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One century of experiments on electron-atom and molecule scattering: a critical review of integral cross-sections

II. – Polyatomic molecules

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1. – Introduction

1˙1. *General remarks.* – Vivid experimental activity in the field of electron scattering on gases has been observed in the period after the first part of this review has been published (A. Zecca, G.P. Karwasz and R.S. Brusa: "One century of experiments on electron-atom and molecule scattering: a critical review of integral cross-sections.

I. Atoms and diatomic molecules". La Rivista del Nuovo Cimento. No. 3, 1996.) This paper will be referred as (Part I) from now on. Many of these works have produced absolute cross-sections. With new precise measurements of total and partial cross-sections, well-documented cross-section databases are available for many polyatomic targets, as it was previously for a few monoatomic and diatomic gases only. In particular the growing interest in atmospheric physics and chemistry, both regarding naturally occurring gases and anthropogenic pollutants, has fostered new experiments on molecules such CO_2, SO_2, N_2O, O_3, ClO_2. Numerous data compilations are available; unfortunately, some of them can be found as Internet files only.

Until a few years ago, the lack of reliable experimental data over a sufficiently large energy range has made the comparison between theory and experiment difficult: as a consequence, theoretical models could not be fully validated by comparison with reliable observations. We proposed in Part I that this situation was going to change; the growth of experimental data in the last years seems to confirm our prediction, even for the subfield of polyatomic molecules.

In the present paper (Part II) we review cross-sections for polyatomic molecules, like H_2O, NH_3, CH_4 and so on. Hydrocarbons and halides will be discussed in (Part III) of this paper. Hydrogen halides, HCl, HF and HBr are discussed in the present paper.

1˙2. *Review papers.* – Integral CS for numerous polyatomic targets have been reviewed in the last ten years by Shimamura (1989), Hayashi (1992), Morgan (1999). Older review papers have been quoted in (Part I).

Shimamura (1989) reviewed total and partial CS between 0–2000 eV in H_2, N_2, O_2, CO, CO_2, H_2O, CsF, HBr, KI, LiF, NO, NH_3, N_2O, SF_6. Hayashi (1992) gave semiempirical total and partial cross-sections in the 0.01–1000 eV energy range for the following targets: He, He 2^3S, Ne, Ar, Kr, Xe, H, O, Na, Cu, Hg; H_2, N_2, O_2, F_2, CO, HCl, H_2O, CO_2, OCS, SO_2, N_2O, C_2H_2, BF_3, NH_3, CH_4, SiH_4, GeH_4, CF_4, C_2H_4, CH_3OH, SF_6, C_2H_6, Si_2H_6, C_2F_2, C_3H_8. Hayashi's paper does not supply references.

A number of review papers for the following targets: N_2, O_2, H_2, CO, CO_2, H_2O, NO, N_2O, SO_2, NH_3, Hg, O, F, Ar, C_2H_2, C_2H_4, C_2H_6, CH_4, SiH_4, Si_2H_6, Cl_2, F_2, HCl, HBr, SF, SF_6, CF_4, C_2F_6, CHF_3, c-C_4F_8, CF_2Cl_2, SiF_4, BCl_3, NF_3, BF_3, C_3F_8 have been quoted by Morgan (1999). The same author has published detailed reviews on Cl_2, F_2, HCl (1992a) and CF_4, SiH_4 and CH_4 (1992b).

A comprehensive list of benchmark measurements of total, swarm-derived and optical emission CS, a discussion of analytical representations for cross-section data, notes on plasma and fusion-related CS, an overview of databases and a guide to bibliographies have been given in a monographic issue of *Advances in Atomic, Molecular and Optical Physics* edited by Inokuti (1994).

Christophorou and Olthoff (1999) reviewed extensively total, integral and differential cross-sections for Cl_2. Inelastic CS in N_2 and O_2 have been reviewed by Majeed and Strickland (1997); CO inelastic CS have been examined by Liu and Victor (1994). Total and partial cross-sections for SO_2 were analysed by Bhardwaj and Michael (1999).

1˙3. *Updating references.* – We quote below some of the most significant partial CS measurements appeared after 1995, in particular dealing with targets discussed in (Part I).

Total cross-sections at low energies have been studied in NO (Alle *et al.* 1996, Randell *et al.* 1996b), Cl_2 (Gulley *et al.* 1998), CO (Randell *et al.* 1996a).

Momentum transfer CS analysis for atomic targets, Ar, Kr, Xe has been done by Suzuki *et al.* (1990, 1989, 1992, respectively).

Elastic CS measurements at low energies were performed on He (Čubrić *et al.* 1999), Ar (Gibson *et al.* 1996a, Cvejanović and Crowe 1997), Kr (Cvejanović and Crowe 1997), Xe (Gibson *et al.* 1998), CO (Gibson *et al.* 1996b), N_2 (Sun *et al.* 1995), O_2 (Green *et al.* 1997), NO (Mojarrabi *et al.* 1995), Cu (Madison *et al.* 1998) and, in an extended angular range, in noble gases (Zubek *et al.* 1999).

Vibrational excitation was studied for O_2 (Brunger *et al.* 1998a), N_2 (Sun *et al.* 1995) and NO (Mojarrabi *et al.* 1995).

Electronic excitation was studied in He (Röder *et al.* 1996, Khakoo *et al.* 1996a, LeClair and Trajmar 1996b, Asmis and Allan 1997, Čubrić *et al.* 1999), He 2^3S (Boffard *et al.* 1999), Ne (Zhong *et al.* 1997b, Brunger *et al.* 1998b), Ar (Ji *et al.* 1996, Panajotović *et al.* 1997), Kr (LeClair and Trajmar 1996a, Guo *et al.* 1999), Xe (Suzuki *et al.* 1996, Khakoo *et al.* 1996b, c, LeClair and Trajmar 1996a, b), CO (Furlong and Newell 1996, LeClair and Trajmar 1996b, Zobel *et al.* 1995, 1996, Zhong *et al.* 1997a, Olszewski *et al.* 1998, Zetner *et al.* 1998, Almeida *et al.* 1999), NO (Mojarrabi *et al.* 1996), NO_2 (LeClair and Trajmar 1996b, Poparić *et al.* 1999), K (Borovik *et al.* 1999), Hg (Burrow *et al.* 1998), Cu (Madison *et al.* 1998). Scattering from excited metal atoms was also extensively studied (Law and Teubner 1995, Li and Zetner 1996, Karaganov *et al.* 1999, Stockman *et al.* 1998, Karaganov *et al.* 1999, Shurgalin *et al.* 1999, Stockman *et al.* 1999, Trajmar *et al.* 1999, Zetner *et al.* 1999).

Absolute DCS for forward-scattering electronic excitation (equivalent to photoabsorption CS, see eq. (16) in Part I) have been extensively measured by Brion and collaborators. Their papers have been reviewed by Olney *et al.* (1997) who discusses: He, Ne, Ar, Kr, Xe; H_2, HD, D_2, N_2, O_2, CO, NO, CO_2, NO_2, N_2O, H_2O, H_2S, SO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, CH_3OH, HCHO, CH_3CHO, $(CH_3)_2CO$, HCl, CH_3F, CH_3Cl, CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, CCl_4, BrCN, NH_3, NH_2CH_3, $NH(CH_3)_2$, $N(CH_3)_3$, SiH_4, SiF_4, PH_3, PF_3, PF_5 and PCl_3.

Optical emission CS was studied for targets like Ne (Kanik *et al.* 1996), Xe (Fons and Lin 1998), CO (Ciocca *et al.* 1997). Atomic and molecular photoemission cross-sections for atomic transitions in the extreme ultraviolet were reviewed by van de Burgt *et al.* (1989).

Ionization. Numerous atoms, molecules and radicals have been recently measured. The AT&T group studied molecules and radicals like N_2, CO, CO_2, CS, S_2, CS_2 (Freund *et al.* 1990); the Houston group, targets like Ar (Straub *et al.* 1995), H_2, N_2, O_2 (Straub *et al.* 1996); the New York group, N_2 (Abramzon *et al.* 1999a, b); the Pasadena groups, F_2 (Rao and Srivastava 1996); the Belfast group, Pb (McCartney *et al.* 1998); Tian and Vidal, N_2, O_2 (1998b), CO, CH_4, C_2H_2 (1998a, 1999). New experimental methods, like the use of a magneto-optical trap (Schappe *et al.* 1996) or comparison with photoionization (Sorokin *et al.* 1998) have been developed. At the same time, semiempirical approaches have been successfully applied for ionization CS in different targets (Kim and Rudd 1994, Hwang *et al.* 1996, Kim *et al.* 1997, 1998, Margreiter *et al.* 1990, Deutsch *et al.* 1996, 1997a, b, Harland and Vallance 1997, Khare *et al.* 1999).

Electron attachment has been reviewed by Chutjian *et al.* (1996) and Smith and Španěl (1994). New measurements have been obtained for CO, NO (Denifl *et al.* 1998) and H_2 (Orient and Chutjian 1999).

In the recent years, a new convergence between experimental and theoretical research was observed for complex targets like, for example, carbon dioxide (Gibson *et al.* 1999). Semi-empirical approaches, like the additivity rule (compare eq. (16) in Part I) were succesfully developed and experimentally tested for the total (Zecca *et al.* 1999, Karwasz *et al.* 1999), elastic (Tanaka *et al.* 1997), ionization (Harland and Vallance 1997), dissociation-into-neutrals (Motlagh and Moore 1999) channels.

1˙4. *Aims of the paper*. – The following lines of this introduction are intended as a guide for the reader and will recall closely the corresponding introduction in Part I.

The aim of this paper is to review updated experimental results on electron scattering by small polyatomic molecules. Both total and partial cross-sections will be presented in the widest possible energy interval. Sporadically, also differential cross-sections (DCS) for elastic and inelastic processes will be presented if they are essential for understanding the physics of the collision process. The present review does not aim at a full completeness: nevertheless we have attempted to include both the new and old data when useful to complete the description of a given target.

Theoretical data will not be reviewed: however theoretical data will be presented occasionally. Theoretical data have been used on the basis of two criteria: a) when experimental data for a given gas were not available, and the addition of a few theoretical results was sufficient to give a view of the scattering phenomena; b) when there was no way to adjudicate between contradictory experimental results from different laboratories. We have to stress here that the choice of these theoretical data has been subjective and does not imply a judgement on other theoretical works performed on the same target.

The present paper does not contain a review of the experimental techniques used for cross-section measurements. Occasionally in the text, some experimental details will be discussed. This will be useful: a) to explain discrepancies among different laboratories; b) to justify results which deviate from the majority of results for the same measured quantity. The same argument applies for data analysis procedures: in particular, normalization procedures will be discussed in a few instances.

Throughout the paper the following acronyms will be used: CS for Cross-Section, TCS for Total Cross-Section and DCS for Differential Cross-Section. These acronyms will be used undifferentiated for singular and plural.

1˙5. *Organization of the paper*. – Molecular targets have been grouped in the three sections. The grouping has been made on the basis of "chemical" or "geometrical" similarities among molecules. How it will be apparent from the reading of the paper, these similarities correlate often with analogies in the shape of the total cross-section. For example, the CH_4, SiH_4, GeH_4 show striking analogies, like a deep Ramsauer-Townsend minimum in the sub- eV region and a single broad maximum in the 10 eV region. Linear triatomic molecules such as CO_2, N_2O, OCS show pronounced resonances in the range below 10 eV while the TCS for bent triatomic molecules NO_2, SO_2 does not show such distinct structures. The TCS maximum in polar hydrides (H_2O, NH_3, HCl) is weaker than in CH_4 and these targets show a low-energy rise of the TCS.

The three sections are the following: tetrahedral hydrides, non-tetrahedral (polar) hydrides, and triatomic molecules. Hydrocarbons and halides including substituted hydrocarbons, substituted silanes and SF_6 are presented in the forthcoming part III. Some other targets, for which little experimental work exist, are mentioned only where it seemed to be the most appropriate. In this manner, the reader will find a few comments and references on disilane Si_2H_6 in subsect. **2**˙2 "Silane (SiH_4)"; on HI in subsect. **3**˙6 "Other hydrogen halides (HF, HBr)".

Each subsection inside the above-mentioned three sections, will describe one or more gases. Usually, a part only of the measured data available in the literature will be discussed. A selection has been made: this has been stronger for those gases which received more attention from experimentalists. The reason for this selection lies in the (already declared) aim of this review. The goal of the work has been to produce a critically selected set of data which should be representative of our best present knowledge of electron scattering phenomena on molecules. Therefore the measurements data have been selected to form a set as much coherent as it is possible.

Each of the subsections contains a variable number of sub-paragraphs: total, elastic, vibrational and electronic excitation, optical emission, ionization cross-sections will be presented where data are available. The last sub-paragraph in each chapter is entitled: "Sum Check". Here we attempt to make a consistency check on the available data by summing up the partial cross-sections and comparing this sum with the measured total cross-section at selected energies. For many targets this sum check is rather rough: in spite of this, it can give useful information on the general quality of the available experimental data. Sometimes, it can give limits about one of the integral cross-sections being affected by a larger error.

The energy range covered by the present review, spans from 0 eV up to 5000 eV. Whenever an energy interval has to be indicated, the following convention will be observed:

- very low energies: $E < 1\,\mathrm{eV}$,
- low energies: $1\,\mathrm{eV} < E < 30\,\mathrm{eV}$,
- intermediate energies: $30\,\mathrm{eV} < E < 300\,\mathrm{eV}$,
- high energies: $E > 300\,\mathrm{eV}$.

Those limits have to be considered with some fuzziness.

Units. $10^{-20}\,\mathrm{m}^2$ ($= 10^{-16}\,\mathrm{cm}^2$) units are used for cross-sections. In some cases, like for the photoionization cross-section smaller units, $10^{-22}\,\mathrm{m}^2$ are used. The cgs units are used for the dipole moment ($1\,\mathrm{Debye} = 3.34 \cdot 10^{-30}\,\mathrm{Cm}$). Townsend units ($1\,\mathrm{Td} = 10^{-21}\,\mathrm{Vm}^2/\mathrm{molecule}$) are implicitly used for the reduced electrical field in swarm measurements; we give the $10^{-21}\,\mathrm{Vm}^2$ quotation in the text. The Bohr radius $a_0 = 0.529 \cdot 10^{-10}\,\mathrm{m}$ is used as the unit for scattering length. E in the text stands for energy (in eV), k for the momentum $E = (h/2\pi)^2 k^2/2m$, where m stands for the electron mass and h for Planck's constant.

Experimental errors. We do not quote experimental errors, unless they are significant for the analysis. From one side, error bars declared by the authors are very often greater than the real discrepancies between different data sets. On the other side, unknown, unexpected or underestimated factors, like for example a poor angular resolution, an inefficient discrimination of inelastically scattered electrons, a poor energy resolution, scattering inside the electron optics and/or gas pressure evaluation errors can cause high systematic errors, above the value of the random ones.

Terminology. Note that the energy resolution in "elastic" cross-section measurements is usually not sufficient to distinguish the scattered electrons which underwent inelastic scattering leading to the rotational excitation of the molecule. Therefore, the "elastic" cross-sections from these experiments (for example, Alle *et al.* 1992) contain an inelastic contribution of the rotational excitation CS. However, we will continue to call them "elastic", following the original terminology. Sometimes, we add the adjective "vibrationally elastic", to stress that only the vibrational excitation is separated. Experimental elastic cross-sections without the rotational contribution will be called “pure elastic” or “rotationally elastic”, for example in HCl subsect. **3**˙5.

Swarm data. In the present Part II (and to an even greater extent in Part III) we will make use of swarm data to evaluate electron scattering cross-sections. This will happen mainly in the very low-energy region, where beam measurements are scarce. For some targets, like for example SiH_4, the momentum transfer cross-section σ_m, see eq. (3) (Part I), has been derived by other authors from measurements of the electron diffusion coefficients; in this case we will refer to the published cross-sections directly. In other targets, like H_2S no cross-sections have been derived in the original papers; therefore we quote only the available diffusion coefficients (the drift velocity, the characteristic energy, the longitudinal diffusion coefficient).

A general feature of swarm experiments is that electrons undergo multiple scattering in the diffusion chamber: typical dimensions of drift cells are of several hundreds cubic centemeters and target gas pressures are in the range of a few hundreds Pa. In the Townsend-Huxley technique (Huxley and Crompton 1974) the D_{T}/μ (ratio of transverse diffusion coefficient to mobility, called also the characteristic energy) and the D_{L}/μ (ratio of the longitudinal diffusion coefficient to mobility) can be determined simultanously. In this technique electrons released from a photocathode by UV radiation pass through a small orifice, drift under action of a uniform electric field and diffuse laterally producing a widening spread of the electron swarm and are finally collected by a sectored anode (see, for instance, Mechlińska-Drewko *et al.* 1999). The drift velocity w can be measured in drift cells equipped some electrical shuttering system (see, for instance, Hasegawa *et al.* 1998).

The derivation of cross-sections from diffusion coefficients requires solving the Boltzmann equation and taking into account all possible inelastic processes. However, to the first approximation, the following simplified relations hold (see, for example, Crompton 1994):

$$w = -\left(\frac{2}{m}\right)^{1/2} \frac{eF}{3N} \int_0^\infty \frac{E}{\sigma_m(E)} \frac{\mathrm{d}f_0(E)}{\mathrm{d}E}\,\mathrm{d}E,$$

$$D_{\mathrm{T}} = \left(\frac{2}{m}\right)^{1/2} \frac{1}{3N} \int_0^\infty \frac{E}{\sigma_m(E)} f_0(E)\mathrm{d}E,$$

where $f_0(E)$ is the leading (symmetric) term in the expansion of the energy distribution function of the electron swarm, F is the electric field intensity, N is the gas target density, and e and m are the electron charge and mass, respectively.

Electron attachment. Electron attachment is an important channel for electron scattering on polyatomic molecules. Some molecules (CCl_4 as an example) attach electrons at very low energies, forming parent molecular negative ions, ${CCl_4}^-$ in this case. Many other targets, like CO_2, form non-stable parent ions which undergo dissociation into negative ions and neutral radicals (for CO_2 according to the scheme $CO_2 + e^- \rightarrow {CO_2}^- \rightarrow O^- + CO$). We use the term “*dissociative* electron attachment” for the latter process while we call “electron attachment” the former one.

The cross-section for electron attachment in molecules like SF_6, CCl_4, C_6F_6 increases strongly in the “zero” energy limit. This behaviour of the cross-section will be illustrated in details while we discuss halomethanes (Part III); different formulae approximating the cross-section proposed in the literature will be cited there. As the molecular negative ions are rather unstable, the excess collisional energy must be transferred from the ion into, for example, the vibrational excitation of another, neutral molecule. Otherwise, the negative ion can decay before being detected. Because of this difficulty, stable molecular ions formed in electronic collisions are still being discovered, even in targets already extensively studied in the past, like O_2 (Matejcik *et al.* 1999).

On the other hand, the *dissociative* attachment is usually related to a resonant scattering, *i.e.* to the formation of a short-lived, negative ion. As far as this formation takes place *via* capture of the incoming electron inside the effective potential energy barrier of the target, the dissociative attachment occurs at well-defined energies, for example at 3.8 eV and 8.1 eV for CO_2. However, both the position as well as the width of the peaks in the dissociative attachment depend also on the exit channel. As an example, the cross-section for the F^- ion production via dissociative attachment from CF_2Cl_2 molecules peaks at 3.1 eV, the FCl^- ion at 2.85 eV and ${CFCl_2}^-$ at 3.55 eV (Illenberger *et al.* 1979).

Analysis of differential and vibrational cross-sections. A semi-empirical analysis of the literature data has been performed by the present authors in some cases. In particular, we have performed numerical integration of differential elastic and electronic excitation cross-sections, when only DCS were available. Simple numerical polynomial fits were used without special emphasis on the choice of the fitting formula. The main source of error in the integral CS derived in this way comes from the extrapolation of experimental DCS outside the measured angular range (in particular toward small angles). We are aware that the errors quoted by us can be underestimated; in addition it must be kept in mind that these errors do not include the experimental uncertainties given by each author.

There is a general lack of integral CS for vibrational excitation. We have evaluated these values by making rough estimates: multiplying experimental DCS at some angles, say 60° or 90° by constant factors or performing a numerical integration. In gases for which the vibrational excitation is expected to be a significant part of the TCS and at energies outside resonances, we used the Born approximation (eq. (15) in Part I) and the known (Bishop and Cheung 1983) transition dipole moments for optically active modes.

Numerical tables. We have decided to avoid printing huge numerical tables containing the data collected from the literature. Most of the tables in this paper will present the results of our "sum check" and aim to give the reader an idea on the most probable partitioning scheme of the total cross-sections among the possible scattering channels. For this reason, several alternative data sets are usually compared. A "summed" value in a row appears in the last column but one of the table and it is obtained by summing the values in this row; if a summed value is given, but no value is given in this row for a specific process, the value from the nearest row above is used in the summation. Values in parenthesis are not used for summation; they usually concern CS which are a complementary manifestation of the same scattering channel, like electronic excitation and dissociation into neutral radicals. No "summed" values are given for rows with high experimental uncertainty.

Figures. This paper will rely heavily upon the use of figures representing integral cross-sections as a function of energy. In order to keep the number of printed pages within reasonable limits, we were forced to compress the result of many experiments in a single figure. Therefore we had to find a few rules to render these figures readable and unambiguous.

In all figures regarding the integral cross-sections, the energy axis will span from 0.001 eV to 5000 eV. This will make easier the comparison of different figures (different targets). Willing to show an energy range of several decades the choice for a logarithmic axis was a must. This implies the absence of a zero-energy abscissa: in all figures where we wanted to show a zero-energy cross-section (σ_0), this has been plotted as a point placed attached to the left vertical axis. Again for the easiness of the comparison, the cross-section axis has a span of two decades for all figures: the reader will check easily that the total cross-sections of most gases vary by a factor smaller than 100 in the above-quoted energy range.

Each integral cross-section figure will report a number of total and partial cross-section measurements (sometimes partially overlapping). Having a limited number of symbols which can be clearly distinguished in the printing, it has been unavoidable to use the same symbol more than once to indicate different measurements. In order to avoid ambiguity the following rules have been adopted in the making of the figures.

- A given symbol has not been used twice to indicate measurements of the same integral cross-sections. The same symbol can be found to indicate different integral cross-sections.
- A further discrimination can be achieved by observing the order in which the symbols are listed within the figure frame in each homogeneous group. This listing is always in an order of increasing energy going from the top to the bottom.
- As a last mean to identify correctly the data from different laboratories, sometimes points of a given symbol are connected by straight line segments. These segments act also as a guide for the eye, every time the measured points are very sparse.

Please note that lines are also used in the figures:

- to represent theoretical results;
- to represent experimental data, whenever the density of points in the original paper was high;
- to represent momentum transfer cross-sections.

References. The standard presentation of references would lead to a single large list. We have considered such a list to be of difficult handling for the reader. On this basis, each paragraph (dealing with a single target) will end with a reference list regarding this target only. This will lead to some redundancy of these lists (about 30%) due to the fact that often a published paper presents results regarding two or more different gases. This organization will yield a better usability of the references from the side of the reader.

In the present review we have used three data files available on Internet sites. Nevertheless we will not quote in our reference list data which can be found as Internet files only. The present organization of Internet is such that these files can be classified as "volatile knowledge". There is no guarantee that those data will be traceable in a few years from now. Therefore future readers cannot make any reference to such sources.

We entirely refer the reader to our previous review (Part I) to remind the definitions and the formulae which will be used in the following.

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2. – Tetrahedral hydrides

Electron scattering on tetrahedral hydrides shows numerous analogies with noble gases (see, *e.g.*, Kauppila and Stein 1990, Karwasz 1995, Przybyla *et al.* 1997). On this basis, CH_4, SiH_4, GeH_4 molecules will be discussed before other polyatomic molecules. Please note that some of these analogies can be found also in other molecules, but are often masked by different features in the partial cross-sections. Tetrahedral hydrides, with a bond length about 2/3 of the crystallographic radius of the central atom (Weast 1986), are frequently considered as "almost spherical" (see Freeman and March 1993 and March *et al.* 1994).

2˙1. *Methane* (CH_4). – Methane is used in many technological processes such as, for example, diamond-like film depositions (Cui and Fang 1997) and radiation counters. It constitutes the main component of the Jovian atmosphere (Wallace and Hunten 1978) and has been detected in the interstellar space. Its importance in Earth's atmosphere warming-up through the greenhouse action has been recently acknowledged and extensively studied (Groedel and Crutzen 1993). A set of recommended cross-sections up to 1000 eV has been published by Kanik *et al.* (1993) and Morgan (1999). A low-energy swarm analysis has been performed by Shimura and Makabe (1992) and by Alvarez-Pol *et al.* (1997).

Total cross-sections have been measured in most of the laboratories active in the field during the last decade. This allows to establish a set of data consistent within 3% (see fig. 1). At energies below 0.1 eV the time-of-flight results of Ferch *et al.* (1985) and Lohmann and Buckman (1986) merge with the modified-effective range analysis of swarm data by Schmidt (1991) and determine the position (0.34 eV) and the depth ($1.32 \cdot 10^{-20}\,\mathrm{m}^2$) of the Ramsauer minimum in a congruent way. Note that the pioneer measurements (Ramsauer and Kollath 1930) yielded a minimum TCS value of $1.36 \cdot 10^{-20}\,\mathrm{m}^2$, close to the recent experiments and better than the determination of Barbarito *et al.* (1979), not shown in fig. 1. Relative "total" CS for CH_4, recorded for scattering into $90° \pm 30°$ angles and obtained with synchrotron-radiation electron source have been reported in the 0.1–6 eV energy range by Lunt *et al.* (1994).

At 1–5 eV the data of Ferch *et al.* (1985) agree well with the measurements of Jones (1985) and are slightly higher than the results of Lohmann and Buckman (1986). Between a few eV and 100 eV the data from the Gdańsk laboratory (Zecca *et al.* 1991) agree very well with those of Kanik *et al.* (1992) and those of Nishimura and Sakae (1990) and merge with the high-energy cross-sections from the Trento laboratory (Zecca *et al.* 1991). The high-energy (400–5000 eV) results of García and Manero (1998) agree with Zecca *et al.* (1991) up to 1000 eV but are about 30% higher at 4000 eV. This discrepancy is higher than the declared angular resolution error in the experiment of Zecca *et al.* (1991); the reason for this divergence is not clear.

TCS reaches its maximum of $26.4 \cdot 10^{-20}\,\mathrm{m}^2$ (Jones 1985, Kanik *et al.* 1992) at about 8 eV. In the region of the maximum the data of Dababneh *et al.* (1988) are slightly higher than this value while those of Ferch *et al.* (1985) and Lohmann and Buckman (1986) are lower. One notes that time-of flight measurements can suffer from systematic errors, leading to underestimation of TCS in the high-energy limit of each apparatus. This could be the case of Ferch *et al.* (1985) and Lohmann and Buckman (1985) measurements above 10 eV, due to the energy determination uncertainty, and Jones (1985) above 25 eV, due to the scattering on exit apertures. On the other hand, the data of Nishimura and Sakae (1990) above 100 eV, Dababneh *et al.* (1988) above 300 eV and Zecca *et al.* (1991) above

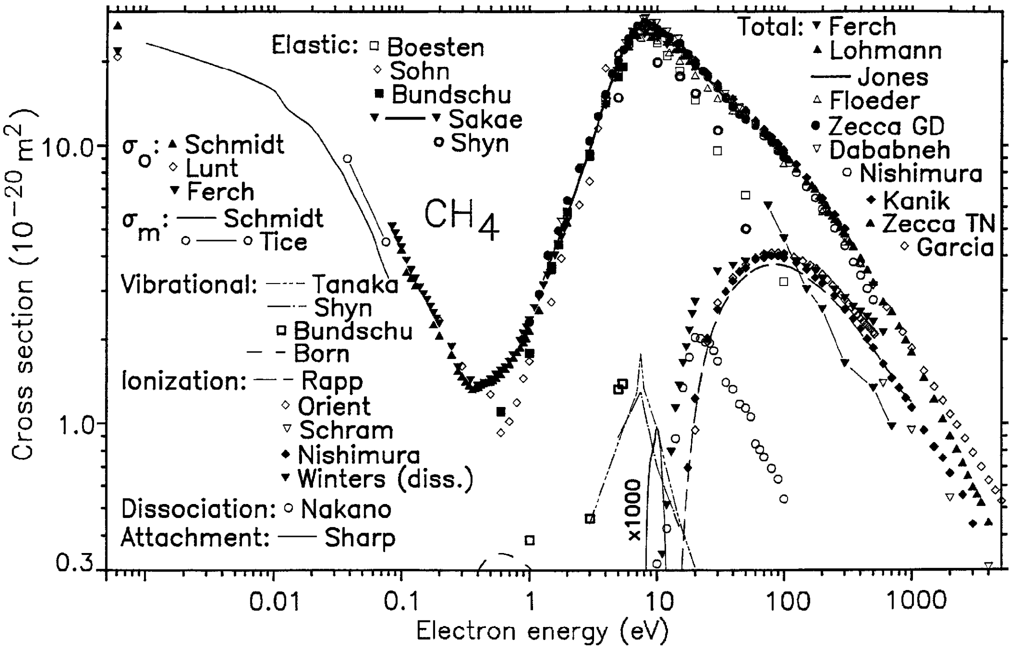

Fig. 1. – Integral cross-sections for electron scattering on CH_4. *Total*: Ferch *et al.* (1985); Lohmann and Buckman (1986); Jones (1985); Floeder *et al.* (1985); Zecca GD, Gdańsk measurements from Zecca *et al.* (1991); Dababneh *et al.* (1988); Nishimura and Sakae (1990); Kanik *et al.* (1992); Zecca TN, Trento measurements from Zecca *et al.* (1991); García and Manero (1998); the data of Ramsauer and Kollath (1930), Barbarito *et al.* (1979), Sueoka and Mori (1986), are not presented for clarity reasons. *Elastic*: Boesten and Tanaka (1991); Sohn *et al.* (1986); Bundschu *et al.* (1997); Sakae *et al.* (1989); Shyn and Cravens (1990). *Momentum transfer*: Schmidt (1991); Tice and Kivelson (1967) from cyclotron resonance experiment. *Zero energy*: Schmidt (1991) from swarm; Ferch *et al.* (1985) and Lunt *et al.* (1994) from total. *Vibrational*: Tanaka *et al.* (1983) normalized (this work) by a factor of 1.3 to the elastic CS of Boesten and Tanaka (1991); Shyn (1991); Bundschu *et al.* (1997), absolute; Born approximation, from Sohn *et al.* (1986). *Ionization*: Rapp and Englander-Golden (1965); Orient and Srivastava (1987); Schram *et al.* (1966); Nishimura and Tawara (1994); Winters (1975), ions + neutral fragments; data of Chatham *et al.* (1984), Durić *et al.* (1991), Straub *et al.* (1997) and Tian and Vidal (1998) are not shown for clarity. *Dissociation into neutrals*: Nakano *et al.* (1991). *Dissociative attachment*: Sharp and Dowell (1967).

1000 eV can be underestimated due to angular resolution errors, see fig. 1.

Above 10 eV the data of Floeder *et al.* (1985) are 5% lower, on the average, than the other sets of data; those of Sueoka and Mori (1986) are on the average 10% lower. We note that the measurements of Sueoka and collaborators are often lower than those of other laboratories (see for instance their data on CO_2, NH_3, N_2). We stress that such a systematic behaviour could arise from errors in the energy scale calibration. In time-of-flight apparatuses, the energy calibration depends on a time-scale definition and overestimating the time of flight gives an underestimation of the energy. This can reach easily the order of 10% at high energy. Our hypothesis could give account also of low values in measurements of Floeder *et al.* Alternatively, these discrepancies can be attributed to an error in the evaluation of the effective scattering length in those two apparatuses, because of the use of a longitudinal focusing magnetic field (see the discussion of this effect by Kauppila *et al.* 1981). The data of Sueoka and Mori up to 400 eV and some early low-energy measurements are not shown in fig. 1 for clarity reasons.

Swarm measurements. At energies below 0.1 eV the momentum transfer cross-sections of Schmidt (1991) agree well with those of Ohmori *et al.* (1986) and Haddad (1985) and the cyclotron-resonance evaluation (Tice and Kivelson 1967). The values of Duncan and Walker (1972) are significantly higher than those of the mentioned groups. It is worth noting that cross-section values at the Ramsauer-Townsend minimum show a "historical trend": more recent momentum transfer analysis (Schmidt 1991, Schmidt and Berkhan 1994) yield a deeper minimum than the earlier determinations (Duncan and Walker 1972, Gee and Freeman 1979, Haddad 1985, Ohmori *et al.* 1986, Davies *et al.*, 1989). We noted (Part I) a similar trend for Kr and Xe. A possible explanation lies in improvements of the target gas purification. A second one relates to a progress in the numerical analysis of the swarm coefficients. According to the analysis which takes into account the rotational excitation and resonant structures in the near-to-threshold vibrational excitation (Schmidt 1993, Schmidt and Berkhan 1994), the CH_4 minimum is placed at 0.35 eV and amounts to $0.2 \cdot 10^{-20}\,\mathrm{m}^2$. In an alternative analysis (Alvarez-Pol *et al.* 1997) a much higher minimum has been obtained with a value close to the TCS determinations.

The scattering length of $-2.48a_0$ from TCS measurements (Ferch *et al.* 1985) agrees reasonably well with the values from recent swarm analysis ($-2.59a_0$ Schmidt 1991) and theories ($-2.9a_0$, McNaughten *et al.* 1990). Phase shifts in the 0.2–5 eV energy range for s, p and d-waves, have been derived from the experimental elastic CS by Sohn *et al.* (1986).

Elastic cross-sections both differential as well integral have been extensively measured at low energies (0.6–5.4 eV) by Bundschu *et al.* (1997). Their DCS agree well in shape with those of Sohn *et al.* (1986) but the integral values are somewhat (20%) higher. Earlier 3–20 eV data by Tanaka *et al.* (1982) have been used as reference values for the normalization of other CS, both elastic (Curry *et al.* 1985, Mapstone and Newell 1992) and vibrational ones (Tanaka *et al.* 1983, Shyn 1991, Mapstone and Newell 1994). More recently, the data of Tanaka *et al.* (1982) were found to be underestimated by about 30%: the remeasured values (Boesten and Tanaka, 1991) are in very good agreement with TCS (Jones, 1985, Ferch *et al.*, 1985) at energies below 8 eV. At 15 eV and 20 eV these remeasured data are in reasonable agreement with the absolute elastic data of Shyn and Cravens (1990). However, at 30 eV the integral data of Boesten and Tanaka (1991) are still 20% lower than the elastic values of Vušković and Trajmar (1983) and of Shyn and Cravens (1990). Similarly, at 100 eV the measurement of Boesten and Tanaka (1991) is 40% lower than that of Sakae *et al.* (1989). The reason for this latter discrepancy is not clear: probably, both values are affected by normalization errors in opposite directions.

The recent measurement of Maji *et al.* (1998) at 300–1300 eV, 30°–120° disagree somewhat with results of Sakae *et al.* (1989). At 300 eV the two measurements (Maji *et al.* and Sakae *et al.*) coincide at 120° but differ by +40% at 30°; at 700 eV they coincide at 30° but differ by −50% at 120°.

The relative determination of Przybyla *et al.* (1997) agrees well in shape with preceding works (Boesten and Tanaka 1991, Sakae *et al.* 1989). Przybyla *et al.* stressed a remarkable similarity between positron scattering on Ar and CH_4. This contrasts with electron scattering, for which the CH_4 integral elastic cross-section at 200 eV is much lower than the argon one (see also Karwasz 1995).

A comparison between CH_4 and SiH_4 DCS at selected energies will be shown in fig. 3 below. Even at low energies (1.0–3.0 eV), DCS are dominated by d-wave scattering

(Bundschu *et al.* 1997). The Ramsauer minimum as seen in elastic CS (Sohn *et al.* 1986) is shallower ($0.92 \cdot 10^{-20}\,\mathrm{m}^2$) than in momentum transfer CS and is shifted to higher energy (0.6 eV).

Vibrational excitations have been studied at low energies by the Kaiserslautern group (Rohr 1980, Sohn *et al.* 1983, Müller *et al.* 1985, Sohn *et al.* 1986), by Tanaka *et al.* (1982), Shyn (1991), Lunt *et al.* (1994) and more extensively by Bundschu *et al.* (1997). Two infrared-active modes (ν_3=0.374 eV, ν_4=0.162 eV) are not separable from nearby Raman modes (ν_1=0.362 eV and ν_2=0.190 eV, respectively). Different low-energy DCS agree generally in shape, but the most recent data (Bundschu *et al.* 1997) are the highest ones.

Müller *et al.* (1985) indicated that the forward-angle DCS at 0.5 eV can be well approximated by the Born approximation. However, both the Kaiserslautern group (Rohr 1980, Sohn *et al.* 1983) and Lunt *et al.* (1994) noticed narrow structures in the ν_2, ν_4 excitation functions just above the threshold. Sohn *et al.* (1983) suggested the presence of a very-short-lived resonant state with a f-wave symmetry; on the other hand, coupling of ν_2, ν_4 with other vibrational modes cannot be excluded. At the energy of the Ramsauer minimum the vibrational integral CS evaluated from the Born approximation (Sohn *et al.* 1986) contributes about 30% of TCS.

Different measurements indicate that around 8 eV the vibrational excitation is enhanced by resonant scattering (Tanaka *et al.* 1983, Curry *et al.* 1985, Shyn 1991, Mapstone and Newell 1994). However, some doubt regards the absolute values: all these measurements were normalized to the underestimated elastic data of Tanaka *et al.* (1982). In addition, the DCS of Mapstone and Newell (1994) are up to a factor of 2 higher than the remeasured data of Tanaka *et al.* (1983). In its maximum at 7.5 eV the vibrational excitation (Shyn 1991) contributes about 5% of TCS and is dominated by a d-wave scattering (Tanaka *et al.* 1993).

Rotational excitation has been measured by Müller *et al.* (1985) via broadening of the energy loss peaks. Due to the T_d symmetry only the $J = 0 \rightarrow 3$ and $J = 0 \rightarrow 4$ pure rotational excitations are effective. At 0.5 eV, *i.e.* in the vicinity of the Ramsauer minimum, the rotational excitation CS is of the order $1 \cdot 10^{-23}\,\mathrm{m}^2$ for the $J = 0 \rightarrow 3$ transition and $1 \cdot 10^{-22}\,\mathrm{m}^2$ for the $J = 0 \rightarrow 4$ transition. The relative contribution to TCS is therefore less than 1%. The rotational excitation becomes isotropic and more effective at higher energies, amounting at 10 eV to about $1.5 \cdot 10^{-20}\,\mathrm{m}^2$ for $J = 0 \rightarrow 4$ transitions and about $1.1 \cdot 10^{-20}\,\mathrm{m}^2$ for $J = 0 \rightarrow 3$ transitions (compare also theories of Jain 1991 and Abusalbi *et al.* 1983).

Electronic excitation has been studied by Vušković and Trajmar (1983) for energy loss between 7.5 and 15 eV. They have normalized their DCS to the early elastic measurements of Tanaka *et al.* (1982). The integral electron excitation CS of Vušković and Trajmar normalized to the more recent elastic CS of Shyn and Cravens (1990) at 20 eV and 30 eV, and to the value of Sakae *et al.* (1989) at 200 eV, amount to 1.50, 1.93 and $0.3 \cdot 10^{-20}\,\mathrm{m}^2$, respectively. These values correspond within the experimental uncertainty (35%) to the cross-section for dissociation into neutrals, as measured by Nakano *et al.* (1991) and Winters (1975). Due to the relatively low energy of the first threshold for molecular fragmentation (4.48 eV, see Heck *et al.* 1996) it is not to be excluded that most of the electronic excitations in CH_4 lead to the dissociation of the molecule. The normalized electronic excitation CS of Vušković and Trajmar (1983) are also in a good accord with the semiempirical values of 1.75 and $0.37 \cdot 10^{-20}\,\mathrm{m}^2$ at 20 eV and 200 eV, respectively (Kanik *et al.* 1993).

Vušković and Trajmar (1983) pointed out differences in angular and energy dependences of DCS for separate energy-loss bands. DCS for the 9.0–13.5 eV energy-loss processes are forward-centered, even at low energies. The integral CS for these excitations decrease with collision energy slower than the near-to-threshold, 7.5–9.0 eV energy-loss CS (Vušković and Trajmar 1983, Dillon *et al.* 1984, Johnson *et al.* 1979). By analogy with, say H_2, see fig. 20 in Part I, the 9.0–13.5 eV energy-loss excitations should be optically allowed. The theory (Bettega *et al.* 1988) predicts the integral CS for the lowest excitation, to the $^3T_2$ state, to fall quickly with energy (Bettega *et al.* 1998). Therefore, one of the possible states with the cross-section slowly varying with energy should be assigned to the $^1T_2$ Rydberg level (Curtis and Walker, 1989).

Inner-shell electronic excitation spectra were studied by Harshbarger and Lassettre (1973), Tronc *et al.* (1976, 1979), Hitchcock *et al.* (1977) and valence ones by Dillon *et al.* (1984). Photoabsorption CS, derived in absolute forward-angle electron scattering experiment (Au *et al.* 1993) reaches maximum of $0.48 \cdot 10^{-20}\,\mathrm{m}^2$ at 14 eV.

Optical emission cross-sections were measured mainly for atomic fragments (see Pang *et al.* 1987 and references therein). Rather big discrepancies exist even for determination of atomic hydrogen Lyman-α emission CS: the data of Pang *et al.* (1987), in good agreement with those of Orient and Srivastava (1981), are by a factor of two higher than the determination of Möhlmann and de Heer (1979). The Ly-α cross-section amounts to $6.3 \cdot 10^{-22}\,\mathrm{m}^2$ at 100 eV (Pang *et al.* 1987) and falls like $1/E$ above 200 eV (Pang *et al.* 1987, Möhlmann *et al.* 1979).

Dissociation into neutrals has been studied in relative measurements by Nakano *et al.* (1991). Dissociation into two radicals were observed: CH_3 reaching a maximum CS of about $1.4 \cdot 10^{-20}\,\mathrm{m}^2$ at 25 eV, and CH_2 reaching a maximum of $0.7 \cdot 10^{-20}\,\mathrm{m}^2$ at 19 eV and disappearing above 50 eV. The presence of the CH_3 radical was also detected in plasma experiments (Childs *et al.* 1992). The CH radical was studied in an optical emission experiment (Donohue *et al.* 1977).

Winters (1975) measured the summed CS for ionization and dissociation, up to 500 eV. He estimated the relative contribution from dissociation into neutrals at 100 eV as 50% of the overall CS for the molecular fragmentation, in agreement with the plasma experiment of Perrin *et al.* (1982). Photofragmentation patterns were studied by Heck *et al.* (1996).

Ionization integral CS were measured in a wide energy range (up to 3000 eV) by Nishimura and Tawara (1994). These data are slightly lower (by 3%) than those of Orient and Srivastava (1987) and Tian and Vidal (1998) at energies below 300 eV and higher by about 10% than the measurements of Durić *et al.* (1991), Chatham *et al.* (1984), Rapp and Englander-Golden (1965) and Straub *et al.* (1997). At 500 eV the total ionization CS of Nishimura and Tawara (1994), Rapp and Englander-Golden (1965), Straub *et al.* (1997) and Tian and Vidal (1998) coincide within 5%; the data of Orient and Srivastava (1987) are 15% higher and those of Schramm *et al.* (1966) 15% lower.

Partial ionization CS measurements of Straub *et al.* (1997) extend up to 1000 eV, while those of Adamczyk *et al.* (1966) up to 2000 eV. The overall ionization at 200 eV branches almost equally into the parent ${CH_4}^+$ and the dissociative processes (Adamczyk *et al.* 1966, Orient and Srivastava 1987, Tarnovsky *et al.* 1996, Staub *et al.* 1997, Tian and Vidal 1998). At 100 eV the relative contributions from ${CH_4}^+$, ${CH_3}^+$ and ${CH_2}^+$ ions amount to 50%, 38% and 6%, respectively (Chatham *et al.* 1984). Dissociated ions easily form dimers (Tian and Vidal, 1997).

Dissociative attachment (Sharp and Dowell 1967) presents two overlapping peaks in the region of the total cross-section maximum: the lower one at 9 eV is due to the production of H^- ions, and the higher one at 10.2 eV is due to ${CH_2}^-$ ions. The contribution to TCS is as low as $4 \cdot 10^{-5}\,\mathrm{m}^2$. Isotope effects in CH_4 and CD_4 dissociative attachment were studied also by Ben Arfa *et al.* (1990).

Resonances. A broad peak at about 8 eV has been attributed to the T_2 d-type shape resonance (see, for example, Gianturco and Scialla 1987). This has been also confirmed by DCS studies in both elastic and vibrational excitation channels (see above for references). The resonance leads to a moderate enhancement of the vibrational excitation. This enhancement is lower than the one found in the case of N_2, see fig. 22 in Part I. No long-lived resonances were observed between 0 and 20 eV in high-resolution, high-sensitivity transmitted electron current experiments (Boness *et al.* 1967, Sanche and Schulz 1973).

Some resonant structures of the Feshbach type at 6.53, 7.37 and 8.15 eV have been

Table I. – *Integral cross-sections for electron scattering on methane (in* 10^{-20} m^2 *units).*

Energy	Elastic	Vibrational	Electronic excitation	Ionization	Neutral dissociation	Summed	Total
0.6	0.92 S	0.34 B				1.26	1.49 L
	1.1 BU					1.44	1.54 F
1.0	1.66 S	0.24 B				1.90	2.13 L
	1.78 BU					2.16	2.34 F
2.0	5.61 BO	0.21 B				5.82	5.24 L
	4.64 BU	0.28 BU				4.92	5.5 J
							6.3 Z
2.5	6.06 S	0.18 B				6.24	8.2 Z
3.0	9.25 BO	0.46 T				9.71	9.06 L
	7.70 BU	0.45 BU				8.15	9.4 J
	7.4 TA					7.85	10.3 Z
5.0	18.0 BO	0.83 T				18.8	18.9 K
	17.5 BU	1.32 BU				18.8	19.9 Z
	13.7 TA						
8.0	26.3 BO	1.33 T				27.6	26.4 K
	19.6* TA						27.4 Z
10	23.0 BO	1.02 T			0.31 N	24.3	25.9 K
	19.8 SH						
	18.4 TA						
15	18.3 BO	0.45 T	1.1 KA	0.21 NI	(1.3) N	20.1	23.0 Z
	17.6 SH						
	15.7 TA						
20	14.4 BO	0.31 T	1.75 KA	1.22 NI	(2.0) N	17.7	20.0 K
	15.3 SH		(1.5 VT)			18.6	
	17.6 V					20.6	
	14.3 TA						

TABLE I. – *Continued.*

Energy	Elastic	Vibrational	Electronic excitation	Ionization	Neutral dissociation	Summed	Total
30	11.3 SH 11.4 V 9.5 BO		1.75 KA (1.93 VT)	2.56 NI	(1.6) N	15.6 15.7	16.5 K
50	6.57 BO 5.0 SH		1.2 KA	3.60 NI	(1.1) N	11.4	13.3 K
100	3.2 BO 4.59 SA		0.67 KA	3.92 NI	(0.5) N	7.79 9.18	9.56 K
150	3.01 SA		0.47 KA	3.55 NI		7.03	7.35 Z 7.61 K
200	2.56 SA		0.37 KA (0.30 VT)	3.17 NI		6.1	6.31 Z 6.42 K
300	1.63 SA		0.26 KA	2.55 NI		4.44	4.76 Z 4.97 K
500	1.33 SA		0.17 KA	1.85 NI		3.35	3.18 Z 3.14 G
700	0.967 SA		0.13 KA	1.44 NI		2.54	2.49 Z 2.47 KA

* - Interpolated value.
( ) - Values not used in the sum.
B - From Born approximation (Part I), Sohn *et al.* (1983).
BU - Bundschu *et al.* (1997).
BO - Boesten and Tanaka (1991).
G - García and Manero (1998).
F - Ferch *et al.* (1985).
J - Jones (1985).
K - Kanik *et al.* (1992).
KA - Kanik *et al.* (1993), recommended.
N - Nakano *et al.* (1991).
NI - Nishimura and Tawara (1994).
L - Lohmann and Buckman (1986).
S - Sohn *et al.* (1986).
SA - Sakae *et al.* (1989).
SH - Shyn and Cravens (1990).
T - Tanaka *et al.* (1983), multiplied (this work) by 1.3.
TA - Tanaka *et al.* (1982).
V - Vušković and Trajmar (1983).
VT - Vušković and Trajmar (1983), normalized (this work) to elastic CS of Boesten and Tanaka (1991).
Z - Zecca *et al.* (1991).

claimed by Botz and Glick (1975) and at 12 eV and 17–19 eV by Mathur (1980) in transmission experiments. We are not aware of other confirmations of these finding. Inner-shell resonances have been reported in the differential elastic (Mathur *et al.* 1984) and energy loss (Tronc *et al.* 1976, Hitchcock *et al.* 1977) spectra. These structures are too weak to be observed in TCS (Zecca *et al.* 1991).

Sum check is presented in table I. At energies below 2 eV the summed values of Bundschu *et al.* (1997) agree very well with TCS (Lohmann and Buckman 1986); data of Sohn *et al.* (1986) are somewhat (20%) lower. On the other hand, the elastic data of Boesten and Tanaka (1991) seem to be slightly overestimated in their low energy limit. The agreement between summed and measured TCS is excellent from 5 eV to 30 eV.

Between 50 eV and 100 eV the summed values are somewhat smaller than the total ones possibly because of underestimation of the elastic part by Boesten and Tanaka (1991). At high energies the elastic data of Sakae *et al.* (1989) sum-up very well with the ionization CS of Nishimura and Tawara (1994) and recommended electronic excitation CS (Kanik *et al.* 1993) to the absolute TCS of Zecca *et al.* (1991). We are not aware of integral elastic CS above 700 eV; a limited angular range of DCS of Maji *et al.* (1998) hinders their use.

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2˙2. *Silane* (SiH_4). – In spite of the great practical importance of this gas for plasma deposition processes in semiconductors technology (Haller 1983, Li *et al.* 1996), few measurements of electron scattering in silane SiH_4 exist. On the other hand, numerous theories were tested for SiH_4 (Bettega *et al.* 1993, 1998, Gianturco *et al.* 1987, 1992, Sun *et al.* 1992, Yuan 1988, 1989, Winstead *et al.* 1991, 1994). Semiempirical cross-sections for swarm-modelling purposes have been reviewed, among others, by Garscadden *et al.* (1983), Hayashi (1987), Ohmori *et al.* (1986), Kushner (1988), Kurachi and Nakamura (1989) and Morgan (1992). A set of selected integral (mainly experimental) CS is presented in fig. 2. At the end of this subsection we mention some measurements in disilane (Si_6H_6).

Total cross-sections have been measured in normalized experiments up to 12 eV by Wan *et al.* (1989) and up to 400 eV by Sueoka *et al.* (1994). These latter data supersede earlier measurements of Mori *et al.* (1985). Both laboratories used a guiding magnetic field; this leads to difficulties in determining the interaction length and normalization procedures were applied. In spite of this, the data of Wan *et al.* and Sueoka *et al.* are in good agreement each with other. The data of Sueoka *et al.* at high energies overlap also very well with the absolute measurements of Zecca *et al.* (1992). Absolute data of Szmytkowski *et al.* (1997) coincide at 100 eV with these two determinations but at 250 eV are 10% lower, probably due to a higher angular resolution error.

TCS exhibits a Ramsauer minimum of about $1.1 \cdot 10^{-20}\,\mathrm{m}^2$ ($\pm 20\%$ error bar) at about 0.25 eV (Wan *et al.* 1989). This minimum coincides with the minimum in momentum transfer CS as given by Kurachi and Nakamura (1989). We note that this is in contradiction with the indications of the modified effective range theory (formula (9), Part I). The minimum in the experimental TCS (Wan *et al.* 1989) is deeper than the theoretical value given by Sun *et al.* (1992) and Jain and Thompson (1991) but shallower than the theoretical value by Yuan (1988). TCS reaches a maximum of $56.6 \cdot 10^{-20}\,\mathrm{m}^2$ at 2.9 eV (Szmytkowski *et al.* 1997).

Swarm. Only a few measurements of electron drift velocities (Cottrell and Walker 1965, Pollock 1968) and characteristic energies (Millican and Walker 1987) exist and this is one of the reasons for strong discrepancies in the derived momentum transfer CS. While Kurachi and Nakamura (1989), Ohmori *et al.* (1986) and Morgan (1992) derived a Townsend minimum of about $1 \cdot 10^{-20}\,\mathrm{m}^2$ depth, Mathieson *et al.* (1987) and Hayashi (1987) reported a lower value, of about $0.3\text{–}0.4 \cdot 10^{-20}\,\mathrm{m}^2$. On the other hand, the data of Mathieson *et al.* (1987) are higher than other swarm analysis (Kurachi and Nakamura 1989) or theories (Yuan 1989, Sun *et al.* 1992) at energies below 0.1 eV. A scattering length of $-4.2a_0$ was calculated by Jain and Thompson (1991).

Elastic cross-sections were studied between 1.8 eV and 100 eV by Tanaka *et al.* (1990a). The integral elastic CS reaches a maximum of $49.0 \cdot 10^{-20}\,\mathrm{m}^2$ at 7.5 eV, in analogy to CH_4. This value is somewhat higher than TCS at this energy but the error remains within the uncertainty of Tanaka's *et al.* measurement. Between 40 eV and 100 eV the decrease of the integral elastic CS with energy is steeper than the E^{-1} dependence (see Part I, formulas (10–11)). This suggests that the value given by Tanaka *et al.* at 100 eV could be slightly (15–20%) underestimated, as was the case of CH_4.

We note some disagreement between different theories in determining not only the absolute value but also the position of the maximum in integral elastic CS. While the calculation of Gianturco *et al.* (1992) and Winstead *et al.* (1994) placed this maximum at about 5–7 eV in agreement with the experiment (Tanaka *et al.* 1990a), other theories (Tossell and Davenport 1984, Gianturco *et al.* 1987, Yuan 1988, 1989, Sun *et al.* 1992, Winstead *et al.* 1991, Bettega *et al.* 1993) localize it at 3–4 eV.

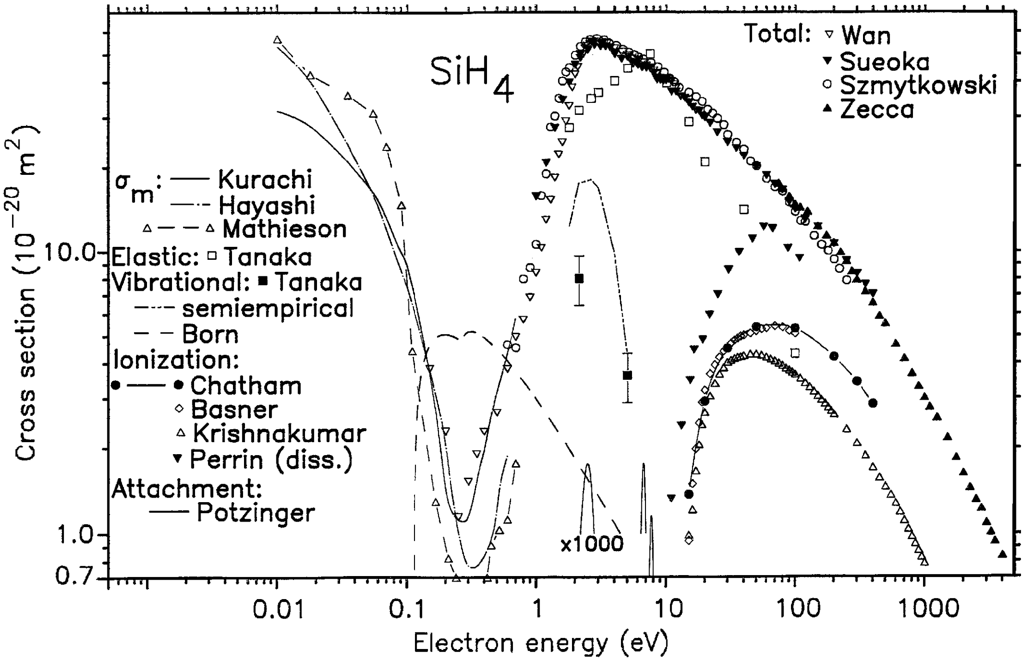

Fig. 2. – Integral cross-sections for electron scattering on SiH_4. *Total*: normalized of Wan *et al.* (1989); normalized of Sueoka *et al.* (1994); absolute of Szmytkowski *et al.* (1997); absolute of Zecca *et al.* (1992). *Momentum transfer*: Kurachi and Nakamura (1989); Mathieson *et al.* (1987); Hayashi (1987). *Elastic*: absolute of Tanaka *et al.* (1990a). *Vibrational*: integrated (this work) DCS of Tanaka *et al.* (1990a); semiempirical, difference between TCS of Sueoka *et al.* (1994) and elastic CS of Tanaka *et al.* (1990a); Born approximation, for direct excitation (see chapter 1.4 Part I). *Ionization*: Chatham *et al.* (1984); Basner *et al.* (1997); Krishnakumar and Srivastava (1995); diss., ionization + dissociation into neutrals of Perrin *et al.* (1982). *Dissociative attachment*: Potzinger and Lampe (1969), multiplied by a factor 1000, apart from the value at 2.5 eV which is arbitrarily chosen, for illustration purposes.

The shape of elastic DCS at the lowest energies measured by Tanaka *et al.* (1990a) resembles a *d*-wave pattern, see fig. 3 for DCS at 2.15 eV. DCS becomes forward-centered just above 5 eV (see fig. 3 for 7.5 eV).

Vibrational excitation CS at near-to-threshold energies can be evaluated from Born approximation (eq. (15), Part I). The vibrational thresholds in SiH_4 for infrared-active modes ν_3 (0.271 eV) and ν_4 (0.113 eV) are lower than the respective thresholds in CH_4 while the dipole transition moments (Bishop and Cheung 1982) are higher. The direct vibrational excitation CS, evaluated from these data (present work), reaches its maximum at about 0.4 eV (see fig. 2) and is higher by a factor of 20 compared to that in CH_4.

A rise in the vibrational excitation was observed between 1.7 eV and 3.0 eV (Tronc *et al.* 1989, Tanaka *et al.* 1990a). Energy loss spectra (Tronc *et al.* 1989) and DCS (Tanaka *et al.* 1990a) indicate the presence of a T_2 shape resonance in the *d*-wave channel at about 2 eV. A rough estimate (present work) of the integral vibrational excitation CS from differential measurements (Tanaka *et al.* 1990a) gives values of $8.0 \cdot 10^{-20}\,\mathrm{m}^2$ and $3.6 \cdot 10^{-20}\,\mathrm{m}^2$ at 2.15 eV and 5 eV, respectively. The intensity of the $\nu_2 + \nu_4$ unresolved excitation is two times more that of the $\nu_1 + \nu_3$ modes at these energies. Similarly, at

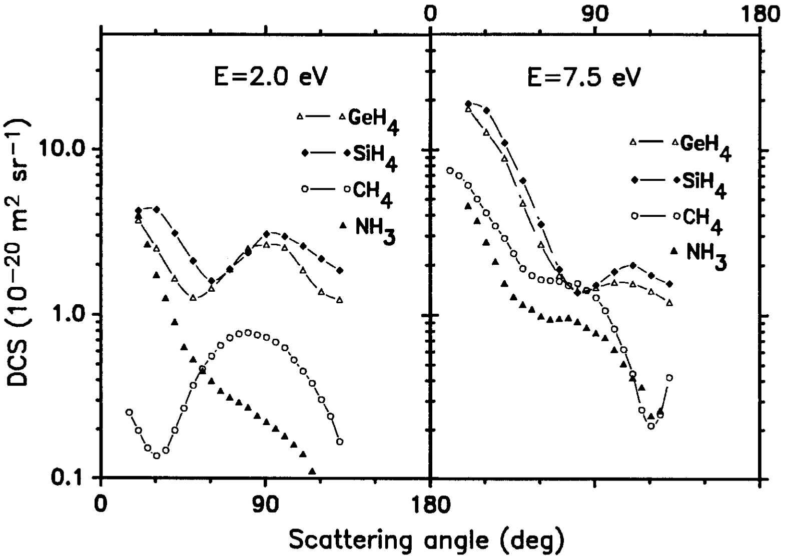

Fig. 3. – Elastic differential cross-sections for electron scattering on CH_4, SiH_4, GeH_4 and NH_3 at 2.0 eV (2.15 eV for SiH_4) and 7.5 eV electron energy. CH_4 data, Boesten and Tanaka (1991); SiH_4, Tanaka *et al.* (1990a); GeH_4, Dillon *et al.* (1993). 5th-order polynomial fits are drawn for eye-guiding only. NH_3, Alle *et al.* (1992).

20 eV and 30° scattering angle the $\nu_{1,3}$ mode dominates over the $\nu_{2,4}$ mode (Tronc *et al.* 1989). In fig. 2 as "semiempirical" data we present the difference between TCS of Sueoka *et al.* (1994) and elastic CS of Tanaka *et al.* (1990a). These values are in a rough agreement with the integrated experimental vibrational CS of Tanaka *et al.* (1990a).

Rotational excitation CS according to the theory of Jain (1991) is one order of magnitude higher than in CH_4 at 1 eV and almost equal to CH_4 at 15 eV. Integral CS for excitation to the lowest allowed states $J = 3$ and $J = 4$, averaged for 300 K gas temperature, amounts at 5 eV to about $0.7 \cdot 10^{-20}\,\mathrm{m}^2$ and $0.5 \cdot 10^{-20}\,\mathrm{m}^2$, respectively.

Electronic excitation spectra have been studied by Dillon *et al.* (1985) at 200 eV collision energy, by Tanaka *et al.* (1990b) at 20–100 eV energies, by Tronc *et al.* (1989) at 25 eV and at near-to-threshold energies by Curtis and Walker (1989). Theoretical estimation of the first singlet and triplet $(2t_2 \to 4sa_1)\ ^{1,3}T_2$ excitation CS has been done by Winstead *et al.* (1994). Their calculations agree pretty well with the experiment as far as regards the experimental elastic CS (Winstead and McKoy 1990); this gives also some credibility to the electronic excitation evaluations. Winstead *et al.* (1994) predicted at 15 eV equal contributions (about 3% each) of the two T_2 excitations to TCS.

Calculations of Winstead *et al.* (1994) indicated the importance of the excitation to the optically allowed $4sa_1{}^1T_2$ state (with threshold at 10.26 eV) at high collision energies: maximum of the integral CS for this state of $0.8 \cdot 10^{-20}\,\mathrm{m}^2$ is reached at 40 eV. The $4sa_1{}^3T_2$-state electron excitation CS (threshold at 10.26 eV) falls quickly with energy above 15 eV (Bettega *et al.* 1998). The calculations (Winstead *et al.* 1994) suggest also that all electronic excitation lead to dissociation of the molecule. Other states seen both at low and high collision energies were extensively discussed by Curtis and Walker (1989) and Dillon *et al.* (1985), respectively.

Forward electron scattering CS for (7.5–350 eV) energy loss were studied by Cooper *et al.* (1995); the corresponding photo-absorption CS reaches a maximum of about $1.1 \cdot 10^{-20}\,\mathrm{m}^2$ at 10.7 eV.

Ionization CS as measured by Chatham *et al.* (1984) and Basner *et al.* (1997) are, on the average, 20% higher than those of Krishnakumar and Srivastava (1995). This discrepancy is probably due to the different normalization procedures chosen (normalization to the Ar ionization cross-sections and by relative flow technique, respectively). No stable $SiH_4{}^+$ ions were observed (Potzinger and Lampe 1969, Morisson and Traeger 1973, Haaland 1990). Presence of $SiH_4{}^+$ ions at a few per cent level was observed only in photoionization studies (Berkowitz *et al.* 1987) near the threshold (11.0 eV). At 100 eV branching ratios for $SiH_3{}^+$, $SiH_2{}^+$, SiH^+, Si^+, H^+ and $H_2{}^+$ amount to 32%, 42%, 10%, 8.5%, 7%, 0.5%, respectively (Krishnakumar and Srivastava 1995, see also Haaland 1990). Ionization of SiD_x ($x = 1$–3) radicals was studied by Tarnovsky *et al.* (1996).

Dissociation cross-section. Combined dissociation into neutral and ionized fragments has been studied by Perrin *et al.* (1982) in a plasma experiment. Differently than for CH_4, due to the fact that the parent $SiH_4{}^+$ ions are not stable, the dissociation into neutrals can be evaluated by subtracting the ionization CS from Perrin *et al.*'s combined cross-section (see table II). The neutral dissociation is the dominant inelastic channel between its threshold (8 eV) and 15 eV. Between 20–100 eV the contributions from ionization and from neutral fragment dissociations are of the same order (about 1/3 of TCS, each). The cross-sections of $1.0 \pm 0.5 \cdot 10^{-20}\,\mathrm{m}^2$ for formation of the SiH free radical have been measured at 40–70 eV impact energy (Schmitt *et al.* 1984).

The studies of Perkins *et al.* (1979) at 8.4 eV photon energy showed that SiH_2 is the dominant (83%) and SiH_3 is the secondary photolysis fragment, in some analogy with the ionization branching ratio. At 100 eV, the neutral-dissociation CS in SiH_4 is about double than that of CH_4. Optical emission measurements (Perrin and Aarts 1983, Tsurubuchi *et al.* 1991, 1992) indicate that only a small part (3%) of the dissociated fragments is created in excited electronically states, with Balmer H_α and SiH ($A\,{}^2\Delta \rightarrow X\,{}^2\Pi$) lines predominant.

Dissociative attachment measurements (Potzinger and Lampe 1969) indicate the presence of several resonance processes between 2.5 eV and 20 eV. At 2.5 eV only the $SiH_3{}^-$ and $SiH_2{}^-$ ions have been observed while between 6.7–8.5 eV also the SiH^- and Si^- fragments. The $SiH_3{}^-$ and $SiH_2{}^-$ cross-sections reach maxima of $0.18 \cdot 10^{-22}\,\mathrm{m}^2$ at 6.7 eV and of $0.07 \cdot 10^{-22}\,\mathrm{m}^2$ at 7.7 eV, respectively. Due to a poor transmission function, no absolute value was determined for the 2.5 ± 0.3 eV peak; in fig. 2 we give an arbitrary value for illustration purposes only. Negative ions $SiH_n{}^-$ ($n = 0$–3) were also observed at about 8.5 eV (Curtis and Walker 1989).

Resonances. Tanaka *et al.* (1990a) and Tronc *et al.* (1989) from vibrational excitation measurements deduced the existence of a T_2 ($l = 2$) shape resonance at about 2.1 eV, in analogy with the 8 eV shape resonance in CH_4 and in agreement with the calculation of Tossel and Davenport (1984). However, from a comparison between fig. 1 and fig. 2 some fundamental differences can be noticed for these two targets. The peaks of TCS and elastic CS coincide in CH_4 and the vibrational contribution at the maximum is small. In SiH_4 the maximum of the elastic CS is at about the same (7.5 eV) energy that for CH_4 but the maximum of TCS is shifted to a lower (2.9 eV) position where the vibrational excitation CS is, roughly, 20% of TCS. Electronic attachment processes (Potzinger and Lampe 1969) were observed both at the elastic and total CS maxima in SiH_4.

Sum check indicates a generally good agreement between partial CS in the 5–15 eV energy range. At 2.15 eV, vibrational excitation CS, as evaluated in the present work,

TABLE II. – *Integral cross-sections for electron scattering on silane (in* 10^{-20} *m*^{2} *units).*

Energy	Elastic	Vibrational	Ionization	Overall dissociation	Neutral dissociation	Summed	Total
1.8	27.5 T						39 S
2.15	31.6 T**	8 T1				39.6	48.9 S
5.0	44.4 T	3.6 T1				48.0	48.7 S
10	39.4 T			0.8 P	(0.8)*	40.2	40.3 S
15	28.7 T		(1.37) C	3.2 P	(1.8)*	31.9	33.6 S
20	20.7 T		(2.92) C	5.5 P	(2.6)*	26.2	29.8 S
30	16.5 T**		(4.50) C	8.3 P	(3.8)*	24.8	24.4 S
50	10.5 T		(5.36) C	11.6 P	(6.2)*	22.1	20.0 S
100	4.3 T		(5.30) C	9.8 P	(4.5)*	14.1	14.1 S 14.7 Z

* - Dissociation into neutrals evaluated (present work) from difference between total (neutral + ionic) dissociation (Perrin *et al.* 1982) and ionization CS (Chatham *et al.* 1984).
** - Interpolated values.
( ) - Values not used in the sum.
C - Chatham *et al.* (1984).
P - Perrin *et al.* (1982), read from figure.
S - Sueoka *et al.* (1994).
T - Tanaka *et al.* (1990a).
T1 - Tanaka *et al.* (1990a), as given in their figure and integrated (present work), ±20% possible extrapolation error.
Z - Zecca *et al.* (1992).

seems to be slightly underestimated, probably due to uncertainties in extrapolating experimental DCS (Tanaka *et al.* 1990a) towards small angles. On the other hand, the integral elastic CS (Tanaka *et al.* 1990a) at 7.5 eV is larger than the TCS measurement (Szmytkowski *et al.* 1997). The flow normalization procedure used by Tanaka *et al.* could explain a proportional shift of the entire measured curve but cannot give account of noise in isolated points. We note that the uncertainty on the CS values at 7.5 and 10 eV reflects in uncertainty in the location of the elastic CS maximum.

At 100 eV the most probable partitioning between elastic, ionization and neutral-dissociation channels is 4.9, 5.3 and $4.5 \cdot 10^{-20}$ m^2, respectively. The extension of the elastic CS measurements above 100 eV and of the TCS measurements below 1 eV would be of interest. New evaluations of swarm parameters are also desirable.

Disilane (Si_2H_6). Disilane is the silicon-based analog of ethane. Elastic and vibrational excitation CS were reported at 2–100 eV by Dillon *et al.* (1994). The integral elastic CS shows a large and broad maximum centered at 4 eV. The CS values rise from $49 \cdot 10^{-20}$ m^2 at 2 eV to $83 \cdot 10^{-20}$ m^2 at 4–5 eV, falling to $9.6 \cdot 10^{-20}$ m^2 at 100 eV. DCS at all the energies studied are rather uniform in angle, apart from 100 eV where a shallow dip appears at 60° and a minimum at 110°.

Enhancement of vibrational excitation at 2 eV was observed, suggesting the trapping of the incident electron into a valence Si-H antibonding orbital (Dillon *et al.* 1994). At 2 eV DCS for the 0.26 eV energy-loss process is uniform in angle while that for the 0.11 eV process shows a minimum at 60° and a maximum at 105°. The position of the resonance in Si_2H_6 is slightly shifted to a lower energy compared to SiH_4. Energy-loss spectra in the region of valence excitations were reported by Dillon *et al.* (1988).

Ionization CS for Si_2H_6 up to 300 eV were reported by Chatham *et al.* (1984). At 100 eV the total ionization CS in Si_2H_6 ($9.4 \cdot 10^{-20}\,\mathrm{m}^2$) is by a factor 1.75 higher than in SiH_4. Both the parent $Si_2H_6{}^+$ (11%) as well as the fragment ions were observed, with $Si_2H_4{}^+$ (25%) and $Si_2H_2{}^+$ (15%) dominating. Ionization and dissociation of Si_2H_6 was studied in plasma experiment by Perrin *et al.* (1982) and Perrin and Aarts (1983). Use of Si_2H_6 and Ge_2H_6 for the epitaxial growth of Si and Ge films was studied by Li *et al.* (1996).

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2˙3. *Germane* (GeH_4). – Electron scattering in germane (GeH_4), in spite of its great importance for understanding discharge mechanisms in processes of plasma deposition and doping in semiconductor industries (see for example Li *et al.* 1996) received, as silane, little experimental attention. Germane is particularly similar to silane as far as the bond length (1.53 Å *vs.* 1.48 Å) and the polarizability (about 5.2 $Å^3$ *vs.* 4.5 $Å^3$) are concerned. The polarizability value for GeH_4 is an estimate made by the present authors from polarizability values for $GeCl_4$ and GeH_3Cl from (Weast 1986).

Total cross-sections. GeH_4 TCS has been recently measured by Możejko *et al.* (1996) between 0.75 eV and 200 eV. The maximum of TCS amounts to $58.8 \cdot 10^{-20}\,m^2$ at 3.8 eV. This value is slightly higher than the maximum of the TCS in SiH_4. March *et al.* (1994) suggested that this difference reflects the difference in the bond length of SiH_4 and GeH_4. The data of Możejko *et al.* (1996) are, in the overlap range between 70 eV and 200 eV, about 10% lower than the intermediate-energy absolute measurements of Karwasz (1995); the reason for this discrepancy is not clear. The optical-model TCS of Baluja *et al.* (1992) are slightly lower than the experimental TCS at intermediate energies. The difference can be due to the theoretical underestimation of electronic excitation and/or dissociation into neutrals.

TCS for GeH_4 almost coincides with TCS for SiH_4 between 150 eV and 300 eV but falls slower with energy in the 300–4000 eV range (Karwasz 1995). At high energies the SiH_4 and GeH_4 TCS approach the values of Ar and Kr, respectively. However, no complete merging was observed up to 3000 eV (Karwasz 1995).

Elastic cross-sections. Measurements of the elastic CS in the 1–100 eV energy range (Dillon *et al.* 1993) indicate the existence of a Ramsuaer minimum below 1 eV. The elastic CS reaches a maximum ($45.5 \cdot 10^{-20}\,m^2$) close to the one in SiH_4 and at an energy (5 eV) somewhat intermediate between those corresponding to the maximum of elastic CS in CH_4 and SiH_4 (see subsect. **2**˙2). At 7.5–10 eV the elastic CS of Dillon is about 10% lower than the TCS (Możejko *et al.* 1996); this difference remains within declared uncertainty of the relative-flow normalization procedure (Dillon *et al.* 1993). The continuum multiple scattering theory (Dillon *et al.* 1993) is somewhat closer to the TCS than the measurement of the same authors.

Different theoretical calculations agree on the existence of a resonant broad peak around 5 eV, but diverge in the prediction of the absolute values of the CS. Bettega *et al.* (1993) pointed out that SiH_4 and GeH_4 integral elastic CS practically coincide in the 1–20 eV energy range. On the other hand, Winstead *et al.* (1991, 1992) and Varella *et al.* (1997) indicated a somewhat lower elastic CS in GeH_4 than in SiH_4 between 5 and 20 eV. The model with a spherical potential obtained from multicenter Hartee-Fock wave-functions (Jain *et al.* 1991, Kumar *et al.* 1995) overestimates the experimental elastic CS both at the maximum and at 100 eV. The same model with the inclusion of an absorption potential (Baluja *et al.* 1992) agrees well with the experimental elastic CS at 100 eV, see fig. 4. Elastic DCS for SiH_4 (Tanaka *et al.* 1990) and GeH_4 (Dillon *et al.* 1993) exhibit similar amplitudes and angular distributions in the whole 2–100 eV energy range (see fig. 3).

Swarm parameters (drift velocity and longitudinal diffusion) coefficient were measured between 0.05 and $50 \cdot 10^{-21}\,Vm^2$ for GeH_4-Ar mixtures by Soejima and Nakamura (1993). The derived momentum transfer CS merges very well at 1 eV with TCS measurements (Możejko *et al.* 1996). Soejima and Nakamura (1993) found a rather shallow Ramsauer-Townsend minimum of $3 \cdot 10^{-20}\,m^2$ at 0.3 eV. Note that the analysis of SiH_4 data from the same group gave also a Ramsauer-Townsend minimum shallower than the results of other authors, see subsect. **2**˙2.

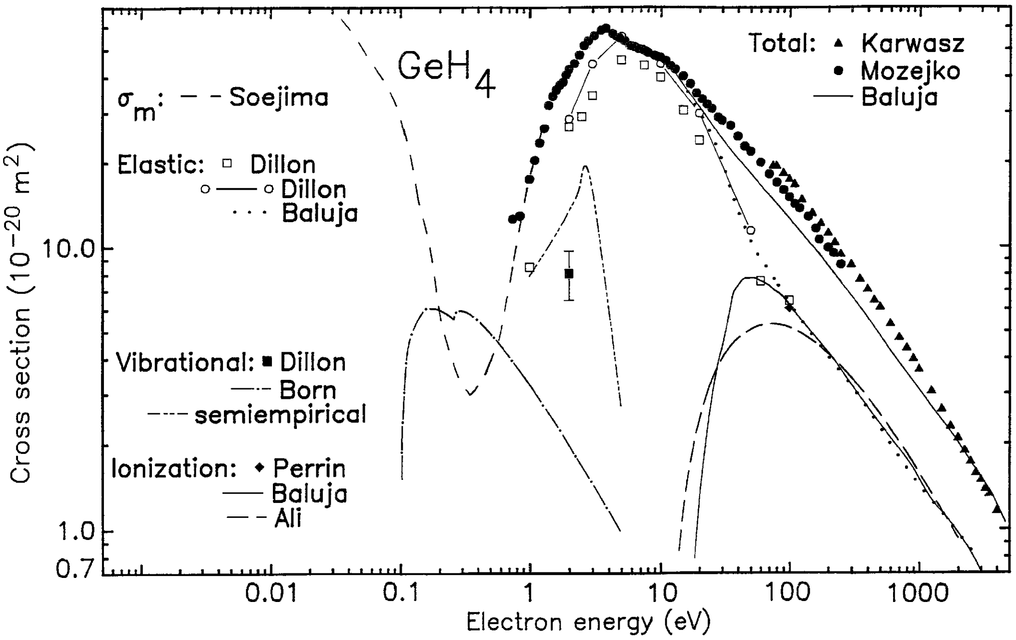

Fig. 4. – Integral cross-sections for electron scattering on GeH_4. *Total*: Możejko *et al.* (1996), absolute; Karwasz (1995), absolute; Baluja *et al.* (1992), optical model. *Elastic*: squares, experimental Dillon *et al.* (1993); open circles with line, theoretical Dillon *et al.* (1993); Baluja *et al.* (1992), optical model. *Momentum transfer*: Soejima and Nakamura (1993). *Vibrational*: Dillon, rough estimate (present work) by integrating DCS of Dillon *et al.* (1993); Born approximation (Part I, eq. (15)); semiempirical, difference between TCS (Możejko *et al.* 1992) and experimental elastic CS (Dillon *et al.* 1993). *Ionization*: 100 eV, plasma experiment of Perrin and Aarts (1983); optical model, Baluja *et al.* (1992); semiempirical model, Ali *et al.* (1997).

Vibrational excitation. DCS for vibrational excitations have been reported by Dillon *et al.* (1993). An enhancement of the vibration excitation around 2.5 eV, indicating the presence of a resonant state, was observed at different scattering angles. Angular distributions for the unresolved bending ($\nu_2 + \nu_4$) as well as for the stretching ($\nu_1 + \nu_3$) modes in GeH_4 at 2.0 eV exhibit a dominant d-wave character, in analogy with the 2.15 eV excitation in SiH_4. Excitation of the $\nu_2 + \nu_4$ mode dominates over $\nu_1 + \nu_3$, by a factor of two approximately. A rough estimation—made in the present work—of the integral CS from differential data (Dillon *et al.* 1993) gives $8 \cdot 10^{-20}\,\mathrm{m}^2$ at 2 eV, see the full square with error bar in fig. 4.

The direct (non-resonant) vibrational CS has been evaluated by the Born approximation with dipole transition moments from Bishop and Cheung (1982). The vibrational CS values obtained in this way for GeH_4 and SiH_4 are similar. The maximum for the ($\nu_2 + \nu_4$) mode ($6.0 \cdot 10^{-20}\,\mathrm{m}^2$ at 0.17 eV) is lower than the swarm-determined value of about $11 \cdot 10^{-20}\,\mathrm{m}^2$ (Soejima and Nakamura 1993). In fig. 4 semiempirical values obtained as the difference betweeen TCS of Możejko *et al.* (1996) and experimental elastic CS of Dillon *et al.* (1993) are also shown.

Rotational excitation—according to the calculation of Varella *et al.* (1997)—is slightly more effective in GeH_4 than in SiH_4: it falls from $5.9 \cdot 10^{-20}\,\mathrm{m}^2$ and $4.9 \cdot 10^{-20}\,\mathrm{m}^2$ at 7.5 eV to $1.6 \cdot 10^{-20}\,\mathrm{m}^2$ and $0.8 \cdot 10^{-20}\,\mathrm{m}^2$ at 30 eV for excitations to the $J' = 3$ and $J' = 4$ states, respectively.

Electronic excitation and dissociation. Energy loss spectra in the region of valence and Rydberg excitations were measured at 200 eV by Dillon *et al.* (1985)—similarities with SiH_4 are noticeable. At 20 eV collision energy the excitation of the lowest spin-forbidden $3t_2(^1A_1) \rightarrow 5s(^3T_2)$ transition dominates, while at 100 eV the excitation of the optically allowed states dominates (Dillon *et al.* 1993).

The cross-section for optical emission at 100 eV (Perrin and Aarts 1983) in GeH_4 has a similar value ($0.15 \cdot 10^{-20}$ m^2) to that in SiH_4 ($0.16 \cdot 10^{-20}$ m^2). Perrin and Aarts show that for the series CH_4, SiH_4, GeH_4, the relative contribution of molecular excited fragments to the overall UV-visible emission decreases while the contribution of the excited central atom (or its ions) increases. In the case of GeH_4, the emission from atomic H and Ge fragments contribute 45% each of the overall signal in the 230–700 nm wavelength range.

Optical absorption in the ultraviolet region was studied by Mitchell *et al.* (1987) and Itoh *et al.* (1986). A maximum of $1.07 \cdot 10^{-20}$ m^2 in the photoabsorption CS at 10.4 eV, almost coincident with the maximum for SiH_4 ($1.14 \cdot 10^{-20}$ m^2), has been reported (Itoh *et al.*). X-ray photoabsorption spectra for excitation of the Ge $2p$ level were studied by Guillot *et al.* (1996).

Dissociation into neutrals. The value of $19 \cdot 10^{-20}$ m^2 at 100 eV for dissociation into neutral fragments, as evaluated from plasma experiments (Perrin and Aarts 1983) is not congruent with TCS measurements (Karwasz 1995). Using an analogy with CH_4 and SiH_4, an upper limit of about $5 \cdot 10^{-20}$ m^2 can be set for GeH_4 at 100 eV.

Ionization cross-sections. Very close values of ionization CS for GeH_4 and SiH_4 have been obtained in plasma experiments (Perrin and Aarts 1983) at 100 eV (5.0 *vs.* $6.0 \cdot 10^{-20}$ m^2, for SiH_4 and GeH_4, respectively). This experimental ionization CS in GeH_4 agrees well with the absorption part of TCS calculated from optical model (Baluja *et al.* 1992) and with a modified binary-encounter semiempirical model for ionization (Ali *et al.* 1997).

Ionization branching ratios are similar for SiH_4 and GeH_4 molecules. No stable parent ions ${GeH_4}^+$ were observed; ${GeH_3}^+$ and ${GeH_2}^+$ ions amount respectively to 35% and 37% of the total yield (Perrin and Aarts 1983). These relative proportions are similar to those observed in photoionization studies—a very weak ${GeH_4}^+$ signal was observed only near to the photoionization threshold (Ruscic *et al.* 1990).

Sum check is presented in table III. At 2 eV the sum of elastic CS of Dillon *et al.* (1993) and the present evaluation of the vibrational CS from the experiment of Dillon *et al.* agrees with the TCS (Możejko *et al.* 1996) within the combined uncertainty for both experiments (15–20% for elastic DCS, 30% for vibrational CS and 3–7% for TCS). A similar, rather good agreement is seen at 5 eV where we have estimated the vibrational CS from the Born approximation (eq. (15), Part I). The Born approximation clearly underestimates the vibrational CS at 3.0 eV. At 10–100 eV the missing part in the summed CS probably accounts of the electronic excitation.

Partitioning of TCS for tetrahedral molecules and noble gases. The similarity of the partitioning scheme at 100 eV among the three spherical-like hydrides CH_4, SiH_4 and GeH_4 has been stressed (Karwasz 1995). In detail, the ionization for all three gases amounts to about 35–40% of TCS (the spread depends on the choice of the experimental data set). On the other hand, the elastic CS at 100 eV is almost the same for these hydrides and the isoelectronic noble gases CH_4-Ne, SiH_4-Ar, GeH_4-Kr (Karwasz 1995). Note, however, that this last conclusion was based on elastic cross-sections for CH_4, SiH_4 and GeH_4 from Tanaka's group. As follows from the present review it is plausible that, at least for CH_4, Tanaka and co-worker's results are somewhat underestimated at 100 eV. More measurements of elastic CS at 100 eV and above would be of interest.

Table III. – *Integral cross-sections for electron scattering on germane (in* 10^{-20} m^2 *units).*

Energy(eV)	Elastic	Vibrational	Ionization	Summed	Total
1.0	8.4 D				17.3 M
2.0	26.4 D	8.0 D1		34.4	42.3 M
2.5	28.8 D				49.3 M*
3.0	34.1 D	1.5 B		35.6	53.9 M*
5.0	45.5 D	0.97 B		46.5	53.8 M*
7.5	43.4 D				49.1 M*
10	39.4 D				46.5 M
15	30.1 D		1.14 A	31.2	39.9 M
20	23.6 D		2.38 A	26.0	34.0 M
60	7.47 D		5.22 A	12.7	19.8 M
100	6.36 D		5.12 A	11.5	14.9 M

* - Interpolated value.
A - Ali *et al.* (1997), semiempirical.
B - Born approximation (eq. (15), Part I), present work.
D - Dillon *et al.* (1993).
D1 - Present evaluation from experimental DCS (Dillon *et al.* 1993).
M - Możejko *et al.* (1996).

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3. – Hydrides

In this section electron scattering on small (few atoms) hydrides, different from tetrahedral ones, is discussed. All these targets possess rather strong dipole moments, which reflects in low-energy TCS, rising towards zero energy. The polar character of these molecules causes also bigger experimental uncertainties due to angular resolution in total and elastic CS measurements.

3˙1. *Ammonia* (NH_3). – Ammonia molecules are present in the interstellar medium; this gas is preferentially used as a source of nitrogen atoms in thin films fabrication by plasma deposition techniques. Analogies between total electron-scattering cross-sections for the first row hydrides CH_4, NH_3, H_2O were already searched for in the pioneer investigations (Brüche 1929). NH_3, due to its pyramidal geometry possesses a rather strong dipole moment of 1.47 D and a smaller polarizability (2.26 $Å^3$) compared to CH_4 (2.59 $Å^3$). Integral cross-sections for NH_3 are shown in fig. 5.

Total cross-sections were measured in absolute experiments by Szmytkowski *et al.* (1989) at low (1–100 eV) and by Zecca *et al.* (1992) and García and Manero (1996) at high energies (75–4000 eV and 300–5000 eV, respectively). Sueoka *et al.* (1987) have obtained normalized TCS in an energy range (1–400 eV) that overlaps with the above experiments. While the data of Szmytkowski *et al.* and of Zecca *et al.* merge well at 100 eV, the results of Suoeka *et al.* are systematically lower above 4 eV, with a difference as big as 25% at the cross-section maximum. We remind that for CH_4 the data of Sueoka and Mori (1986) were also lower in the maximum than other measurements (Jones 1985, Zecca *et al.* 1991, Kanik *et al.* 1992). Results of Brüche (1929) are lower than those of Szmytkowski *et al.* (1989) by 13% at the maximum.

The two high-energy data sets (Zecca *et al.* 1992 and García and Manero 1996) coincide up to 1000 eV but diverge as much as 28% at 4000 eV. Part of this discrepancy can be attribuited to the poor discrimination of inelastically scattered electrons in the apparatus of Zecca *et al.* (1992); however, the relative difference between the two experiments is lower in NH_3 than in CH_4, in spite of the permanent dipole of ammonia. Both the data of Zecca *et al.* (1992) and those of García and Manero (1996) fall between the two alternative optical-potential models of Jain (1988), see fig. 5.

Swarm measurements. Due to the relatively large dipole moment of NH_3, the low-energy momentum transfer CS rises quickly with decreasing energy. Analysis of Hayashi (1992), see also Shimamura (1989), practically coincide with the early swarm determination of Pack *et al.* (1962). (In fig. 5 for the data of Pack *et al.* their two-parameters fit containing the $1/(E^{1/2} + E^{3/2})$ term was taken.) The swarm data also agree well with the thermal-energies determination of Tice and Kivelson (1967) obtained by a cyclotron-resonance technique. The analysis of swarm data in NH_3 is difficult, due to the expected high CS for rotational de- and excitation at low energies.

At sub-thermal energies momentum transfer (and rotational excitation) CS were studied by Rydberg atoms techniques. The linear dependence of the Rydberg atoms quenching rate on their principal quantum number n suggests an $1/E$ energy dependence of the CS (Ling *et al.* 1993, Kellert *et al.* 1980, Petitjean *et al.* 1986). Experiments with very high number $n = 400$ potassium Rydberg atoms yielded the ionization rate constant of about $2 \cdot 10^{-6}\,\mathrm{cm^3 s^{-1}}$ (Ling *et al.* 1993). The relation between the quantum number n and the corresponding collision energy, and between the rate constant and the electron-scattering CS is not straightforward. Roughly, the measurement of Ling *et al.* (1993) indicate CS of the order of $10^{-16}\,\mathrm{m}^2$ at 0.1 meV (see also Petitjean *et al.* 1986).

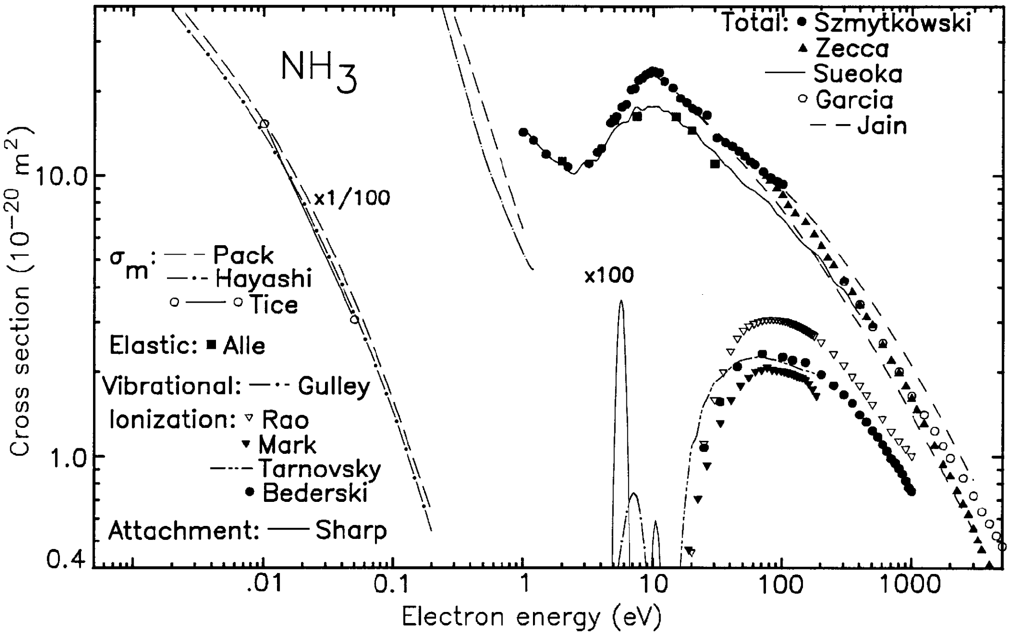

Fig. 5. – Integral cross-sections for electron scattering on NH_3. *Total*: Szmytkowski *et al.* (1989) absolute; Zecca *et al.* (1992) absolute; García and Manero (1996) absolute; Sueoka *et al.* (1987) normalized; Jain (1988) optical model, upper curve—polarized orbitals absorption potential, lower curve—non-polarized orbitals; data of Brüche (1929) are not shown for clarity. *Elastic*: Alle *et al.* (1992), absolute. *Momentum transfer*: Pack *et al.* (1962), "σ_1" model; Hayashi (1992) swarm compilation; Tice and Kivelson (1967) from cyclotron resonance. *Vibrational*: Gulley *et al.* (1992), $v_{1,3}$ unresolved mode. *Electron attachment*: Sharp and Dowell (1969). *Ionization*: Märk *et al.* (1977), Rao and Srivastava (1991); Tarnovsky *et al.* (1997); Bederski *et al.* (1980).

Elastic cross-sections (rotationally inelastic) have been extensively measured by Alle *et al.* (1992) for scattering angles from 20° to 120° at energies from 2 to 30 eV and by Ben Arfa and Tronc (1988) at 7.5 eV. DCS at 2 eV and 7.5 eV are compared in fig. 3 to those in CH_4. At 2 eV the NH_3 DCS is forward centered; it changes by one order of magnitude between 20° and 60° (Alle *et al.* 1992). This should be attributed to the direct rotational excitation. On the other hand, DCS at 2 eV, 60°–120° is lower in NH_3 than in CH_4, see fig. 3.

At 7.5 eV the DCS of Ben Arfa and Tronc (1988) are in good agreement with those of Alle *et al.*, 1992) from 30° to 120°. DCS in NH_3 and CH_4 have a similar shape at this energy but the NH_3 DCS are lower by a factor of about 1.5, see fig. 3. The integral cross-sections in NH_3 given by Alle *et al.* (1992) at all energies almost coincide with the TCS of Sueoka *et al.* (1987) and at 5–20 eV are in good agreement with the calculations of Gianturco (1991) and Varella *et al.* (1999). The maximum of the integral elastic CS (Alle *et al.* 1992) occurs at the same energy, about 9 eV, as the maximum in TCS (Sueoka *et al.* 1987, Szmytkowski *et al.* 1989). Relative DCS at 25 eV and 50 eV have been reported by Furlan *et al.* (1990).

Forward (2°–10°) elastic DCS at 300, 400 and 500 eV were reported by Harshbarger *et al.* (1971) and Bromberg (1975). DCS for the momentum transfered K approaching zero

($K < 3$ a.u.) rises more quickly in NH_3 and H_2O than in non-polar molecules N_2, O_2 and noble gases (Bromberg 1975). DCS becomes energy-independent below $K = 0.8$ a.u., like in Ne, see fig. 2 in Part I. The near-to-zero angle DCS in NH_3 is higher than in H_2O, in spite of the smaller dipole moment and at $K = 0.2$ a.u. amounts to about $17 \cdot 10^{-20}\,m^2/sr$ compared to $14 \cdot 10^{-20}\,m^2$ in H_2O. On the other hand, for the momentum transfer larger than 6 a.u. the NH_3 DCS are lower than those in H_2O (Bromberg 1975).

Lahmam-Bennani *et al.* (1979) measured the zero-angle elastic DCS of $13.5 \cdot 10^{-20}\,m^2/sr$ at 35 keV. Differences between experimental near-to-zero DCS (Lahmam-Bennani *et al.*, 1979, 1980) and those predicted by an independent-atom model indicate the importance of electron-correlation effects in NH_3 molecule (Duguet *et al.* 1983, Breitenstein 1987).

Vibrational excitation in the region of the maximum of TCS was studied by Cvejanović *et al.* (1987), Ben Arfa and Tronc (1985, 1988), Ben Arfa *et al.* (1990) and Gulley *et al.* (1992). In all these measurements a large maximum of the $\nu_{1,3}$ (unresolved symmetric and asymmetric stretch) modes between 5 eV and 9 eV was observed. Angular distributions (Gulley *et al.* 1992) at 7.5 eV are d-wave like, indicating the decay of the ^2E shape resonance. The vibrational excitation (Gulley *et al.* 1992) contributes only to 4% of the TCS (Szmytkowski *et al.* 1989).

Between 12 and 50 eV no enhancement of vibrational excitations was observed (Furlan *et al.* 1990) indicating a direct (non-resonant) scattering mechanism. At 50 eV the ν_2 mode (out-of-plane symmetric deformation) is forward-peaked while the remaining modes are almost isotropic.

Rotational excitation, according to the theory (Gianturco 1991), amounts to 20% of TCS at 10 eV. Note, however, that this theory overestimates the rotational excitation at energies below 2 eV, where the theoretical rotational excitation exceeds the TCS. Swarm and Rydberg-atoms experiments point out on the importance of rotational de- and excitation processes at very low energies. According to the recent theory (Varella *et al.* 1999) the $00 \rightarrow 20$ rotational excitation reaches maximum at the same energy as the elastic CS (10 eV) while the $00 \rightarrow 01$ cross-section continues to rise towards low energies.

Electronic excitation spectra for optically allowed transitions have been studied by Lassettre *et al.* (1968), Harshbarger (1970, 1971), Harshbarger *et al.* (1971), Furlan *et al.* (1985) and for forbidden transitions by Furlan *et al.* (1987) and Cvejanović *et al.* (1992). Energy loss spectra for different collision energies (50 eV, Johnson and Lipsky 1977, Furlan *et al.* 1985; 300 eV, Harshbarger *et al.* 1971) show several overlapping electronic states with well-pronounced vibrational structures in the 5.5–11 eV energy loss range.

Forward-angle scattering of 35 keV electrons was studied by Lammam-Bennani *et al.* (1980). Absolute oscillator strengths (formula (16), Part I) have been obtained for excitation energies 5–200 eV by Wigth *et al.* (1977) and Burton *et al.* (1993). Two maxima in the derived photoabsorption CS, at 11.5 eV and 16 eV, the latter amounting to $0.33 \cdot 10^{-20}\,m^2$, were observed above the ionization threshold (Burton *et al.* 1983). Photoabsorption CS for lower states show well-resolved vibrational structures.

Optical emission investigations of atomic hydrogen Balmer series (Möhlmann and de Heer 1979, Sato *et al.* 1986, Kurepa *et al.* 1989, Tasić *et al.* 1989) in spite of some differences, indicate coherently an about 4-folds higher emission for NH_3 than for H_2. At 100 eV the Balmer H_α emission cross-section amounts to $3.8 \cdot 10^{-22}\,m^2$ (Kurepa *et al.* 1989). At 1000 eV its value $0.59 \cdot 10^{-22}\,m^2$ is an average of H_2O ($0.73 \cdot 10^{-20}\,m^2$) and CH_4 ($0.42 \cdot 10^{-20}\,m^2$) values (Möhlmann and de Heer 1979). CS at 100 eV for emission from excited NH radicals in $c(^1\Pi) \rightarrow a(^1\Delta)$ and $A(^3\Pi) \rightarrow X(^3\Sigma)$ bands are of the same order, about $2 \cdot 10^{-22}\,m^2$, of the Balmer H_α cross-section (Sato *et al.* 1986).

Ionization cross-sections has been recently measured by Syage (1992) and Tarnovsky *et al.* (1997) normalizing the data to Ar ionization CS and by Rao and Srivastava (1991, 1992) who used a relative-flow normalization method. Earlier data of Crowe and McConkey (1977) up to 300 eV and Bederski *et al.* (1980) up to 1000 eV are in good agreement being both normalized to the calculations of Jain and Khare (1976). Some discrepancies exist in determining the maximum value of the ionization CS at 80 eV. Rao and Srivastava (1991) obtained the highest value, $3.0 \cdot 10^{-20}\,\mathrm{m}^2$ while Märk *et al.* (1977) the lowest one, $2.0 \cdot 10^{-20}\,\mathrm{m}^2$. Three determinations, $2.2 \cdot 10^{-20}\,\mathrm{m}^2$ of Tarnovsky *et al.* (1997), $2.3 \cdot 10^{-20}\,\mathrm{m}^2$ of Syage (1992) and a single-point determination of $2.3 \cdot 10^{-20}\,\mathrm{m}^2$ at 85 eV (Sharp and Dowell 1969) coincide within the error bars. Lampe *et al.* (1957) in their single-energy study of numerous targets obtained a somewhat higher value $3.5 \cdot 10^{-20}\,\mathrm{m}^2$ for NH_3 at 75 eV.

It is worth remembering that H_2O measurements from the Innsbruck group (Märk and Egger 1976) were lower than other data, probably due to the incomplete detection of light ions (see the discussion for CCl_4 in Part III). On the other hand, the ionization CS for H_2O from the Pasadena group (Orient and Srivastava 1987) are the highest set of data, see subsect. **3**˙2. Note, finally, that two recent semiempirical approaches (Hwang *et al.* 1996, Deutsch *et al.* 1997) give ionization CS values close to the upper experimental limit (Djurić *et al.* 1981, Rao and Srivastava 1992). More absolute measurement would be desirable.

Branching ratios are almost constant between 100 and 1000 eV: about 50% of the ions are formed as parent ${NH_3}^+$ and 45% as the dissociated ${NH_2}^+$ ion (Bederski *et al.* 1980, Rao and Srivastava 1991). The H^+, N^+, NH^+ and ions are created with 1% to 3% branching ratios, roughly; the ${H_2}^+$ and ${NH_3}^{+2}$ with about 0.1%.

Dissociative attachment. Two peaks at 5.65 eV and at about 10 eV were observed in the dissociative attachment channel (Sharp and Dowell 1969, Compton *et al.* 1969). At the first peak, the dissociative attachment CS is about 0.2% of TCS. Both ${NH_2}^-$ and H^- ions were observed with approximately the same intensity. At the second peak, one order of magnitude smaller, the H^- ion dominates (Sharp and Dowell 1969). At the first peak a vibrational structure with spacing corresponding to ν_2 was observed (Stricklett and Burrow 1986, Tronc *et al.* 1988). The angular distribution of H^- ions produced at 5.7 eV is almost isotropic (Tronc *et al.* 1988).

Resonances. Two low-energy resonances in NH_3, a broad shape one and a Feshbach one, partially overlap in the 5–9 eV range. The first one, visible in the vibrational $\nu_{1,3}$ channel as a broad (almost 2 eV FWHM) hump (Ben Arfa and Tronc 1985, Gulley *et al.* 1992) is due to the trapping of an extra electron to the antibonding σ^* valence orbital and has the ^2E symmetry. Measurements of the vibrational DCS at 7.5 eV (Ben Arfa and Tronc 1985, Gulley *et al.* 1992) indicate that this shape resonance state is of the *d*-type, like the one in CH_4. Similarities among shape resonances occurring in small hydrides have been discussed by Ben Arfa and Tronc (1985). The shape resonance position rises from 6.5 eV in H_2O to 7.3 eV in NH_3 and about 8 eV in CH_4 (Ben Arfa *et al.* 1990).

The $^2A_2''$ Feshbach resonance manifests in the dissociative attachment (Tronc *et al.* 1988). The $^2A_2''$ Feshbach resonance is planar at equilibrium configuration (the $D_{3\mathrm{h}}$ point group), similarly to its parent, the $^1A_2''$ Rydberg state. A vibrational structure due to the excitation of the ν_2 mode of this resonance has been seen in electron energy loss spectra (Furlan *et al.* 1985), negative ion yield (Stricklett and Burrow 1986, Tronc *et al.* 1988) and electron transmission spectra (Stricklett and Burrow 1986).

It is important to stress, that unlike in CH_4, the three maxima in NH_3 (in the dissociative attachment, in the vibrational excitation and in TCS) are significantly shifted

Table IV. – *Integral cross-sections for electron scattering on ammonia (in* 10^{-20} m^2 *units).*

Energy	Elastic	Vibrational	Ionization	Summed	Total
2.0	11.2 A				10.9 S
5.0	15.8 A				15.7 SZ
					14.5 S
7.5	16.2 A	0.7 G		16.9	21.0 SZ
					17.5 S
15	16.2 A		0.19 T	16.4	19.8 SZ
					16.0 S
20	14.4 A		0.5 R	14.9	17.4 SZ
			1.1 T	15.5	14.2 S
30	11.0 A		1.6 R	12.6	14.3 SZ
			1.8 T	12.8	12.1 S

A - Alle *et al.* (1992).
G - Gulley *et al.* (1992).
R - Rao and Srivastava (1991).
S - Sueoka *et al.* (1987).
SZ - Szmytkowski *et al.* (1989).
T - Tarnovsky *et al.* (1997).

in energy. We are not aware of any attribution of a resonant state to explain the 10 eV maximum in the electron attachment CS (Sharp and Dowell 1969).

Sum check does not resolve the controversy between TCS of Szmytkowski *et al.* (1989) from one side and TCS of Sueoka *et al.* (1987) and elastic CS of Alle *et al.* (1992) from other side. It seems clear that Sueoka *et al.*'s data are somehow underestimated being lower than the summed and/or the elastic values, (see table IV) almost for all considered energies. This is the same kind of discrepancy that was observed in Sueoka's data for other gases, like CH_4 or HCl. On the other hand, at 7.5 eV in particular, on the basis of the CH_4 partitioning scheme, it is hard to expect that the difference between Szmytkowski's and Alle's values (20% of TCS) can be explained by the lack of the electronic excitation in the sum. Independent measurements of total and elastic CS would be of interest.

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3˙2. *Water vapour* (H_2O). – Cross-sections for electron scattering on H_2O, in spite of their crucial importance for understanding the biological effects of radiations and the atmospheric processes, do not form a coherent set of data. In particular, rather serious controversies regard total and ionization cross-sections. Recent compilations of CS for plasma modeling have been given by Shimamura (1989) and Phelps (1999). A set of integral CS is presented in fig. 6 and in table V.

Total cross-sections have been measured in absolute experiments by Szmytkowski (1987) in the 0.5–80 eV energy range, by Nishimura and Yano (1988) between 7 and 500 eV, by Saglam and Aktekin (1991, 1990) between 4–20 eV and 25–300 eV, respectively, and by Zecca *et al.* (1987) between 80 and 3000 eV. The overlapping measurements agree reasonably well above 20 eV. At lower energies the data of Szmytkowski (1987) constitute the highest set, being at 8 eV 9% and 30% higher than the measurements of Saglam and Aktekin (1991) and Nishimura and Yano (1988), respectively. The measurements of Saglam and Aktekin (1990) and of Nishimura and Yano (1988) in the 30–80 eV energy range agree within 5% with the results of Szmytkowski *et al.* (1991) and in the 80–200 eV range with the data of Zecca *et al.* (1987). Normalized data of Sueoka *et al.* (1986) are on the average 15–25% lower than other measurements. In fig. 6 we have renormalized their data by a factor 1.12 to the value of Nishimura and Yano (1988) at 400 eV. In spite of this the data of Sueoka *et al.* (1986) remain generally lower than the other measurements. We note a larger discrepancy among the TCS data below 20 eV. The optical-model results of Jain (1988), not shown in fig. 6, exhibit the same type of differences with the high-energy experiment (Zecca *et al.* 1987) as noted for NH_3, see fig. 5. At high energies (above 1000 eV) TCS of H_2O is 5% higher than NH_3. In turn, this last one is 5% higher than CH_4 (see Zecca *et al.* 1992).

Elastic cross-sections (vibrationally elastic) have been given in the 15°–165° angle range and 2.2–20 eV energy range by Shyn and Cho (1987), in the 10°–120°, 5–40 eV range by Johnstone and Newell (1991), in the 20°–120°, 4–200 eV range by Danjo and Nishimura (1985), in the 5°–130°, 100–1000 eV range by Katase *et al.* (1986). Rotationally elastic CS were measured at 15°–105°, 2.14 eV and 6 eV by Jung *et al.* (1982). DCS in the limit of low angles rises quickly with decreasing scattering angle (see fig. 8 in the H_2S paragraph).

At 2.2 and 6 eV DCS of Shyn and Cho (1987) for scattering angles below 60° are slightly higher than the summed (elastic + rotational excitation) values of Jung *et al.* (1982); a similar discrepancy is observed at 6–20 eV between the data of Shyn and Cho (1987) and Johnston and Newell (1991). This discrepancy can hardly be attributed to normalization procedures (to helium CS in both experiments) or to differences in the angular resolution (equal to 2° in the experiment of Johnston and Newell and 3° as evaluated from the divergence of the primary electron beam in the experiment of Shyn and Cho). A small shift in the angle determination should rather be hypothesized. The data of Danjo and Nishimura (1985) are systematically lower than other measurements above 8 eV (Shyn and Cho 1987, Katase *et al.* 1986, Johnston and Newell 1991); an error due to the normalization procedure cannot be excluded.

At 100 eV the integral elastic CS of Katase *et al.* (1986) is 25% (40% at 200 eV) higher than that of Danjo and Nishimura (1985). Note that also in CH_4 the data of Katase and collaborators are somewhat higher than other determinations.

The integral elastic CS exhibits a broad maximum at about 10 eV (Johnston and Newell 1991, Shyn and Cho 1987). The integral elastic value (Shyn and Cho 1987) is lower than TCS (Szmytkowski 1987) by 20% at 6–10 eV. Both the finite angular resolution as well as the integration procedure can lead to high errors in integral elastic

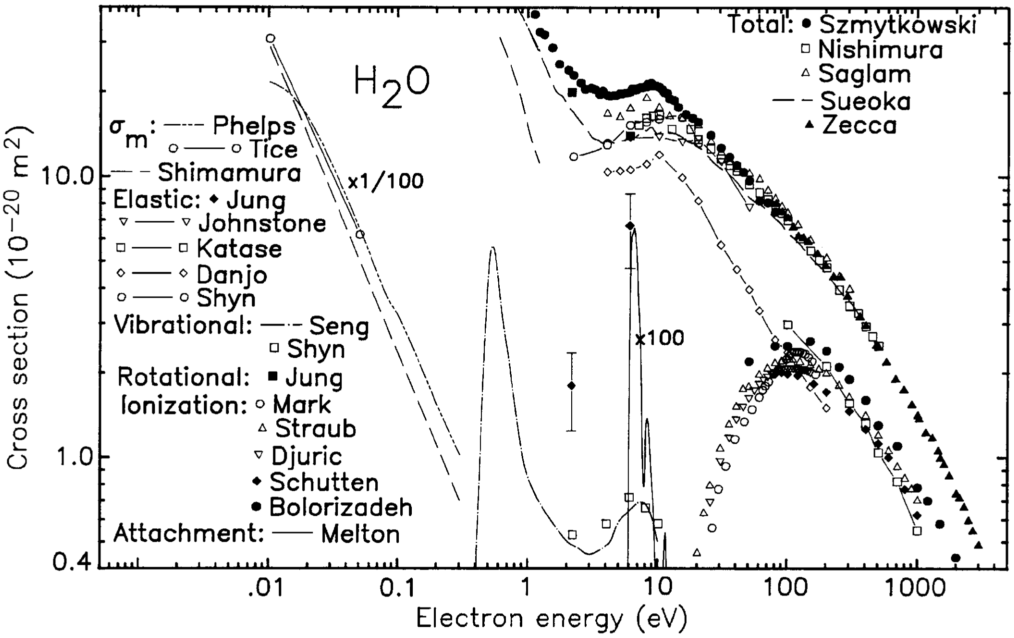

Fig. 6. – Integral cross-sections for electron scattering on H_2O. *Total*: absolute of Szmytkowski (1987); Nishimura and Yano (1986); Saglam and Aktekin (1990, 1991); Zecca *et al.* (1987); normalized of Sueoka *et al.* (1986) multiplied (this work) by 1.12. *Elastic* (vibrationally): Danjo and Nishimura (1985); Shyn and Cho (1987); Johnstone and Newell (1991), Katase *et al.* (1986); rotationally elastic, Jung *et al.* (1982), present rough estimate from DCS. *Momentum transfer*: Phelps (1999); Shimamura (1989); Tice and Kivelson (1967), cyclotron resonance. *Vibrational*: Seng and Linder (1976), read from figure; Shyn *et al.* (1988). *Rotational*: Jung *et al.* (1982), presently integrated (±30% error bar). *Ionization*: Straub *et al.* (1998); Djurić *et al.* (1988); Schutten *et al.* (1966); Bolorizadeh and Rudd (1986); Märk and Egger (1976), H_2O^+ normalized for partitioning, see text; results of Orient and Srivastava (1987) and of Rao *et al.* (1995) are not shown for clarity. *Dissociative attachment*: Melton (1972).

CS for polar molecules at low energies. Note that theoretical evaluations (Okamoto *et al.* 1993) reproduce well the experimental differential CS but give much higher integral values ($28.4 \cdot 10^{-20}\,\mathrm{m}^2$ at 6 eV).

Seng and Linder (1974) reported absolute vibrationally elastic DCS at 90° between 0.5 eV and 10 eV. These data indicate a maximum of the elastic CS at 7–8 eV and a minimum at about 2 eV. A similar result is confirmed by rotationally elastic measurements of Jung *et al.* (1982). A rough evaluation (present work ±30% error bar) of the rotationally elastic integral CS from DCS Jung *et al.* indicates a much lower integral value at 2.14 eV ($1.8 \cdot 10^{-20}\,\mathrm{m}^2$) than at 6 eV ($6.7 \cdot 10^{-20}\,\mathrm{m}^2$), see squares with error bars in fig. 6. The possible existence of a deep Ramsauer minimum in the elastic CS at 1 eV and the influence of the finite angular resolution on measured TCS were discussed, among others, by Yuan and Zhang (1992).

Forward (2°–10°) elastic DCS have been measured at 500 eV by Lassettre and White (1973). At 4° DCS in H_2O is 20% lower than in NH_3 (Harshbarger *et al.* 1971); at 10° this difference is still 10%. At 300–500 eV the NH_3 and H_2O differential CS coincide for the momentum transfer values between $K = 1$ and 5 a.u. (Bromberg 1975), compare DCS *vs.* K for He, Ne, Ar in fig. 2 in Part I.

Scattering potentials have been derived from elastic CS at intermediate energies through inversion procedures using the Born approximation (Katase *et al.* 1986) and a quantum mechanics complex formalism (Lun *et al.* 1994).

Swarm data (Pack *et al.* 1962, Christophorou and Pittman 1970, Wilson *et al.* 1975, Petrović 1986) indicate a continuous rise of momentum transfer CS in the limit of the zero energy. The data from the compilation of Phelps (1999) based on measurements of Pack *et al.* (1962) are at 0.02–1 eV higher than the data of Shimamura (1989) and merge better with TCS (Sueoka *et al.* 1986, Szmytkowski 1987). The two swarm data sets differ also in giving the zero energy CS value: $5 \cdot 10^4 \cdot 10^{-20}\,\mathrm{m}^2$ (Phelps 1999) and $5 \cdot 10^3 \cdot 10^{-20}\,\mathrm{m}^2$ (Shimamura 1989). The more recent swarm measurements (Cheung and Elford 1990) indicate that momentum transfer CS derived by Pack *et al.* (1962) should be corrected upward by 9%. Momentum transfer CS of Tice and Kivelson (1967) obtained by a cyclotron-resonance technique at thermal energies coincide with the data of Phelps (1999). An extensive semiempirical analysis of swarm parameters in H_2O was done by Ness and Robson (1988).

Vibrational cross-section exhibits a sharp near-to-threshold peak (Seng and Linder 1976). The peak value (about $4 \cdot 10^{-20}\,\mathrm{m}^2$) for unresolved stretching $\nu = (100) + (001)$ modes exceeds roughly by a factor of 20 the Born approximation result (eq. (15), Part I) and that for the bending mode $\nu = (010)$ by a factor of 5. At 1 eV the sum of the two integral values falls down to about 0.51–$0.63 \cdot 10^{-20}\,\mathrm{m}^2$ (Seng and Linder, 1976, Wong and Schulz, 1975, respectively).

A resonant enhancement of the vibrational excitation was observed between 4 and 10 eV (Seng and Linder 1974, 1976). The maximum for the $\nu = (010)$ bending mode occurs at about 6 eV and amounts to $0.56 \cdot 10^{-20}\,\mathrm{m}^2$ while that for unresolved $\nu = (100) + (001)$ stretching modes amounts to $0.18 \cdot 10^{-20}\,\mathrm{m}^2$ at 10 eV (Shyn *et al.* 1988). It is worth noting that, for NH_3 and H_2O the integral vibrational CS at the position of the shape resonance are almost equal.

The excitation of the $\nu = (010)$ mode is forward peaked in the whole 0.35–8 eV energy range studied by Seng and Linder (1976). DCS for unresolved $\nu = (100, 001)$ modes is backward peaked at 0.6 eV, isotropic at 1 eV and shows a *d*-like character at 8 eV (Seng and Linder 1976, Shyn *et al.* 1988), see fig. 8 for 2.2 eV.

Excitation of high vibrational levels between 4 eV and 10 eV have been studied by Cvejanović *et al.* (1993). Two vibrational progressions $(n, 1, 1)$ and $(n, 0, 1)$ have been observed. The amplitudes of higher excitations fall quickly with n: by more than two orders of magnitude from $n = 1$ to $n = 5$. This quick fall with n reminds the short-lived resonance in H_2 at a similar energy (see fig. 19, Part I).

At 15 eV and 20 eV the $\nu = (010)$ and $\nu = (100, 001)$ vibrational CS are almost isotropic (Shyn *et al.* 1988, Trajmar *et al.* 1973). Surprisingly large, comparable to the electronic excitation CS, and forward peaked $\nu = (001, 100)$ vibrational CS have been measured at 53 eV (Trajmar *et al.* 1973).

Rotational excitation CS have been extracted by studying the broadening of the elastic peak in the beam experiment of Jung *et al.* (1982). As pointed out by Jain and Thompson (1983), at the temperature of the measurements (450 K) different levels up to $J = 7$ can be populated. About 1/4 of amplitude of the measured CS comes from the $\Delta J = -1$ de-excitation.

At 2.14 eV the sum of DCS for rotational excitation and de-excitation is forward peaked (Jung *et al.* 1982), indicating a direct (non-resonant) dipole interaction. Also at 6 eV the angular distribution is strongly forward-peaked but exhibits an additional shallow maximum at 75°. Both at 2.14 eV as well as at 6.0 eV the rotational excitation and/or de-excitation dominates over the (rotationally) elastic CS. The present rough evaluation of integral values from DCS of Jung *et al.* (1982) gives rotational excitation CS of $20 \cdot 10^{-20}\,\mathrm{m}^2$ and $14 \cdot 10^{-20}\,\mathrm{m}^2$ at 2.14 eV and 6 eV, respectively.

Electronic excitation spectra were studied by Lassettre and White (1974) at 500 eV collision energy and by Chutjian *et al.* (1975) at low energies. Trajmar *et al.* (1973) obtained relative DCS in the 0°–90° angular range for five singlet and one triplet state at 15 eV, 20 eV and 53 eV collision energy. At 15 eV the DCS for the lowest optically allowed $\tilde{X}(^1A_1) \rightarrow \tilde{A}(^1B_1)$ excitation (7.4 eV energy loss) is forward peaked, similarly to the elastic DCS but smaller than it roughly by a factor of 50. At 20 eV the transitions to the optically allowed $\tilde{A}(^1B_1)$ and $\tilde{B}(^1A_1)$ (9.7 eV energy loss) and to the Rydberg $\tilde{D}(^1A_1)$ (10.16 eV) state are forward centered and roughly of similar magnitude (Trajmar *et al.* 1973). The recent calculation (Morgan 1998) gave at 20 eV an integral CS of $0.3 \cdot 10^{-20}\,\mathrm{m}^2$ and $0.1 \cdot 10^{-20}\,\mathrm{m}^2$ for the $\tilde{A}(^1B_1)$ and $\tilde{B}(^1A_1)$ states, respectively.

Some ambiguity regards triplet states. The lowest $\tilde{a}(^3B_1)$ triplet state was assigned to the 7.0 eV energy loss process (Chutjian *et al.* 1975). The 4.5 eV energy loss, weak state reported by Trajmar *et al.* (1973) was not confirmed (Lassettre and Huo 1974, Edmonson *et al.* 1978); the observation resulted from a dissociative attachment process (Chutjian *et al.* 1975). The 9.81 eV energy loss triplet state observed by Trajmar *et al.* (1973) was assigned (Chutjian *et al.* 1975, Kaldor 1987) to the $\tilde{d}(^3A_1)$ excitation. At 20 eV the DCS for this state shows a maximum at 60°; the integral CS for this excitation is smaller by about one order of magnitude than the above-mentioned three optical-allowed excitations (Trajmar *et al.* 1973).

Forward-angle electron scattering measurements in the 6–200 eV energy loss range were performed by Chan *et al.* (1993). The derived photoabsorption CS, differently from NH_3, does not show vibrational structures for the two lowest optically allowed states that peak at 7.4 and 9.7 eV. On the contrary, the vibrational structure is well visible for the 10–12.4 eV energy loss (Chan *et al.* 1993). The maximum (about $0.24 \cdot 10^{-20}\,\mathrm{m}^2$) at 13.5 eV in photoabsorption CS of H_2O is the lowest in the CH_4, NH_3, H_2O series.

Optical emission was studied from dissociated fragments, OH (Becker *et al.* 1980 and references therein) and H (Möhlmann and de Heer 1979). At 100 eV the sum of atomic hydrogen Balmer radiation from H_2O corresponds to a CS of $4.7 \cdot 10^{-22}\,\mathrm{m}^2$ (Möhlmann and de Heer 1979), *i.e.* about 10% of the CS for the OH^+ ion formation.

Laser-induced fluorescence of OH fragments was used by Darrach and McConkey (1991) to determine CS for dissociation into neutrals but no absolute values were given. The CS for $O(^1S)$ atoms production reaches its maximum of $1.5 \cdot 10^{-22}\,\mathrm{m}^2$ at 100 eV (Kedzierski *et al.* 1998).

Ionization. Some disagreement exists between different experimental ionization CS. Results of Djurić *et al.* (1988), Straub *et al.* (1998), high-energy (100 eV–20 keV) data of Schutten *et al.* (1966) and, to a less extent, the integrated (from DCS) cross-sections of Bolorizadeh and Rudd (1986) coincide within the declared experimental errors. The data of Djurić *et al.* and Schutten *et al.* were obtained with a similar set-up and agree well also with the calculation of Khare and Meath (1987).

The data of Orient and Srivastava (1987) are higher than those of Djurić *et al.* by almost a factor of two at 100 eV. It is worth remembering that the data of Orient and Srivastava (1987) for CH_4 from the same experiment were also higher than other measurements. The results of Rao *et al.* (1995), obtained on the same apparatus but with an improved ion collection, show a similar to other data energy dependence but are still 20% higher than the values of Straub *et al.* (1998) and Schutten *et al.* (1996). The semiempirical models (Kim and Rudd 1994, Deutsch *et al.* 1997) agree within the error bar with the data of Djurić *et al.* (1988) at 100 eV and those of Schutten *et al.* (1966) at 1000 eV.

Branching ratios (mean of different experiments) amount to 60%, 20%, 15% and 5% for H_2O^+, OH^+, H^+ and O^+, respectively, in the 100–400 eV energy range (Dolan 1993). Märk and Egger (1976) measured CS for the H_2O^+ ion formation only. Using the experimental branching ratios for formation of other types of ions (Orient and Srivastava 1987), we have evaluated the integral ionization CS from the measurements of Märk and Egger: it agrees with the uncertainty of this procedure with the measurements of Djurić *et al.* (1988), see fig. 6.

Triple (in angle and energy loss) DCS have been studied by Bolorizadeh and Rudd (1986) for collision energies 50–2000 eV. Their data are well reproduced by the semiempirical model of Kim and Rudd (1994).

Dissociative electron attachment CS (Compton and Christophorou 1967, Melton and Neece 1971, Melton 1972, Jungen *et al.* 1979) exhibits three peaks at 6.4, 8.6 and 11.2 eV. At the first two peaks all possible anion radicals H^-, O^-, OH^- are produced, with the H^- dominating (see table VI). At the third peak the intensity of H^- ions is very low (about 600 times smaller than at 6.4 eV) and the O^- dominates. The OH^- ion contributes to the 10^{-3} part of the total negative ions current in all three processes (Melton 1972). Belić *et al.* (1981) studied the kinetic energy and angular distributions of the H^- ion produced at 6.5, 8.8 and 12.0 eV collision energies in order to identify the types of resonances.

Resonances. A broad maximum observed in the $\nu = (001, 100)$ vibrational CS (Seng and Linder 1974, 1976) between 2 eV and 10 eV, and in the transmission spectra (Sanche and Schulz 1973, Mathur and Hasted 1975) have been attributed to the short-lived, $^2B_2$ symmetry (Ben Arfa *et al.* 1990) shape resonance. Note, however, that this assignment is still not clear (Cvejanović 1993). Comparison of shape resonances in CH_4, NH_3 and H_2O has been done by Ben Arfa *et al.* (1990). We resume their data and the dissociative attachment data in table VI.

Three peaks observed in the dissociative attachment (Melton 1972, Belić *et al.* 1981) at 6.5 eV, 8.6 eV and 11.8 eV have been attributed (Jungen *et al.* 1979) to Feshbach resonances of the $^2B_1$, $^2A_1$ and $^2B_2$ symmetry, respectively. These resonant states are formed by binding two $3sa_1$ electrons to the H_2O^+ core obtained by the excitation of one electron from the valence orbitals $1b_1$, $3a_1$ and $1b_2$, respectively. Angular distributions of H^- ions indicate a pure *p*-wave character of the resonance at 6.5 eV, a *d*-wave one at 12.0 eV while at 8.8 eV a mixed one, probably resulting from the *s*- and *d*-waves scattering (Belić *et al.* 1981). The $^2B_1$ Feshbach resonance at 6.5 eV overlaps the above-mentioned broad shape resonance: enhancement of the $(n, 0, 1)$ and $(n, 1, 1)$ vibrational modes due to its presence is clearly visible in the shape-resonance background (Cvejanović *et al.* 1993).

Sum check shows large insonsistencies for H_2O, mainly because of discrepancies between elastic and total CS. At 2.2 eV, where the vibrational CS exhibits a minimum, the integral elastic value of Shyn and Cho (1987) amounts only to one a half of the experimental TCS (Szmytkowski 1987). Momentum transfer CS derived in the same experiment at 2.2 eV (Shyn and Cho 1987) equals half of the semiempirical value of Phelps (1999). On the other hand, a rough evaluation (present work) of the sum of integral elastic and rotational excitation CS from measurements of Jung *et al.* (1982) agrees pretty well with the experimental TCS. The uncertainty in extrapolating DCS to low scattering angles, being bigger for polar molecules, like H_2O, can influence more the integral CS value. Note that recent TCS measurements of (Sueoka 1998), not shown in fig. 6, corrected for the angular resolution (Sueoka 1998), are in the whole 10–80 eV energy range about 10%

TABLE V. – *Integral cross-sections for electron scattering on water vapour (in* 10^{-20} m^2 *units).*

Energy	Elastic	Vibrational	Ionization	Summed	Total
2.2	11.8 SH	0.53 SH		12.3	23.5* SZ
	1.8[20.2] JU			22.5	
4.0	13.0 SH	0.58 SH		13.6	19.5 SZ
	10.4 DA				16.9 SA
6.0	15.3 SH	0.72 SH		16.0	20.0 SZ
	13.8 J				17.7 SA
	6.7[14.3] JU			21.7	
8.0	15.7 SH	0.66 SH		16.4	20.9 SZ
	11.1 DA				19.2 SA
10	16.1 SH	0.58 SH		16.7	20.9 SZ
	13.9 J			14.5	17.8 SA
15	16.3 SH	0.32 SH	0.107 D	16.7	17.5* SZ
	13.3 J				16.3 SA
20	13.2 SH	0.18 SH	0.384 D	13.8	15.7 SZ
	13.7 J			14.3	15.4 SA
30	11.3 J		0.965 D	12.3	12.7 SZ
	5.72 DA		0.68 O		12.4 SA
50	7.76 J		2.2 B	10.0	9.7 SZ
	3.97 DA		1.62 D		10.4 SA
100	2.98 K		4.36 O	7.34	7.18 Z
			2.5 B	5.5	7.49 SA
	2.37 DA		2.07 D		
200	2.11 K		2.40 B	4.51	4.80* Z
			3.39 O	5.50	5.17 SA
	1.50 DA		1.71 S		
300	1.56 K		1.97 O	3.53	3.69* Z
			1.9 B	3.46	4.01 SA
400	1.32 K		1.6 B	2.92	2.97 Z
			1.26 S	2.58	
500	1.04 K		1.3 B	2.34	2.48 Z
			1.12 S	2.16	

TABLE V. – *Continued.*

Energy	Elastic	Vibrational	Ionization	Summed	Total
700	0.82 K		1.1 B	1.92	1.89* Z
			0.88* S	1.70	
1000	0.55 K		0.78 B	1.33	1.42 Z
			0.62 S	1.17	

$*$ - Interpolated value.
B - Bolorizadeh and Rudd (1986).
D - Djurić *et al.* (1988).
DA - Danjo and Nishimura (1985).
J - Johnstone and Newell (1991).
JU - Jung *et al.* (1982), present rough estimate (±30% error) of the rotationally elastic CS; in parenthesis the rotational excitation CS, present estimate.
K - Katase *et al.* (1986).
O - Orient and Srivastava (1987).
S - Schutten *et al.* (1966).
SA - Saglam and Aktekin (1990, 1991).
SH - Shyn and Cho (1987) elastic and Shyn *et al.* (1988) vibrational.
SZ - Szmytkowski *et al.* (1987).
Z - Zecca *et al.* (1987).

TABLE VI. – *Positions and assignments of shape resonances for second-period hydrides. Shape resonances data are from Ben Arfa and Tronc (1985) and Ben Arfa et al. (1990). Electron attachment data:* CH_4, *Sharp and Dowell (1967);* NH_3, *Sharp and Dowell (1969);* H_2O, *Melton (1972); electron attachment CS are given in* (10^{-22} m^2). *TCS (in* 10^{-20} m^2*) are of Szmytkowski (1987) and co-workers, see corresponding paragraphs for* NH_3 *and* CH_4 *references. Energies E are given in eV.*

Gas	Vibrational excitation			TCS		Electron attachment		
	E	symmetry	partial waves	E	value	E	value	ions
H_2O	6.5	^2B	$l = 2 + 1$	9.0	21.1	6.4	6.6	H^-, O^-, OH^-
						8.6	1.6	H^-, O^-, OH^-
						11.2	0.6	O^-, OH^-
NH_3	7.3	^2E	$l = 2 + 1$	9.7	23.5	5.65	2.7	${NH_2}^-$, H^-
						10.5	0.43	${NH_2}^-$, H^-
CH_4	8.0	$^2T_2$	$l = 2 + 1$	8.0	27.4	9.2*	$\cong 0.7$	H^-
						9.7	$\cong 0.5$	${CH_2}^-$

* - Two overlapping peaks are observed in CH_4 (Sharp and Dowell) 1967.

higher than the measurements of Szmytkowski (1987) but at 1 eV rise up to the value of $110 \cdot 10^{-20}\,\mathrm{m}^2$. Independent, absolute measurement of the elastic and total CS at low energies in H_2O would be desirable.

At 15 eV the integral elastic and vibrational values of Shyn and co-workers sum-up well to the TCS (Szmytkowski 1987). The electronic excitation CS, according to the four-state calculation of Morgan (1998) amounts to $0.5 \cdot 10^{-20}\,\mathrm{m}^2$ at this energy, compared to the TCS value of $17.5 \cdot 10^{-20}\,\mathrm{m}^2$.

A rather poor agreement between different sets of data exists at 100 eV. At this energy the sum of the elastic CS (Katase *et al.* 1986) with the ionization of Orient and Srivastava (1987) overestimates the total CS (Zecca *et al.* 1987) but the sum with the ionization of Djurić *et al.* (1988) or Bolorizadeh and Rudd (1986) underestimates it. Between 200 eV and 1000 eV the ionization CS of Bolorizadeh and Rudd (1986) sums up very well with the elastic data of Katase *et al.* (1986) to TCS (Zecca *et al.* 1987). The difference of less than 10% is to be attributed to the missing electronic excitation CS.

Isotope effects. Deuterated water (D_2O) TCS have been measured from 7 eV to 500 eV by Nishimura and Yano (1988) and from 0.4 eV to 2700 eV by Szmytkowski *et al.* (1991). In this last paper, the Gdańsk apparatus has been used in the range 0.4 to 100 eV, while the Trento apparatus has been used from 81 to 2700 eV. The two measurements merge well in the overlap range and are in good agreement with the data of Nishimura and Yano (1988) from 10 to 500 eV. These last data are lower than those of Szmytkowski *et al.* (1988) from 7 to 10 eV. The TCS in D_2O shows absolute values very close to those of H_2O. Below 1 eV the D_2O cross-section is larger than for H_2O (10% at 0.5 eV). The difference was attributed (Szmytkowski *et al.*) to the bigger momentum of inertia of D_2O and therefore to the increased probability of direct (non-resonant) rotational excitation. This leads to a higher TCS for the D_2O compared to H_2O. A small difference (−5%) has been eventually recorded between 3 and 20 eV. This was explained (Szmytkowski *et al.* 1991) by a smaller probability of the resonant vibrational excitation for the heavier target. The broad maximum centered at 8 eV has the same, structureless shape as the one seen in H_2O (see fig. 6). The two cross-sections coincide within the error bars from 20 eV to 2700 eV.

Ionization CS in D_2O have been measured by Märk and Egger (1976) up to 170 eV and Djurić *et al.* (1988). The ionization CS for D_2O tends to be lower than that for H_2O, by about than 2%; the difference is slightly higher at the near-to-threshold region. This can be due to a slightly higher (by 0.2 eV) ionization threshold for D_2O compared to H_2O (Märk and Egger 1976). A similar difference was observed for ionization in other deuterated species, ND_3 (Märk *et al.* 1977) and PD_3 (Märk and Egger 1977). Note, however, that observed differences remain within the experimental uncertainty.

Isotope effects for deuterated hydrides were observed also in the dissociative attachment (Compton and Christophorou 1967, Jungen *et al.* 1979 and Belić *et al.* 1981). The competition between the two, negative-ion and vibrational-excitation decay channels of resonances, leads to a depletion of the dissociative attachment process for both deuterated species, ND_3 and D_2O (compare Ben Arfa *et al.* 1990, Cvejanović *et al.* 1993).

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3˙3. *Phosphine* (PH_3). – Phosphine is a heavy analog of NH_3. Due to its highly poisonous properties it was measured sporadically. This is also the case of other heavy hydrides AsH_3, SbH_3, SnH_4 which were studied mainly theoretically, in spite of their importance in semiconductor industry.

We are not aware of any total or elastic CS measurements for PH_3. Integral and differential elastic CS for the hydrides of the Vth group (PH_3, AsH_3, SbH_3) and the 5th row (SnH_4, TeH_2, HI) of the periodic table have been calculated by Bettega *et al.* (1996). The elastic CS in PH_3 and AsH_3 at 1–40 eV were calculated by Winstead *et al.* (1992).

In PH_3, Millican and Walker (1987) in swarm experiment measured the ratio (characteristic energy) of transverse diffusion coefficient D_{T} to mobility μ at $2\text{–}80 \cdot 10^{-21}\,\mathrm{Vm}^2$ reduced fields. The ratio D_{T}/μ in PH_3 assumes the same values like in H_2S but for reduced fields by a factor of two lower.

Tronc *et al.* (1981) measured vibrational excitation functions for the $\nu_{2,4}$ and $\nu_{1,3}$ unresolved modes between 0.5 and 4.5 eV incident energy. DCS at 90° shows a large resonant peak, extending from 1.5 to about 3.5 eV and reaching at 2.2 eV a maximum of $0.38 \cdot 10^{-20}\,\mathrm{m}^2/\mathrm{sr}$ and of $0.58 \cdot 10^{-20}\,\mathrm{m}^2/\mathrm{sr}$ for the $\nu_{2,4}$ and $\nu_{1,3}$ excitations, respectively. The out-of-resonance vibrational DCS, say, at 1.2 and 4.5 eV, amount scarcely to $0.1 \cdot 10^{-20}\,\mathrm{m}^2/\mathrm{sr}$ and $0.08 \cdot 10^{-20}\,\mathrm{m}^2/\mathrm{sr}$, for the two modes, respectively. Energy loss spectra at 90° suggest that as much as 30% of TCS at 2.2 eV can result from vibrational excitation. We remind a similarly high amount observed in SiH_4.

Märk and Egger (1977) measured ionization CS in PH_3 up to 180 eV. Ionization CS in PH_3 is higher than that in NH_3 by a factor of two (Märk *et al.* 1977). Whereas in the NH_3 molecule the NH^+ ion constitutes a few per cent of the total ionization, in PH_3 at 180 eV the PH^+ ion dominates over the parent ${PH_3}^+$.

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3˙4. *Hydrogen sulfide* (H_2S). – H_2S is a small (bond length 1.34 Å), weakly polar (0.97 D) molecule of a relatively high polarizability ($\alpha = 3.78 \cdot 10^{-30}\,\mathrm{m}^3$). Emission of H_2S from natural sources influences heavily the atmospheric sulphur balance (Bates *et al.* 1992). Figure 7 presents the H_2S integral CS.

Total cross-sections have been measured by absolute transmission methods at 1–100 eV by Szmytkowski and Maciąg (1986) and between 75–4000 eV by Zecca *et al.* (1992). These two measurements agree well in the range of energy overlap. TCS rises from about $25 \cdot 10^{-20}\,\mathrm{m}^2$ at 1.5 eV to $32 \cdot 10^{-20}\,\mathrm{m}^2$ at 2.3 eV, remains constant within the experimental error up to 5 eV and reaches a broad maximum of $38 \cdot 10^{-20}\,\mathrm{m}^2$ at about 8 eV (Szmytkowski and Maciąg 1986). At 4000 eV the H_2S TCS is only 4% lower than that for SiH_4 (Zecca *et al.* 1992).

Theoretical TCS obtained by the optical-potential model (Jain and Baluja 1992) agree well with experimental data at 30 eV and at 3000 eV. They are somewhat underestimated in the intermediate energy range, see fig. 7. A similar behaviour has been observed in the theoretical calculations of Jain and Baluja (1992) for GeH_4 (see fig. 4) and SiH_4 (see fig. 2): these values are on the average lower than the experimental counterpart.

Elastic cross-sections have been obtained in the 1–30 eV energy range by Gulley *et al.* (1993) who used the relative flow technique and normalization to helium data. These elastic CS are compatible with the TCS of Szmytkowski *et al.* (1986). The difference at 10 eV and above is to be attributed to the increasing contributions from inelastic scattering; the 25% difference at 3 eV can be due to the vibrational excitation.

The angular distributions of Gulley *et al.*'s DCS at 20 eV and 30 eV agree very well with the relative data of Marinković (1985). Poorer agreement exists with the data of Rohr (1978) at 3 eV, which are higher by almost 50%, possibly due to some error in the normalization procedure.

The integral elastic CS exhibits a maximum at 5 eV, decreasing smoothly at higher energies (Gulley *et al.* 1993). However, the momentum transfer CS (not shown in fig. 7) presents another local maximum at 2.0 eV. This reflects changes in the angular distribution of elastically scattered electrons, indicating the presence of a resonant process.

In the very low energy limit (below 1 eV) the elastic scattering is strongly forward peaked (Rohr 1978). The energy dependence of the elastic DCS at 80° shows a minimum at about 1.2 eV and two shallow maxima at 2.2 eV and 5.7 eV (Rohr 1978). The minimum shifts to 2 eV for the 40° scattering angle. Also Tronc and Edard (1989) reported a broad minimum in the 90° elastic DCS extending from 0.6 to 1.3 eV. DCS at 2 eV (2.2 eV) for H_2S (H_2O) are shown in fig. 8. Whereas the elastic DCS in H_2O shows a single minimum at about 120°, the DCS in H_2S has a more complex dependence on the scattering angle.

Different theoretical models were applied in limited energy ranges: Jain and Thompson (1983) up to 10 eV, Gianturco (1991) between 10 eV and 30 eV, Nishimura and Itikawa (1996) at 3–30 eV, Greer and Thompson (1994) at 2–10 eV, Yuan and Zhang (1993) at 0.1–50 eV, Jain and Baluja (1992) at 10–5000 eV. In particular, the models differ in the treatment of the polarization and exchange interactions, important at low energies. Calculations of Jain and Thompson (1983) indicate the existence of Ramsauer minimum in the integral vibrationally elastic CS (*i.e.* with rotational excitation included) CS at 1 eV (see fig. 7). Ramsauer minimum of $0.6 \cdot 10^{-20}\,\mathrm{m}^2$ for the pure (rotationally and vibrationally) elastic CS in H_2S is predicted at a lower energy (0.5 eV) than in H_2O (Yuan and Zhang 1993, the data are not shown in fig. 7 for clarity reasons).

Swarm experiments regarded the ratio of transverse diffusion D_T to mobility μ (the characteristic energy) at 5–$200 \cdot 10^{-21}\,\mathrm{Vm}^2$ (Millican and Walker 1987) but no cross-sections were derived. Qualitatively, the D_T/μ coefficient in H_2S—lower by a factor of 2

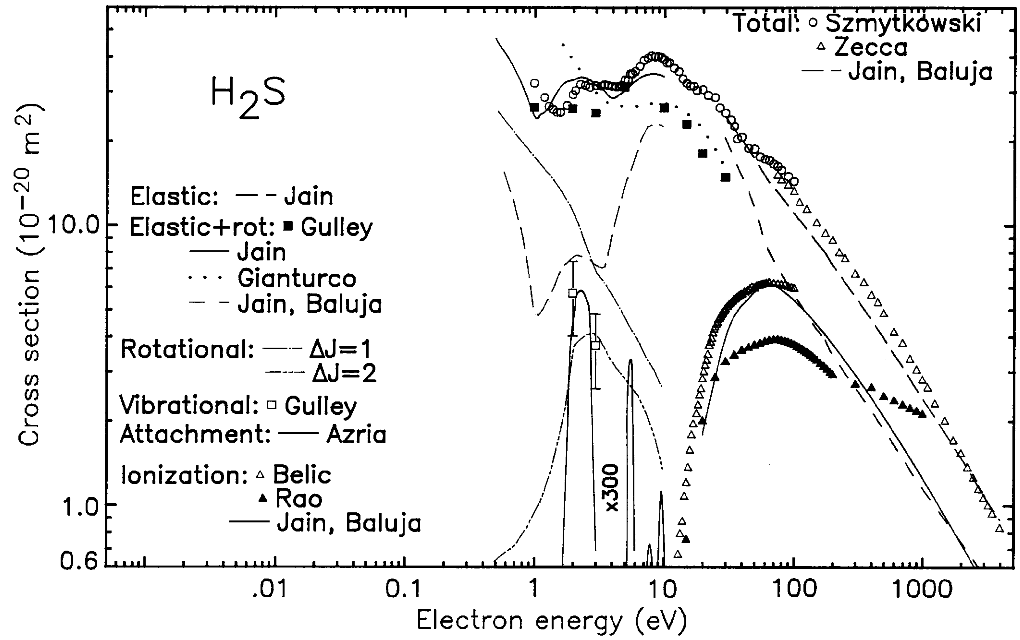

Fig. 7. – Integral cross-sections for electron scattering on H_2S molecule. *Total*: Szmytkowski and Maciąg (1986); Zecca *et al.* (1992); Jain and Baluja (1992), optical model. *Elastic* (rotationally): Jain and Thompson (1983), theory. *Elastic + rot* (vibrationally elastic): Gulley *et al.* (1993), absolute experimental; Jain and Thompson (1983), theory; Gianturco (1991), theory; Jain and Baluja (1992), optical model. *Rotational excitation*: $J = 0_0 \to 1_0$ and $0_0 \to 2_{-2}$, Jain and Thompson (1983). *Vibrational excitation*: Gulley *et al.* (1993), integrated in this work. *Ionization*: Belić and Kurepa (1985); Rao and Srivastava (1993); Jain and Baluja (1992), optical model. Electron *attachment*: Azria *et al.* (1972).

compared to SiH_4 (Millican and Walker 1987)—would indicate a higher cross-section for the first molecule. A dip-like structure is observed in H_2S at the characteristic energy D_T/μ of about 0.5 eV.

At the sub-milli-eV energies CS were studied by Rydberg-atoms quenching method (Frey *et al.* 1994). It was evidenced that the quenching rate as a function of the Rydberg atoms quantum number n (*i.e.* collision energy) has a different dependence for H_2S than for other polar molecules, like HF, NH_3, CH_2Br_2, $C_6H_5NO_2$. For the latter targets the rate constant *vs.* n indicated a $1/E$ dependence of TCS in the zero-energy limit. For H_2S the quenching rate is independent of n so an $1/\sqrt{E}$ dependence of CS is expected. It is worth noting that, differently from other molecules reported by Frey *et al.* (1994), for H_2S no long-lived negative ions were observed at such very low energies. A possible reason for this can be that a relatively weak dipole moment does not sustain a permanent negative ion and that the high polarizability of the molecule can dominate the scattering at very low energy.

Vibrational excitation exhibits a near-threshold peak (at 0.4 eV for 120° scattering angle) and a broad resonant maximum around 2.3 eV (Rohr 1978, Tronc and Edard 1989). DCS for the vibrational excitation at 2 eV of the (010) and (100) + (001) modes (Gulley *et al.* 1993) are shown in fig. 8. At the resonant position (about 2.3 eV) overtones

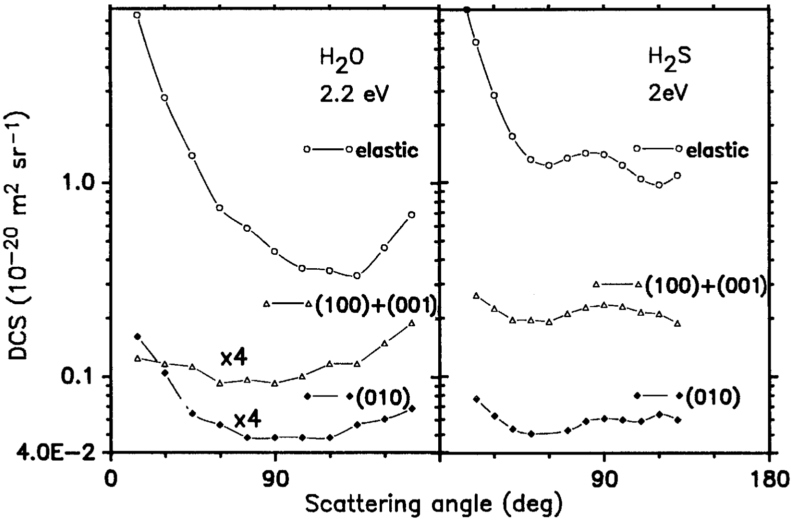

Fig. 8. – Differential cross-sections for elastic (rotationally summed) and vibrational excitation cross-sections at 2.2 eV in H_2O (Shyn and Cho 1987, Shyn *et al.* 1988) and 2.0 eV in H_2S (Gulley *et al.* 1993).

up to $n = 4$ of the $(n01) + (10n)$ and of the $(n10) + (01n)$ composite modes were observed (Rohr 1978). The relative intensities for the excitation of the $(10n)$ + $(n01)$ overtones with $n > 1$ amount to 50% of the (100) + (001) mode; overtones with $n > 1$ of the $(n10, 01n)$ mode amount to almost 100% of the (010) mode (Rohr 1978). A rough estimate (±30% error bar, present work) of the integral CS from DCS of Gulley *et al.* (1983) gives $0.9 \cdot 10^{-20}\,\mathrm{m}^2$ and $3.6 \cdot 10^{-20}\,\mathrm{m}^2$ for (010) and (100 + 001) modes at 2 eV, respectively, falling down to $0.7 \cdot 10^{-20}\,\mathrm{m}^2$ and $1.5 \cdot 10^{-20}\,\mathrm{m}^2$ at 3 eV, respectively. In fig. 7 we present the summed values for both modes of Gulley *et al.*, multiplied by the corresponding factors for overtones, according to Rohr (1978).

Angular distributions at 2.0 eV suggest that both s- and d-waves are involved in the scattering process (Tronc and Edard 1989, Gulley *et al.* 1993), see fig. 8. At this energy and 90° scattering angle DCS for the $(n00, 10n)$ excitation is about 20% of the elastic DCS (Tronc and Edard 1989). A disagreement by a factor of 2 has to be noticed between DCS of Rohr (1978) and Gulley *et al.* (1993); it was attributed (Gulley *et al.*) to different transmission functions of the two analyzers.

Rotational excitation. Due to the close spacing between energy levels the rotational excitation has not been measured. Therefore, the low-angle rise of DCS for "elastic" scattering in the experiment of Rohr (1978) and Gulley *et al.* (1993) includes at low energies the direct rotational excitation. The calculation of Jain and Thompson (1983) shows that, as it was observed experimentally for HCl, the $\Delta J = 1$ excitation diminishes approximately like $1/E$ at low energies while the $\Delta J = 2$ excitation exhibits a resonant peak at about 2.3 eV.

Electronic excitation and ionization in the limit of forward-scattering was studied up to 90 eV electron impact energy by Brion *et al.* (1986). The corresponding photoabsorption CS reaches a maximum of $0.65 \cdot 10^{-20}\,\mathrm{m}^2$ at 15 eV.

Theoretical calculations for the excitation to the three lowest triplet states $X\,^1A_1 \rightarrow {}^3A_2\ (2b_1 \rightarrow 3b_2)$, ${}^3B_1(2b_1 \rightarrow 6a_1)$ and ${}^3A_1(5a_1 \rightarrow 6a_1)$ were performed up to 50 eV by

Michelin *et al.* (1997). At 12 eV the summed CS for these states amounts to $2.0 \cdot 10^{-20}\,\mathrm{m}^2$, the three contributions being almost equal. Note a similar CS value ($1.5 \cdot 10^{-20}\,\mathrm{m}^2$) for the excitation to the triplet ${}^3T_2$ state in SiH_4 at the same energy (Bettega *et al.* 1998).

Optical emission cross-section for the H_α Balmer line from H_2S exceeds the H_2O value at low energies but almost coincides with it above 500 eV (Möhlmann and de Heer 1979). It amounts to $6.2 \cdot 10^{-22}\,\mathrm{m}^2$ at 100 eV. Emission in H_β line was studied also by Ogawa *et al.* (1991).

Ionization CS were measured by Rao and Srivastava (1993) and Belić and Kurepa (1985): the data of Rao and Srivastava are lower by almost of factor of 2. This discrepancy is of opposite sign respect to the H_2O measurements from the same laboratories, compare fig. 6. We note also a visible change in the energy dependence of ionization CS above 300 eV in the measurements of Rao and Srivastava, see fig. 7. On the other hand, the data of Belić and Kurepa agree at 75 eV with a single point determination of $6.42 \cdot 10^{-20}\,\mathrm{m}^2$ by Lampe *et al.* (1957). Also the optical-model absorption CS (Jain and Baluja 1992, Joshipura and Vinodkumar 1997) agrees with this experiment. The semiempirical binary-encounter-Bethe mode (Kim *et al.* 1997), not shown in figure, coincides with the experiment of Rao and Srivastava (1993) up to 200 eV but at 1000 eV is 50% lower. On the other side, the semiempirical model of Khare and Meath (1987), not shown in fig. 7, is even lower that the experiment of Rao and Srivastava.

Branching ratios at 100 eV for the H_2S^+ and HS^+ fragments, 50% and 21%, respectively, are similar to those in H_2O (Rao and Srivastava 1993). The proportion between S^+ and H^+ fragments, 22% and 5%, are inverted compared to O^+ and H^+ ions from H_2O. Kinetic energies of ionized fragments were studied by Cordaro *et al.* (1986).

Dissociative attachment. Four peaks are observed in the dissociative attachment CS at 2.3 eV (mainly HS^-, with a smaller contribution of S^-) at 5.4 and 8 eV (mainly H^-, with a smaller contribution of S^-) and at 9.7 eV (S^- ions) (Azria *et al.* 1972, Tronc *et al.* 1973, Belić and Kurepa 1985). Angular and kinetic energy distributions of H^- ions have been studied in the 4.5–9 eV region by Azria *et al.* (1979). At 2.3 eV the attachment CS amounts to about $5\text{–}6 \cdot 10^{-4}$ of TCS (Belić and Kurepa 1985, Rao and Srivastava 1993).

Resonances. Some controversy on the configuration of resonant states exists. TCS shows two maxima at 2.3 eV and 8 eV and a weak structure close to 3.5 eV (Szmytkowski and Maciąg 1986). Nothing can be said on the detailed shape of the elastic CS due to the sparseness of measured points. The calculations of Gianturco (1991) show a broad maximum centered at 10 eV, while Jain and Thompson (1983) an additional maximum at 2 eV. The first maximum in TCS corresponds to resonant structures observed in the vibrational excitation (Rohr 1978, Gulley *et al.* 1993) and in the dissociative attachment (Azria *et al.* 1972, Fiquet-Fayard 1972) channels. As stressed by Gulley *et al.* (1993) it is not possible, at present, to assign a single configuration to this shape resonance. Different theories (Jain and Thompson 1983, Gianturco 1991, Greer and Thompson 1994) predict a ${}^2B_2$ configuration, while the analysis of the dissociative attachment (Fiquet-Fayard *et al.* 1972) and vibrational excitation (Rohr 1978) suggests a ${}^2A_1$ configuration with a superposition of *s*- and *d*-wave contributions. An interesting feature of the 2.3 eV resonance is the big, 20–25% contribution of the vibrational excitation CS (Tronc and Edard 1989) to the TCS. Analogies with the shape resonances observed at about 2 eV in SiH_4, PH_3, H_2S and HCl were discussed by Tronc and Edard (1989).

${}^2B_1$ and ${}^2A_1$ resonant configurations have been attributed to the dissociative attachment peaks at 5.5 eV and 8 eV, respectively, on the basis of angular distributions of H^- ions (Azria *et al.* 1979). These states should be probably classified as Feshbach resonances lying near to the thresholds for electronic excitation (see Brion *et al.* 1986).

TABLE VII. – *Integral cross-sections for electron scattering on* H_2S *(in* 10^{-20} m^2 *units).*

Energy (eV)	Elastic	Vibrational	Ionization	Sum	Total
1.0	26.3 G				32.0 SZ
2.0	26.0 G	5.7 G1		31.7	29.2 SZ
3.0	25.1 G	3.7 G1		28.8	31.5 SZ
5.0	31.1 G				33.0 SZ
10.0	26.2 G				38.9 SZ
15.0	22.9 G		0.75 R 1.21 B	23.7 24.1	32.0 SZ
20.0	18.0 G		2.0 R 3.0 B	20.0 21.0	30.4 SZ
30.0	14.8 G		3.3 R 5.1 B	18.1 19.9	25.1 SZ

B - Belić and Kurepa (1985).
G - Gulley *et al.* (1993).
G1 - Gulley *et al.* (1993), vibrational DCS integrated (±30% extrapolation uncertainty) and normalized for overtones, this work.
R - Rao and Srivastava (1993).
SZ - Szmytkowski and Maciąg (1986).

Sum check for the 1–30 eV region is presented in table VII. The integral vibrational CS has been obtained by a rough integration (±30% possible error) of DCS (Gulley *et al.* 1993) and then multiplying by a factor of 1.5 for the (100, 001) and by a factor of 2 for the (010) vibrational modes, in order to account for overtones. At 2 and 3 eV the summed and total CS differ slightly; experimental errors in the determination of the collision energy in a highly reactive gas like H_2S are not to be excluded. The elastic CS is closer to the TCS at 5 eV, outside the resonance, where energy-shift errors are probably smaller.

At 2–2.5 eV the vibrational CS contributes as much as 20–25% (Tronc and Edard 1989) to the TCS. This partitioning is similar in SiH_4 at about the same energy. Like in SiH_4 and GeH_4, maxima in the elastic, vibrational and total CS occur at different energies.

At 20 eV the summed value is 1/3 lower than the experimental TCS (Szmytkowski and Maciąg): electronic excitation to optically forbidden (Michelin *et al.* 1997) and allowed states (we are not aware of any data) can account for this difference. We recall also a large value (about 1/3 of TCS) of the dissociation-into-neutrals CS in SiH_4 and GeH_4 molecules.

At 100 eV the ionization CS (Belić and Kurepa 1985) amounts to 45% of TCS (Zecca *et al.* 1992). A similar sharing has been found in CH_4. Independent measurements both of partial and total CS in H_2S are desirable to solve these discrepancies.

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3˙5. *Hydrogen chloride* (HCl). – Hydrogen chloride is used as a halogen donor in the XeCl excimer lasers (Nighan and Brown 1980, Kligler *et al.* 1981, Kannari *et al.* 1990). Therefore, the major number of investigations in the field of electron scattering for this molecule was devoted to the Cl^- formation cross-section (see Teillet-Billy and Gauyacq 1984 and references therein). We are aware of only a few measurements of total cross-sections; the reason for this scarcity is the highly corrosive character of HCl. Vibrational structures observed in the dissociative attachment (Abouaf and Teillet-Billy 1977) triggered numerous theoretical works. Semiempirical CS values have been reviewed by Penetrate and Bardsley (1983), Hayashi (1987) and Morgan (1992) and HCl plasma models were studied by Caledonia and Center (1976) and Capitelli *et al.* (1979).

Total cross-section was measured by Brüche (1927) on a Ramsauer-type apparatus from 4 eV to 30 eV and more recently by Hamada and Sueoka (1994) in a time-of-flight apparatus using a longitudinal guiding magnetic field at energies between 0.7 eV and 400 eV. Hamada and Sueoka have corrected their data for the angular resolution error introduced by the guiding magnetic field. Above 15 eV their data agree well with those of Brüche but are lower about 15% at 9 eV. Note that the needed angular resolution correction, due to the use of the magnetic field, rises towards low scattering energies.

According to Hamada and Sueoka (1994) TCS exhibits a maximum at about 9 eV and rises sharply at the low energy limit, similarly to other polar molecules, like H_2O and NH_3. A shoulder structure was observed at about 4 eV, indicating a possible shape resonance, of the $^2\Sigma$ configuration as predicted by the theory (McCartney *et al.* 1990, Malegat and Le Dourneuf 1990). The optical model results of Jain and Baluja (1992) are higher than the measurements of Hamada and Sueoka (1994), in the whole 10–400 eV energy range.

Elastic cross-sections (rotationally elastic, $\Delta\nu = 0$, $\Delta J = 0$) were measured between 0.5–10 eV and 15°–135° by Rädle *et al.* (1989) and between 5–200 eV and 10°–160° by Gote and Ehrhardt (1995). Integral values were given only by Rädle *et al.* (1989); the integral CS exhibits a Ramsauer minimum of about $8 \cdot 10^{-20}\,\mathrm{m}^2$ at 2 eV, see fig. 9.

For the sake of comparison with TCS, we have performed a rough estimate of the vibrationally elastic CS. The DCS of Rädle *et al.* (1989) for rotational excitation have been integrated by us and then summed with rotationally elastic integral CS read from their fig. 3. The rotationally elastic as well as the rotational excitation DCS from Gote and Ehrhardt (1995) have been integrated and then summed. The integral vibrationally elastic CS obtained from the data of Gote and Ehrhardt are reported in table VIII and in fig. 9. The integral vibrationally elastic CS from Rädle *et al.* are separated into the two contributions in table VIII and shown both as rotationally as well as vibrationally elastic in fig. 9. The minimum in the vibrationally elastic CS, see fig. 9, is less visible than the minimum in rotationally elastic CS, because of the different energy dependences of the DCS for specific rotational $\Delta J = 0, 1, 2$ transitions.

At 5 eV and 10 eV the integral vibrationally elastic CS of Rädle *et al.* (1989) and of Gote and Ehrhardt (1995) are well compatible with TCS of Brüche (1927), see fig. 9, but are slightly higher than the elastic calculation of Shimoi and Itikawa (1999)—not shown in fig. 9—and the experimental TCS of Hamada and Sueoka (1994). In the 50–200 eV range the elastic CS of Gote and Ehrhardt are close to the TCS of Hamada and Sueoka.

The angular distribution of rotationally elastic DCS at 1.5 eV shows a shallow minimum at 75°; the one at 2 eV a sharp deep at 105° (see fig. 10). Similarily to the other polar hydrides H_2O and H_2S, the HCl low-energy differential cross-sections are forward centered (compare figs. 8 and 10).

The energy dependences of vibrationally elastic DCS were reported at 60°, 90° and

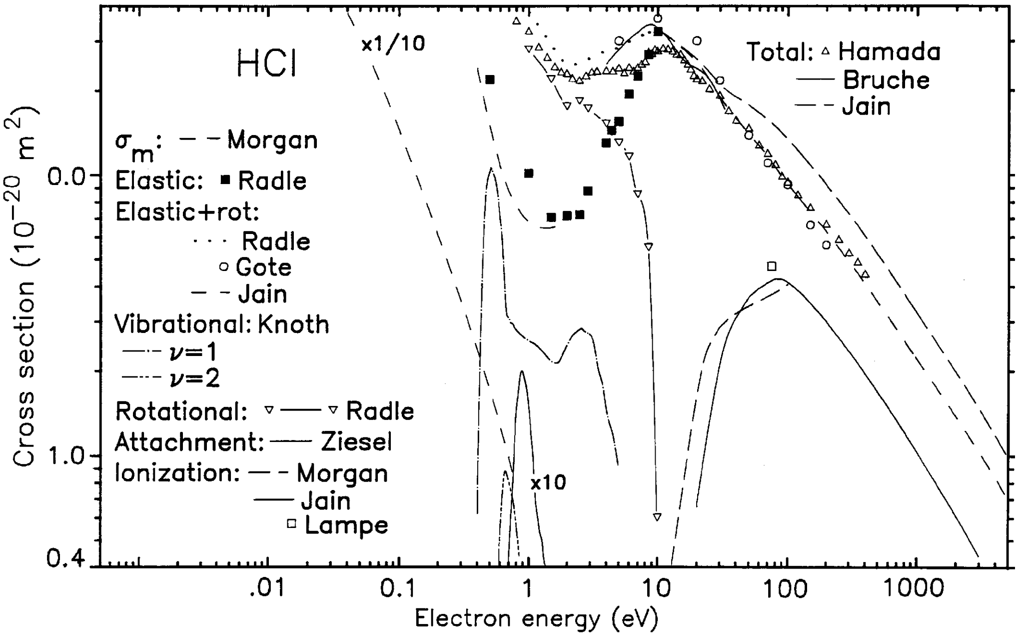

Fig. 9. – Integral cross-sections for electron scattering on HCl. *Total*: Hamada and Sueoka (1994), transmission method with magnetic field; Brüche (1927), Ramsauer set-up; Jain and Baluja (1992), optical model. *Elastic*: Rädle *et al.* (1989), rotationally elastic. Elastic + rot: Rädle *et al.* (1989) and Gote and Ehrhardt (1995), presently integrated, vibrationally elastic; Jain and Baluja (1992), optical model, electronically elastic. *Momentum transfer*: Morgan (1992), swarm-data compilation. *Vibrational*: $\nu = 1$ Knoth *et al.* (1989a), $\nu = 2$ Knoth *et al.* (1989b). *Rotational excitation*: sum of $\Delta J = 1, 2, 3$, Rädle *et al.* (1985), presently integrated from DCS. *Electron attachment*: Ziesel *et al.* (1975), normalized at maximum to the theoretical value of Teillet-Billy and Gauyacq (1984). Ionization: Jain and Baluja (1992), optical model; Morgan (1992), swarm-data; Lampe *et al.* (1957), beam experiment.

135° by Knoth *et al.* (1989a). These dependences show prominent cusp structures at about 0.35 eV, corresponding to the opening of the $\nu = 1$ vibrational channel (Knoth *et al.* 1989a).

Swarm data were compiled by Morgan (1999) who quotes a zero energy CS of $1340 \cdot 10^{-20}\,\mathrm{m}^2$, *i.e.* much less than the values for H_2O and NH_3 (Shimamura 1989). A sharp rise of the elastic CS in the zero-energy limit, to $1000 \cdot 10^{-20}\,\mathrm{m}^2$ at 0.01 eV, is also predicted by theories (Pfingst *et al.* 1992, Thümmel *et al.* 1992).

Momentum transfer CS (Morgan 1999) exhibits a minimum at a lower energy than the minimum in elastic CS (Rädle *et al.* 1989), see fig. 9. Swarm coefficients in HCl have been compiled by Gallagher *et al.* (1983) and Penetrate and Bardsley (1983).

Vibrational excitation. Sharp threshold peaks were observed for vibrational excitation of $\nu = 1$ (Rohr and Linder 1975, 1976, Knoth *et al.* 1987, Knoth *et al.* 1989a) and $\nu = 2, 3$ (Knoth *et al.* 1989b) levels. Note that the earlier data (Rohr and Linder 1975) were probably overestimated by almost a factor of two. The integral CS for excitation of $\nu = 1$ (Knoth *et al.* 1989a) and $\nu = 2$ (Knoth *et al.* 1989b) levels exhibit minima at the opening of the successive vibrational levels, $\nu = 2$ or $\nu = 3$, respectively. The width of these threshold structures is about 0.15 eV (see fig. 9).

TABLE VIII. – *Integral cross-sections for electron scattering on hydrogen chloride (in* 10^{-20} *m*^{2} *units).*

Energy	Elastic	Rotational	Vibrational	Inelastic	Summed	Total
0.5	21.8 R	51 R1	10.2 K		83	49* H
1.0	10.1 R	28 R1	2.5 K		41	32.6 H
1.5	7.0 R	21 R1 45 R2	2.1 K		29	25.2 H
2.0	7.1 R	17 R1	2.5 K		27	23.0 H
2.5	7.2 R	18 R1	2.8 K		28	21.7 H
4.0	13.0 R	13.6 R1	1.5 K		28.1	23.4 H 24.9 B
5.0	15.5 R	12.1 R1	1.0 K		28.6	23.1 H 28.5 B
10.0	32.4 R 36 G	0.6 R1	0.5 K		33.5 36.5	28.3 H 34.0 B
20	30.0 G			0.7 J	30.7	21.7 H
50	13.8 G			3.7 J	17.5	12.8 H
100	9.2 G			4.1 J	13.3	9.4 H
200	5.6 G			3.0 J	8.6	6.7 H

* - Extrapolated from the 0.8–1.6 eV data slope.
B - Brüche (1927), read from figure.
G - Gote and Ehrhardt (1995), elastic + rotational, in this work integrated.
H - Hamada and Sueoka (1994).
J - Jain and Baluja (1992), theoretical absorption CS.
K - Knoth *et al.* (1989a, b).
R - Rädle *et al.* (1989), rotationally elastic, read from their figure.
R1 - Present rough estimate (±30% error up to 2 eV, ±10% at 5 eV) by integrating the vibrationally elastic DCS for 15°–180° and subtracting the elastic integral CS (Rädle *et al.* 1989).
R2 - Rädle *et al.* (1989), integral value for the $\Delta J = 1$ transition.

More recently, Cvejanović and Jureta (1989), Schafer and Allan (1991), Cvejanović *et al.* (1993) have found additional faint "boomerang" oscillations in the energy dependences of the $\nu = 1$ and $\nu = 2$ DCS. These structures, with spacing of about 0.04 eV, are superimposed on a slowly varying background and appear at the opening of the successive vibrational channels. They are much weaker than, say, in N_2 (compare fig. 22 in Part I). The structures in HCl have been attributed to near-threshold resonant states (Domcke and Mündel 1985).

The integral vibrational CS reaches the peak values of $10.5 \cdot 10^{-20}$ m^2, $0.85 \cdot 10^{-20}$ m^2

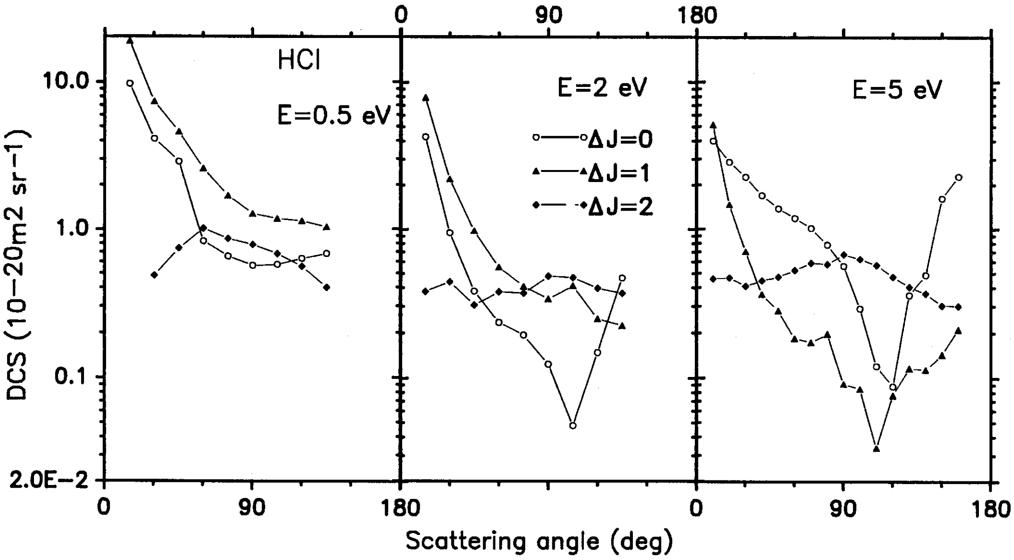

Fig. 10. – Differential cross-sections for elastic ($\Delta J = 0$) and rotational-excitation electron scattering on HCl: 0.5 eV and 2 eV, Rädle *et al.* (1989); 5 eV, Gote and Ehrhardt (1995).

and $0.22 \cdot 10^{-20}\,\mathrm{m}^2$ for $\nu = 1$, $\nu = 2$ and $\nu = 3$ excitations, respectively (Knoth *et al.* 1989a, b). At near-to-threshold energies, 0.5 eV for $\nu = 1$ and 0.8 eV for $\nu = 2$ (Knoth *et al.* 1989a and 1989b, respectively) the vibrational excitation DCS diminishes for scattering angles below 60°, independently of the rotational sub-channel. This is in contradiction with a simple model assuming *s*-wave scattering exclusively and indicates the coupling between the vibrational excitation and the ($\Delta J = 1$, $\Delta\nu = 0$) rotational excitation which is forward peaked, see fig. 10.

Both $\nu = 1$ (Rohr and Linder 1975) as well as higher ($\nu = 2, 3$) vibrational excitation CS exhibit resonant-like enhancements around 2.7 eV. The angular dependence of the $\nu = 0 \rightarrow 1$ vibrational excitation CS is essentially isotropic at this energy (Rädle *et al.* 1989).

Rotational excitation. Due to the permanent dipole moment of the HCl molecule, enhancement of rotational excitation, especially in the low energy limit is expected. For a gas temperature of 400 K and in the 0.5–2 eV energy range, the DCS for $\Delta J = 1$ transitions are roughly double than the elastic ($\Delta J = 0$) DCS (Rädle *et al.* 1989), see fig. 11. Only at energies higher than 3 eV the elastic scattering dominates over the rotational de- and excitation. Generally, the $\Delta J = 2$ DCS angular dependences follow the elastic DCS shapes, up to energies of 200 eV (Gote and Ehrhardt 1995). The $\Delta J = 1$ angular distributions do not follow elastic DCS but, as shown in fig. 10, are more uniform or exhibit flat maxima at angles where elastic DCS reach a minimum. This peculiarity is an example of parity conservation in the case of diatomic molecules (Rädle *et al.* 1983).

The integral CS for all measured (Rädle *et al.* 1989) rotational $\Delta J = 1$–4 transitions at 2 eV and 400 K gas temperature is 10% lower than in H_2O at a similar energy and temperature, compare tables V and VIII. The integral rotational CS in HCl falls like $1/E$ in the 0.5–1 eV energy range. DCS for the $\Delta J = 1$ excitation below 2 eV are well described by Born approximation (formula (14), Part I). This indicates a direct (non-

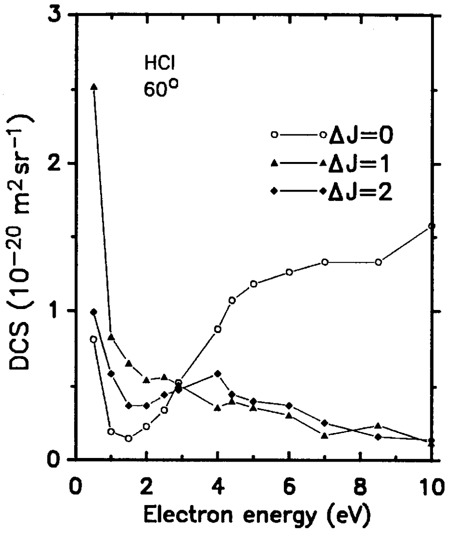

Fig. 11. – Energy dependence of the elastic and rotational-excitation differential cross-section at 60° for electron scattering on HCl molecule (Rädle *et al.* 1989).

resonant) scattering mechanism. At higher energies and angles above 60° the measured data are somewhat higher that the Born values (Rädle *et al.* 1989).

The rise of the $\Delta J = 2$ excitation in the zero energy limit, see fig. 11 for 60°, indicates the presence of a near-to threshold resonance (Rädle *et al.*, 1989). The $\Delta J = 2$ excitation exhibits another resonant maximum at 3–4 eV, in correspondence to the peak in the vibrational $\nu = 0 \to 1$ transition (Rädle *et al.* 1989). The even $\Delta J = 2, 4$ rotational excitations are effective up to 10 eV; at higher energies the CS for excitation into $J > 1$ levels become quite low compared to other diatomic molecules, like Cl_2 or CO (Gote and Ehrhardt 1995). As stated by Ernesti *et al.* (1995) this is due to the fact that the center of mass in HCl is very close to the Cl atom and the interference effects in rotational excitation are small.

Electronic excitation. Valence energy-loss spectra were measured by York and Comer (1984) at 100 eV incident energy and by Wang *et al.* (1983) at 200 eV. Both valence as well as inner-shell energy loss spectra at 1500 eV incident energy were acquired by Shaw *et al.* (1984). Three Rydberg progressions converging to the ionization energy of 12.83 eV were observed (York and Comer 1984). Threshold electron impact excitation was studied by Compton *et al.* (1968) and Jureta *et al.* (1989).

Photoabsorption cross-section, as obtained in zero-angle electron scattering (Daviel *et al.* 1984), exhibits three maxima: at 9.5 eV (of $0.29 \cdot 10^{-20}\,\mathrm{m}^2$), 12 eV ($0.6 \cdot 10^{-20}\,\mathrm{m}^2$) and 15 eV ($0.55 \cdot 10^{-20}\,\mathrm{m}^2$).

Cross-section for Balmer H_α emission from HCl is lower than that in H_2S, amounting to $4.9 \cdot 10^{-22}\,\mathrm{m}^2$ at 100 eV (Möhlmann and de Heer 1979). Theoretical electron-impact dissociation CS through the $X^1\Sigma^+ \to A^1\Pi$ process amounts to $0.23 \cdot 10^{-20}\,\mathrm{m}^2$ at 100 eV (Borges Jr. *et al.* 1989).

Ionization. Nier and Hanson (1936) have measured relative cross-sections for ionization of HCl up to 500 eV. Thresholds for formation of HCl^+, Cl^+, H^+, HCl^{2+} and Cl^{2+} ions have been determined at 12.9 eV, 17.2 eV, 18.6 eV, 35.7 eV and 45.7 eV, respectively;

at 140 eV the corresponding partial cross-sections scale as 100 : 15 : 3 : 0.4 : 3.5. Kinetic energies of ions were measured by Hanson (1937). Lampe *et al.* (1957) determined an integral cross-section of $4.70 \cdot 10^{-20}\,\mathrm{m}^2$ at 75 eV. According to the additivity-rule model of Deutsch *et al.* (1997) the ionization CS reaches a maximum of $3.7 \cdot 10^{-20}\,\mathrm{m}^2$ at 50 eV. This is somewhat lower than the ionization CS of $5.4 \cdot 10^{-20}\,\mathrm{m}^2$ in SiH_4 at the same energy, see table II. In fig. 9 we have adopted the semiempirical values from swarm measurements given by Morgan (1999) and we have compared them with the inelastic (electronic excitation + ionization) CS from the optical model (Jain and Baluja 1992).

Photoionization cross-section reaches a maximum of $0.55 \cdot 10^{-22}\,\mathrm{m}^2$ at 18 eV (Daviel *et al.* 1984). Thresholds for HCl^+, Cl^+ and H^+ photoionization are close to those determined by Nier and Hanson (1936).

Dissociative attachment has been widely studied by swarm (Christophorou *et al.* 1968, Kligler *et al.* 1981, Sze *et al.* 1982, Petrović *et al.* 1988), by beam (Hanson 1937, Azria *et al.* 1974, Ziesel *et al.* 1975, Orient and Srivastava 1985) and flowing afterglow (Adams *et al.* 1986) methods.

Cl^- formation CS exhibits a peak at about 0.85 eV (Orient and Srivastava 1985) and a step-like fall up to 2 eV (Ziesel *et al.* 1975, Abouaf and Teillet-Billy 1977). This kind of fall was explained (Fiquet-Fayard 1974) as caused by the opening of successive, vibrationally excited exit channels for the decay of the compound HCl^- state.

In spite of the numerous measurements there is still some controversy on the absolute value of the peak at 0.85 eV. In fig. 9 the data of Ziesel *et al.* (1975) have been normalized to the theoretical (Teillet-Billy and Gauyacq 1984) value of $0.2 \cdot 10^{-20}\,\mathrm{m}^2$ at the peak, in agreement with several experiments (Christophorou *et al.* 1968, Orient and Srivastava 1985). Enhancement of the threshold Cl^- formation peak by a factor of 40 and 880, compared to the $\nu = 0$ state, was observed for scattering on $\nu = 2$ and $\nu = 3$ excited states, respectively (Allan and Wong 1981).

H^- formation CS exhibits two maxima: a structureless at 7.1 eV and another, somewhat weaker, at 9.3 eV with fine structures superimposed (Azria *et al.* 1974 and 1980, Tronc *et al.* 1979). The two peaks have been attributed to $^{+}\Sigma$ and $^{2}\Pi$ resonant HCl^- states, respectively (Taylor *et al.* 1977, Goldstein *et al.* 1978). Relative values of these H^- peaks are by a factor 25 and 50, respectively, smaller than the Cl^- peak at 0.85 eV (Azria *et al.* 1974). The fine structures in the second peak are associated with a series of Feshbach resonances (Azria *et al.* 1980). Around the first peak (at 6.6–7.6 eV) the angular distributions are dominated by the δs partial-wave while at 8.7–10.2 eV by the δp wave (Tronc *et al.* 1979, Azria 1980).

Resonances. Feshbach resonances between 9 and 11 eV were observed in the H^- dissociative attachment (Azria *et al.* 1980) and in the electron transmission (Spence and Noguchi 1975) experiments. The peak at the threshold and a maximum at about 2.5 eV in the $\nu = 1$ vibrational CS have been attributed (Knoth *et al.* 1989a) to the $3^2\Sigma^+$ and to the intermediate $1^2\Sigma^+$ shape resonant states, respectively. The 2.5 eV shape resonance is also visible in TCS (Hamada and Sueoka 1994). The vibrational excitation (Knoth *et al.* 1989a) amounts to about 10% of the TCS at this resonance, see fig. 9. Time-dependent calculations (Gertitschke and Domcke 1990) show that the lifetimes of the shape resonances in HCl are extremely short (10^{-15} s).

Sum check for HCl evidences inconsistencies among the various measurements. This is caused both by experimental difficulties in handling such a corrosive gas as well as from the polar character of the target. At low energies elastic (and total) CS are extremely forward peaked. As noticed by Hamada and Sueoka (1994) changing the exit apertures in their TCS apparatus from 8 mm to 1 mm rises the measured cross-sections by a factor of about 5 at 0.8 eV. Measurements of rotational excitation and elastic DCS at energies below 5 eV have been performed only for angles above 15° (Rädle *et al.* 1989); any attempt to integrate these data is subject to a big error. We estimate this error to be as big as 30% below 2 eV, diminishing to 10% at 5 eV. For the data of Gote and Ehrhardt (1995) we estimate the uncertainty due to the integration of DCS performed in the present work to be 10% at 5 eV and 20% at 200 eV.

Rädle *et al.* (1989) reported at 1 eV a value of $45 \cdot 10^{-20}\,\mathrm{m}^2$ for the integral CS for the rotational $\Delta J = 1$ transition and a value of $7.0 \cdot 10^{-20}\,\mathrm{m}^2$ for the elastic CS. Our present evaluation of the rotational excitation CS at this energy is lower by a factor of two. On the other hand, the vibrationally elastic integral CS obtained by us from DCS of Rädle *et al.* (1989) and those of Gote and Ehrhardt (1995) practically coincide at 5 eV, see fig. 9.

The summed values in table VIII have been obtained by adding the rotational CS of Rädle *et al.* (1989) integrated in this work, their integral elastic CS and the vibrational CS of Knoth *et al.* (1989a, b). Apart from the lowest energies, the difference between the summed values and the TCS of Hamada and Suoeka (1984) remains within the combined error bars.

As somewhat larger (20%) difference between the (elastic + rotational) integral CS from data of Gote and Ehrhardt (1995) and of Rädle *et al.* (1989) and the total CS (Hamada and Sueoka 1994) is observed at 10 eV, where the CS for the vibrational excitation is already quite low. Note that the two sets of (elastic + rotational) CS are in good agreement with the pioneer measurement of Brüche (1927). At 100 eV the sum of the elastic CS from Gote and Ehrhardt (1995) plus the theoretical absorption CS (Jain and Baluja 1992) is 40% higher than the TCS of Hamada and Sueoka (1994); the difference diminishes to about 15% at 200 eV. Probably TCS of Hamada and Sueoka (1994) are somewhat underestimated.

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3˙6. *Other hydrogen halides* (HF, HBr). – Little experimental work was done on other halon hydrides. The main interest was focused on vibrational excitation, because of the existence of near-to-threshold resonant structures, similar to those observed in HCl.

Hydrogen fluoride (HF). We are not aware of TCS measurements in HF. Elastic scattering (and rotational excitation) was studied by Rädle *et al.* (1989) in the 0.63–10 eV energy range. These experimental CS are in good agreement with theory (Padial and Norcross 1984). Rotationally elastic ($\Delta J = 0$) integral CS reaches a minimum at about 3–4 eV and at lower energies rises less steeply than what is predicted by the theory (Rädle *et al.* 1989). At 45° scattering angle the DCS for the dipole-induced $\Delta J = 1$ rotational excitation descends monotonically with collision energy and exceeds the elastic DCS. The two, $\Delta J = 0$ and $\Delta J = 1$, DCS are equal at 10 eV. At 1 eV an integral value of $110 \cdot 10^{-20}\,\mathrm{m}^2$ for the $\Delta J = 1$ rotational excitation at 1 eV has been reported (Rädle *et al.* 1989).

Vibrational excitation CS shows a sharp near-to-threshold peak both for the $\nu = 0 \rightarrow 1$ mode (Rohr and Linder 1976, Knoth *et al.* 1989a) as well as for the $\nu = 0 \rightarrow 2$ one (Knoth *et al.* 1989b). At 0.63 eV the $\nu = 0 \rightarrow 1$ vibrational excitation for different rotational transition $\Delta J = 0, 1, 2, 3$ is depleted in the forward direction, similarly as in HCl (Knoth *et al.* 1989a). In contrast to HCl, no resonance enhancements in the vibrational nor in the rotational channel were observed up to 10 eV.

In the zero-energy limit, experiments on Rydberg-atoms quenching indicate a quick rise of the rotational excitation CS (Ling *et al.* 1993, Hill *et al.* 1996). This rise exceeds the values predicted by the Born formula (see Part I) and has been explained assuming the existence of a virtual state with a binding energy of 1.0–1.5 meV (Hill *et al.* 1996). A scattering length value of about $-100a_0$ was derived.

Electronic excitation and ionization in the zero-angle limit was studied by Carnovale *et al.* (1981) and Carnovale and Brion (1983). The photoabsorption CS obtained in these papers shows three maxima, at about 10 eV, 15 eV and 21 eV. The first maximum (in the electronic excitation range) amounts to $0.05 \cdot 10^{-20}\,\mathrm{m}^2$, compared to $0.17 \cdot 10^{-20}\,\mathrm{m}^2$ for the remaining two, above the ionization threshold (Carnovale *et al.* 1981). Energy-loss spectra at 70 eV collision energy and 11–16 eV energy loss were studied by Salama and Hasted (1976).

Carnovale *et al.* (1981) comparing the photoabsorption CS above 20 eV of Ne with the ones of isoelectronic molecules noticed that the fall of CS with increasing energy becomes steeper going from Ne to HF, H_2O, NH_3, CH_4. The photoabsorption CS for the four molecules intersect at about 30 eV.

We are not aware of experimental determinations of ionization CS. The additivity-rule model (Deutsch *et al.* 1997) yields a maximum of $1.4 \cdot 10^{-20}\,\mathrm{m}^2$ at 90 eV, compared to $3.9 \cdot 10^{-20}\,\mathrm{m}^2$ in CH_4, see subsect. **2**˙1. Just above the ionization threshold (16 eV) only HF^+ ions were detected; the H^+ ions appear above 19 eV. Branching ratios at 60 eV amount to 66%, 22.5% and 11.5% for HF^+, H^+ and F^+ ions, respectively (Carnovale and Brion 1983).

In analogy with HCl, enhancement of the dissociative attachment CS by one order of magnitude for scattering on the vibrationally ($\nu = 1$) excited molecule has been observed in HF (Allan and Wong 1981). The cross-section for F^- formation from vibrationally excited HF reaches a maximum at 2.0 eV. The flowing-afterglow technique has been used to study the $e^- + HF$ attachment rate but the ion yield was below the experimental sensitivity (Adams *et al.* 1986).

Feshbach resonances have been identified in HF, HCl, HBr and HI by Spence and Noguchi (1975). In HF one resonance series resulting from the addition of a pair of

TABLE IX. – *Comparison of threshold and shape resonances for* HF*,* HCl*, and* HBr *(from Rohr, 1978). "cross-sections" refer to integral CS for excitation of $\nu = 1$ modes. For* HF *and* HCl *we give re-measured values (Knoth et al. 1989a, Rädle et al. 1989) in parenthesis, whenever different from those quoted by Rohr (1978).*

	Threshold resonance ($\nu = 1$)		Shape resonance ($\nu = 1$)		Number of vibrations observed
	Position (eV)	Cross-section ($10^{-20}\,\mathrm{m}^2$)	Position (eV)	Cross-section ($10^{-20}\,\mathrm{m}^2$)	
HF	0.51 (0.7)	7	*	1	2
HCl	0.51	20 (10)	2.5	3	3
HBr	0.41	40	0.9	27	6

* - No clear maximum observed in the 1–5.5 eV range (Rädle *et al.* 1989).

$3s\sigma$ electrons to the positive $X\,^2\Pi$ ion core has been observed between 12.8 and 13.9 eV collision energy (Spence and Noguchi 1975).

Hydrogen bromide (HBr). HBr possesses a smaller dipole moment (0.82 D) than HF (1.82 D) and HCl (1.11 D) molecules. A few experiments only and several calculations (Malegat and Le Dourneuf 1990, Fandreyer and Burke 1996, Rescigno 1996) were performed on HBr.

Rohr (1978) measured vibrationally elastic and vibrational excitation CS up to 7 eV. The integral elastic CS rises towards zero energy, amounting to $100 \cdot 10^{-20}\,\mathrm{m}^2$ and $70 \cdot 10^{-20}\,\mathrm{m}^2$ at 1 eV and 5 eV, respectively. DCS dependences on energy show a minimum at 2 eV ($\theta = 80°$) and 3 eV ($\theta = 20°$). Theoretical calculations (Fandreyer *et al.* 1993, Rescigno 1996) predict the zero-energy rise of the integral elastic CS, a shallow minimum at about 1 eV, a weak maximum at 2.0 eV and almost a constant value of about $30 \cdot 10^{-20}\,\mathrm{m}^2$ between 4 eV and 10 eV (Rescigno 1996). We recall that, like for HCl, absolute values of Rohr (1978) could be overestimated.

The vibrational excitation exhibits near-to-threshold peaks, similar to HF and HCl (Rohr 1978, Sergenton *et al.* 1999). The peak in the $\nu = 1$ integral CS amounts to about $40 \cdot 10^{-20}\,\mathrm{m}^2$ and is followed by a broader maximum of $27 \cdot 10^{-20}\,\mathrm{m}^2$ at 0.9 eV (Rohr 1978). Threshold peaks and broad maxima were observed also for higher overtones, up to $\nu = 5$. The maxima in DCS, as observed at 60°, scale roughly by a factor of three, passing from $\nu = 1$ to $\nu = 2$ and so on. The near-to-threshold peaks are well reproduced by theories (Fandreyer *et al.* 1993, Horáček and Domcke 1996).

As pointed out by Rohr (1978), the vibrational excitation CS differ from Born's approximation much more in the case of HBr than in HF and HCl targets. In HBr higher overtones are excited and the threshold resonance is stronger (see table IX). Similarly, also the shape resonance leads to a higher vibrational excitation in HBr than in HF and HCl.

Optical emission CS for H_α Balmer series amounts to $7.1 \cdot 10^{-22}\,\mathrm{m}^2$ at 100 eV (Möhlmann and de Heer 1979). Valence and inner-shell electronic excitation energy-loss spectra were studied by Shaw *et al.* (1984).

Electron attachment CS exhibits a large maximum that peaks at 0.39 eV; a weak structure related to the opening of higher vibrational states is superimposed on it (Ziesel *et al.* 1975, Abouaf and Teillet-Billy 1980). The peak value amounts to $4.0 \cdot 10^{-20}\,\mathrm{m}^2$

(Christophorou *et al.* 1968). This value as well as the shape of the experimental curve well reproduced by the theory (Horáček and Domcke 1996). Attachment rate coefficients for HI and HBr are one order of magnitude higher than for HCl (Adams *et al.* 1986, Alajajian and Chutjian 1988, Chutjian *et al.* 1990, Smith and Španěl 1994).

Rohr (1978) postulated the existence of two resonant states at low energies, both of them of the $^2\Sigma^+$ symmetry. The shape resonance, responsible for the broad maximum in elastic and vibrational excitation CS as well as for the gross structure in dissociative attachment, is located at about 0.9 eV. A second resonance, at the vibrational excitation threshold, is responsible for the appearance of steps in dissociative-attachment CS and sharp peaks in the vibrational excitation CS. A comparison between these two types of resonances in HF, HCl and HBr is given in table IX.

Feshbach resonances in HBr were studied by Spence and Noguchi (1975) and Čubrić *et al.* (1994).

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4. – Triatomic molecules

In this section the triatomic molecules formed by second and third row periodic-table atoms will be considered. Some of them (CO_2, CS_2, N_2O) are linear, other (NO_2, SO_2, O_3) have a bent configuration.

4˙1. *Carbon dioxide* (CO_2). – Electron scattering on CO_2 has been extensively studied, due to its importance for gas lasers (Lowke *et al.* 1973). The impact of anthropogenic CO_2 emission on the Earth's radiation budget, although known since one century, has been recently admitted in the scientific community (Hansen *et al.* 1981). The growing consequences of the global warming will possibly lead in the next years to an increase of both experimental and theoretical investigation on CO_2 and on other atmospheric trace gases (as for instance H_2O, SO_2, CH_4, ClO_2, O_2, O_3, NO_x). Figure 12 gives a view of integral cross-sections for CO_2. Sets of momentum transfer cross-sections were reported by Lowke *et al.* (1973), Nakamura (1995), Hasegawa *et al.* (1998) and inelastic cross-sections by (Waibel and Grosswendt 1991) and Beuthe and Chang (1997).

Total cross-sections have been measured between 0.1 eV and 5000 eV. TCS rises in the limit of very low energies reaching as much as $60 \cdot 10^{-20}\,\mathrm{m}^2$ at 0.1 eV (Ferch *et al.* 1981, Buckman *et al.* 1987). The rise of TCS below 1 eV has been also confirmed by Field *et al.* (1991) in a synchrotron-radiation electron-source experiment. This rise, much above the near-to-zero values in the heavier noble gases, is somehow unexpected considering that CO_2 does not possess a permanent dipole moment in its ground state. The presence of a virtual-state resonance at zero energy has been postulated (Estrada and Domcke 1985).

TCS reaches a minimum of $5.8 \cdot 10^{-20}\,\mathrm{m}^2$ at 1.9 eV (Szmytkowski *et al.* 1987), exhibits a resonant structure around 3.8 eV and another, wide maximum at 25 eV. At low energies the TCS of Szmytkowski and Zubek (1978), Buckman *et al.* (1987), Szmytkowski *et al.* (1987), Ferch *et al.* (1981) and Hoffman *et al.* (1982) agree within 10%. The normalized cross-sections of Suoeka and Mori (1984) were lower than other data sets at 20–400 eV and are not reported in fig. 12. The more recent results from the same laboratory (Kimura *et al.* 1997) agree well with the data of Szmytkowski *et al.* (1987) up to 10 eV. In the 10–50 eV range the data of Kimura *et al.* agree with the Detroit measurements (Kwan *et al.* 1983) but are higher than Gdańsk results (Szmytkowski *et al.* 1987). On the other hand, the data of Szmytkowski *et al.* coincide with integral elastic CS of Tanaka *et al.* (1998). As at energies above 10 eV some contribution from the electronic excitation is expected, we suppose that the data of Szmytkowski *et al.* are slightly underestimated between 10 and 50 eV. One possible reason could be an imperfect screening against inelastically scattered electrons.

At high energies, the data from Trento laboratory in Szmytkowski *et al.* (1987) practically coincide with the more recent measurements of García and Manero (1996) up to 1000 eV but are about 20% lower at 2500 eV. A partial reason for that can be a lack of retarding field analyzer for scattered electrons in the Trento apparatus that can lead to an underestimation of measured TCS. On the other hand, more recent linear-transmission experimental results of Xing *et al.* (1997) in the 1000–4000 eV range in N_2O lie somewhat below the data of García and Manero (1996).

Due to the peculiar features of low-energy TCS and the use of CO_2 in infrared lasers, special attention has been devoted to scattering from the vibrationally excited molecule. It has been noticed by Buckman *et al.* (1987) and by Ferch *et al.* (1989) that TCS in the low energy limit rises with the temperature of the gas. The TCS for scattering on the vibrationally excited $\nu_2 = (010)$ molecule has been deduced to exceed that for the ground

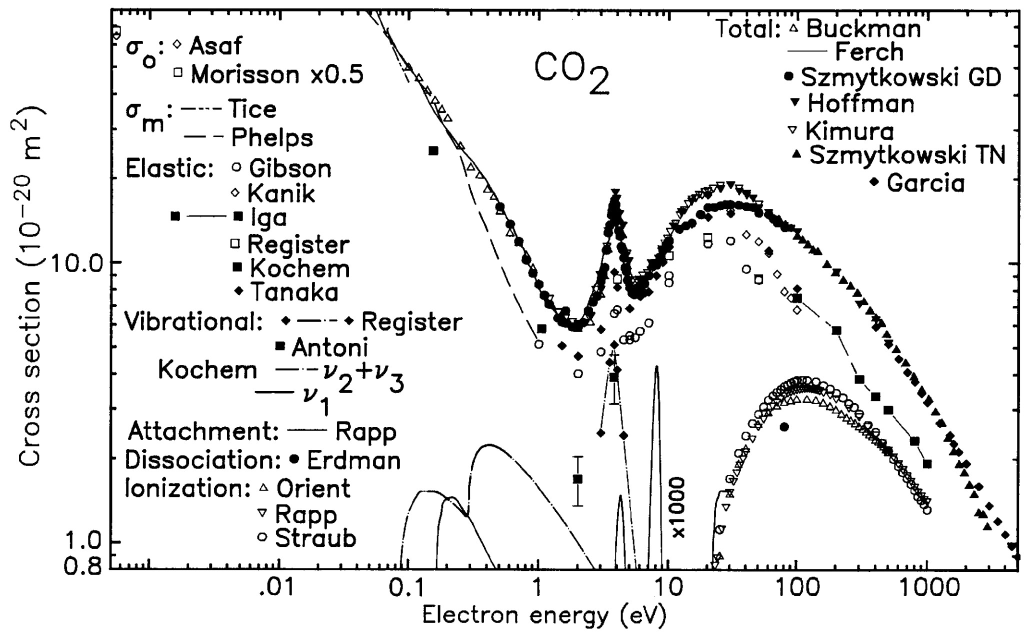

Fig. 12. – Integral cross-sections for electron scattering on CO_2. Total (absolute): Ferch *et al.* (1981); Buckman *et al.* (1987); Szmytkowski GD, Gdańsk data from Szmytkowski *et al.* (1987); Kimura *et al.* (1997); Hoffman stands for Kwan *et al.* (1983) and Hoffman *et al.* (1982); Szmytkowski TN, Trento data from Szmytkowski *et al.*; García and Manero (1996); Sueoka and Mori (1984), not shown. *Momentum transfer*: Phelps (1999); Tice and Kivelson (1967), cyclotron resonance. *Zero-energy*: Asaf *et al.* (1991), Fano method; Morrison (1982) theory. *Elastic*: Kochem *et al.* (1985); Gibson *et al.* (1999), data from two laboratories, see text; Register *et al.* (1980); Tanaka *et al.* (1998); Iga *et al.* (1984), squares with full line; Iga *et al.* (1999b), squares with broken line; Shyn *et al.* (1978), not shown for clarity. *Vibrational excitation*: Kochem *et al.* (1985), sum of (010) and (001) modes from Born approximation, and theory of Estrada and Domcke (1985) for (100), in agreement with experiment; Antoni *et al.* (1986), absolute; Register *et al.* (1980), sum, around 4 eV data of Čadež *et al.* (1977) normalized to Register *et al.* (1980). *Electron attachment*: Rapp and Briglia (1965). *Dissociation into neutrals*: Erdman and Zipf (1983) plus LeClair and McConkey (1984). *Ionization*: Orient and Srivastava (1987); Rapp and Englander-Golden (1965); Straub *et al.* (1996).

state by a factor of about two at low energies. This is to be attributed to a non-zero dipole moment of the molecule in the bending vibrational mode.

Swarm measurements (Pack *et al.* 1962, Hake and Phelps 1967, Elford and Haddad 1980, Roznerski and Leja 1984) and cyclotron-resonance measuerements (Tice and Kivelson 1967) agree with the beam data and indicate a rise of the momentum transfer CS in the zero-energy limit. According to Lowke *et al.* (1973), Tice and Kivelson (1967) and the recent compilation of Phelps (1999) the momentum transfer CS falls with energy approximately as $E^{-1/2}$ between 0.001 eV and 0.1 eV. The more recent drift parameter measurements include works by Roznerski and Mechlińska-Drewko (1994) and Hasegawa *et al.* (1996, 1998).

Zero-energy cross-section obtained from a Rydberg-atoms quenching experiment (Asaf *et al.* 1991) amounts to $64 \cdot 10^{-20}\,\mathrm{m}^2$ and is in a rather serious disagreement both with the swarm-derived value ($600 \cdot 10^{-20}\,\mathrm{m}^2$, Phelps, 1999) as well as with the theory

($134 \cdot 10^{-20}\,\mathrm{m}^2$, Morrison, 1982). We note however, some discrepancies in the theoretical evaluations of the low-energy TCS (Takekawa and Itikawa 1996, Gianturco and Stoecklin 1996). The modified effective range theory of Fabrikant (1984) yields a scattering length value between $-7.2a_0$ and $-6.8a_0$ (TCS of about $170 \cdot 10^{-20}\,\mathrm{m}^2$). Experiments on Rydberg atoms quenching (Ling *et al.* 1993) indicate CS with the order of magnitude of $100 \cdot 10^{-20}\,\mathrm{m}^2$ at energies of 1 meV or so.

Elastic cross-sections have been studied in numerous experiments. In spite of this, the data are somewhat contradictory, especially for integral cross-sections (see a comparison by Gibson *et al.* 1999). The measurements at low energies (Kochem *et al.* 1985) reproduce the general rise of TCS towards low energies. The angular distributions at the lowest investigated energy (0.155 eV) indicate a high contribution from *p*-wave scattering. A rough estimate of the integral elastic CS obtained in this work from the differential data of Kochem *et al.* gives $25 \cdot 10^{-20}\,\mathrm{m}^2$ at 0.155 eV and $5.8 \cdot 10^{-20}\,\mathrm{m}^2$ at 1.05 eV.

The integral elastic CS of Shyn *et al.* (1978), obtained by normalization to helium, exceed TCS at energies below 50 eV; this suggests a normalization error. The renormalization of Shyn *et al.*'s by a factor of 0.75 to the elastic CS of Register *et al.* (1980) at 10 eV eliminates this discrepancy. However, the renomalized data of Shyn *et al.*'s are still significantly higher than the elastic CS of Register *et al.* at 4 eV. This difference is probably due to the poorer energy resolution (60 meV FWHM) of Shyn *et al.*'s apparatus in comparison to that of Register *et al.* (23 meV). Such a resolution did not allow Shyn *et al.* to resolve completely the lowest vibrational excitation (with 83 meV threshold) at the $^2\Pi$ resonance position.

The recent absolute determination of Tanaka and co-workers (Tanaka *et al.* 1998, Sakamoto *et al.* 1999) merges well with the integral CS from measurements of Kochem *et al.* (1985) and practically coincides with Register *et al.*'s one at 4–10 eV. The data of Shyn *et al.* renormalized by a multiplicative factor 0.75 are in agreement with Tanaka *et al.* (1998) at 50 eV and 100 eV. On the other hand, the two independents sets of CS by Gibson *et al.* (1999)—from the Flinders University at 5–50 eV and from Australian National University in Canberra at 1–10 eV fall between the integral CS of Tanaka *et al.* (1998) and that of Register *et al.* (1980). Below 10 eV the DCS of Gibson *et al.* practically coincide within the error bars with measurements of Shyn *et al.*, Register *et al.* and Tanaka *et al.* Some discrepancies start to be visible at 10 eV and above, with the DCS from Canberra being lower, at small scattering angles, than the DCS from Flinders University.

The differential CS of Kanik *et al.* (1989), measured with a resolution of about 200 meV, agree well at 20 eV and 50 eV with the measurements of Shyn *et al.* (1978) but are somewhat higher than the latter at 90 eV. Due to the limited angular range (20°–120°) of the measurements of Kanik *et al.*, the integral values (obtained in this work) can be subject to extrapolation errors of about ±20%. Iga *et al.* (1984) have obtained elastic CS values at 500–1000 eV by normalization to the N_2 data. Their values at 500 eV agree well with the values of Bromberg (1974). Also at 300 eV the recent DCS (Iga *et al.* 1999a) agree well with Bromberg's data. The data of Iga *et al.* (1999b) agree both with the integral CS of Register *et al.* (1980) and Tanaka *et al.* (1998) up to 100 eV as well as with the DCS of Kanik *et al.* (1989) and those of Bromberg. This is not the case of the measurements of Maji *et al.* (1998) which at 500 eV are lower than Bromberg's data by a factor of five at 30° and by a factor of three at 40°.

Low angle DCS at high-energies were given by McClelland and Fink (1985) and by Breitenstein *et al.* (1984). DCS at 2°–5° at 300–500 eV are in CO_2 roughly twice those in O_2, compare fig. 26 in (Part I). Absolute DCS in the 20°–130°, 1.5–100 eV range have been recently measured by Sakamoto *et al.* (1999) and in the 20°–120°, 2–10 eV range by Ono *et al.* (1999).

Vibrational excitation at energies below 1 eV (Kochem *et al.* 1985) indicates the presence of non-direct (resonant) processes. The angular distributions at collision energies of 0.2 eV and 1.0 eV for the infrared inactive symmetric-stretch (100) mode are isotropic, within the experimental error (Kochem *et al.* 1985). Experimental results for this mode are higher than the values obtained by the Born approximation but are in agreement with more advanced theories (Estrada and Domcke 1985, Whitten and Lane 1982). The integrated CS for this mode reaches a maximum of $1.3\cdot 10^{-20}\,\mathrm{m}^2$ at about 0.2 eV (Estrada and Domcke 1985).

The infrared active (010) bending and (001) asymmetric stretching modes in the near-to-threshold region follow the Born approximation. The angular distributions are forward-peaked, both in 0.3 eV–1 eV range (Kochem *et al.* 1985) as well as 2 eV and 3.6 eV (Antoni *et al.* 1986). Differential CS at a fixed angle of 20° for the (010) and (001) modes descend monotonically with energy up to 6 eV (Johnstone *et al.* 1995). The sum of the two integral vibrational CS in the Born approximation, using dipole transition moments of 0.063 a.u. for (010) and 0.126 a.u. for (001) modes (Bishop and Cheung 1982), reaches a maximum of $2.2\cdot 10^{-20}\,\mathrm{m}^2$ at 0.4 eV. Note, however, some discrepancies among the absolute magnitudes of low-energy vibrational excitation CS obtained by different methods: swarm (Hake and Phelps 1967, Bulos and Phelps 1976), crossed beam (Boness and Schulz 1968, Field 1991), SF_6-scavenger method (Stamatovic and Schulz 1969).

Vibrational excitation is highly enhanced in the region of the resonance at 3.8 eV. The enhancement regards mainly the symmetric stretch (100) mode and the bending (020) mode with its higher overtones (Antoni *et al.* 1986, Johnstone *et al.* 1995). According to Register *et al.* (1980) one third of TCS in the resonance region is due to vibrational excitation. Overtones up to 10th order of the symmetric stretching mode have been observed (Čadež *et al.* 1977). With one quantum of bending $(n,1,0)$, the modes up to $n=23$ were observed (Boness and Schulz 1974, Čadež *et al.* 1977).

It has been recently pointed out (Cartwright and Trajmar 1996) that angular distributions for odd overtones, (11^10), (03^10), (05^10) and so on exhibit zero DCS values for 0° and 180° scattering angles, due to symmetry violation reasons (compare pag. 117 in Part I, for the $X\,^3\Sigma_g^- \to b\,^1\Sigma_g^+$ electronic transition in O_2). The (010) mode shows a mixed angular distribution, influenced by a dipole interaction at low angles.

An enhancement of the (100) excitation has been observed around 10 eV and 30 eV (Tronc *et al.* 1979b). The (200) mode is excited at these energies with an intensity 5 and 7 times lower, respectively.

Vibrational energy loss spectra for both inelastic and superelastic scattering from thermally excited molecules were studied by Johnstone *et al.* (1993, 1999). The recent measurements of vibrational excitation CS by Ono *et al.* (1999) and Watanabe *et al.* (1999) at 2–10 eV and 2–30 eV, respectively, agree well with the data of Register *et al.* (1980).

Rotational excitation has been studied *via* broadening of the vibrational excitation peak at 2 eV and 3.8 eV by Antoni *et al.* (1986). Outside the resonance, at 2 eV, rotational excitations accompany the infrared active vibrational modes, with the $\Delta J = \pm 1$ change in the half of the (010) transition events and in all (001) transitions (the latter due to the symmetry requirements). Resonant scattering enhances the rotational $\Delta J = \pm 2$ transitions in symmetric stretch (100) excitations. For the resonant excitation of the (010) bending mode all seven $\Delta J = 0, \pm 1, \pm 2, \pm 3$ transitions are almost equally probable.

Electronic excitation. Electronic excitation energy-loss spectra for valence transitions have been studied by Meyer and Lassettre (1965), Hall *et al.* (1973), Klump and Lassettre (1978), McDiarmid and Doering (1984). The most complete study in the forward-scattering configurations is that one of Chan *et al.* (1993), covering the 6 to 203 eV energy-loss range. The most prominent structures in the photoabsorption CS below the ionization threshold are due to excitations to the $^1\Sigma_u^+$ and $^1\Pi_u$ states at 11.05 eV (with CS maximum of $1.0 \cdot 10^{-20}\,\mathrm{m}^2$) and at 11.40 eV, respectively (Chan *et al.* 1993).

Inner-shell excitation was studied experimentally by Tronc *et al.* (1979a), Hitchcock and Ishii (1986), Letardi *et al.* (1989), Boechat Roberty *et al.* (1991) and theoretically by de Miranda and Bielschowsky (1993) and Fomunung *et al.* (1996).

Optical emission from CO_2 excited by electron impact up to 350 eV collision energy was studied in several works (Ajello 1971, Mumma *et al.* 1972, Kanik *et al.* 1993). Emission from the ${CO_2}^+$ ion, from the metastable $a^3\Pi$ CO radical and the CO^+ ion, and from atomic fragments dominate in the intervals 280–450 nm, 195–250 nm and 126–195 nm, respectively (Ajello 1971). The emission CS for the ionized molecule transitions ${CO_2}^+$ ($\tilde{A}\,^2\Pi_u \rightarrow \tilde{X}\,^2\Pi_g$) and ${CO_2}^+$ ($\tilde{B}\,^2\Sigma_u \rightarrow \tilde{X}\,^2\Sigma_g$) amount to $0.8 \cdot 10^{-20}\,\mathrm{m}^2$ and $0.5 \cdot 10^{-20}\,\mathrm{m}^2$, respectively at 200 eV (Ajello 1971). These values compare to $2.6 \cdot 10^{-20}\,\mathrm{m}^2$ of the overall CS for ionization into ${CO_2}^+$ (Orient and Srivastava 1987), indicating that the parent ion is produced in excited states in half of the ionizing events.

Surprisingly high seems to be the emission CS from the at $^3\Pi \rightarrow X\,^1\Sigma^+$ transition in CO (Cameron band) produced in dissociation of CO_2. Ajello (1971) reported a maximum value of $0.1 \cdot 10^{-20}\,\mathrm{m}^2$ for the $(0, 1)$ vibronic band of the CO ($a\,^3\Pi \rightarrow X\,^1\Sigma^+$) electronic transition. Erdman and Zipf (1983) argued that the total CS for the CO ($a\,^3\Pi \rightarrow X\,^1\Sigma^+$) transition amounts to as much as $2.4 \cdot 10^{-20}\,\mathrm{m}^2$ at 80 eV, *i.e.* almost 20% of TCS.

At 200 eV the summed CS for the ultraviolet emission from the C radical and the C^+ ion in the 130–170 nm range amounts to $0.02 \cdot 10^{-20}\,\mathrm{m}^2$ and $0.01 \cdot 10^{-20}\,\mathrm{m}^2$, respectively (Mumma *et al.* 1972). At the same energy the emission CS from ionized atomic species in the extreme ultraviolet range (40–125 nm) amounts to $0.03 \cdot 10^{-20}\,\mathrm{m}^2$ (Kanik *et al.* 1993). At the same impact energy the CS for the formation of atomic ions amounts to $1.0 \cdot 10^{-20}\,\mathrm{m}^2$ (Tian and Vidal 1998a).

Ionization. The recent measurements of total ionization CS (Orient and Srivastava 1987, Straub *et al.* 1996, Tian and Vidal 1998a) coincide within the error bars with the experiment of Rapp and Englander-Golden (1965) performed up to 1000 eV and the data of Shyn and Sharp (1979) in the 50–400 eV range obtained from differential measurements. In particular, CS for the formation of the ${CO_2}^+$ ion of Straub *et al.* (1996), Tian and Vidal (1998a) and Adamczyk *et al.* (1972) coincide at 100 eV and they are bounded within ±20% limits by the data of Krishnakumar (1990) and Orient and Srivastava (1987) from above and Freund *et al.* (1990) and Märk and Hille (1978) from below.

Somewhat bigger discrepancies exist for dissociative ionization CS: only the data of Tian and Vidal (1998a) and those of Straub *et al.* (1996) coincide. The share of non-dissociative (${CO_2}^+$) ionization remains constant in the whole 100 eV–500 eV energy range (Orient and Srivastava 1987) and amounts to about 60% of total ionization CS (Tian and Vidal 1998a). At 100 eV the O^+, CO^+, C^+ ionization CS amount to 0.7, 0.5, $0.35 \cdot 10^{-20}\,\mathrm{m}^2$ approximately (Tian and Vidal 1998a, b).

Double ionization to ${CO_2}^{++}$ at 100 eV amounts to 1% of the ${CO_2}^+$ yield (Märk and Hille 1978, Tian and Vidal 1998a). DCS for dissociative ionization were studied by Zhukov *et al.* (1990) and for overall ionization by Shyn and Sharp (1979) and Ogurtsov (1998). The threshold ionization has been studied by Winkler and Märk (1994) indicating a linear rise of the CS with energy, in contrast to Wannier's law.

Dissociative attachment ($O^- + CO$) exhibits two peaks of $0.15 \cdot 10^{-20}\,\mathrm{m}^2$ and $0.44 \cdot 10^{-20}\,\mathrm{m}^2$ at 4.4 eV and 8.1 eV, respectively (Asundi *et al.* 1963, Rapp and Briglia 1965). It does not exceed one part in 10^3 of the TCS. Structures in negative-ion yield due to vibrational excitation in the region of the 4.4 eV resonance were studied by Stamatovic and Schulz (1973), Abouaf *et al.* (1976), Dressler and Allan (1985), Cicman *et al.* (1998). Weak structures for production of $O_2{}^-$ and C^- ions have been observed in the 11.3–13 eV and 17–19 eV range (Spence and Schulz 1974, Orient and Srivastava 1983).

Dissociation into neutrals has been studied by metastable-fragments detection (Misakian *et al.* 1975, Allcock and McConkey 1976, Barnett *et al.* 1992, LeClair and McConkey 1994). A cross-section as high as $2.4 \cdot 10^{-20}\,\mathrm{m}^2$ at 80 eV has been deduced from fluorescence studies of the CO ($a^3\Pi$) fragment (Erdman and Zipf 1983); the O atom is produced mainly in the ^5S state in this process (Misakian *et al.* 1975). The cross-section for another possible channel ($\mathrm{CO}\,{}^1\Sigma^+ + \mathrm{O}\,{}^1S_0$) amounts to only $0.16 \cdot 10^{-20}\,\mathrm{m}^2$ at this energy (LeClair and McConkey 1994).

Resonances. The peak in TCS at 3.8 eV has been attributed to an intermediate lifetime resonance of the $^2\Pi_\mathrm{u}$ symmetry (Claydon *et al.* 1970, Dill *et al.* 1979). In the vibrational excitation functions (Boness and Schulz 1974, Čadež *et al.* 1974, 1977), in the spectroscopy of threshold electrons (Cvejanović *et al.* 1985) and in the transmitted electron currents (Boness and Hasted 1966, Burrow and Sanche 1972, Sanche and Schulz 1973, Szmytkowski and Zubek 1978) some oscillatory structure superimposed on the resonant maximum has been detected. However, this effect is to small to be visible in TCS.

High-resolution ($\Delta E = 17\,\mathrm{meV}$) vibrational excitation studies in the 3.5 eV–4.2 eV region (Allan 1989, Currell and Comer 1993, 1995, Currell 1996) evidenced the presence of three vibrational progressions in the energy loss spectra. This indicates (Currell 1996) a possible decay of the temporarily negative $CO_2{}^-$ state to the Π_u and, with a smaller probability, to the Σ_g state. Also recent calculations (Kazansky 1995) indicate that the parent configuration of the 3.8 eV resonance is probably bent rather than linear because of a similar configuration of the $CO_2{}^-$ ion (Pacansky *et al.* 1975). A possible core-excited mechanism for this resonance has been discussed (Cartwright and Trajmar 1996).

The second peak at 8.1 eV in the dissociative attachment CS (Rapp and Briglia 1965) and the enhancement of the vibrational CS in this region (Tronc *et al.* 1979b) have been attributed to the formation of the CO_2^- ($^2\Sigma_\mathrm{g}{}^+$) resonant state (Claydon *et al.* 1970). The enhancement of stretching vibration mode at 30 eV has been associated to a resonant state with Σ_u symmetry (Tronc *et al.* 1979b).

Inner shape resonances in the regions of both C and O atom core-excitations, between 300–320 eV and 540–580 eV, respectively, have been observed in photoionization studies (Schmidbauer *et al.* 1995), photoelectron (Truesdale *et al.* 1984) and in electron energy-loss studies (Wight and Brion 1974). The inner-shell resonance observed in the ionization channel at 290 eV amounts to 0.2% of the overall positive ions signal (King *et al.* 1980).

Sum check indicates a limited consistency of the measured partial cross-sections, see table X. At 0.155 eV the sum of the elastic and vibrational cross-section of Kochem *et al.* (1985) are 30% lower than the absolute total value (Buckman *et al.* 1987); the main source of uncertainty is due to the integration error of the elastic part. At 4 eV and 10 eV the sum, using the elastic and vibrational values of Register *et al.* (1980), agrees with the TCS of Szmytkowski *et al.* (1987) and Kimura *et al.* (1997) within 10%.

Between 20 eV and 100 eV the sum of elastic and ionization CS is about 10–20% lower than different evaluations of the TCS (Szmytkowski *et al.* 1987, Kimura *et al.* 1997). Using for the electronic excitation CS the re-normalized (Erdman and Zipf 1983) optical emission CS for the $a\,{}^3\Pi$ state of CO (Ajello 1971) one brings the summed CS into a good agreement with TCS. It is worth stressing the high contribution from the dissociation into neutral CO in electron scattering on CO_2 at intermediate energies, equal

TABLE X. – *Integral cross-sections for electron scattering on carbon dioxide (in 10–20 m^2 units).*

Energy (eV)	Elastic	Vibrational	Dissociation	Ionization	Summed	Total
0.155	25 K	1.3 K			26.3	35.3 F
1.05	5.8 K	1.4 K			7.2	7.7 F
2.0	4.62 T	1.69 A			6.3	5.84 B
4.0	8.73 R	4.13 R			12.9	14.2 SZ
	11.0 S	3.90 A			14.9	15.4 B
10.0	10.61 R	0.59 R			11.2	12.0 SZ
	11.4 T				12.0	
20.0	12.32 R	0.26 R	1.4 E	0.41 O	14.4	16.2 SZ
	14.59 T			0.56 ST	16.8	18.5 KI
	17.5 KA				19.7	
50.0	11.7 S	0.05 R	2.3 E	2.66 O	16.7	15.1 SZ
	8.75 R				13.8	
	11.9 KA				16.9	17.0 KI
60.0	11.0 T		2.3 E	3.24 ST	16.5	16.2 SZ
	10.8 KA				16.3	15.1 KI
90.0	7.14 S		2.5 E	3.23 O	12.9	13.4 SZ
	7.5 KA				13.2	
100	8.1 T		2.5 E	3.81 ST	14.4	12.5 SZ
	6.8 KA				13.1	
500	2.98 I			2.14 RE	5.12	5.47* SZ
800	2.31 I			1.57 RE	3.88	3.88* SZ
1000	1.92 I			1.4 RE	3.32	3.33* SZ

* - Interpolated values.
A - Antoni *et al.* (1986).
B - Buckman *et al.* (1987).
E - CO $a\,^3\Pi$ of Erdman and Zipf (1983) at 80 eV plus CO $^1\Sigma^+$ of LeClair and McConkey (1994).
F - Ferch *et al.* (1981).
I - Iga *et al.* (1984).
K - Kochem *et al.* (1985), elastic CS integrated in this work, vibrational from theory (Estrada and Domcke 1985 and Born approximation).
KA - Kanik *et al.* (1989), DCS integrated in this work.
KI - Kimura *et al.* (1997), read from figure.
O - Orient and Srivastava (1987).
R - Register *et al.* (1980).
S - Shyn *et al.* (1978), normalized (this work) by 0.75 to Register *et al.* (1980) at 10 eV.
ST - Straub *et al.* (1996).
RE - Rapp and Englander-Golden (1965).
SZ - Szmytkowski *et al.* (1987).
T - Tanaka *et al.* (1998).

to that of the ionization. At 50 eV the sum of recent elastic CS (Tanaka *et al.* 1998) with inelastic contributions agrees better with TCS measurement of Kimura *et al.* (1997) than with that of Szmytkowski *et al.* (1987).

At 800 and 1000 eV the sum of the elastic cross-section of Iga *et al.* (1984) and of the ionization measurements of Rapp and Englander-Golden coincides with the total values (Szmytkowski *et al.* 1987). At 1000 eV the ionization cross-section constitutes 42% of TCS.

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4·2. *Nitrous oxide* (N_2O). – Relatively few electron scattering experiments have been performed on N_2O, in spite of its basic importance in biochemistry and in atmospheric chemistry (Wang and Sze 1980). N_2O is a linear, asymmetric (N-N-O) molecule, with a slight (0.28 D) dipole moment. A semiempirical set of cross-sections was given by Hayashi (1992). The integral CS for N_2O are shown in fig. 13.

Total cross-sections have been measured by Ramsauer and Kollath (1930) between 0.1 eV and 2 eV, by Brüche (1927) between 2 eV and 50 eV, by Zecca *et al.* (1974) between 0.2 eV and 7 eV, by Szmytkowski and co-workers (1984, 1989, 1996) between 0.4 eV and 250 eV, by Kwan *et al.* (1984) between 1 eV and 500 eV and by Xing *et al.* (1997) at 600–4250 eV. The agreement between different sets of data is not perfect. In particular, CS of Brüche (1927), not shown in figure, are in 1–20 eV energy range 10%–15% lower than the measurements of Szmytkowski *et al.* (1984) and merge with the latter at 30 eV. The results of Zecca *et al.* (1974) normalized to Brüche at 4 eV merge with those of Szmytkowski *et al.* at 1 eV and 5 eV but are lower by a factor of two in the maximum of TCS at 2.3 eV. The poor energy resolutions of the experiment of Zecca *et al.* (1974) is the reason for this discrepancy.

The data of Szmytkowski *et al.* up to 10 eV agree well with those of Kwan *et al.* (1984) but are systematically (about 20%) lower at 20–80 eV; the reason for this discrepancy is not clear. Remeasured data by Szmytkowski *et al.* (1996) are closer at 20–250 eV to the determination of Kwan *et al.* (1984) than to the previous data from the same laboratory (Szmytkowski *et al.* 1989). The high-energy data of Xing *et al.* (1997) merge well with the measurements of Kwan *et al.*

TCS exhibits a sharp, resonant peak of $28 \cdot 10^{-20}\,\mathrm{m}^2$ at 2.3 eV (Szmytkowski *et al.* 1984), a broad maximum at about 20 eV and a rise in the low energy limit. Theoretical calculations (Sarpal *et al.* 1996, Morgan 1997, Winstead and McKoy 1998) reproduce only qualitatively this resonance peak. The rise in the low energy limit should be attributed to the permanent dipole moment of the molecule, as it was the case for NO (see Part I). Kwan *et al.* (1984) pointed out close similarities in TCS for electron and positron scattering on N_2O and CO_2.

In several works (Joshipura and Patel 1994 and 1996, Jiang *et al.* 1997, Zecca *et al.* 1999) the additivity rule was applied to derive TCS at intermediate energies. As far as all these models agree with the high-energy experiment (Xing *et al.* 1997), at 100 eV they do not allow any judgment on the experimental discrepancy. In fact, the data of Szmytkowski *et al.*'s (1984, 1989) are in agreement with Jiang *et al.* (1997) and Zecca *et al.* (1999) models and those of Kwan *et al.* (1984) and Szmytkowski (1996) are in better agreement with the model of Joshipura and Patel (1994, 1996).

Elastic CS have been measured between 10 eV and 80 eV by Marinković *et al.* (1986), by Gulley and Buckman (1999) between 2 eV and 20 eV, by the Tokyo group (Kitajima *et al.* 1999, Sakamoto *et al.* 1999) between 1.5 eV and 100 eV, by Johnstone and Newell (1993) between 5 eV and 80 eV, and by Nogueira *et al.* (1989) at 200, 500, 1000 eV. DCS of Kubo *et al.* (1981) at 5, 10 and 20 eV are in general agreement with the measurements of Marinković *et al.* (1986) but the limited angle range does not allow to obtain reliable integral CS. DCS of Kitajima *et al.* (1999) coincide at 5 eV with those of Kubo *et al.* (1981) but are lower than the measurements of Johnstone and Newell (1983) by 10–20%. At 10 eV the DCS of Kitajima *et al.* are by a similar amount lower than the measurements of Gulley and Buckman (1999).

The integral elastic CS of Johnstone and Newell (1993) agrees well with those of Marinković *et al.* (1986) at low energies, but is substantially lower than the latter at 80 eV. This discrepancy could be caused by an underestimation of the forward scattering

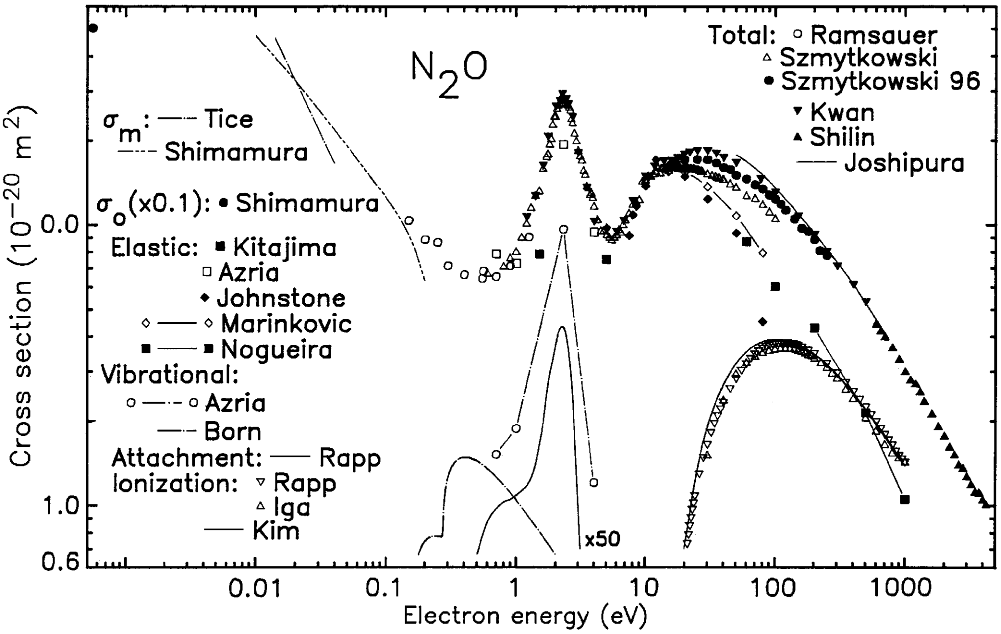

Fig. 13. – Integral cross-sections for electron scattering on N_2O. Total: Szmytkowski *et al.* (1984 and 1989); Szmytkowski *et al.* (1996); Ramsauer and Kollath (1930); Kwan *et al.* (1984); Shilin (Xing *et al.* 1997); Joshipura and Patel (1996), additivity rule; absolute value of Brüche (1927) and normalized of Zecca *et al.* (1974) are not shown for clarity. *Momentum transfer*: Tice and Kivelson (1967), cyclotron resonance; Shimamura (1989), semiempirical. *Zero-energy*: Shimamura (1989), semiempirical. *Elastic*: Kitajima *et al.* (1999), integrated in this work; Azria *et al.* (1975), DCS at 40° multiplied by 4π and normalized by a factor 2.4 to TCS of Szmytkowski *et al.* (1984) at 2.3 eV; Marinković *et al.* (1986); Johnstone and Newell (1993); Nogueira *et al.* (1989), integrated in this work. *Vibrational*: summed of Azria *et al.* (1975) renormalized by a factor of 2.4, see elastic; Born approximation, (eq. (15) Part I), sum of all 3 modes. *Ionization*: Kim *et al.* (1997), semiempirical model; Rapp and Englander-Golden (1965); Iga *et al.* (1996). *Dissociative attachment*: Rapp and Briglia (1965).

in the measurements of Johnstone and Newell (1993). The elastic data of Marinković *et al.* (1986) at 10 eV coincide with the TCS of Szmytkowski *et al.* (1984) and in the high energy limit merge well with the integrated (in present work) CS of Nogueira *et al.* (1989). The theory (Michelin *et al.* 1996) overestimates the experimental elastic CS (Marinković *et al.* 1986) by 40% at 10 eV and by 15% at 80 eV.

Azria *et al.* (1975) measured elastic (and vibrational) DCS at 40° at low energies (0.7–4.0 eV). They gave a rough estimate for integral CS by multiplying these DCS by a factor 4π. We verify that an additional factor of 2.4 has to be applied in order to normalize their sum of elastic and vibrational CS to the TCS value at 2.3 eV (Szmytkowski *et al.* 1984). The renormalized sum is compatible also quite well with TCS at 1 eV and 4 eV (Szmytkowski *et al.* 1984, Kwan *et al.* 1984).

No integral values were given in the most recent studies (Gulley and Buckman 1999, Kitajima *et al.* 1999, Sakamoto *et al.* 1999). The present rough estimates of integral values (±10% uncertainty due to the extrapolation and integration of DCS at 5 eV and ±20% at 100 eV) from DCS measurements of Sakamoto *et al.* (1999) are in a reasonable agreement with other low-energy determinations: presently renormalized data of Azria *et al.* (1975) at low energies and absolute values of Marinković *et al.* (1986) at intermediate energies.

High-energy DCS in the 10°–140° angle (Nogueira *et al.* 1989) obtained by the relative flow technique agree well with the independent-atoms model (Nogueira *et al.* 1989). In fig. 13 we present integral CS obtained in the present work from experimental DCS of Nogueira *et al.* (±20% extrapolation and integration uncertainty). In the low energy limit (200 eV) these integral values merge well with the measurements of Sakamoto *et al.* (1999). Positron-scattering relative DCS at 5–100 eV have been obtained by Przybyla *et al.* (1999).

Swarm. Quite few measurements of drift coefficients in N_2O were performed. Bailey and Rudd (1932) measured transversal diffusion to mobility ratio D_T/μ up to $100 \cdot 10^{-21}\,\mathrm{Vm}^2$ and more recently Mechlińska-Drewko *et al.* (1999) up to $200 \cdot 10^{-21}\,\mathrm{Vm}^2$. Momentum transfer CS in the very low energy range were given by Pack *et al.* (1962). Swarm-based CS (Pack *et al.* 1962, Shimamura 1989) are in good agreement with the cyclotron-resonance measurements of Tice and Kivelson (1967). A zero-energy CS value of $500 \cdot 10^{-20}\,\mathrm{m}^2$ was given by Shimamura (1989).

Vibrational excitation. Differential cross-sections for vibrational excitation at 40° were measured between 0.7 eV and 4.0 eV in an absolute experiment (Azria *et al.* 1975). At the TCS maximum (2.3 eV) the (100), (010) and (001) modes are excited in proportions 4 : 2 : 1. As discussed for the elastic CS, the data of Azria *et al.* (1975) should be renormalized by a factor of 2.4; the renormalized vibrational CS contributes to about 1/3 of TCS at 2.3 eV. This share is as high as in the case of the low-energy shape resonance in CO_2. Excitations up to $n = 12$ overtones of the (n00) and (n01) series were observed at 2.4 eV (Andrić and Hall 1984). DCS at 40° for these modes fall rather quickly with the quantum number n (Azria *et al.* 1975), by two orders of magnitude between (100) and (700). A broad peak in vibrational excitation DCS was also observed at 8 eV (Tronc *et al.* 1981, Andrić and Hall 1984). In fig. 13 we present also the sum of infra-red active modes in the Born approximation (Part I, eq. (15)); the calculated CS are in agreement with measurements of Azria *et al.* (1975) at 0.7 eV.

Electronic-excitation DCS at 0°–148° for the $C\,^1\Pi$ (8.5 eV energy loss) and $D\,^1\Sigma^+$ (9.6 eV energy-loss) states were measured by Marinković *et al.* (1986) at collision energies between 15 eV and 80 eV. Marinković *et al.* gave only relative integral CS at all energies except 80 eV. In a further paper Marinković *et al.* (1999) have used a new normalization at 80 eV to the generalized oscillator strength. This gives correction factor for the previous DCS values of 2.5 and 0.5 for the $D\,^1\Sigma^+$ and $C\,^1\Pi$ states, respectively. The related contributions to the integral CS (evaluated in the present work) amount to $0.48 \cdot 10^{-20}\,\mathrm{m}^2$ and $0.015 \cdot 10^{-20}\,\mathrm{m}^2$. The renormalization (Marinković *et al.* 1999) to the generalized oscillator strength (see Part I, eq. (16)) gives at 80 eV correction factors for the previous (Marinković *et al.* 1986) DCS of 2.5 and 0.5 for the $D\,^1\Sigma^+$ and $C\,^1\Pi$ states, respectively and brings integral CS to $0.48 \cdot 10^{-20}\,\mathrm{m}^2$ and $0.015 \cdot 10^{-20}\,\mathrm{m}^2$, respectively. The renormalized value for the $C\,^1\Pi$ state is half of the theoretical CS at this energy (Michelin *et al.* 1996). No calculations were performed for the $D\,^1\Sigma^+$ state. Note that the values obtained in the present work by integrating the DCS given by Marinković *et al.* (1999) are slightly higher than this theory, see table XI.

Forward-angle inelastic electron scattering has been studied in the 5.5–203 eV energy-loss range, 2000 eV collision energy by Chan *et al.* (1994). The valence excitation spectrum in N_2O shows a structure similar to the one in CO_2 but shifted by about 1 eV towards lower energies (Chan *et al.* 1994). Note a similar difference in the ionization threshold, 13.8 eV for CO_2 and 12.9 eV for N_2O. Also the maximum of the photoabsorption CS, of $1 \cdot 10^{-20}\,m^2$ for the $D\,^1\Sigma^+$ state at 9.65 eV is of a similar amplitude to that for the $^1\Sigma^+$ state in CO_2.

Energy-loss spectra were investigated also by Lassettre *et al.* (1968), Weiss *et al.* (1971), Hall *et al.* (1973), Lee (1977) and in core-level range by Camilloni *et al.* (1987) and Cavanagh and Lohmann (1999). Threshold-electron spectra for valence and Rydberg excitations were studied by Čubrić *et al.* (1986).

Optical emission cross-sections were studied at 0–2000 eV energy, in the 185–900 nm wavelength range by van Sprang *et al.* (1978). The main feature is the emission from the N_2O^+ molecular ion ($A\,^2\Sigma^+ \rightarrow C\,^1\Pi$) transition, located between 330–400 nm (van Sprang *et al.*, Kume *et al.* 1991). The sum of the vibronic CS for this transition amounts to $0.53 \cdot 10^{-20}\,m^2$ at 100 eV. The cross-sections for emission in the 220–330 nm range, probably from the NO ($B\,^2\Pi_r \rightarrow X\,^1\Pi_r$) transition, amounts to $0.23 \cdot 10^{-20}\,m^2$ at 100 eV (van Sprang *et al.* 1978). The NO radical is likely to be produced by secondary reactions between atomic fragments and N_2O (Lee and Suto 1984).

Ionization CS were measured by Rapp and Englander-Golden (1965) and Iga *et al.* (1996) up to 1000 eV: the two set of data agree very well. Partial ionization CS into the N_2O^+ ion up to 175 eV by Märk *et al.* (1981) agree well (within 20%) with the determination by Iga *et al.* only if both stable and metastable ions detected by Märk *et al.* are included. The partitioning of the ionization channel into N_2O^+ and NO^+ ions remains almost constant in the 200–1000 eV range: 54% and 25%, respectively (Iga *et al.* 1996). Semi-empirical models (Deutsch *et al.* 1997, Kim *et al.* 1997) agree well with experiments (Rapp and Englander-Golden, 1965, Iga *et al.* 1996).

Dissociation into neutrals. N_2O shows a reach pattern of dissociation into neutral fragments ($N_2 + O$), ($NO + N$) in different final electronic states (Clampitt and Newton 1969, Allcock and McConkey 1978). The lowest threshold, for the $N_2(A\,^3\Sigma^+) + O(^3P)$ dissociation channel, is found at 7.9 eV (Allcock and McConkey 1978, Mason and Newell 1989, Barnett *et al.* 1991).

Absolute CS for production of metastable $O(^1S)$ atoms were measured up to 1000 eV (LeClair *et al.* 1992, LeClair and McConkey 1993). The $O(^1S)$ state is produced together with the N_2 molecule in the ground state through the excitation of the N_2O molecule to the purely repulsive $D\,^1\Sigma^+$ state. The $O(^1S)$ dissociation CS reported by LeClair and McConkey (1993) at 80 eV is one half ($0.2 \cdot 10^{-20}\,m^2$) than the electronic excitation CS for the $D^1\Sigma^+$ state reported by Marinković *et al.* (1999).

Dissociative attachment CS for the O^- production reaches a maximum of $0.08 \cdot 10^{-20}\,m^2$ at 2.2 eV. A shoulder has been observed below 1 eV (Schulz 1961, Curran and Fox 1961, Rapp and Briglia 1965, Christophorou *et al.* 1971, Krishnakumar and Srivastava 1990). The shoulder structure rises with rising gas temperature (Chantry 1969) and shifts towards zero-energy (Brüning *et al.* 1998). An activation energy of 0.21 eV for the O^- ion has been estimated (Brüning *et al.* 1998).

A broad maximum approximately 10 times weaker (outside of the scale of fig. 13) was observed by Rapp and Briglia (1965) at 10.5 eV while Krishnakumar and Srivastava (1990) reported three faint peaks at 5.4, 8.1 and 13.2 eV. Another broad structure rises above the 18 eV threshold and reaches a maximum at 40 eV (Rapp and Briglia 1965, Krishnakumar and Srivastava 1990). Existence of anion states at about 7 eV, 9 eV and 16 eV was also confirmed in electron trapping experiment for condensed N_2O (Bass *et al.* 1997).

Microwave (Warman *et al.* 1972) and swarm methods (Phelps and Voshall 1968, Dutton *et al.* 1975) were also used to determine the attachment coefficients.

Table XI. – *Integral cross-sections for electron scattering on nitrous oxide (in* 10^{-20} m^2 *units).*

Energy	Elastic	Vibrational	Electronic	Ionization	Summed	Total
0.7	7.8 A	1.5 A			9.3	6.9* SZ1
1.0	7.2 A	1.9 A			9.1	8.0 SZ1
2.3	19.3 A	9.6 A			28.9	28.3 SZ1
4.0	9.3 A	1.2 A			10.5	11.6 SZ1
10.0	14.4 M				14.4	14.4 SZ1
12.0	15.5 M				15.5	15.5 SZ1
15.0	15.4 M			0.2 R	15.6	15.6 SZ1
20	15.3 M		0.1 M1	0.6 R	16.0	17.0 SZ2
30	13.6 M		0.3 M1	1.6 R	15.5	17.0 SZ2
50	10.7 M		0.5 M1	2.8 R	14.0	15.0 SZ2
80	7.9 M		0.7 M1	3.6 R	12.2	14.4 SZ2
100	6.0 K		0.6 M1**	3.7 R	10.3	12.3 SZ2
200	4.28 N		0.5 M1**	3.45 R	8.23	8.83 SZ2
600	2.13 N		0.2 M1**	2.23 R	4.56	4.44 X
1000	1.05 N		0.1 M1**	1.42 R	2.57	3.05 X

* - Interpolated values.
** - Extrapolated values.
A - Azria *et al.* (1975), DCS at 40°, multiplied by $2.4 \cdot 4\pi$.
K - Kitajima *et al.* (1999), integrated (this work).
M - Marinković *et al.* (1986).
M1- Marinković *et al.* (1999), presently integrated (±20% error) DCS for the $D^1\Sigma^+$ state.
N - Nogueira *et al.* (1989), integrated in this work.
R - Rapp and Englander-Golden (1965).
X - Xing *et al.* (1997).
SZ1 - Szmytkowski *et al.* (1984).
SZ2 - Szmytkowski *et al.* (1996).

Resonances. From vibrational excitation DCS measurements in the 1.4–3.1 eV energy range, Andrić and Hall (1984) deduced the presence of two overlapping resonances of the $^2\Sigma$ and $^2\Pi$ symmetries. At 2.4–3.1 eV the $^2\Sigma$ contribution is twice that of the $^2\Pi$ state and below 1.8 eV only the $^2\Sigma$ state is present in the vibrational excitation and dissociative excitation CS (Andrić and Hall 1984). Studies of angular distributions of O^- ions at 1.9–2.9 eV indicate contributions from p and s partial waves (Tronc *et al.* 1977). Theoretical discussions of low-energy resonant states in N_2O were published by

Bardsley (1969), Chantry (1969), Hopper *et al.* (1976).

At 8 eV a maximum in the vibrational excitation CS (Andrić and Hall 1986), a peak in dissociative attachment (Krishnakumar and Srivastava 1990) and threshold-electrons spectra (Čubrić *et al.* 1986) indicate another $^2\Sigma$-type resonance (Andrić and Hall 1986); however, this is too weak to be seen in TCS. Two series of resonances, between 10 eV and 11 eV and above 12 eV were observed in the transmitted electron current by Sanche and Schulz (1973). Intermediate energy resonances at about 400 eV, related to inner-shell excitations were observed in the ionization channel by King *et al.* (1980). The effect is about half of that observed for CO_2.

Sum check indicates a pretty good agreement at 1 eV and 4 eV between the renormalized elastic and vibrational CS of Azria *et al.* (1975) and the TCS of Szmytkowski *et al.* (1984). Between 20 eV and 80 eV the sum of the elastic data of Marinković *et al.* (1986), the ionization CS of Rapp and Englander-Golden (1965) and the electron excitation CS (evaluated in this work) from the DCS of Marinković *et al.* (1999) is slightly lower than the TCS (Szmytkowski *et al.* 1996). Probably, other electronic states apart from the $D\,^1\Sigma^+$ should be included.

The summed CS at 600 eV (in good agreement with experimental TCS, Xing *et al.*, 1997) is for N_2O ± 25% lower than that for CO_2 and NO_2. This difference is to be attributed to a smaller elastic CS in N_2O. On the contrary, the ionization part for N_2O exceeds that for CO_2 in the whole energy range from the threshold up to 1000 eV (Rapp and Englander-Golden 1965). At 1000 eV the summed value is lower than the experimental TCS (Xing *et al.* 1997) and lower than the theoretical value of Joshipura and Patel (1994) obtained from an additivity model.

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4˙3. *Nitrogen dioxide* (NO_2). – NO_2 is a bent molecule (bond angle 134°), weakly polar (dipole moment 0.32 D). NO_2 is one of the most difficult air pollutants to control chemically (Okumara *et al.* 1994, Seinfeld and Pandis 1998). It acts in the troposphere as a catalyst of the ozone distruction and, in a cycle of oxidation processes involving methane and/or carbon monoxide, also of the ozone formation (Crutzen 1973). In spite of this, NO_2 has received little experimental attention. In particular, we are not aware of any measurements of elastic CS and absolute total ionization CS. In fig. 14 the few existing data are shown. The analysis of swarm-based CS has been done by Sakai *et al.* (1995).

Total cross-section has been measured by Szmytkowski *et al.* (1992) from 0.6 eV to 220 eV and by Zecca *et al.* (1995) from 100 eV to 4000 eV: these sets of data are congruent in the region of energy overlap. The rise of TCS in the limit of low energies, from $12.5 \cdot 10^{-20}\,\mathrm{m}^2$ at 3.5 eV to $17.0 \cdot 10^{-20}\,\mathrm{m}^2$ at 0.6 eV has been attributed to a direct scattering process (Szmytkowski *et al.* 1992). A local maximum of $15.0 \cdot 10^{-20}\,\mathrm{m}^2$ is centered around 11 eV. At high energies TCS is only slightly (a few per cent) lower than that for CO_2 (Zecca *et al.* 1995). Note that the statistical errors in NO_2 measurements by Zecca *et al.* are somewhat higher than in other high-energy experiments from this laboratory. Above 500 eV the experimental TCS (Zecca *et al.*) agrees well with the theoretical values of Joshipura and Patel (1994) obtained from a sum rule. We are not aware of swarm either elastic scattering CS measurements.

Vibrational excitation studies indicate a resonant process in the energy region below 2 eV (Sanche and Schulz 1973). At 0.65 eV collision energy all three fundamental modes and their overtones are visible in the energy-loss spectra (Benoit and Abouaf 1991). The bending mode disappears at 1.3 eV and by contrast, the symmetric stretch overtones up to the order $n = 5$ order increase in intensity. The angular dependence at 0.55 eV is quite uniform for the (010) mode and forward peaked for the (001) and (100) stretching modes; at 1.4 eV the DCS for the (200) mode is *p*-wave like (Benoit and Abouaf 1991).

Electronic excitation spectra were measured at 100 eV in the 1.3–4.3 eV range by Krauss *et al.* (1974) and at 3 keV impact energy for N and O inner-shell excitations by Zhang *et al.* (1990). A recent detailed study of the forward (photon-like) electron scattering has been performed by Au and Brion (1997) who used two spectrometers: a low-resolution (1 eV) one, working at 8 keV collision energy and covering the 6–200 eV energy-loss range and a high-resolution (0.05 eV FWHM) one, at 3 keV collision energy, 1.6-50 eV energy loss. The lowest-energy, broad absorption band centered at 3.12 eV was attributed to the $4b_2 \rightarrow 6a_1(^2A_1 \rightarrow {}^2B_2)$ and $6a_1 \rightarrow 2b_1(^2A_1 \rightarrow {}^2B_1)$ transitions with the ν_2 bending mode vibronic progression. The maximum of the photoabsorption CS below the photoionization threshold (11.23 eV) amounts to $0.44 \cdot 10^{-20}\,\mathrm{m}^2$ and is centered at 9.7 eV. Note a rather high electronic excitation CS with a maximum of about $30 \cdot 10^{-20}\,\mathrm{m}^2$ derived from swarm measurements (Sakai *et al.* 1995).

Dissociation into neutrals was studied by photon scattering. The photodissociation threshold is as low as 3.1 eV (Jost *et al.* 1996 and reference therein).

Ionization cross-section has been measured from threshold to 180 eV by Stephan *et al.* (1980). According to this measurement, at 100 eV the dominant ion is NO^+; the parent ${NO_2}^+$ constitutes about 40% of the signal, while the fragment O^+ and N^+ ions about 10% and 2%, respectively. The ratio for both NO^+ and ${NO_2}^+$ is about 10^{-4} at 100 eV.

Note that the absolute values of Stephan *et al.* (1980) are uncertain, due to the unknown ion collection efficiency of their apparatus. The relative ${NO_2}^+$ cross-sections have been normalized to the Ar^+ signal using the molecular flow method. The forward-

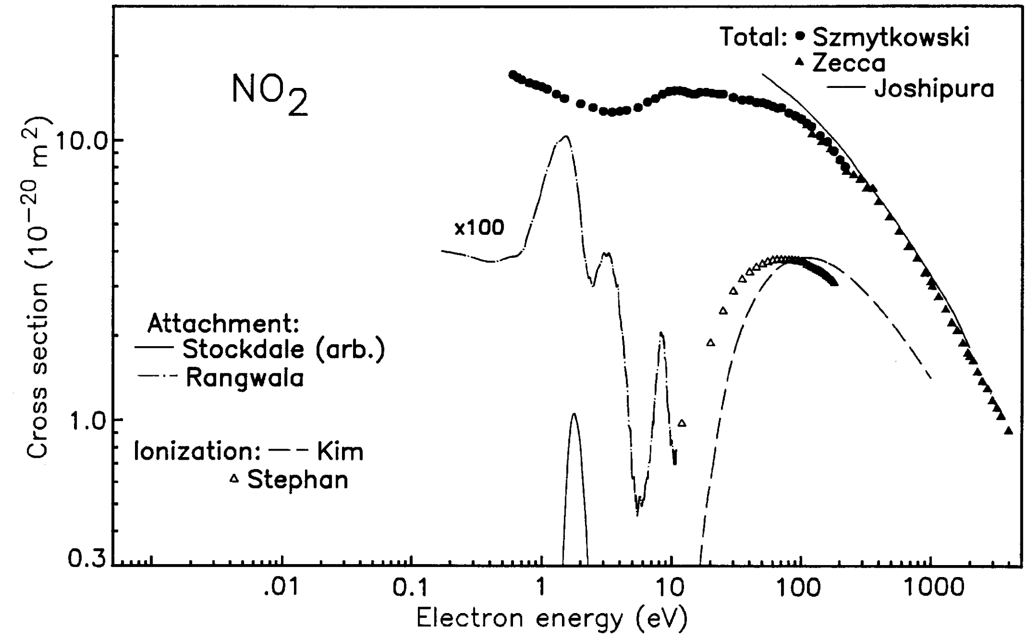

Fig. 14. – Integral cross-sections for electron scattering on NO_2. *Total*: Szmytkowski *et al.* (1992), Zecca *et al.* (1995); Joshipura and Patel (1996), additivity rule. *Ionization*: Stephan *et al.* (1980), yield of ${NO_2}^+$ multiplied by a factor 15; Kim *et al.* (1997), semiempirical. *Electron attachment*: Stockdale *et al.* (1969), O^- yield, arbitrary units; Rangwala *et al.* (1999), O^- yield, absolute units.

angle scattering experiment of Au and Brion (1997) gives partitioning rates somewhat different than Stephan *et al.* (1980). Their partial photoionization CS for the formation of NO^+, O^+, N^+ and ${NO_2}^+$ ions scale as 44%, 34%, 16% and 6%, respectively at 80 eV.

In fig. 14 we have normalized the ${NO_2}^+$ ionization CS of Stephan *et al.* (1980) by a multiplicative factor of 15 to the semiempirical model of Kim *et al.* (1997) at 100 eV. This factor is congruent with Au and Brion's partitioning scheme. Note that the measurements from the Innsbruck laboratory for other triatomic gases (Märk and Hille 1978, Märk *et al.* 1981) agree well with more recent experiments, see subsects. **4**·1 and **4**·2.

Some discrepancy exists also on the shape of ionization CS, see fig. 14, as well as on the ionization threshold: 10.4 eV as measured by Stephan *et al.*, 11.3 eV from other electron-scattering measurements (Kiser and Hisatsune 1961, adopted also by Kim *et al.* 1997) and 9.7 eV from photoionization studies (see Weast 1986). Gas contamination by N_2O_4 dimers or other oxygen-nitrogen compounds (*e.g.*, see O'Connor *et al.* 1996, Georges *et al.* 1996) could explain these discrepancies. Semiempirical models (Deutsch *et al.* 1997, Kim *et al.* 1997) indicate for NO_2 a maximum value of ionization CS slightly lower than for N_2O.

Dissociative attachment. All possible products of dissociative attachment in NO_2 have positive electron affinities. The yields for O^-, NO^- and ${O_2}^-$ ions reach their maxima at 1.8 eV, 3.2 eV and 4.4 eV, respectively (Abouaf *et al.* 1976) and the relative intensities scale as 1000:3:10 (Stockdale *et al.* 1969). More recent measurements (Abouaf *et al.* 1976, Rangwala *et al.* 1999) show three maxima in the O^- formation cross-section: at 1.5, 3.2

and 8.4 eV, see fig. 14. A vibrational structure, much weaker than the one observed in OCS (Tronc *et al.* 1982) is visible in NO_2 (Abouaf *et al.* 1976) inside the 1.8 eV peak. At 1.5 eV the dissociative attachment CS (Rangwala *et al.* 1999) amounts to as much as 0.8% of TCS. We note a similarly large dissociative attachment CS in other triatomic molecules at the energy of shape resonances, *e.g.*, about 0.5% for OCS and 0.3% for N_2O (see figs. 13 and 17). The data of Rangwala *et al.* indicate the rise of the O^- formation peak in the limit of zero energy. Electron attachment at thermal energies was studied by Shimamori and Hotta (1986).

Resonances. The NO_2 molecule has a stable negative ion and its electron affinity is 2.27 eV (Erwin *et al.* 1988). A rich vibrational structure with progression of the symmetric-stretch and bending modes was observed in transmitted current between 0.1 eV and 1.8 eV (Sanche and Schulz 1973). A detailed study of the vibrational excitation (Benoit and Abouaf 1991) has attributed these structures to a long-lived $^1A_1$ shape resonance below 1 eV and an intermediate lifetime $^3B_1$ shape resonance above 1.1 eV. The presence of these resonances is hardly visible in TCS (Szmytkowski *et al.* 1992) but produces well visible structures in transmitted current (Boness *et al.* 1968, Larkin and Hasted 1972, Sanche and Schulz 1973) and in the electron-impact energy loss spectra (Krauss *et al.* 1974). Attribution of the 3–4 eV (Stockdale *et al.* 1969, Rangwala *et al.* 1999) and 8.5 eV peaks seen in electron attachment CS to a resonant state is not clear.

Sum check is not possible due to the lack of elastic CS measurements. In several works (Joshipura and Patel 1994, 1996, Zecca *et al.* 1999) the additivity rule was applied to derive partial or total CS at intermediate energies. According to these models the high-energy TCS in NO_2 is slightly higher, 3% at 1000 eV (Joshipura and Patel 1994), than that in N_2O.

New measurements of ionization CS are needed in order to resolve discrepancies between the available experiments and the semiempirical model (Kim *et al.* 1997). Serious discrepancies regard also the dissociative attachment processes.

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4·4. *Ozone* (O_3). – Ozone is a bent molecule (Jones 1985), possessing a permanent dipole moment of $0.53D$ (Steinfeld *et al.* 1987). Due to this configuration, some analogies can be expected between O_3, NO_2 and SO_2 molecules. Electron scattering and ultraviolet absorption in O_3 are of basic importance in atmospheric phenomena. Formation of ozone in the atmosphere (Toumi *et al.* 1996) and in electrical discharges (Eliasson and Kogelschatz 1986) are still intensively studied. For these reasons, numerous new electron scattering experiments on O_3 have been recently done (see Mason 1999). A critical survey on spectroscopy and kinetics of atmospheric ozone was performed by Steinfeld *et al.* (1987).

Total cross-sections. No absolute measurements of TCS exist to our knowledge. Low-energy TCS has been evaluated from backward-angles scattering between 9 meV and 9.7 eV (Gulley *et al.* 1998). These data indicate a rise of TCS in the limit of low energies, up to $120 \cdot 10^{-20}\,\mathrm{m}^2$ at 10 meV. This rise can be explained as a direct rotational excitation and is in a reasonable agreement (Gulley *et al.* 1998) with the Born approximation (Part I, formula (14)). Some enhancement of TCS was observed around 4 eV, but the absolute accuracy is rather poor, due to the lack of detection of forward-scattering events (Gulley

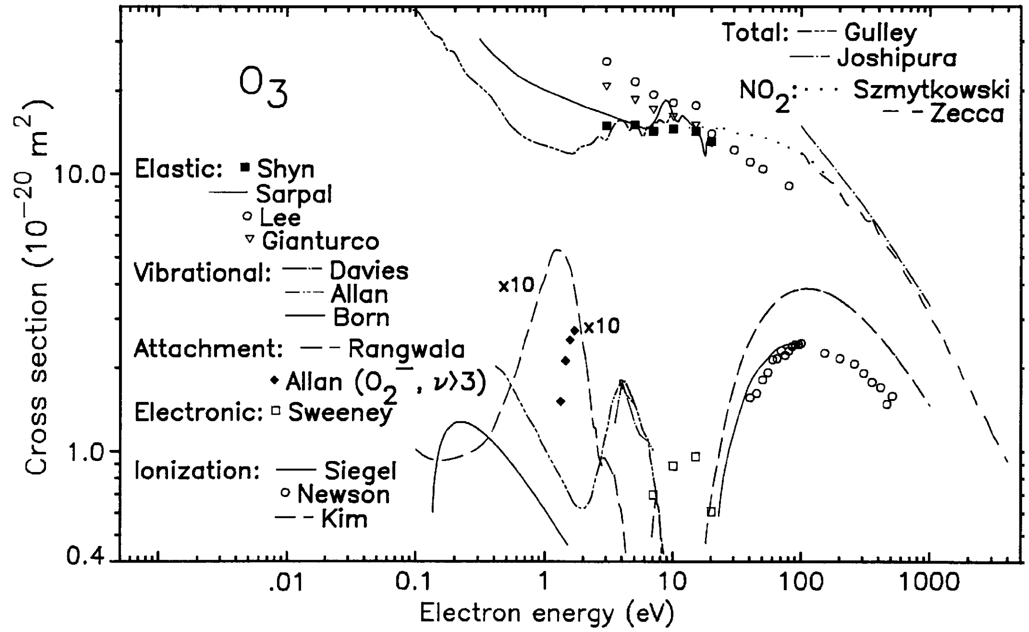

Fig. 15. – Integral cross-sections for electron scattering on O_3. *Total*: Gulley *et al.* (1998), backward scattering; Joshipura and Patel (1994), additivity rule; NO_2 total CS above 10 eV are reported in this figure to allow a comparison: Szmytkowski *et al.* (1992), Zecca *et al.* (1995); *Elastic*: Shyn and Sweeney (1993), absolute; Sarpal *et al.* (1994), R-matrix calculations; Lee *et al.* (1998), Schwinger variational method; Gianturco *et al.* (1998), sum of elastic and rotational excitation. *Vibrational*: summed, present estimate from DCS given by Allan *et al.* (1996); Davies *et al.* (1993), presently normalized to elastic; Born approximation (eq. (15) Part I). *Electronic excitation*: Sweeney and Shyn (1996), Hartley band (4.9 eV energy-loss), absolute. *Ionization*: Siegel (1982), absolute; Newson (1995), normalized; Kim *et al.* (1997), semiempirical. Dissociative attachment: Rangwala *et al.* (1999a), sum of O^- and ${O_2}^-$ signals; Allan *et al.* (1996), formation of ${O_2}^-$ ions in high ($\nu' > 3$) vibrational states.

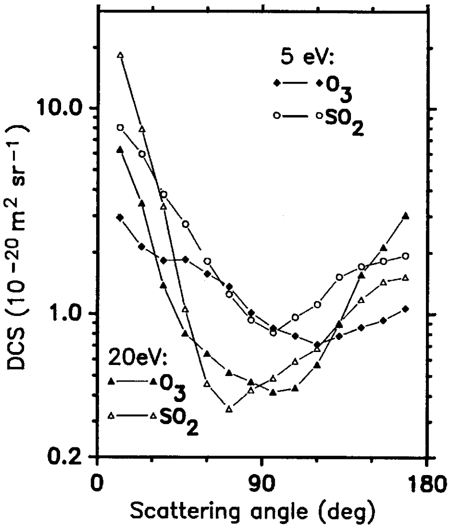

Fig. 16. – Differential cross-sections for elastic scattering on O_3 (Shyn and Sweeney 1993) and SO_2 (Trajmar and Shyn 1989) at 5 eV and 20 eV.

et al. 1998). Therefore, for illustration purposes we present in fig. 15 the TCS for the NO_2 molecule above 10 eV (Szmytkowski *et al.* 1992, Zecca *et al.* 1995). The calculations of Joshipura and Patel (1994), based on the additivity rule (and successfully applied to CO_2 and NO_2 above 500 eV) predict a TCS value for O_3 at 1000 eV equal to that for CO_2.

Elastic cross-section measurements of Shyn and Sweeney (1993) indicate essentially little variation in the integral values between 3 eV and 20 eV: from $14.8 \cdot 10^{-20}\,\mathrm{m}^2$ to $13.0 \cdot 10^{-20}\,\mathrm{m}^2$, respectively. Relative measurements at 0.2–15 eV (Allan *et al.* 1996a) show more rapid variations only at low energies: the 30° elastic DCS shows a deep minimum at 1.5 eV while the 90° DCS a maximum at 2 eV.

At all studied energies between 2 eV and 20 eV (Shyn and Sweeney 1993, Allan *et al.* 1996a) some rise of DCS is observed at low scattering angles: this is probably due to the permanent dipole moment of the molecule. However, forward angle scattering is less pronounced than in the case for SO_2 molecule (see fig. 16). At 3 eV the angular distribution is uniform within 30% between 30° and 150° (Shyn and Sweeney 1993). At 2 eV the DCS rises visibly only below 20° scattering angles (Allan *et al.* 1996a). At 20 eV DCS exhibits a minimum at 90° (Shyn and Sweeney 1993).

The R-matrix calculations (Sarpal *et al.* 1994, 1998) predict a rise of the integral cross-section in the low energy limit. Calculations of Okamoto and Itikawa (1993) in the 5–20 eV energy range are about 50% higher than the experimental values (Shyn and Sweeney 1993). Calculations of Gianturco *et al.* (1998) and of Lee *et al.* (1998) agree somewhat better with the experiment, especially at 20 eV.

Vibrational excitation in the 3.5–7 eV, 40°–120° range was first studied by Davies *et al.* (1993). Energy loss spectra show maxima at 130, 260, 380 meV; the energy resolution of this experiment did not allow to separate contribution from specific modes. Approximately, the fundamental modes are contained in the first energy-loss peak and multiple excited modes overlap in higher peaks. DCS at 90° for the first energy-loss peak reaches a maximum at 4.5 eV; it suggests the existence of a resonant state close to this energy. A rise of the vibrational excitation DCS with increasing angle observed at 6.5 eV (Davies *et al.* 1993) has not been confirmed by further studies (Allan *et al.* 1996a). At 6 eV and 60° angle the vibrational excitation DCS for the first energy-loss peak amounts to 4.6% of the elastic-scattering DCS; the second and third energy-loss peaks are smaller by a factor of three each (Davies *et al.* 1993).

Subsequent studies (Allan *et al.* 1996a) allowed to resolve the bending ν_2 mode at all excitation quanta and the stretching modes ν_1 and ν_3 at high quanta, for example the (400) and (004) energy-loss peaks were well separated. Rise of the vibrational excitation CS in the limit of zero-energy for all three fundamental (infra-red active) modes was observed. Note, however, that the direct vibrational excitation in O_3, according to Born's approximation is rather weak, say by a factor of two less than in SO_2 (compare the transient dipole moments in Bishop and Cheung 1982).

A sharp rise of the vibrational excitation CS between 3 eV and 6 eV, peaking at 4.2 eV for all modes was reported (Allan *et al.* 1996a). The stretching (001) + (100) modes dominate over the bending (010) mode at this energy: at 90° scattering angle the two DCS differ by a factor of four. Angular distributions of vibrationally inelastic scattered electrons are almost uniform at 6.5 eV; at 4.2 eV the angular distribution rises below 40° scattering angles.

We evaluated absolute values of integral CS for vibrational excitation in two ways. First, we have normalized the height of energy loss peaks at 3.5–7.0 eV collision energy from Davies *et al.* (1993) to the elastic CS of Shyn and Sweeney (1993). In the second way, we have multiplied the 30° vibrational excitation DCS of Allan *et al.* (1996a) for the (100) + (001) mode by 4π and by a factor of two due to the branching ratio, as can be deduced from that work. A seen from fig. 15, the two evaluations are in a reasonable agreement. The vibrational excitation integral CS amounts in its maximum to roughly 10% of the elastic CS, somewhat more than in the O_2 resonance at 10 eV and less than in the N_2 resonance at 2.5 eV (figs. 21 and 27 in Part I). In the low energy limit the present evaluation of the integral CS agrees reasonably well with the Born approximation (eq. (15), Part I), taking into account that the quoted factor of two overestimates the branching ratio at low energies.

Rotational excitation has been calculated by Gianturco *et al.* (1998). The $J = 0 \rightarrow J = 1$ excitation falls in the 5–20 eV range. The excitations to $J = 2, 3, 4$ states show rather flat maxima at about 15 eV; at this energy the sum of the rotational CS equals the elastic CS.

Electronic excitation. Electron energy-loss spectra for dipole allowed excitation have been studied by Celotta *et al.* (1974) and Johnstone *et al.* (1992). A prominent peak in the energy-loss spectrum at about 4.9 eV corresponds to the Hartley $X^1A_1 \rightarrow {}^1B_2$ transition, important for the ultra-violet absorption in atmosphere. The photoabsorption CS ($0.11 \cdot 10^{-20}\,\mathrm{m}^2$) for this transition has been obtained in synchrotron-radiation studies (Mason *et al.* 1996). Three more strong absorption bands corresponding to the excitation to Rydberg states have been observed between 9.0 eV and 11.5 eV photon energy, with a maximum photoabsorption CS of $0.3 \cdot 10^{-20}\,\mathrm{m}^2$ at 10.2 eV (Mason *et al.* 1996).

Studies at low collision energies (4–8 eV) and large ($\geq 45°$) scattering angles have evidenced a large band in the energy loss spectra, extending from 1.3 eV to 2.4 eV and corresponding to excitations to different optically forbidden states (Swanson and Celotta 1975). Detailed studies (Allan *et al.* 1996b) under conditions favoring singlet (scattering angle $\vartheta = 10°$ and residual energy $E_\mathrm{r} = 20\,\mathrm{eV}$) or triplet ($\vartheta = 30°$–$135°$, $E_\mathrm{r} = 1$–$3\,\mathrm{eV}$) excitations allowed to separate those states. The energy loss spectra under "singlet" conditions resemble the photoabsorption spectra (Mason *et al.* 1996), although the dipole forbidden singlet-singlet transitions (*e.g.*, in the Hartley 4.9 eV band) are sightly enhanced. At $E_{\rm r} = 20\,{\rm eV}$, $\vartheta = 10°$ the excitation of two singlet states, $^1A_2$ and $^1B_1$ with thresholds 1.44 eV and 1.88 eV, respectively (Borowski *et al.* 1995) was observed. Under "triplet" conditions ($E_{\rm r} = 1.0\,{\rm eV}$, $\vartheta = 135°$) two vibrational progressions, assigned in a photoelectron detachment experiment (Arnold *et al.* 1994) to the $^3B_1$ and $^3B_2$ states are well visible in the energy loss spectra (Allan *et al.* 1996b). An additional vibronic peak at 2.05 eV, assigned to the Chappuis $^1B_1$ state (Arnold *et al.* 1994) was also observed (Allan *et al.* 1996b).

DCS measurements for the Hartley band are forward centered at low-scattering angles and vary slowly with energy between 7 eV and 20 eV (Allan *et al.* 1996b, Sweeney and Shyn 1996). However, DCS at larger angles show that at least one optically forbidden transition is present in the Hartley band (Sweeney and Shyn 1996). The integral value for this band amounts to $0.95 \cdot 10^{-20}\,{\rm m}^2$ at 15 eV (Sweeney and Shyn 1996).

Dissociation. We are not aware of measurements of ozone dissociation into neutrals by electron impact. The photolysis studies in the UV range show two possible exit channels: the first with molecular oxygen in the ground state O_2 ($X\,^3\Sigma_{\rm g}$) + O (^3P) and the second one with the oxygen molecule in a long-lived metastable state O_2 ($a^1\Delta_{\rm g}$) + O (^1D). The two channels are approximately equally probable at wavelengths shorter than 310 nm. In the first process a significant part (1%) of O_2 molecules is formed in very high ($\nu \geq 24$) vibrational states (Miller *et al.* 1994, Syage 1996). The formation of O_2 in high vibrational states was also observed in studies of electron auto-detachment in ${O_2}^-$ ion, formed from O_3 in the dissociative attachment process (Allan *et al.* 1996c). At 1.7 eV electron collision energy the ${O_2}^-$ ion (autodetaching to O_2) is formed in $\nu' = 4, 6, 8$ states with almost the same probability (Allan *et al.* 1996c). A dissociation threshold of 1.06 eV has been established in that measurement (Allan *et al.* 1996c).

Ionization. Total and partial ionization CS were measured up to 100 eV by Siegel (1982) and from 40 eV to 500 eV by Newson *et al.* (1995). The observed (Siegel 1982) thresholds for ${O_3}^+$ and ${O_2}^+$ ions formation are congruent with the values of 12.67 eV and 13.14 eV, respectively, obtained from the photoionization experiments (Rosenstock *et al.* 1977) but the threshold for the O^+ appearance is somehow too high (18–19 eV). According to Siegel, at 100 eV the total ionization CS would amount to about $2.4 \cdot 10^{-20}\,{\rm m}^2$, *i.e.* it would be equal to that of O_2 (Rapp and Englander-Golden 1965) within the experimental error. The branching ratio between ${O_3}^+$, and ${O_2}^+$ and O^+ ions is 1:0.9:0.35 (Siegel 1982).

Newson *et al.* (1995) have normalized their measurements at 100 eV to the data of Siegel (1982); the two data sets agree well in shape. The branching ratio at 500 eV (Newson *et al.*, 1995) remains the same as at 100 eV. However, the semiempirical model (Kim *et al.* 1997) gives a ionization CS 50% higher than the data of Newson *et al.*

Dissociative attachment has been studied by Curran (1961) and more recently by Walker *et al.* (1996), Allan *et al.* (1996a), Skalny *et al.* (1996) and Rangwala *et al.* (1999a, b) in beam experiments between 0–10 eV. A good agreement exists on both energy positions as well as the values of the peaks in dissociative attachment CS (Skalny *et al.* 1996, Rangwala *et al.* 1999a). The ${O_2}^-$ peak is centered at 1.2 eV and is by a factor of two lower than the O^- peak at 1.4 eV (Rangwala *et al.* 1999a). A substantial part of the ${O_2}^-$ ions is formed in high ($\nu' \geq 4$) vibrational states (Allan *et al.* 1996c), see fig. 15 for the cross-section.

A shoulder structure was observed in the dissociative attachment CS at about 4 eV and another weaker peak at 7.5 eV (Walker *et al.* 1996, Rangwala *et al.* 1999a), see fig. 15.

A similarity between the shape of the dissociation attachment CS for O^- formation from NO_2 and from O_3 has been stressed (Rangwala 1999b); the absolute values in O_3 are higher by more than a factor of three. The share of dissociative attachment CS (Walker *et al.* 1996, Rangwala *et al.* 1999) is probably as high, almost 1% of TCS, as for other triatomic molecules, NO_2, OCS, N_2O.

A rise of the dissociative attachment CS for the formation of the O^- ion in the limit of zero-energy has been recently reported (Senn *et al.* 1999). The $1/E$ dependence of the CS indicates an s-wave scattering for the process. ${O_3}^-$ ion formation has been observed in electron attachment experiments on mixed ozone-oxygen clusters (Matejcik *et al.* 1996).

Resonances. There is no clear evidence about the existence of shape resonances in O_3. The static-exchange R-matrix (Sarpal *et al.* 1994), Schwinger variational method (Lee *et al.* 1998) and *ab-initio* with model exchange (Curik *et al.* 1999) elastic CS calculations yielded several structures in the elastic CS in the 5–20 eV energy range, attributed to two shape resonances, ${}^2A_1$ and ${}^2B_2$ (Curik *et al.*). The calculation of Gianturco *et al.* (1998) and the experiment (Shyn and Sweeney 1993) did not show such structures. Vibrational excitation measurements (Davies *et al.* 1993, Allan *et al.* 1996a) indicate a rather wide shape resonant state at about 4.2 eV. The ${}^2A_1$ symmetry has been proposed for this state (Allan *et al.* 1996a). A core-excited resonance has been postulated for the 1.3 eV peak in the dissociative attachment CS (Rangwala *et al.* 1999a). This resonance is visible also in the energy-loss spectra at 1–2 eV collision energy as a long progression of the symmetric stretch vibration (Allan *et al.* 1996b). A Feshbach resonance has been postulated (Allan *et al.* 1996a) for the 7.5 eV peak in the dissociative attachment CS.

Sum check. The scarcity of data, in particular the poor reliability of the experimental ionization CS and lack of total CS measurements does not permit a sum check.

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4·5. *Carbonyl sulfide* (OCS). – The OCS molecule, similarly to CO_2 has a linear configuration; it possesses a weak permanent dipole moment of 0.71 D. OCS is a source of biogenic sulphur in the atmosphere (Hines and Morisson 1992) and is also present in the interstellar medium (Jefferts *et al.* 1971). Integral cross-sections for OCS are given in fig. 17 and table XII.

Total cross-section was measured by Szmytkowski *et al.* (1984, 1989) in the energy range from 0.2 to 100 eV, by Dababneh *et al.* (1986) between 0.8 and 40 eV, by Zecca *et al.* (1995) at 90–4000 eV and recently by Sueoka *et al.* (1999) at 0.8–600 eV. TCS exhibits a rise in the very low energy limit and three local maxima: at 1.15 eV, at 4.1 eV and at about 10 eV (Szmytkowski *et al.* 1984). The data of Dababneh *et al.* (1986) are generally lower compared with those of Szmytkowski *et al.* (1984), apart the minimum at 2 eV. A part of this discrepancy can be attributed to a poorer energy resolution of the apparatus of Dababneh *et al.* (1986).

The absolute TCS of Szmytkowski *et al.* (1984) at the CS maximum (1.15 eV) practically coincides with the summed (elastic + vibrational excitation) CS of Sohn *et al.* (1987) but is lower at 0.4 eV and 0.6 eV. A plausible explanation of this discrepancy could be some systematic error in the measurements of Szmytkowski *et al.* (1984) due to the drift of the electrometer's zero at very low (10^{-13} A) currents (Karwasz 1982).

The data of Szmytkowski *et al.* (1989) merge with the high-energy measurements of Zecca *et al.* (1995). The re-measured TCS from the Gdańsk group at 20–250 eV (Szmytkowski *et al.* 1996) practically coincide with previous data (Szmytkowski *et al.* 1984) and the high-energy measurements (Zecca *et al.* 1995). The optical model (Raj and Tomar 1997) reproduces well the experimental TCS above 200 eV.

The most recent data of Sueoka *et al.* (1999) at 0.8–600 eV practically coincide with the measurements of Dababneh *et al.* (1986) and agree well in shape with other determinations. However, in the 4–600 eV they are 15% lower on the average than the results of Szmytkowski *et al.* (1984, 1989) and Zecca *et al.* (1995). Note that both the apparatus of Sueoka *et al.* (1999) and that of Dababneh *et al.* (1986) used a longitudinal magnetic field to guide electrons. Sueoka *et al.* (1999) corrected their measurements for the forward-scattering error introduced by the field but they themselves stressed some uncertainty in this correction.

The resonant peak at 1.15 eV according to Sueoka *et al.* (1999) is by a factor of almost two lower than the value measured by Szmytkowski *et al.* (1984). This discrepancy is probably due to the poorer energy resolution (about 1 eV) in the experiment of Sueoka *et al.* (1999) compared to that of Szmytkowski *et al.* (1984), about 70 meV.

A general similarity between the shapes of total CO_2 and OCS cross-sections has to be mentioned. On the average, apart from the resonance region, the OCS total cross-section is double than that of CO_2. One notices also that the position of the lowest-energy maximum in the OCS total cross-section is shifted to a lower energy.

Elastic cross-section, as measured by Sohn *et al.* (1987), exhibits maxima at 1.15 eV and at about 4 eV. The maximum at 1.15 eV is not so well pronounced as in the fixed-nuclei calculation of Lynn *et al.* (1979). Both the calculation as well as the experimental DCS (Sohn *et al.* 1987) indicate the presence of a resonant $^2\Pi$ state around this energy. At 4 eV DCS indicate a dominant *d*-wave scattering.

Absolute DCS in the 20°–130°, 1.5–100 eV range were measured by Sakamoto *et al.* (1999 a, b). At 1.5 eV and 5 eV the OCS differential cross-sections exceed those of CO_2; at 60 eV and 100 eV both gases show similar absolute values. Whereas the CO_2 differential CS at 100 eV shows a single minimum at 90°, the OCS differential cross-section develops additionally some shoulder structure between 60° and 80°, see fig. 18.

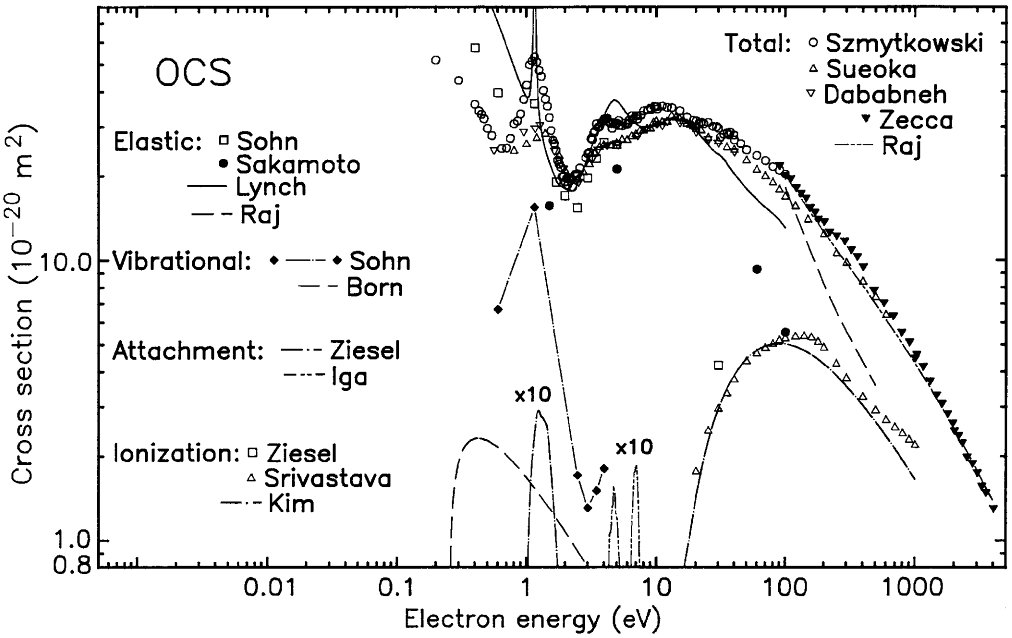

Fig. 17. – Integral cross-sections for electron scattering on OCS. *Total*: Szmytkowski *et al.* (1984, 1989); Dababneh *et al.* (1986), digitized from their figure; Zecca *et al.* (1995); Sueoka *et al.* (1999); Raj and Tomar (1997), optical model. *Elastic*: Sohn *et al.* (1987); Sakamoto *et al.* (1999b), integrated in this work; Lynch *et al.* (1979), theory; Raj and Tomar (1997), optical model. *Vibrational excitation*: Sohn *et al.* (1987), sum of all 3 modes; Born approximation (eq. (15) Part I), sum of all 3 modes. *Electron attachment* (S^- ion yield): Ziesel *et al.* (1975); Iga *et al.* (1996), shown only above 3 eV for clarity. *Ionization*: Srivastava (1997); Ziesel *et al.* (1975) at 30 eV; Kim *et al.* (1997), semiempirical.

The integral elastic CS obtained in the present work (±15% uncertainty due to integration) from DCS of Sakamoto *et al.* (1999a, b) agrees reasonably well with the TCS of Szmytkowski *et al.* (1984) only at 5 eV; at 100 eV it falls down to 25% of the TCS value (Szmytkowski *et al.* 1989). The presently integrated elastic CS at 100 eV is much lower than the theory of Lynch *et al.* (1979). The optical model in the independent-atoms approximation (Raj and Tomar 1997) departs from the calculations of Lynch *et al.* (1979) in the opposite direction. In analogy to other optical-model calculations on linear targets (Jain and Baluja 1992) we expect the theory of Raj and Tomar to be reliable only above 200 eV.

Vibrational excitation is highly enhanced in the region of the $^2\Pi$ resonance. The (010) bending mode and its overtones amount to almost 20% of TCS (Sohn *et al.* 1987). At energies above the resonance the vibrational CS falls down rapidly, approaching at 3 eV the values calculated from the Born approximation (eq. (15), Part I). At 4 eV the excitation of the stretching modes (001) and (100) rises again. At the lowest energy investigated by Sohn *et al.* (0.6 eV), the angular shape of DCS for stretching modes is well described by the Born approximation but the absolute values are underestimated. Similarly, the value calculated from the Born approximation for the three modes (100), (010), (001) is at 0.6 eV a factor of three lower than the sum of experimental integral

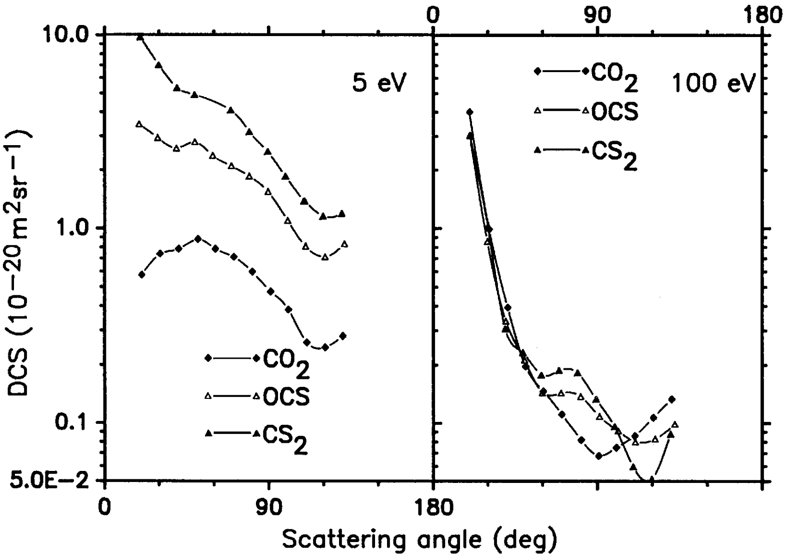

Fig. 18. – Differential cross-sections for electron scattering on CO_2, OCS and CS_2 (from Sakamoto *et al.* 1999)

CS. Threshold peaks were observed below 0.5 eV in DCS for excitation of higher bending overtones, (040), (050), (060) (Abouaf *et al.* 1994). A possible virtual e^- + OCS bound state has been hypothesized (Sohn *et al.*, Abouaf *et al.* 1994) in the zero-energy limit.

Electronic excitation at 30 eV and 55 eV collision energy was studied by Flicker *et al.* (1978). The energy-loss spectrum at 30 eV and 60° scattering angle shows two pairs of overlapping bands: a weak one centered at 4.94 eV and 5.53 eV, and a strong one at 7.36 eV and 8.11 eV. DCS at 55 eV collision energy for the first energy loss state has the typical shape of the spin-forbidden transitions, with a maximum at 40°. A probable assignment is $X\,^1\Sigma^+ \rightarrow {}^3\Sigma^+$. DCS at 55 eV for three more transitions are forward centered and their intensity scale down approximately by a factor of five for the 8.11 eV, 7.36 eV and 5.53 eV energy loss, respectively. Possible configurations of these states are $1^1\Sigma^+$, $^1\Pi$ and $^1\Delta$, respectively (Flicker *et al.* 1978).

Extensive studies of electronic excitation at 10 eV and 60 eV impact energies and 5–17 eV energy loss were performed with 25 meV energy resolution by Leclerc *et al.* (1981).

The electronic excitation above the ionization threshold was studied by Borovik *et al.* (1993). Spectra of threshold electrons (up to 40 meV of residual energy) at 11–16 eV impact energies and of ejected electrons at 19, 28, 60 eV impact energies were recorded. Structures corresponding to autoionization of Rydberg levels of the $X\,^2\Pi$ and $A\,^2\Pi$ ionic states were observed. Inner shell transitions were studied by electron (Tronc *et al.* 1979) and photon impact (Truesdale *et al.* 1984).

Ionization CS was measured by Srivastava (1997) up to 1000 eV. His data agree quite well with the semiempirical model of Kim *et al.* (1997). A single-point determination of Ziesel *et al.* (1975) of $4.2\cdot10^{-20}$ m^2 at 30 eV is slightly higher than the result of Srivastava.

Measurements of forward-angles electron scattering in the 10–50 eV energy range were used to determine the absolute photoionization CS (Carnovale *et al.* 1982). Just above the ionization threshold (11.2 eV) only OCS^+ ions were observed. At 50 eV the dominant ion is S^+ with 60% yield, followed by CO^+ and OCS^+ (about 15%, each). Whereas Carnovale *et al.* (1982) did not report double ionization at 50 eV, Masouka and Doi (1993) observed a high (0.34) branching ration between double and single photoionization at 60 eV photon energy.

The dissociation into metastable states was studied by Barnett *et al.* (1992); kinetic energies of three metastable fragments O (^5S), S (^5S) and CO ($a^3\Pi$) were measured.

Dissociative attachment CS is unusually high: its maximum of $0.29 \cdot 10^{-20}\,\mathrm{m}^2$ is located at the same energy (1.15 eV) as the TCS maximum, as we have seen for CO_2 (Ziesel *et al.* 1975). The relative contribution of the dissociative attachment to TCS is by a factor of 50 higher for OCS than for CO_2. S^- is the main ion observed; as stated by Iga *et al.* (1996) the signals due to O^- and C^- ions observed in some works (Hubin-Franskin *et al.* 1976, Iga *et al.* 1993) are too weak to give reliable cross-section data. The residual CO molecules can be created in vibrationally excited states (Abouaf and Fiquet-Fayard 1976, Tronc *et al.* 1982). Structures in the energy dependences of DCS for the S^- yield, corresponding to vibrational levels of CO, indicate a competition between vibrational excitation and dissociation attachment channels (Abouaf *et al.* 1994).

Broad peaks in the S^- yield were found at 4.7, 7.0 and 10.2 eV, two orders of magnitude weaker than the one at 1.2–1.4 eV (Iga *et al.* 1996, Krishnakumar *et al.* 1999).

Resonances. A $^2\Pi$ shape resonant state was observed between 1.2–1.4 eV. The positions of this resonant state practically coincide when observed in the different channels, the TCS (Szmytkowski and Zubek 1978, Szmytkowski *et al.* 1984), the vibrational excitation (Sohn *et al.* 1987) and the dissociative attachment one (Ziesel *et al.* 1975). At 4 eV, two overlapping resonances (Lynch *et al.* 1979), of the $^2\Delta$, and the $^2\Sigma$ symmetries (the latter dominating) cause some enhancement in the elastic and vibrational CS. The effect is particularly well visible in the stretching vibrational excitations (Sohn *et al.* 1987). In the dissociative attachment channel, the onset of the S^- yield observed at 3.9 eV was attributed to a resonant process (Iga *et al.* 1996). We are not aware of assignments of resonant states to the 7.0 eV and 10.2 eV peaks in the dissociative attachment CS (Iga *et al.* 1996).

Sum check. The small number of experimental determinations of partial CS allow only a limited validity of the sum check. In the very low energy limit, the summed data (Sohn *et al.* 1987) indicate that the experimental TCS of Szmytkowski *et al.* (1984) can be underestimated. The agreement between these two sets of data is very good at 1.15 eV. At 2–5 eV the sum check does not allow to choose between the two TCS data sets (Szmytkowski *et al.* 1984, Sueoka *et al.* 1999).

At 100 eV the sum of experimental elastic (Sakamoto *et al.* 1999) and ionization (Srivastava 1997) CS is almost 50% lower than the TCS (Szmytkowski *et al.* 1984, Sueoka *et al.* 1999). Part of this difference can be attributed to the unknown electronic excitation CS. On the other hand, DCS of Sakamoto *et al.* (1999a, b) can suffer from some underestimation, as can be seen at 5 eV by comparing the integral CS due to Sakamoto *et al.* to that of Sohn *et al.* (1987). A good agreement between summed and exprimental TCS in the 10–100 eV range can be obtained using the theoretical elastic CS of Lunch *et al.* (1979), instead. At 1000 eV the ionization CS (Srivastava 1997) sums with the theoretical (Raj and Tomar 1997) elastic CS up to 93% of TCS (Zecca *et al.* 1995).

TABLE XII. – *Integral cross-sections for electron scattering on carbonyl sulfide (in* $10^{-20}\,\mathrm{m}^2$ *units)*

Energy (eV)	Elastic	Vibrational	Ionization	Summed	Total
0.4	57.2 S			57.2	35.9 SZ
0.6	39.4 S	6.7 S		46.1	26.1* SZ
1.15	36.1 S	15.4 S		51.5	53.1 SZ
1.5	15.6 SA	2.0**		17.6	32.2 SZ
	27.5 **S			29.5	27.7* SU
2.0	16.9 S	1.8**		18.7	19.0 SZ
					21.0 SU
3.0	19.6 S	1.3 S		20.9	24.0 SZ
	23.0 L			24.3	21.6* SU
5.0	25.8 S	2.0**		27.8	30.8 SZ
	21.1 SA			23.1	26.4 SU
10.0	30.3 L			30.3	35.3 SZ
					31.5 SU
20.0	28.9 L		1.8 SR	30.7	31.4 SZ
					29.5 SU
60	9.3 S		4.7 SR	14.0	23.6 SZ
	16.4 L			21.1	21.1 SU
100	5.5 SA		5.3 SR	10.8	20.2 SZ
	13.0 L			18.3	16.9 SU
200	8.2 R		4.9 SR	13.1	12.4 SU
					13.6 Z
400	4.31 R		3.25 SR	7.56	8.4 SU
					9.4 Z
500	3.56 R		2.92 SR	6.48	7.4 SU
					7.6* Z
1000	1.93 R		2.20 SR	4.13	4.43 Z

** - Extrapolated data.
* - Interpolated data.
L - Lynch *et al.* (1979), theory.
R - Raj and Tomar (1997), optical model.
S - Sohn *et al.* (1987).
SA - Sakamoto *et al.* (1999b), read from their figure, integrated in this work, ±15% integration error.
SR - Srivastava (1997).
SZ - Szmytkowski *et al.* (1984, 1989).
SU - Sueoka *et al.* (1999).
Z - Zecca *et al.* (1995).

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4˙6. *Sulphur dioxide* (SO_2). – SO_2 is present as the main constituent of the atmosphere of Jupiter's satellite Io (Bhardwaj and Michael 1999a) and it is also abundant in the Venus atmosphere. Its importance in counteracting the greenhouse warming has also been recognized (Zecca and Brusa 1991). In spite of the fact that the cross-sections (total and elastic) have been measured by several groups, SO_2 remains one of the gases with the biggest discrepancies in the measured data. Similar big discrepancies were observed for another highly reactive gas, O_2, see fig. 27 in Part I. The SO_2 molecule has a bent structure (119°) and in consequence possesses a high (1.63 D) dipole moment. A recent comprehensive review of total and partial CS to be used in Monte Carlo simulations of electron degradation in SO_2 has been performed by Bhardwaj and Michael (1999b).

Total cross-sections measurements of Dababneh *et al.* (1986) and of Szmytkowski and Maciąg (1986) are only in general agreement as far as regards the shape of the curves. Remeasured data of Szmytkowski *et al.* (1996a, b) at 2–10 eV fall in-between the previous measurements (Szmytkowski and Maciąg 1986, Dababneh *et al.* 1986) while at higher energies agree within the error bar with other determinations (Dababneh *et al.* 1986, Zecca *et al.* 1995). Probably, above 10 eV no correct discrimination against inelastically scattered electron was performed in the experiment of Szmytkowski and Maciąg (1986). Absolute measurements in a trochoidal spectrometer at 0.2–12 eV (Wan *et al.* 1993) practically coincide with those of Szmytkowski *et al.* (1996a, b). The measurements of Zubek *et al.* (1981) at 0.2–8 eV, not shown for clarity in fig. 19, are in the 2–8 eV almost a factor of two higher than the TCS of Dababneh *et al.* (1986). This discrepancy is probably due to a systematic error in the pressure reading (Zubek *et al.* 1999). Below 1.5 eV the TCS of Zubek *et al.* rise quickly with lowering energy. A similar rise is visible in the TCS of Dababneh *et al.* below 2 eV but this part of their data seems to be "downwards" shifted.

TCS between 4 eV and 100 eV diminishes smoothly with no sharp structure. A shallow minimum visible in Dababneh *et al.*'s data at 7–8 eV remains within the experimental error bar. At 10 eV the SO_2 total cross-section value of $32 \cdot 10^{-20}\,\mathrm{m}^2$ (Szmytkowski *et al.* 1996a, b) is approximately equal to that of OCS; the two cross-sections merge again at about 1000 eV (Zecca *et al.* 1995). The low-energy end TCS by Zecca *et al.* seems to be somewhat (10% at 90 eV) underestimated. The additivity model based on optical-potential calculations (Raj and Tomar 1997, Joshipura and Vinodkumar 1997) reproduce pretty well the experimental TCS (Szmytkowski *et al.* 1996a, b, Zecca *et al.*, 1995) above 100 eV.

Swarm. Cyclotron-resonance measurements of Tice and Kivelson (1967) and of Sokolov and Sokolova (1981) indicate a rise of the momentum transfer CS in the limit of low energies as one can expect from the polar character of the molecule. However, the data of Sokolov and Sokolova (not shown in fig. 19, see Trajmar *et al.*, 1983, for tabulated values) seem to suffer from a serious error in the energy determination. Tice and Kivelson (1967) quoted a momentum transfer CS value of $660 \cdot 10^{-20}\,\mathrm{m}^2$ at 0.025 eV energy. The low-energy rise is visible also in different TCS measurements (Zubek *et al.* 1981, Dababneh *et al.* 1986, Szmytkowski *et al.* 19986b) but the absolute values disagree rather seriously. TCS of Szmytkowski *et al.* (1996b) at 0.2 eV agree well with the extrapolated momentum transfer CS of Tice and Kivelson (1967).

Elastic cross-sections. Large discrepancies regard also the elastic CS. The most recent data of Gulley and Buckman (1994) indicate a smooth dependence of the integral elastic CS, with a rapid fall above 20 eV. These CS are compatible with the TCS of Szmytkowski and Maciąg (1986) apart at the energy of 1 eV where the discrepancy is 25%. The theory (Gianturco *et al.* 1997) coincides at 2–30 eV with the experimental integral CS (Gulley and Buckman 1994) within the error bar.

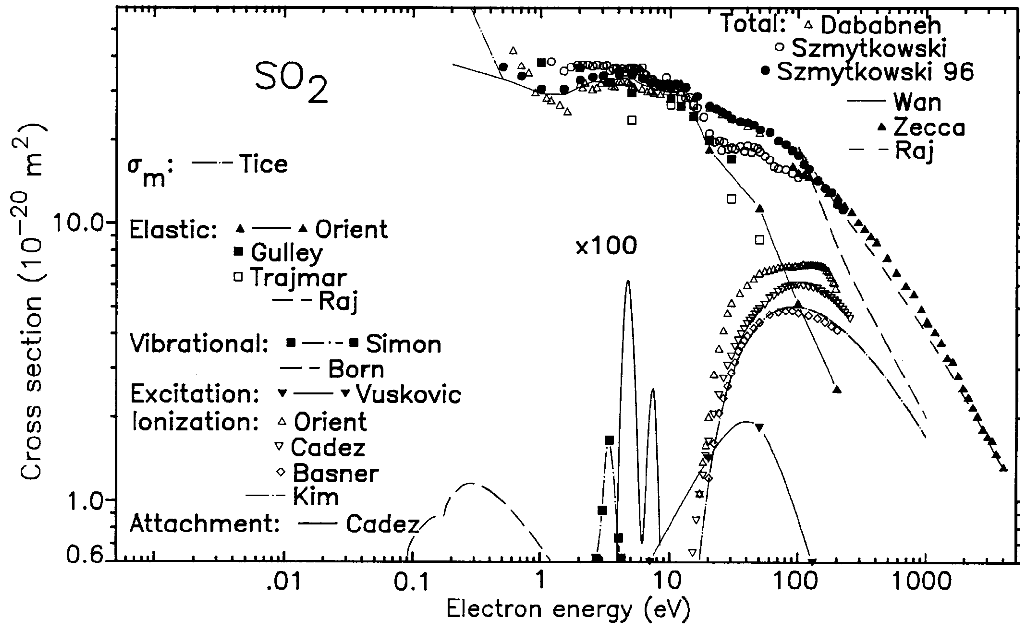

Fig. 19. – Integral cross-sections for electron scattering on SO$_2$. *Total*: Szmytkowski and Maciąg (1986); Szmytkowski *et al.* (1996b); Dababneh *et al.* (1986); Wan *et al.* (1993); Zecca *et al.* (1995); Raj and Tomar (1997), additivity rule; Zubek *et al.* (1981) and Sokolov and Sokolova (1981) not shown for clarity. *Momentum transfer*: Tice and Kivelson (1967), cyclotron resonance. *Elastic*: Orient *et al.* (1982), multiplied by a factor of 2; Trajmar and Shyn (1989), absolute; Gulley and Buckman (1994), absolute; Raj and Tomar (1997), optical model. Vibrational: the (300) excitation function of Simon *et al.* (1978) normalized to Andrić *et al.* (1983) at 3.4 eV; Born approximation (eq. (15), Part I), sum of all three modes. *Electronic excitation*: Vušković and Trajmar (1982). Ionization: Orient and Srivastava (1984); Čadež *et al.* (1983); Basner *et al.* (1995), New York results, Greifswald results not shown for clarity; Kim *et al.* (1997), semiempirical model. Dissociative attachment: Čadež *et al.* (1983); the data of Krishnakumar *et al.* (1997), not shown for clarity, are higher by a factor of two, roughly.

DCS is much forward-centered at 1 eV, due to influence of the permanent dipole moment. At 3–20 eV DCS exhibit a pronounced minimum at 80° (Gulley and Buckman 1994), see fig. 16. The measurements of Orient *et al.* (1982) and of Trajmar and Shyn (1989), normalized to He data, are much lower than those of Gulley and Buckman (1994). This discrepancy, similar to that in H$_2$ (see Part I), can be caused by the normalization procedure. In fact, the DCS measurements of Orient *et al.* and Trajmar and Shyn at 12–50 eV give the same angular dependence but the absolute values are scaled. Therefore, in fig. 19 and in table XIII we present the data of Orient *et al.* (1982) re-normalized by a factor of two to the result of Gulley and Buckman (1994) at 20 eV.

The optical model (Raj and Tomar 1997) seems to overestimate the integral elastic CS at 100 eV being higher than the TCS (Szmytkowski *et al.* 1996a, b, Zecca *et al.* 1995). We note a similar discrepancy for other triatomic molecules between the experimental TCS and the integral elastic CS calculated in the optical model. On the other hand, at 300–1000 eV the theoretical DCS (Raj and Tomar 1997) agree reasonably well with the experiment of Iga *et al.* (1995). High-energy (54 keV), low-angle elastic scattering was studied by Holder and Fink (1981).

TABLE XIII. – *Integral cross-sections for electron scattering on sulphur dioxide (in* $10^{-20}\,\mathrm{m}^2$ *units).*

Energy	Elastic	Vibrational	Ionization	Excitation	Summed	Total
3.4	32.1 G	1.6 A			33.7	35.4 SZ86
5.0	23.5 T					34.0 SZ
10.0	28.1 G			0.8**	28.9	31.5 SZ
	26.7 T					
12.0	27.9 T					31.1* SZ
15.0	26.6 T					29.4* SZ
20	19.9 G		1.6 C	1.4 V	22.9	21.0 SZ
	19.8 T				22.8	
30	12.2 T					23.7 SZ
50	11.3 O		4.9 C	1.8 V	18.0	21.6 SZ
	8.7 T		4.33 K		14.8	18.5 SZ86
100	5.1 O		6.0 C	1.0*	12.1	15.2 Z
						17.5 SZ
200	2.5 O		5.2 C	0.4 V	8.1	12.4 Z
	8.2 R				13.8	11.7 SZ
500	3.56 R		2.69 K	0.2**	6.5	7.25* Z
1000	1.99 R		1.69 K	0.1**	3.8	4.47* Z

* - Interpolated value.
** - Extrapolated value.
A - Andrić *et al.* (1983).
C - Čadež *et al.* (1983).
K - Kim *et al.* (1997), semiempirical.
O - Orient *et al.* (1982) normalized by a factor 2 to Gulley and Buckman (1994) at 20 eV.
R - Raj and Tomar (1997).
SZ - Szmytkowski *et al.* (1996), digitized from their figure.
SZ86 - Szmytkowski and Maciąg (1986).
T - Trajmar and Shyn (1989).
V - Vušković and Trajmar (1982).
Z - Zecca *et al.* (1995).

Vibrational cross-section for direct excitation, as evaluated from the Born approximation (eq. (15), Part I) and using infrared intensities from Bishop and Cheung (1982) is quite weak: $1.2 \cdot 10^{-20}\,\mathrm{m}^2$ at 0.3 eV, with the (001) anti-stretching mode dominating. In the resonance region (3.4 eV), excitation up to $n = 23$ overtones of the (100) mode with some additional bending quanta was observed (Andrić *et al.* 1983, Simon *et al.* 1978). Moreover, vibrational CS shows an unusual dependence on n, see fig. 20. This

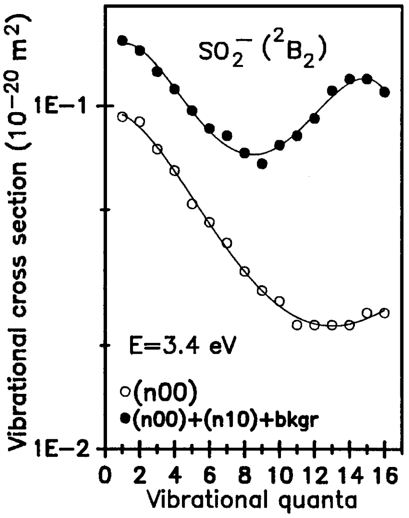

Fig. 20. – Vibrational excitation of overtones in SO_2 in the region of the shape resonance (Andrić *et al.* 1983).

dependence is much different than for other low-energy shape resonances, for example in diatomic molecules (see fig. (19), Part I). The integral vibrational CS in SO_2 obtained by summing the excitations up to $n = 16$ amounts to $1.6 \cdot 10^{-20}\,\mathrm{m}^2$ (Andrić *et al.* 1983), *i.e.* 5% of TCS at 3.4 eV (Szmytkowski *et al.* 1996b). This value is less than the share of vibrational CS in low-energy resonances of some other triatomic molecules, like for example CO_2.

Cross-sections for excitation of single vibrational modes show similar energy dependences: a large peak extending from about 2.5 eV to 4.0 eV with some structure superimposed (Andrić *et al.* 1983). These structures were explained theoretically in terms of a "boomerang" model of the resonant state (Andrić *et al.* 1983). To evaluate the integral vibrational CS in fig. 19 we have normalized the (300) excitation function of Simon *et al.* (1978) to the absolute value of $1.6 \cdot 10^{-20}\,\mathrm{m}^2$ by Andrić *et al.* (1983) at 3.4 eV. The angular distribution at 3.4 eV shows a minimum at 90° and indicates the presence of a B_2 shape resonance (Andrić *et al.* 1983).

Electronic excitation differential and integral CS covering all states between the lowest one (3.1 eV energy loss, optically forbidden $\tilde{X}(^1A_1) \rightarrow \tilde{a}(^3B_1)$ excitation) and the ionization limit (12.34 eV) has been measured by Vušković and Trajmar (1981, 1982). The summed excitation CS amounts to 10% of TCS at 50 eV and drops to 3% of TCS at 200 eV (Vušković and Trajmar 1982). The absolute value of the electron excitation CS at 200 eV ($0.39 \cdot 10^{-20}\,\mathrm{m}^2$) is three times more than the optical emission CS in molecular bands of SO_2 (Ajello *et al.* 1992b). That is because more than two thirds of the excitation cross-section at 200 eV is due to transitions to high $\tilde{G}$, $\tilde{H}$ (9.6–11.3 eV energy loss) levels or predissociating ($\tilde{D}$, 5.5–7.1 eV) states (Vušković and Trajmar, 1982). DCS for all but the lowest at $\tilde{a}(^3B_1)$ states are forward centered (Flicker *et al.* 1978, Vušković and Trajmar 1982).

Forward-angle electron scattering for valence and core excitation was studied by Cooper *et al.* (1991). Below the ionization threshold the derived photoabsorption CS reaches a maximum of $0.25 \cdot 10^{-20}\,\mathrm{m}^2$ at about 9.5 eV, *i.e.* at the maximum of the energy-loss spectra shown by Vušković *et al.* (1982).

The maximum of photoabsorption CS above the ionization threshold amounts to about $0.5 \cdot 10^{-20}\,\mathrm{m}^2$ at 19.5 eV (Cooper *et al.* 1991, Hamdy *et al.* 1991); the $SO_2{}^+$ and SO^+ ions are produced with almost 50% yield, each (Cooper *et al.*).

Optical emission CS in the 40–200 nm and 200–430 nm range due to electron impact at collision energies up to 1000 eV have been studied by Ajello *et al.* (1992a) and (1992b), respectively. In the first spectral range the emission from O and S neutral and ionized atoms was observed. At 200 eV the summed emission CS in this wavelength range amounts to $0.12 \cdot 10^{-20}\,\mathrm{m}^2$ (Ajello *et al.* 1992a, see also Becker *et al.* 1983). In the 264–430 nm wavelength range the emission from $\tilde{A}(^1A_2)$, $\tilde{B}(^1B_1)$, and probably (Ajello *et al.* 1992b) from the $\tilde{E}$, triplet (Vušković and Trajmar 1981) state of the SO_2 molecule were observed. In the 240–265 nm range the emission from $\tilde{A}\,(^3\Pi) \rightarrow \tilde{X}\,(^3\Sigma^-)$ transition in the SO radical dominates. The sum of the emission cross-sections from $\tilde{A}\,(^1A_2)$, $\tilde{B}\,(^1B_1)$, and $\tilde{a}\,(^3B_1)$ at molecular states reaches a maximum of $0.37 \cdot 10^{-20}\,\mathrm{m}^2$ at 9 eV (Ajello *et al.* 1992b). At 100 eV the 264–430 nm range CS (containing also contribution from the ionic $SO_2{}^+$ ($\tilde{C}\,(^2B_2) \rightarrow \tilde{X}\,(^2A_1)$) transition, Tsuji *et al.* 1978) amounts to $0.13 \cdot 10^{-20}\,\mathrm{m}^2$ (Ajello *et al.* 1992b), in excellent agreement with the measurements of Miller and Becker (1987); at 1000 eV it still amounts to $0.09 \cdot 10^{-20}\,\mathrm{m}^2$. The optical emission at 230–400 nm wavelength between 4 eV and 12 eV collision energies was also studied by Zubek (1989) but no cross-sections were given.

Metastable fragment production has been studied by van der Burgt *et al.* (1992) up to 300 eV but no cross-sections have been determined. The dissociation into-neutrals CS reaches a maximum at 130 eV; it rises sharply between the threshold and 50 eV, up to 80% of the maximum value (Kedzierski *et al.* 1999).

Ionization. Large discrepancies exist between different experimental determinations. Even in the recent joint paper from the New York and Greifswald laboratories (Basner *et al.* 1995) discrepancy of 10% exists in the CS maximum as measured by the two groups. On the one side, the results of Čadež *et al.* (1983), Lindsay *et al.* (1996) and "mass spectroscopy" (Greifswald laboratory) data from Basner *et al.* (1995) agree within the error bar, on the other side, the New York results from Basner *et al.* (1995) and the semi-empirical model (Kim *et al.* 1987) practically coincide. The measurements of Čadež *et al.* (1983) are somehow (15–30%) lower than those of Orient and Srivastava (1984) but higher than the normalized values of Smith and Stevenson (1981) by a factor of three at 40 eV.

The overall ionization CS reaches a maximum of $6.0 \cdot 10^{-20}\,\mathrm{m}^2$ at 95 eV (Čadež *et al.* 1983). The parent $SO_2{}^+$ and the radical SO^+ ion productions dominate at 100 eV amounting to 60% and 25%, respectively; the S^+ ion yield rises gradually reaching 17% of the total ionization at 200 eV (Orient and Srivastava 1984).

Electron attachment integral CS exhibits two peaks as it has been shown for CO_2: at 4.7 eV ($0.62 \cdot 10^{-20}\,\mathrm{m}^2$) and at 7.5 eV ($2.5 \cdot 10^{-20}\,\mathrm{m}^2$) (Čadež *et al.* 1983). These data agree very well with both beam and swarm measurements of Spyrou *et al.* (1986) and with relative data of Harland *et al.* (1973) but are significantly lower (by a factor of four at 4.5 eV) than those of Orient and Srivastava (1983) and still lower by a factor of two than those of Krishnakumar *et al.* (1997) and Wan *et al.* (1993). Note that according to the most recent data (Krishnakumar *et al.* 1997) dissociative attachment CS constitutes at its maximum 0.3% of TCS, as in other oxygen or sulphur containing triatomic molecules, OCS, NO_2, N_2O. At both dissociative attachment peaks, the O^- production dominates over that of SO^- (Čadež *et al.* 1983). The S^- yield peaks at a slightly lower (4.0 eV) energy (Orient and Srivastava 1983, Sauers *et al.* 1993). Fine structures due to the vibrational excitation of the neutral fragments SO and O_2 in the dissociative attachment around 4.7 eV were observed (Abouaf and Fiquet-Fayard 1976).

Strong dependence of dissociative attachment CS on the gas temperature was observed (Spyrou *et al.* 1985). This CS varies more than a factor of two between 300 K and 700 K. Dissociative attachment from laser-excited SO_2 was studied by Jaffke *et al.* (1993) and Krishnakumar *et al.* (1996, 1997). Both O^- and SO^- ions were observed at near-to-zero energies, peaking at 0.4 eV and 0.6 eV, respectively (Krishnakumar *et al.* 1996). The summed dissociative attachment CS for the excited $\tilde{B}\,(^1B_1)$ state at 0.4 eV is $0.4 \cdot 10^{-20}\,\mathrm{m}^2$; this value is by a factor of two higher than the maximum of the CS at 4.6 eV for the ground state (Krishnakumar *et al.* 1997). Attachment of electrons to SO_2 in three-body collision at thermal energies was studied by Shimamori and Nakatani (1992).

Resonances. The presence of a resonant state between 2.5 and 4 eV has been first recognized by Sanche and Schulz (1973) in transmitted-current measurements. The structures observed between 2.8 eV and 3.8 eV exhibits a single progression of vibrational levels of a temporary state of ${SO_2}^-$; at energies above 3.8 eV this progression is perturbed by other structures, possible due to the presence of another state of ${SO_2}^-$. Sanche and Schulz stressed an unusual character of the SO_2 resonance. Differently than in SO_2, in other gases with stable negative ions, like O_2 and NO, vibrational structures in transmitted electron current start at near-to-zero energies, see figs. 27 and 29 in Part I. In detailed studies (Andrić *et al.* 1983), the 2.8–3.8 eV state has been classified as an intermediate lifetime shape resonance of the B_2 symmetry and the boomerang model, developed for CO_2, has been used to describe it.

Sum check indicates a quite good consistency between elastic cross-sections of Gulley and Buckman (1994), ionization CS of Čadež *et al.* (1983) and TCS of Dababneh *et al.* (1986) at low energies. If one re-normalizes the elastic cross-section of Orient *et al.* (1982) by a factor of two, to the data of Gulley and Buckman at 20 eV, a good consistency is also found at 50 eV. At higher energies the summed CS are significantly lower than the experimental TCS (Zecca *et al.* 1995). Different partial CS can be underestimated. At 200 eV the presently re-normalized experimental elastic CS (Orient *et al.* 1982) are three times less than the theoretical (Raj and Tomar 1997) value. Similarly, recent calculations (Fomonung *et al.* 1996) show that the electronic excitation integral CS (Vušković and Trajmar 1982) could be underestimated at 200 eV. Note also that the semiempirical model of ionization by Kim *et al.* (1997), differently than in many other gases, in SO_2 coincides with the lower bound of different experimental determinations. Serious discrepancies exist between the two sets of dissociative attachment CS (Spyrou *et al.* 1986, Čadež *et al.* 1983 and Wan *et al.* 1993, Krishnakumar *et al.* 1997). More precise, absolute measurement of partial cross-sections would be of interest.

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ZUBEK, 1999, private information.

4˙7. *Chlorine dioxide* (ClO_2). – Chlorine dioxide plays an important role in catalytic ozone decomposition in stratosphere (Farman *et al.* 1985). Few electron-scattering experiments have been performed on this molecule. Both ClO_2 and Cl_2O molecules are bent (118.5° and 110.8°, respectively), ClO_2 being more compact (1.49 Å bond length *vs.* 1.70 Å for Cl_2O, Weast 1986).

Total cross-sections by the backward-scattering method have been measured between 0.02 eV and 10 eV (Gulley *et al.* 1998). Above 6 eV TCS in ClO_2 is comparable to that of O_3. TCS in ClO_2 exhibits a maximum of about $120 \cdot 10^{-20}$ m^2 at 0.06 eV, followed by a minimum of about $40 \cdot 10^{-20}$ m^2 at 0.04 eV and a low-energy rise.

Vibrational and electronic excitation. Photoabsorption and threshold-electrons spectra were examined in the 2.5–10.8 eV and 0–10 eV energy range, respectively by Marston *et al.* (1998). Near-to-threshold energy-loss spectra show enhanced vibrational excitation around 1 eV due to scattering *via* a resonant state. At energies between 3 and 10 eV electron energy-loss peaks (the most prominent at 3.5 and 8 eV) coincide with photoabsorption bands. A general resemblance between ClO_2 (Davies *et al.* 1995) and O_3 (Johnstone *et al.* 1992) electron energy-loss spectra under the same collisional conditions (near-to-zero scattering angle and 150 eV collision energy) has to be stressed. The ClO_2 spectrum is shifted to lower energies by about 1 eV, with respect to the O_3 spectrum. The photoabsorption CS in the UV and visible region reaches a maximum value of $0.12 \cdot 10^{-20}$ m^2 at 3.5 eV for the $X\,(^2B_1) \rightarrow A(^2A_2)$ transition (Wahner *et al.* 1987, Marston *et al.* 1998); vibrational progressions are well visible in the spectrum. In the VUV region three bands dominate, with a maximum photoabsorption CS of $0.45 \cdot 10^{-20}$ m^2 at 9.3 eV (Marston *et al.* 1998).

Dissociative attachment has been studied in a joint Berlin-Innsbruck experiment in the 0–10 eV range (Senn *et al.* 1999). The dominant feature is the formation of a transient negative (${ClO_2}^{-*}$) ion in an excited state by resonant capture in the vicinity of 0.7 eV and its subsequent decay. The cross-sections for the formation of ClO^-, Cl^- and ${O_2}^-$ ions peak in the range 0.5–0.8 eV and that of the O^- at 1.15 eV. The absolute value of the dissociative attachment CS obtained by normalizing the measurements to the thermal-electrons attachment coefficient from cyclotron-resonance study (Wecker *et al.* 1981) amounts to $8 \cdot 10^{-20}$ m^2 in its maximum (Senn *et al.* 1999). $ClO^- + O$ is the dominant channel. Although the $O_2 + Cl^-$ exit channel is exothermic by nearly 4 eV, the Cl^- ion appears with a mean kinetic energy of only 0.4 eV indicating an effective vibrational excitation of neutral O_2, as is in the case of the O_3 dissociation. Additionally, ${O_2}^-$ and Cl^- ion yields exhibit maxima at zero collision energy; both exit channels are exothermic. The presence of these threshold peaks is analogous to that in O_3 and in some chlorofluoromethanes (see respective paragraphs). Core-excited resonances located around 4 eV and 8 eV appear only in the atomic Cl^- and O^- channels (Senn *et al.* 1999, Marston *et al.* 1998). At higher target gas pressures the parent ${ClO_2}^-$ ion is observed, formed by the collisions of ClO^- and ClO_2 (Senn *et al.* 1999).

Relatively less works (Wecker *et al.* 1981, Nelson *et al.* 1994, Nickolaisen *et al.* 1996) were performed on other chlorine-containing molecule important in atmospheric chemistry, like Cl_2O.

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4˙8. *Carbon disulphide* (CS_2). – Carbon disulphide and its radicals were observed in cometary atmospheres (Cosmovici and Ortolani 1984). In mixtures with NO_2, the CS_2 molecule has an important application in CO chemical lasers (Azoulay and Rosenwaks 1979). The CS_2 molecule is non-polar but possess high electric dipole polarizability ($8.8 \cdot 10^{-30}\,\mathrm{m}^3$). Integral cross-sections are shown in fig. 21.

Total cross-sections have been measured between 0.4 eV and 80 eV (Szmytkowski 1987). The total cross-section in most of the studied energy range exceeds $20 \cdot 10^{-20}\,\mathrm{m}^2$, exhibiting a minimum at about 0.3 eV and rising again towards the zero-energy limit. A flat maximum of $53 \cdot 10^{-20}\,\mathrm{m}^2$ is reached at 4 to 12 eV. No total cross-section measurements have been performed above 80 eV.

The high-energy optical model TCS (Raj and Tomar 1997), differently than in SO_2 and OCS, does not agree with the experiment (Szmytkowski 1987) in the 100 eV limit. On the other hand, the recent optical-model TCS (Lee *et al.* 1999) agrees very well with the experimental TCS (Szmytkowski 1987) in the whole 1–100 eV energy range.

Swarm experiments. Electron mobility in liquid phase and ionization yield in gas and liquid phase were studied by Gee and Freeman (1989 and 1990, respectively).

Elastic cross-section measurements and partial wave analysis were performed between 0.3 eV and 5 eV by Sohn *et al.* (1987). Angular distributions in this energy range exhibit a *d*-wave behavior. Comparison of the summed (elastic + vibrational excitation) values of Sohn *et al.* (1987) with the absolute total ones (Szmytkowski 1987) indicate the elastic CS can be underestimated by about 30%. The structure, predicted at 1.85 eV by a continuum multiple-scattering model (Lynch *et al.* 1979) was not observed nor in elastic (Sohn *et al.* 1987) neither TCS (Szmytkowski 1989). This theoretical artifact was probable due to neglecting the nuclear motion in the calculation (Lynch *et al.* 1979). The recent optical model calculations (Lee *et al.* 1999) agree very well with the measurements of Sohn *et al.* (1987) in the 0.8–3.5 eV energy range and do not show any sharp resonance structures. Below 0.8 eV the theoretical integral value diverges from the experiment and shows a Ramsauer-Townsend minimum at 0.2 eV.

Absolute DCS in the 20°–130°, 1.5–100 eV range were measured by Sakamoto *et al.* (1999a, b). At 2 eV the carbon disulphide DCS resembles in shape that for OCS but is by a factor of two higher (Sakamoto *et al.* 1999a). At 100 eV the three gases CO_2, OCS and CS_2 show similar shapes and amplitudes of DCS. The shoulder structure between 60° and 80° observed in OCS becomes more pronounced in CS_2, see fig. 18. The integral elastic CS diminishes monotonically in the 1.5–100 eV energy range (DCS of Sakamoto *et al.* 1999b, integrated in this work). At 100 eV this integral value is by a factor of two lower than the theoretical value obtained in a continuum multiple-scattering model (Lynch *et al.* 1979) and the optical model calculation (Lee *et al.* 1999). A part of this discrepancy can be attributed to the uncertainty in extrapolating DCS below 30°; in fact a half of the presently evaluated integral value at 100 eV comes from scattering at angles below 30°. On the other hand, some underestimation of experimental DCS cannot be excluded.

The optical model calculation in the independent-atoms approach (Raj and Tomar 1997) overestimates experimental elastic CS at 100 eV (Sakamoto *et al.* 1999a, b), like in SO_2; this theory is probably more reliable at higher energies.

Vibrational excitation is rather important at low energies. At 0.3 eV the CS for the (100) symmetric stretching mode amounts to $1.1 \cdot 10^{-20}\,\mathrm{m}^2$, for the (010) bending mode to $2.0 \cdot 10^{-20}\,\mathrm{m}^2$ and for the (001) asymmetric stretching to $3.3 \cdot 10^{-20}\,\mathrm{m}^2$, compared with $18.7 \cdot 10^{-20}\,\mathrm{m}^2$ for the elastic CS (Sohn *et al.* 1987). For collision energies above 1 eV only fundamental modes were observed (Sohn *et al.* 1987), while at lower energies also the first overtone of the bending mode. The Born approximation describes well angular shapes for infrared-active modes (010) and (001) in the 0.5–3 eV range; however to reproduce absolute values for the (010) mode the literature (Bishop and Cheung 1982) dipole transition moments, see eq. (15) in Part I, should be multiplied by a factor of five. Angular distributions for the infrared inactive (100) mode at low energies are forward peaked, according to the Born approximation, while at 3.5 eV they become rather isotropic.

The rise of vibrational CS above the Born approximation at 0.3 eV, see fig. 19, suggests the existence of threshold phenomena, as observed for example in CH_4. On the other hand, maxima at about 3.5–5 eV for the (100) and (010) modes indicate the presence of resonant processes in this energy region.

Electronic excitation has been measured by Flicker *et al.* (1978) at 25, 40 and 70 eV. The energy loss spectrum at 25 eV collision energy resembles to some extent the one in OCS (at 55 eV): the two low energy loss peaks are much weaker than the 6–7 eV energy loss bands. At 40 eV collision energy the DCS for the 6.27 eV energy loss, optically allowed $X^1\Sigma_g^+ \rightarrow 1^1\Sigma_g^+$ transition is by a factor of 10 higher than the DCS for the 6.79 eV energy loss transition. The configuration of the 6.79 eV transition has not been identified but the shape of the DCS strongly suggested an optically allowed transition (Flicker *et al.* 1978). The DCS for 3.36 eV energy loss is almost uniform in angle, *i.e.* it suggests a singlet-triplet transition, while the 3.91 eV energy loss process is somewhat forward-peaked. The superposition of several states in the 3–4.5 energy-loss region has been hypothesized (Flicker *et al.* 1978).

The sum of the electronic excitation CS at 100 eV obtained from optical measurements in the 110–510 nm range amounts to $1.7 \cdot 10^{-20}\,\mathrm{m}^2$ (Ajello and Srivastava 1981), two thirds of the optical emission at this energy have been attributed to the excited ${CS_2}^+$ ion. An extensive energy loss spectroscopy in the 3–10 eV energy-loss range, 10–100 eV collision energies and 4°–90° scattering angles was performed to identify the excited states (Hubin-Franskin *et al.* 1983).

The optical emission of CS_2 was studied at 3.6–12 eV collision energies (Zubek 1989). Several structures in optical emission CS in the 300–395 band were observed: a first peak at 5.8 eV due to de-excitation of the $^1B_2$ state, the next one at 7.6 eV due to the $^1\Pi_g$ state and at 9.8 eV due to de-excitation of a Rydberg state. In the 240–300 band, a large structure, with the threshold at 9.15 eV, due to de-excitation of the dissociated CS ($A^1\Pi_g$) radical was seen (Zubek 1989). Valence shell photoelectron spectra were studied by Baltzer *et al.* (1996).

Ionization CS of Rao and Srivastava (1991) are in pretty good agreement with the semi-empirical models (Deutsch *et al.* 1997, Kim *et al.* 1997) and with a single point determination of Ziesel *et al.* (1976). At 30 eV the CS_2 ionization cross-section is the highest ($7.5 \cdot 10^{-20}\,\mathrm{m}^2$) compared to OCS and CO_2, 4.2 and $1.7 \cdot 10^{-20}\,\mathrm{m}^2$, respectively (Ziesel *et al.* 1976).

Measurements of the ionization CS into the parent ion of Freund *et al.* (1990) agree within the error bar with those of Rao and Srivastava (1991) at 50 eV and 100 eV and are slightly (14%) higher at 200 eV. The partitioning varies slowly between 100 eV and 1000 eV: from 60% to 72% for ${CS_2}^+$, and from about 17% to 12% for S^+ and CS^+ ions (Rao and Srivastava 1991). The ratios of multiply-charged ions ${CS_2}^+/{CS_2}^{2+}$ and ${CS_2}^{2+}/{CS_2}^{3+}$ amount to about 35 at 1000 eV (Rao and Srivastava). The ionization CS rises from 30% of TCS (Szmytkowski *et al.* 1987) at 50 eV to 37% at 80 eV.

Dissociation. The threshold for dissociation into neutrals (CS and S radicals) is as low as 4.5 eV (Okabe 1972), compared to the ionization threshold (10.08 eV). Therefore, one can expect a high CS for the dissociation, similarly as it was, for example, in SiH_4

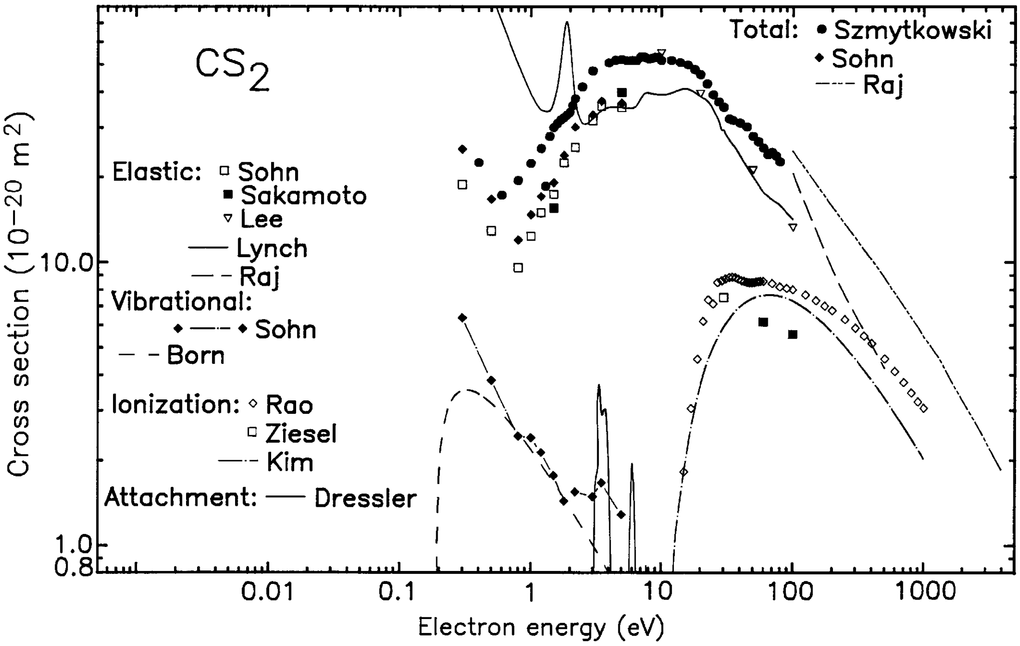

Fig. 21. – Integral cross-sections for electron scattering on CS_2. *Total*: Szmytkowski (1989), absolute; Sohn *et al.* (1987), sum of elastic and vibrational; Raj and Tomar (1997), optical model. *Elastic*: Sohn *et al.* (1987), absolute; Sakamoto *et al.* (1999b), integrated in this work with ±15% uncertainty; Lee *et al.* (1999), optical model, shown at 10–100 eV only; Raj and Tomar (1997), optical model; Lynch *et al.* (1979), continuum multiple-scattering model. *Vibrational*: Sohn *et al.* (1987), sum of all 3 modes; Born approximation (eq. (15) Part I), (010) + (001) modes. *Ionization*: Rao and Srivastava (1991); Ziesel *et al.* (1975) at 30 eV; Kim *et al.* (1997), semiempirical. *Dissociative attachment*: Dressler *et al.* (1987), normalized to Ziesel *et al.* (1975) at 3.35 eV.

and GeH_4.

Dissociative attachment threshold is located at 2.41 eV (Dressler *et al.* 1987). The S^- ions yield reaches a maximum of $3.7 \cdot 10^{-20}\,m^2$ at 3.35 eV (Ziesel *et al.* 1975), where it amounts to less than 10^{-4} of TCS. This yield is of the same relative order of magnitude as the O^- production from CO_2 (Ziesel *et al.* 1975). Other dissociative attachment bands, at 3.65 eV (overlapping with the first one), at 6.2 eV, 7.8 eV (Dressler *et al.* 1987) and a broad one at 25 eV (Krishnakumar and Nagesha 1992) were also observed. At 6.2 eV cross-sections for production of S^-, CS^-, ${S_2}^-$ and C^- ions amount to 23, 6.7, 2.5 and $0.22 \cdot 10^{-20}\,m^2$, respectively (Krishnakumar and Nagesha 1992).

Electron attachment, with formation of ${CS_2}^-$ ion was observed at very low energies in Rydberg atoms quenching experiment of Hotop and collaborators (Harth *et al.* 1989, Desfrancois *et al.* 1993). Studying quenching of neon atoms with principal quantum numbers between $n = 5$ and $n = 30$, they observed a maximum in the electron attachment rate coefficient for n about 20, corresponding to the mean electron energy of 40–50 meV (Harth *et al.* 1989). The maximum rate coefficient in CS_2 is about 1/10 of the rate in SF_6 for the same n.

Resonances. A sharp $^2\Pi_g$ resonance, at about 1.8 eV, predicted by the theory of Lynch *et al.* (1979), was observed in the elastic (Sohn *et al.* 1987) and in the total (Szmytkowski 1987) cross-section only as a weak cusp structure. The presence of a weak resonance in this region was reported in the transmission experiment by Dressler *et al.* (1987) and in the threshold spectra by Dance *et al.* (1978). The vibrational excitation CS hardly shows the presence of a resonant state at 1–2 eV, being almost equal to the value from the Born approximation, see fig. 21.

An enhancement of the elastic cross-section at about 5 eV has been attributed by Sohn *et al.* (1987) to overlapping Σ_u and Σ_g resonances, with an asymptotic *d*-wave dominating. A different symmetry ($^2\Sigma_g$) and position (4.2 eV) has been assigned to this structure on the basis of electron transmission spectroscopy (Dressler *et al.* 1987). Core-excited Feshbach resonances have been attributed to 3.35 and 3.65 eV peaks in the S^- yield (Dressler *et al.* 1987).

Sum check. The big difference between total (Szmytkowski 1987) and theoretical elastic CS (Lynch *et al.* 1979) at 10 eV indicate the importance of inelastic, probably electronic excitation (Zubek 1999) processes. As in the case of other polyatomic molecules, see for example CH_4, the electronic excitation leads mainly to the dissociation of the molecule. At 60 eV the sum of elastic (Lynch *et al.* 1979, Sakamoto *et al.* 1999b) and ionization (Rao and Srivastava 1991) CS exceeds the total value (Szmytkowski 1987) by 10%. Note that the experimental TCS value (Szmytkowski 1987) can be underestimated, as was noted in SO_2.

An additivity rule was applied to derive partial and total CS at intermediate energies (Jiang *et al.* 1997, Raj and Tomar 1997).

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