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BY

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EXCITATION OF THE CO FOURTH POSITIVE BAND SYSTEM BY ELECTRON IMPACT ON CARBON MONOXIDE AND CARBON DIOXIDE[†]

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ABSTRACT

Absolute excitation cross sections were measured for five vibrational bands of the CO($A^1\Pi$ - $X^1\Sigma^+$) Fourth Positive band system. The bands were produced by electron impact on CO and CO_2 and the cross sections were measured from threshold to 350 eV. Relative intensity measurements on 28 bands were used to determine the dependence of R_e on the r-centroid, which is $R_e = 1.9(1.0 - 0.6\ \bar{r}_{v'v''})$. Absolute transition probabilities were computed using this functional form for R_e and normalizing the total transition probability of the v' = 2 level to published experimental results. The total f-value for this transition is then 0.15. Absolute excitation cross sections for the first five vibrational levels ($v' = 0 \rightarrow 4$) of the $A^1\Pi$ state were determined for each parent gas using the measured cross sections of specific bands and the absolute transition probabilities. When CO was the parent gas, the relative populations of these vibrational levels were proportional to the Franck-Condon factors, $q_{v'o}$. The sum of the cross sections for these levels is 1.87×10^{-17} cm^2 ± 15% at 300 eV. This represents 87.4% of the total excitation cross section for the $A^1\Pi$ state. The relative populations of the first five vibrational levels were also determined for dissociative excitation of CO_2 and they differed from the relative populations which resulted from direct excitation of CO. The sum of the cross sections for these five levels is 1.4×10^{-18} cm^2 ± 17% at 300 eV.

INTRODUCTION

The importance of carbon monoxide and carbon dioxide in planetary atmospheres has recently been emphasized by the Mariner space probe investigations of Mars and Venus. In particular, the recent Mariner VII probe toward Mars detected a strong emission spectrum in the vacuum ultraviolet, dominated below 2000 Å by the Lyman alpha radiation from atomic hydrogen and the Fourth Positive band system of carbon monoxide, $CO(A^1\Pi - X^1\Sigma^+)$.[1] Absolute electron excitation cross sections are needed to determine the relative importance of producing the Fourth Positive band system by photoelectron impact on CO and CO_2 in the Martian atmosphere.

Laboratory measurements of the intensities of these bands in emission have been sparse. Krupenie[2] reports some visual estimates made from photographic plates. We report here accurate relative intensity measurements on 28 bands of this system.

Hesser[3] has measured the transition probabilities for the A-X transition from vibrational levels ($v' = 0 \rightarrow 4$) of the CO $(A^1\Pi)$ state in a radiative lifetime experiment. Wells and Isler[4] have measured the radiative lifetime for the $v' = 2$ level in a level-crossing spectroscopic experiment and found good agreement with Hesser's value. Hesser also calculated the total absorption oscillator strength for this transition and found $f = 0.094$, in essential agreement with Rich's[5] value of 0.12 from shock tube work. Lassettre and Skerbele[6], however, obtained a value $f = 0.195$ from electron energy loss spectra measurements and thus the existing data are in serious disagreement. A nonconstant electronic transition moment (R_e)

will change the total f-value calculated from Hesser's absolute transition probabilities. It is therefore of interest to measure the variation in R_e across the band system and thus to determine if this effect is the cause of the disagreement in the f-values.

THEORY

In a region containing diatomic molecules in an electronically excited state, the number of photons emitted per unit volume per second[8] in a transition from the v' vibrational level of the upper state to the v" vibrational level of the lower state is

$$I_{v' v''} = n_{v'} A_{v' v''} \qquad (1)$$

where $n_{v'}$ is the number density of excited molecules in the v' vibrational state, and

$$A_{v' v''} = q_{v' v''} \nu^3_{v' v''} R_e{}^2 (\bar{r}_{v' v''}) \qquad (2)$$

is the transition probability for an electric dipole allowed transition. The usual factor $64\pi^4/3h$ on the RHS of [2] has been included in the definition of $R_e{}^2$ and R_e is then written in atomic units. $q_{v' v''}$ is the Franck-Condon factor for the two vibrational states involved; $\nu_{v' v''}$ is the wave number (cm^{-1}) of the emitted photon; R_e is the electronic transition moment; and $\bar{r}_{v' v''}$ is the r-centroid, a measure of the mean internuclear distance for the transition.

Values of the Franck-Condon factors and r-centroids for the Fourth

Positive band system of carbon monoxide ($A^1\Pi$ - $X^1\Sigma^+$ transition) have been calculated to a high degree of accuracy by Albritten et al.[9] using a Rydberg-Klein-Rees potential function for $v' = 0$ to 9 and $v'' = 0$ to 24. The assumption that R_e is a function of the r-centroid alone has been studied by Drake and Nicholls[10] and found to be good to within one or two percent for oxides and nitrides.

If the molecule is excited to the upper electronic state by electron impact and the Born approximation holds, then the probability of excitation from the ground state ($v'' = 0$) to the v' vibrational level of the upper state is proportional to the Franck-Condon factor for the transition, $q_{ov'}$.[11] Thus, the relative volume emission rates for vibrational bands belonging to a molecular band system are given by

$$\frac{I_{v_1'v_2''}}{I_{v_3'v_4''}} = \frac{q_{ov_1'}\, A_{v_1'v_2''}}{q_{ov_3'}\, A_{v_3'v_4''}} \quad \frac{\sum\limits_{v_4''} A_{v_3'v_4''}}{\sum\limits_{v_2''} A_{v_1'v_2''}} \qquad (3)$$

The relative volume emission rates for vibrational bands belonging to a v'' progression (v' = constant) are given by a much simplified version of [3].

$$\frac{I_{v'v_i''}}{I_{v'v_j''}} = \frac{A_{v'v_i''}}{A_{v'v_j''}} \qquad (4)$$

Thus the relative counting rates ($S_{v'v''}$) for vibrational bands belonging to a v" progression will be

$$\frac{S_{v'v_i''}}{S_{v'v_j''}} = \frac{Q(\lambda_{v'v_i''})}{Q(\lambda_{v'v_j''})} \quad \frac{q_{v'v_i''}\,\nu^3_{v'v_i''}R_e^2\,(\bar{r}_{v'v_i''})}{q_{v'v_j''}\,\nu^3_{v'v_j''}R_e^2\,(\bar{r}_{v'v_j''})} \tag{5}$$

where $Q(\lambda_{v'\,v''})$ is the spectral response of the photon detection system at the wavelength $\lambda_{v'\,v''}$. Equation [5] may be inverted to yield the relative electronic transition moments for the bands in question.

APPARATUS AND CALIBRATION

The apparatus used in making these measurements has been described in detail by Mumma and Zipf[12] (see Figure 1). A small collision chamber was filled with CO or CO_2 to a known pressure (typically 5 x 10^{-5} torr). A beam of electrons (typically 5 x 10^{-5} amperes) was passed through the gas at energies which were varied from 1 to 350 eV. Photons emitted in the interaction region were observed at 90° to the direction of the electron beam with a vacuum monochromator and a solar-blind photomultiplier tube. Excitation functions were measured manually and in a multi-scaling mode at energy intervals of 0.7 volts.

The vibrational bands of the CO Fourth Positive system were produced by direct excitation of CO or dissociative excitation of CO_2, i.e.

$$\begin{aligned} e + CO(X^1\Sigma^+) &\rightarrow CO(A^1\Pi) + e \\ CO(A^1\Pi) &\rightarrow CO(X^1\Sigma^+) + h\nu_{v'\,v''} \end{aligned} \tag{6}$$

or

$$e + CO_2 \rightarrow CO(A^1\Pi) + O + e$$

$$CO(A^1\Pi) \rightarrow CO(X^1\Sigma^+) + h\nu_{v',v''} \qquad (7)$$

The slits of the monochromator were set so that the entire rotational structure of the band was included in the unity portion of the trapezoidal transfer function. The bands for which excitation cross sections were measured were selected on the basis of freedom from contamination by overlapping bands and atomic emissions. Absolute cross section and relative intensity measurements were made at electron energies of 300 eV, where the Born approximation is known to be accurate.[6] The method of calibration of the optical system has been described in detail by Mumma and Zipf[7]. The method uses intensity[13] measurements made on vibrational bands of the Lyman-Birge-Hopfield (LBH) ($a^1\Pi_g - X^1\Sigma_g^+$) band system of molecular nitrogen and on selected multiplets of atomic nitrogen whose branching ratios are known. The relative transition probabilities of the LBH bands were calculated using the Franck-Condon factors of Benesch et al.[14]. The electronic transition moment (R_e) is a constant for this band system[15,16]. A comparison of the calculated intensities with the measured intensities of these bands (via equation [5] then gives the relative response of the optical system as a function of wavelength. A comparison of known branching ratios for NI multiplets with measured intensities is used in a similar manner (See Figure 2).

Absolute calibration of the cross sections was achieved by comparing them to the cross section for producing Lyman alpha radiation (1215 Å) by electron impact on molecular hydrogen.[12,17]

ELECTRONIC TRANSITION MOMENT

The intensities of twenty-eight bands of the CO(A-X) system belonging to v'' progressions with $v' = 0 \rightarrow 6$ were measured by scanning the monochromator over each band. Bands belonging to a given v'' progression (v' constant) were scanned sequentially, thus minimizing the effects of long term drifts in the gas pressure and electron beam current. These parameters were monitored continuously and drifted by less than 1% over the time required to scan a given band. The monochromator slits were set to yield .88Å resolution and the electron energy was set at 300 eV. The detected photon counts were fed into a multi-channel analyzer which was operated in the multi-scaling mode with an equivalent channel width of 0.45 Å. The resulting readout showed the shape of the band and gave visible evidence as to whether the band was overlapped or otherwise contaminated. The total number of counts in the histogram of a band was taken to be the intensity of the band. The relative electronic transition moment was then calculated using Equation [5], the Franck-Condon factors of Albritten et al.[9], and the relative spectral response values shown in Figure 2. This procedure was employed for the bands of each v'' progression. The results for each progression were multiplied by an arbitrary constant and the values of the constants which gave a least squares fit of the data to a linear relation with the r-centroid were determined. This procedure has the advantage that it does not assume anything about how the levels of the $A^1\Pi$ state are populated, whether by direct excitation or cascade, and it does not assume that the relative populations of the upper vibrational levels are related to the Franck-Condon factors, $q_{v',0}$.

The values for $R_e(\bar{r}_{v'\,v''})$ are plotted vs. the r-centroid values in Figure 3. The error bars represent the statistical counting noise ($N^{\frac{1}{2}}$) in the total number of counts in each band or 2.5%, whichever is greater.

The relationship between R_e and $\bar{r}$ based on our measurements is

$$R_e(\bar{r}_{v'\,v''}) = 1.9\ (1.0 - 0.60\ \bar{r}_{v'\,v''}) \qquad (8)$$

where $\bar{r}_{v'\,v''}$ is given in Å and R_e is in atomic units. Hesser's absolute transition probability measurements are interpreted (see discussion below) as best fitting the relation

$$R_e(\bar{r}_{v'\,v''}) = 2.7\ (1.0 - .68\ \bar{r}_{v'\,v''}) \qquad (9)$$

Relative transition probabilities for each vibrational level of the $A^1\Pi$ state ($v' = 0 \rightarrow 9$) were computed using the Albritten et al. Franck-Condon factors and r-centroids, and the measured dependence of R_e given in equation [8]. The transition probabilities were put on an absolute scale by normalizing $A_{v'=2}$ to the average of the published values[3,4], i.e. $A_{v'=2} = 10.3 \times 10^{+7}\ \text{sec}^{-1}$ (Table I). Hesser[3] measured the radiative lifetimes of vibrational levels of the $A^1\Pi$ state using a radio-frequency phase shift technique. His results show a slight increase in transition probability as v' varies from 0 to 5. Our results show a modest decrease (Table I, column three). As an exercise, we determined what slope gave best agreement with Hesser's measurements. The resulting relation is equation [9] and the corresponding computed values of the transition probabilities are displayed in Column four of Table I. We have used equations [2] and [8] to calculate an array of absolute transition probabilities for the system (Table II). We are then able to calculate the total absorption oscillator strength for the CO(A - X) transition. The total absorption oscillator strength is given by

$$f = \sum_{v'} f_{o\,v'} = \sum_{v'} 1.499\ (G'/G'')\ A_{v'o}\ \lambda^2_{v'o} \qquad (10)$$

where λ is in cm, A in $\sec^{-1}$, and G'/G" has the same value as the ratio of the electronic statistical weights g'/g" [where g is (2S + 1) for Σ states and 2 (2S + 1) for states with $\Lambda \geqslant 1$]. For the CO $(A^1\Pi - X^1\Sigma^+)$ transition, G'/G" = 2. We find a total absorption oscillator strength of 0.15. We interpret this as a corrected value of Hesser's f = 0.094, which is thus in better agreement with Lassettre and Skerbele's[6] value of 0.19. The discrepancy between the f-values as measured by optical means and by electron energy loss spectra is thus substantially reduced.

CO

Excitation functions for several vibrational bands of the CO Fourth Positive system, produced by electrons impacting on CO, were measured as a function of electron energy from threshold to 350 eV. The shapes of the excitation functions were obtained using the multi-scaling technique discussed earlier. The cross sections were put on an absolute scale by comparing them to the cross section for production of Lyman alpha radiation by dissociative excitation of H_2 at 300 eV. The vibrational bands whose cross sections have been measured are listed in Table III along with the values of their absolute excitation cross sections at 300 eV. The ratios $n_{v'}/n_o$ have been calculated from the relative band intensities $[I_{v'v''}]$ and the branching ratios are given in Column 6, Table III. These ratios should be compared to the theoretical Franck-Condon factor ratio $q_{v'o}/q_{oo}$. The agreement is quite good. This demonstrates that the populations of the vibrational levels of the $A^1\Pi$ state are proportional to the Franck-Condon factors, $q_{v'o}$. Lassettre[18] has observed similar results for the direct excitation (i.e. excluding cascade) of the $CO(A^1\Pi)$ state from electron energy loss spectra. Our results show that the total emission cross sections for the vibrational levels of the $A^1\Pi$ state (including cascade) are proportional to the Franck-Condon factors $(q_{v'o})$ to within experimental error. Hence, relative emission intensities (photons/sec) for the bands of this system may be calculated using

$$E_{v'v''} = q_{v'o}\, q_{v'v''}\, \nu^3_{v'v''}\, [1.9(1.00 - .60\bar{r}_{v'v''})]^2 \qquad (11)$$

We have calculated the emission intensities relative to the intensity of the (2,0) band using equation [11]. The results are shown in Table IV. These band intensities may now be used for the calibration of monochromators using the molecular vibrational branching ratio technique.[7]

The total cross sections for excitation of vibrational levels of the $A^1\Pi$ state were calculated via

$$\sigma_{v'} = \sigma_{v'v''} \frac{A_{v'}}{A_{v'v''}} \qquad (12)$$

and are shown in Figure 4. The absolute cross section of a specific band belonging to one of these v" progressions (v' = 0 → 4) may be obtained from the total level cross section, $\sigma_{v'}$, by multiplying by the appropriate branching ratio $A_{v'v''}/A_{v'}$. The total cross section for exciting the levels v' = 0 → 4 at 300 eV is 1.87 x 10^{-17} cm^2 ± 15%. If higher vibrational levels are also populated according to the Franck-Condon factors, $q_{v'o}$, then the cross section for the first five levels represents 87.4% of the total excitation cross section for all levels of the $A^1\Pi$ state (which then is 2.13 x 10^{-17} cm^2 at 300 eV). The total cross section for exciting the $A^1\Pi$ state becomes ~ 5.0 x 10^{-17} cm^2 at the peak (25 eV).

Aarts and de Heer[19] have recently measured the shape of the excitation cross section for the (0,1) band of this system from 100 - 6000 eV. They assumed a constant electronic transition moment and then calculated the branching ratio $A_{01}/A_{v'=o}$. The absolute cross section for direct excitation of the v' = 0 vibrational level was calculated from the inelastic electron scattering cross-sections of Lassettre and Skerbele[6] at 500 eV. The calculated branching ratio was then used to obtain the emission cross section for the (0,1) band at 500 eV although Aarts and de Heer recognized that the electronic transition moment was not constant for this system. The assumption of a constant electronic transition moment leads to a branching ratio equal to 0.289 whereas the branching ratio which results from using the variation of R_e determined in this work (Equation 8) is 0.323. Thus we expect the absolute value of the cross section for the (0,1) band to be 11.5% greater at 500 eV than the value quoted by Aarts and de Heer. We compare our cross section for the (0,1) band to that given by Aarts and de Heer in Figure 5. We have multiplied the cross section values of Aarts and de Heer by 1.115 in order to correct for the non-constant electronic transition moment of this band system. There is some disagreement in the shape of the emission cross section over the energy range 100 - 340 eV, but the absolute values agree within the experimental error at 300 eV. The shape of our cross section curve is estimated to be accurate to better than 10%.

CO_2

Excitation cross sections were measured for five vibrational bands of the CO Fourth Positive system which were produced by electron impact dissociative excitation of CO_2. The cross sections were measured over the energy range 0 - 350 eV. Excitation functions were measured using the multi-scaling technique described earlier, and the cross sections were put on an absolute scale by comparing them to the Lyman alpha cross section as in the case of CO. The absolute cross sections, $\sigma_{v' v''}$, at 300 eV are given in Table V, Column 3.

The absolute transition probabilities of the Fourth Positive system (Table II) may be used to determine the total level cross sections, $\sigma_{v'}$, from $\sigma_{v' v''}$ since the branching ratios from a particular v' level are properties only of the CO($A^1\Pi$ - $X^1\Sigma^+$) transition and not of the intermediate dissociation process. Total level cross sections have been calculated in this way and are shown in Figure 6. The relative populations of vibrational levels of the $A^1\Pi$ state will no longer be related to the Franck-Condon factors, $q_{v'0}$, of the CO(A - X) transition but will be a property of the dissociation mechanism of the CO_2 molecule. This can readily be verified by comparing the observed relative populations (Table V, column 6) to the theoretical Franck-Condon ratios $q_{v'o}/q_{oo}$ (Table III, column 7).

The sum of the cross sections for exciting the v' = 0 → 4 levels of the $CO(A^1\Pi)$ state by dissociative excitation of CO_2 is 1.4×10^{-18} cm^2 ± 17% at 300 eV. We cannot calculate what fraction of the total excitation cross section for the $A^1\Pi$ state this represents, although it seems likely that it is a sizeable fraction of the total. The shapes of the level cross sections (v' = 0 → 4) exhibit reproducible differences even out to 200 eV (see Figure 5). The sum of the cross sections for these five vibrational levels peaks near 40 eV where it is 2.6×10^{-18} cm^2.

SUMMARY AND CONCLUSIONS

The dependence of the electronic transition moment on the r-centroid has been measured for the $CO(A^1\Pi - X^1\Sigma^+)$ Fourth Positive band system. This has enabled us to calculate the array of absolute transition probabilities for this system and thus to calculate the total absorption oscillator strnegth (f-value). The f-value obtained in this way (f = 0.15) is 20% lower than the f-value obtained from electron energy loss spectra measurements (f = 0.195). Thus the apparent discrepancy between f-values obtained by lifetime measurements and by electron scattering measurements has been resolved.

Absolute excitation cross sections for bands of the CO Fourth Positive system have been measured for electron impact on CO and on CO_2. We have shown that the intensities of these bands in emission from CO may be calculated on the assumption that the vibrational levels of the $A^1\Pi$ state are populated according to the Franck-Condon factors. This agrees with Lassettre's results for the direct excitation of the $A^1\Pi$ state, and thus we conclude that cascade effects are unimportant for the calculation of relative band intensities. A table of relative emission intensities has been calculated and these are useful in the calibration of vacuum ultraviolet monochromators using the vibrational branching ratio technique.

The relative importance of exciting the CO ($A^1\Pi$) state by direct electron impact exictation of CO and by electron impact dissociative excitation of CO_2 has been calculated from our measured absolute cross sections. The electron on CO cross section peaks at ~ 5.0×10^{-17} cm^2 while the electron on CO_2 cross section peaks at greater than 2.6×10^{-18} cm^2. Since the absolute cross sections have been measured as a function of electron energy, they may be folded into the photoelectron energy spectrum for the Mars upper atmosphere and should provide a way of deciding how the CO Fourth Positive bands are produced as an emission feature in the Mars upper atmosphere.

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LIST OF FOOTNOTES AND REFERENCES

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Table I

Transition Probabilities For Vibrational Levels of The CO($A^1\Pi$) State.

v'	Hesser[3]	Wells and Isler[4]	$R_e\alpha(1. - .6\bar{r})$	$R_e\alpha(1 - .68\bar{r})$
0	9.2 x $10^7 sec^{-1}$		a) 10.5 x 10^7	b) 9.0 x 10^7
1	9.2		10.4	9.2
2	9.5 ± 10%	11.1 x 10^7 ± 10%	10.3	9.4
3	9.5		10.2	9.6
4	9.6		10.0	9.8
5	9.8		9.8	9.9
6			9.6	10.0
7			9.3	10.0
8			9.1	10.1
9			8.9	10.1

a) Calculated using $A_{v'} = \sum_{v''} q_{v'\,v''}\, \nu^3_{v'\,v''}\, R_e^2$ and normalizing $A_2 = 10^7 sec^{-1}$.

b) Calculated by finding the dependence of R_e vs. $\bar{r}$ which gave a best fit of calculated transition probabilities to those shown in column 1.

Table II

CO($A^1\Pi$ - $X^1\Sigma^+$)
Absolute Transition Probabilities
(10^{+7} Sec^{-1})

v' =	v'' = 0	1	2	3	4	5	6	7	8	9	10	11	12
0	1.87	3.41	2.92	1.56	.581	.159	.0333	.00544	.000707	.000074	.000006	0	0
1	4.21	2.34	.0290	.760	1.44	1.04	.444	.130	.0278	.00454	.000578	.000057	.000004
2	5.16	.172	1.35	1.27	.0289	.436	.884	.638	.267	.0758	.0156	.00241	.000285
3	4.57	.0533	1.89	.000454	.996	.638	.000	.372	.582	.373	.142	.0372	.00702
4	3.31	2.28	.522	1.01	.722	.104	.768	.250	.0286	.328	.373	.202	.0680
5	2.08	3.46	.0490	1.58	.0100	.969	.135	.288	.492	.0545	.0811	.263	.221
6	1.18	3.50	1.07	.661	.860	.428	.326	.550	.000961	.360	.236	.000502	.112
7	.626	2.82	2.37	.00222	1.36	.0306	.839	.00206	.499	.157	.0853	.287	.0723
8	.314	1.97	3.02	.494	.723	.749	.269	.460	.282	.132	.348	.00521	.161
9	.152	1.24	2.90	1.57	.0519	1.20	.0417	.701	.0255	.481	.00644	.263	.123

Table III

Absolute Cross Section for Excitation of the CO($A^1\Pi$ - $X^1\Sigma^+$) Fourth Positive Band System by Electron Impact on Carbon Monoxide

Band (v', v'')	Bandhead Wavelength (Å)	Absolute Cross Section[a] $\sigma_{v'\,v''}$	Band Intensity[b] $[I_{v'\,v''}]^c$	Branching Ratio $A_{v'\,v''}/A_{v'}$	Relative Number Density $[n_{v'}]^c$	Relative Franck-Condon Factors $q_{v'o}/q_{oo}$
(0,1)	1597	7.5×10^{-19}	1.00	.323	1.00	1.00
(1,4)	1729	6.2	.85	.138	1.93	1.94
(2,2)	1576	6.3	.87	.131	2.08	2.06
(3,0)	1447	17.6	2.30	.473	1.52	1.60
(4,0)	1419	7.7	1.17	.331	1.11	1.02

a) At 300 eV, absolute accuracy ± 13%.

b) Photons/sec; probable error ± 5%.

c) [ ] denotes normalization to the (0,1) band or $v' = 0$ progression.

d) Based on the dependence of R_e on r-centroid given in equation 8.

Table IV

Relative Volume Emission Rates for Bands of the $CO(A^1\Pi - X^1\Sigma^+)$ Fourth Positive System Excited by Electron Impact on CO[a]

v'	v'' = 0	1	2	3	4	5	6	7	8	9	10	11	12
0	.172	.313	.269	.144	.053	.015	.003	.0005	.0001	0	0	0	0
1	.759	.421	.0052	.137	.260	.187	.080	.023	.0050	.0008	.0001	0	0
2	1.000	.033	.262	.246	.0056	.085	.171	.124	.052	.015	.0030	.0005	.0001
3	.699	.081	.289	.0001	.152	.097	0	.057	.089	.057	.022	.0057	.0011
4	.327	.226	.052	.100	.071	.010	.076	.025	.0028	.032	.037	.020	.0067
5	.117	.194	.0027	.089	.0006	.054	.0076	.016	.028	.0030	.0045	.015	.012
6	.034	.101	.031	.019	.025	.012	.0094	.016	.000	.010	.0068	.0000	.0032
7	.0088	.040	.033	.0000	.019	.0004	.012	.0000	.0070	.0022	.0012	.0040	.0010
8	.0020	.013	.020	.0032	.0047	.0048	.0017	.0030	.0018	.0008	.0022	.0000	.0010
9	.0004	.0036	.0084	.0045	.0001	.0035	.0001	.0020	.0001	.0014	.0000	.0008	.0004

a) Calculated for electron impact on CO using equation 11. The calculation holds for electron energies greater than ~ 50 eV.

Table V

Absolute Cross Sections for Excitation of the CO($A^1\Pi$ - $X^1\Sigma^+$) Fourth Positive Band System by Electron Impact on CO_2

Band (v', v'')	Bandhead Wavelength (Å)	Absolute Cross Section at 300 eV[a] $\sigma_{v', v''}$ (cm^2)	Band Intensity $[I_{v', v''}]$[c]	Branching Ratio[d] $A_{v' v''}/A_{v'}$	Relative Number Density $[n_{v'}]$[c]
(0,1)	1597	11.1×10^{-20}	1.00	.323	1.00
(1,4)	1729	6.0	.417	.138	.974
(2,2)	1576	4.4	.390	.131	.960
(3,0)	1447	5.2	.452	.473	.308
(4,0)	1419	4.1	.352	.33	.344

a) Estimated absolute accuracy ± 17%.

b) Photons/sec;
Probable error ± 10%.

c) [ ] denotes normalization to (0,1) band or v' = 0 progression.

d) Based on the dependence of R_e on r-centroid of equation (6).

List of Figures

Figure 1 A schematic drawing of the experimental apparatus.

Figure 2 The relative spectral response of the window-monochromator-detector combination. The crosses are derived from measurements on the N_2 Lyman-Birge-Hopfield band system and the dots are derived from measurements on multiplets of atomic nitrogen. The smooth curve represents the least squares fit to the data.

Figure 3 The dependence of the electronic transition moment on the r-centroid for the CO Fourth Positive band system. Bands represented by the same symbol belong to the same v" progression, Viz: • (v' = 0); x (v' = 1); 0 (v' = 2); ◇ (v' = 3); ⋆ (v' = 4); Δ (v' = 5); and □ (v' = 6).

Figure 4 Absolute cross sections for excitation of vibrational levels (v' = 0 → 4) of the CO ($A^1\Pi$) state by electrons impacting on CO.

Figure 5 The cross section for excitation of the (0,1) band of the CO($A^1\Pi$ - $X^1\Sigma^+$) band system by electron impact on CO. The continuous curve represents the present data and the crosses represent the data of ref. 19 which have been renormalized as described in the text.

Figure 6 Absolute cross sections for excitation of vibrational levels (v' = 0 → 4) of the CO ($A^1\Pi$) state by electrons impacting on CO_2.

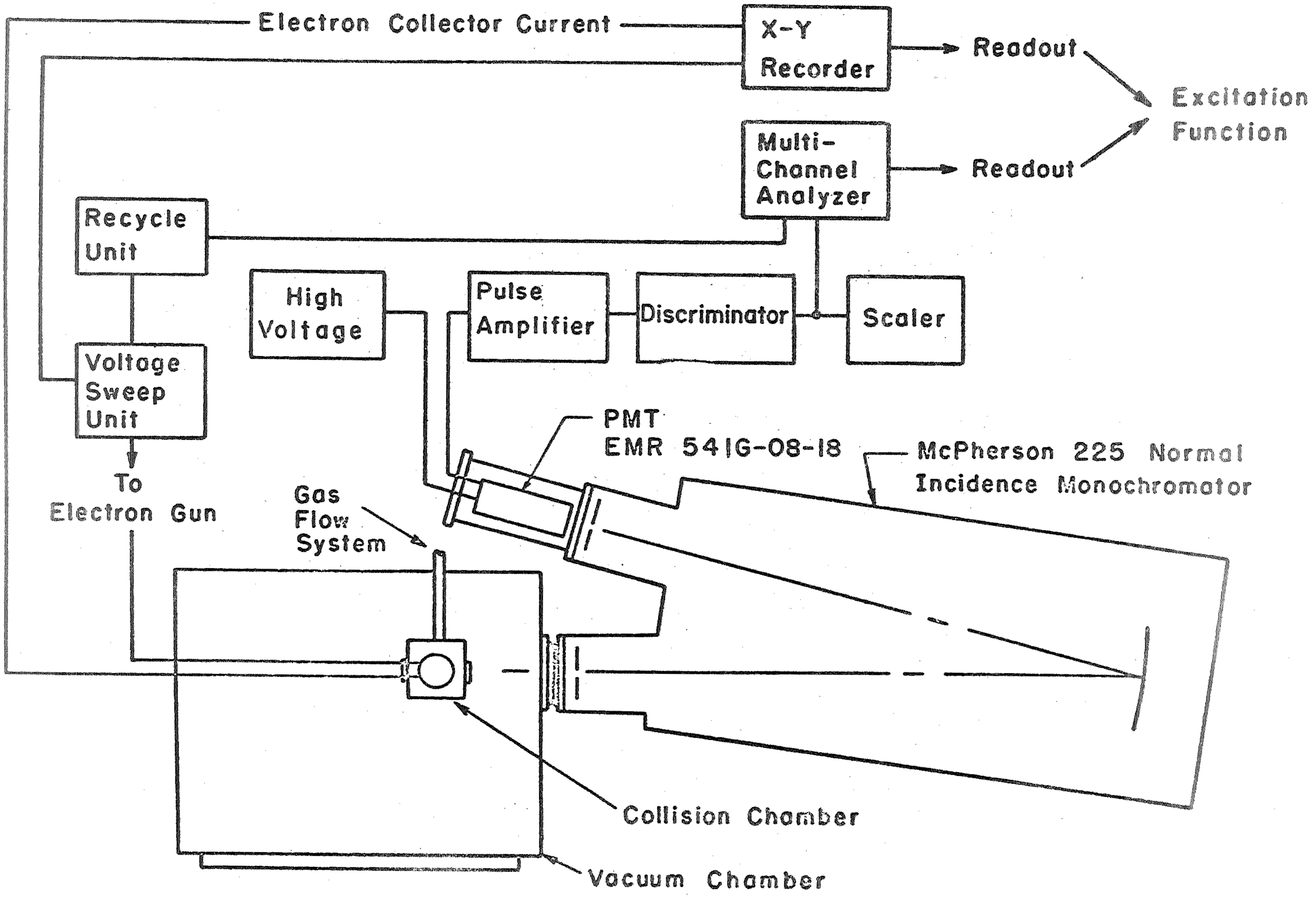
Electron Collector Current
X-Y Recorder
Readout
Excitation Function
Multi-Channel Analyzer
Readout
Recycle Unit
High Voltage
Pulse Amplifier
Discriminator
Scaler
Voltage Sweep Unit
To Electron Gun
Gas Flow System
PMT EMR 541G-08-18
McPherson 225 Normal Incidence Monochromator
Collision Chamber
Vacuum Chamber

Figure 1

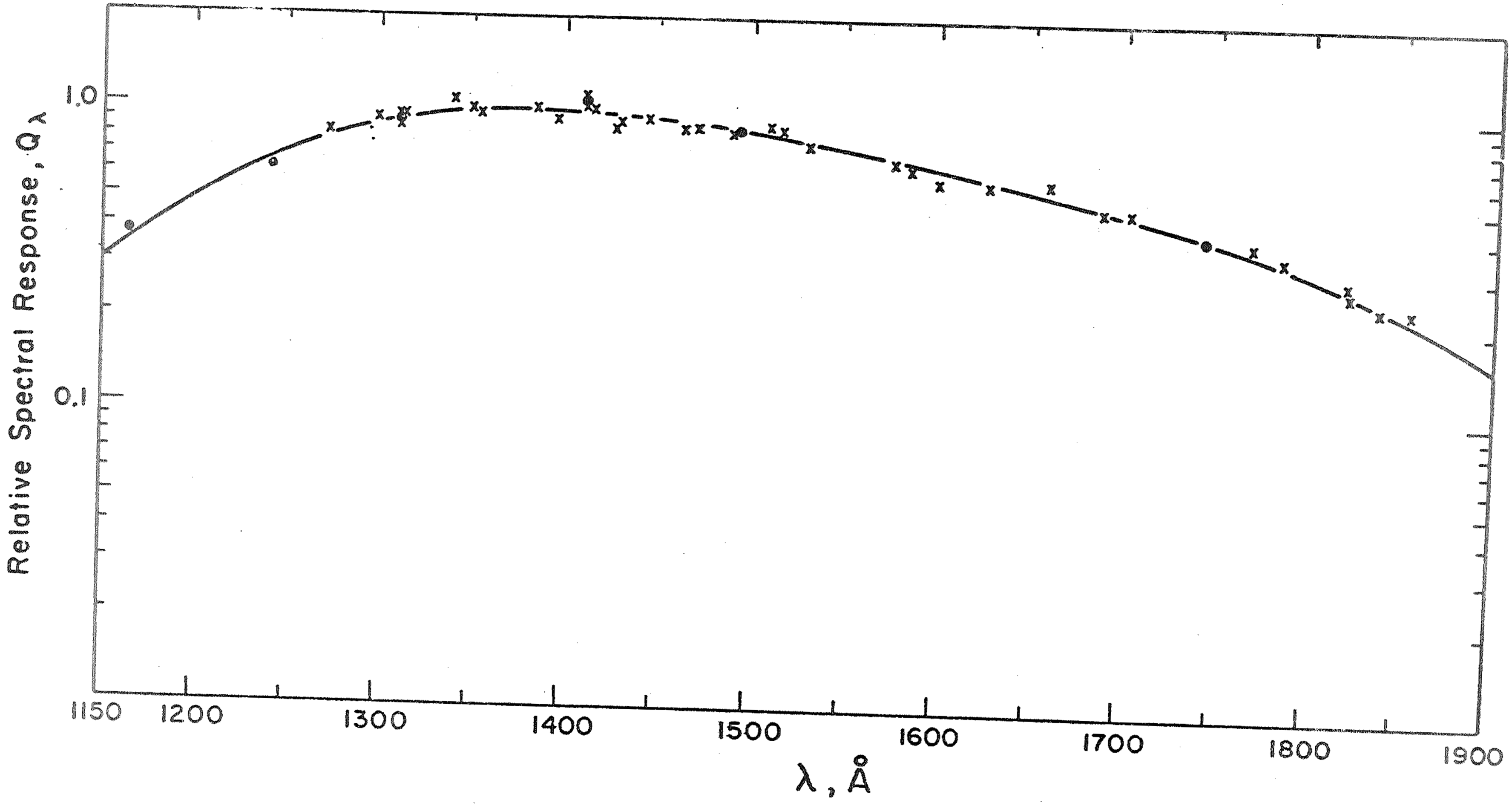
Relative Spectral Response, Q_λ
1.0
0.1
1150
1200
1300
1400
1500
1600
1700
1800
1900
λ, Å

Figure 2

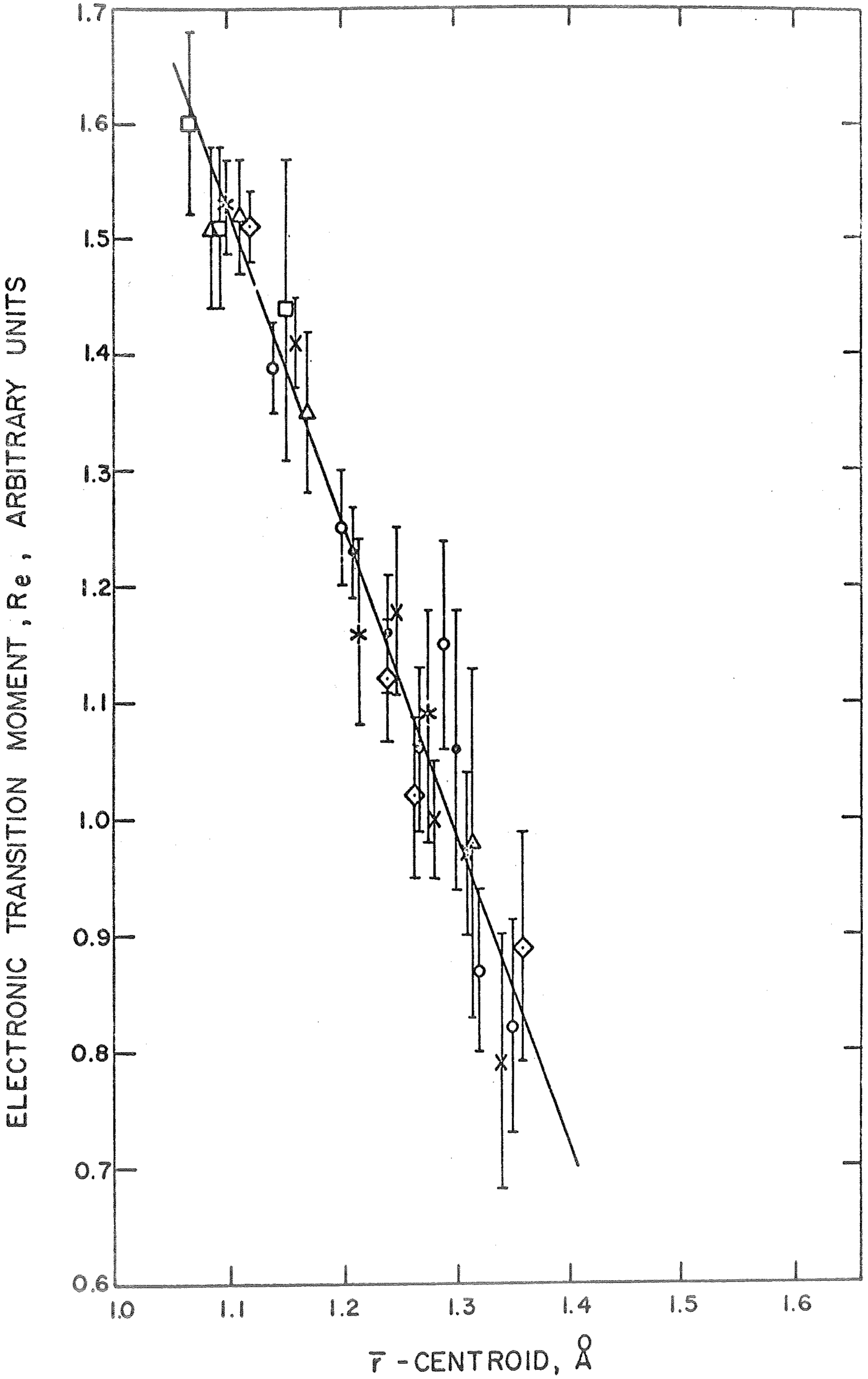
ELECTRONIC TRANSITION MOMENT, Re, ARBITRARY UNITS
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
1.0
1.1
1.2
1.3
1.4
1.5
1.6
r̄ -CENTROID, Å

Figure 3

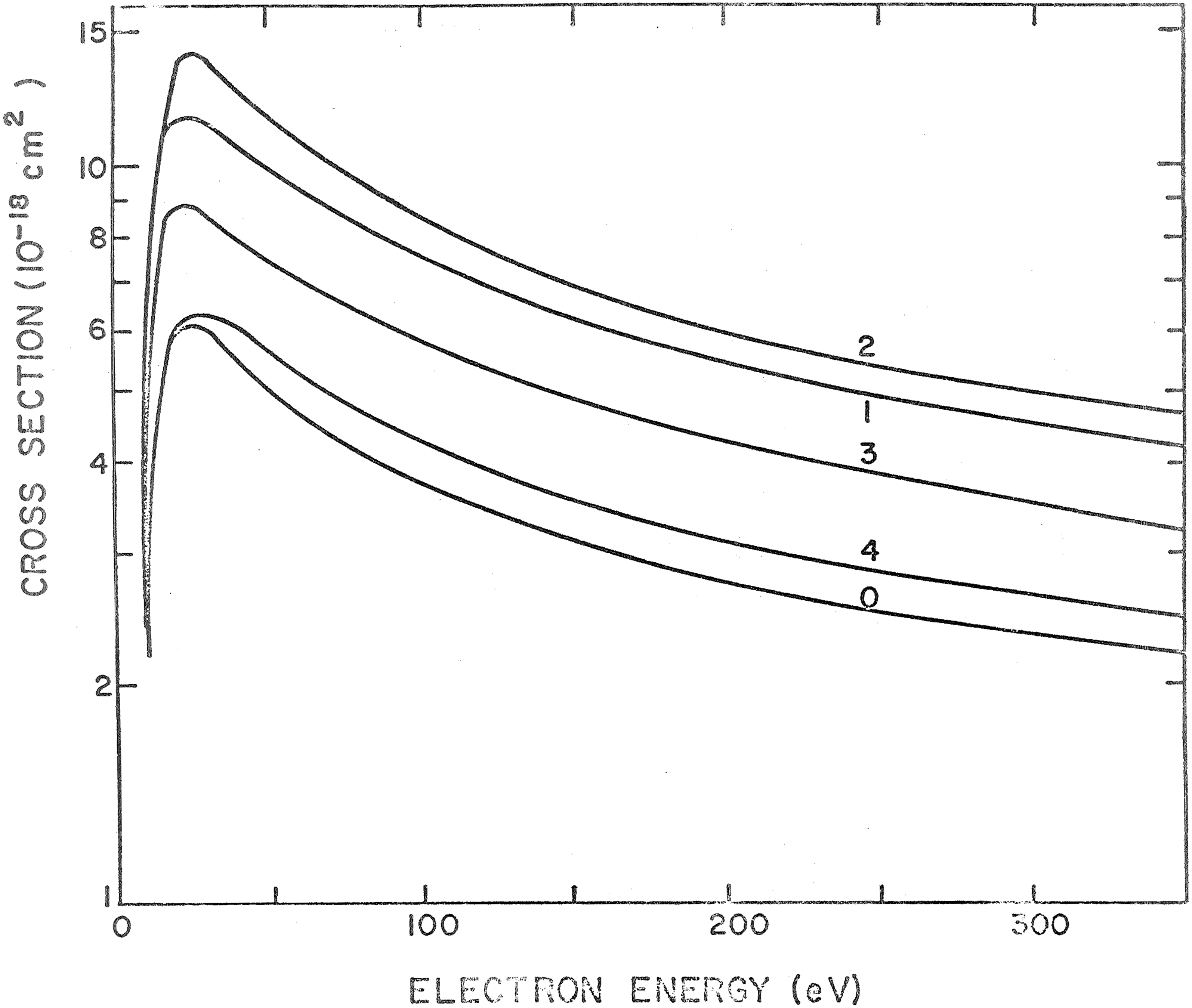
15
10
8
6
4
2
1
0
100
200
300
CROSS SECTION (10^{-13} cm^2)
ELECTRON ENERGY (eV)
2
1
3
4
0

Figure 4

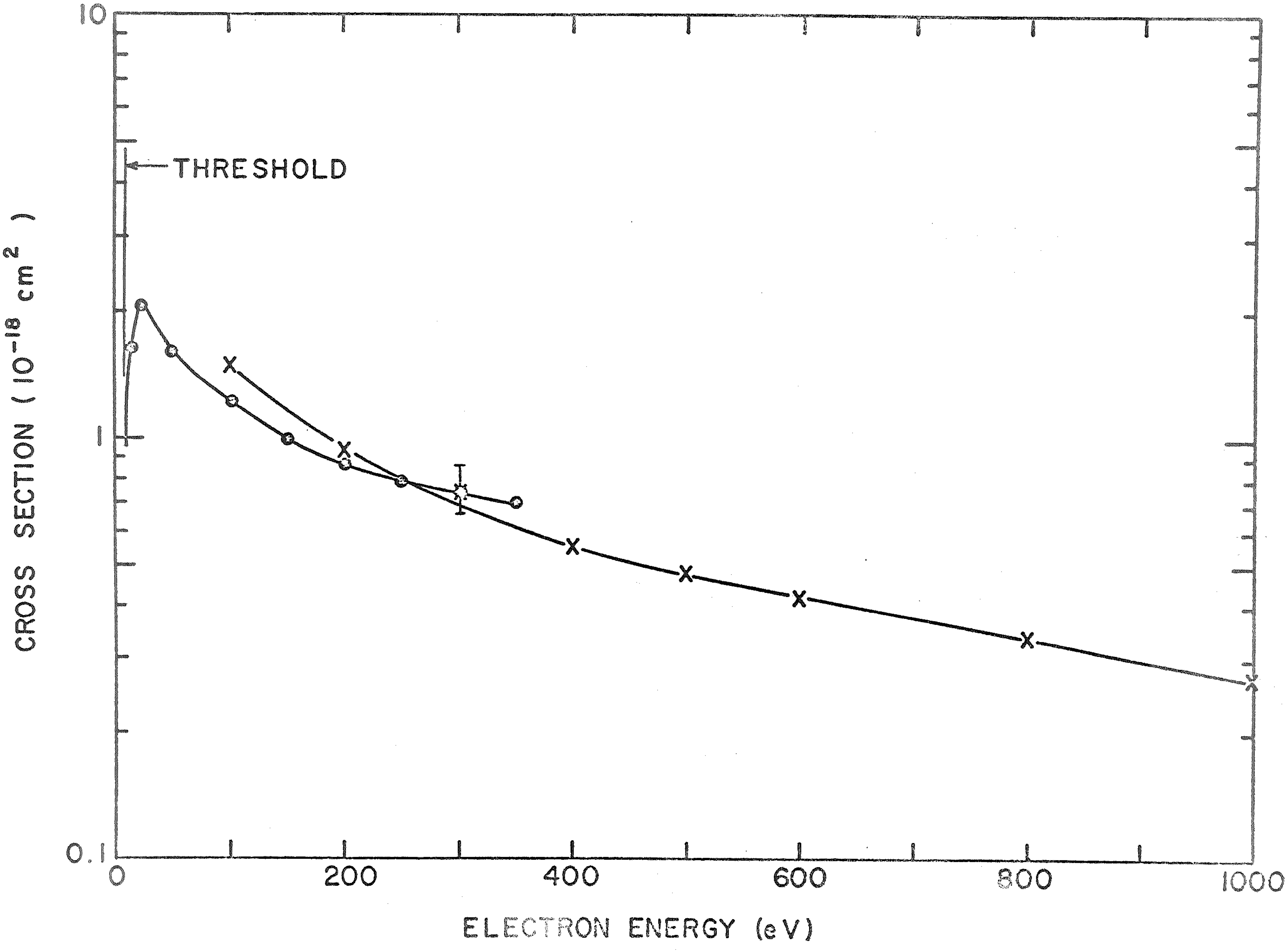
10
1
0.1
CROSS SECTION (10⁻¹⁸ cm²)
THRESHOLD
0
200
400
600
800
1000
ELECTRON ENERGY (eV)

Figure 5

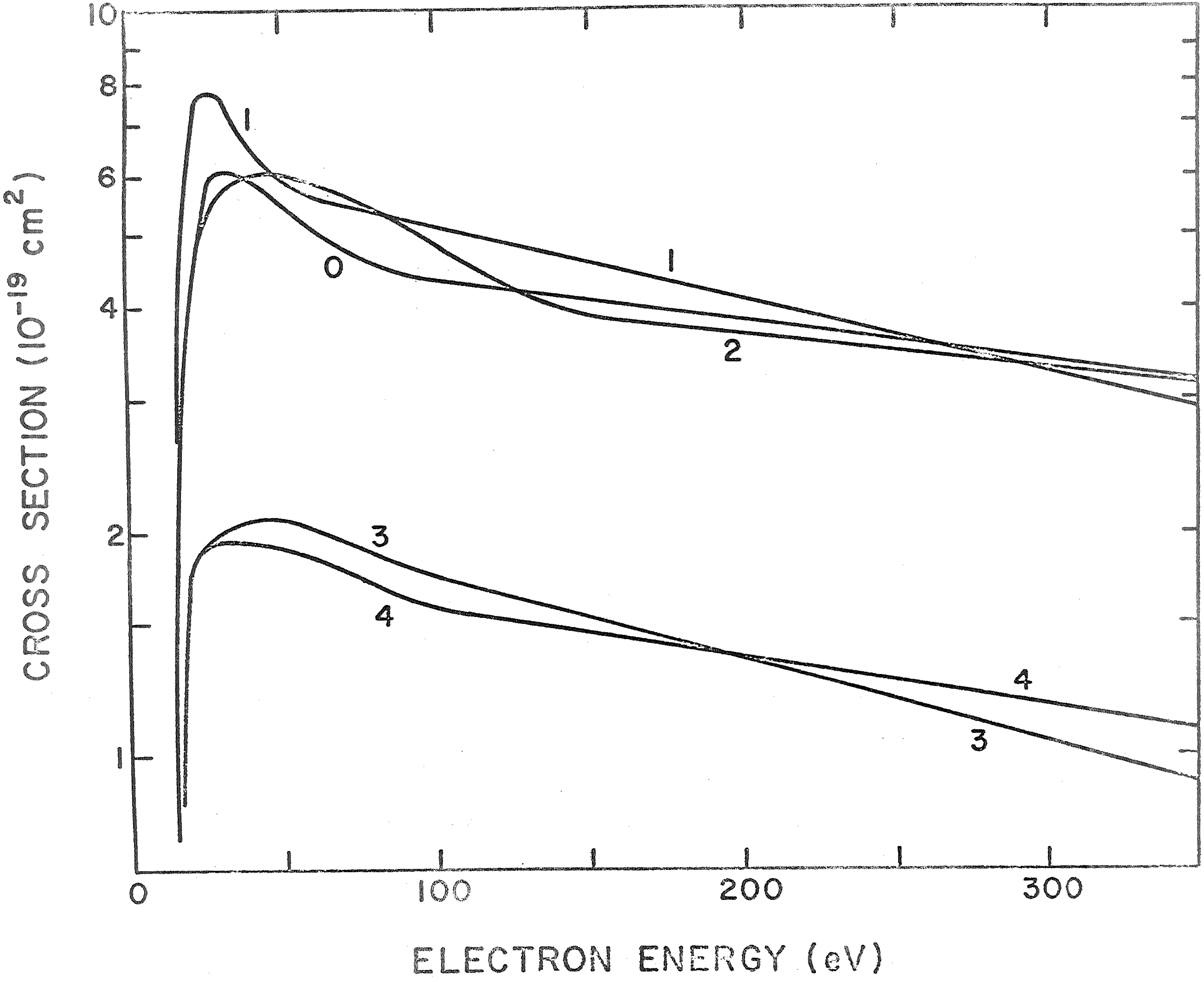
10
8
6
4
2
1
CROSS SECTION (10^{-19} cm^2)
0
100
200
300
ELECTRON ENERGY (eV)
1
0
1
2
3
4
4
3

Figure 6