Selection of Raman Laser Materials

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Abstract—In order to select Raman laser materials for a specific purpose, it is important to know which frequency shifts and excitation power thresholds can be expected from various substances. The thresholds are strongly dependent on the peak scattering cross sections of the corresponding incoherent Raman lines, and these cross sections can vary by several orders of magnitude between Raman lines from different molecules as well as between Raman lines from a single molecule. This paper points out how the rules concerning frequencies, intensities, degrees of depolarization, and line widths, established for incoherent Raman scattering, can be used as a guide for the prediction of Raman laser performance for new materials. Subsequently, all substances and participating vibrations which have been reported to exhibit stimulated Raman scattering to date are listed and discussed.

I. INTRODUCTION

THREE YEARS have passed now since the discovery [1] and explanation [2] of stimulated Raman scattering (SRS). The effect has proven to be a very effective method for the coverage of a large spectral range with intense coherent lines, produced by converting a sizable portion of the output of a Q-switched laser (up to 30 percent) into laser light of different frequencies.

Most of the papers on SRS have dealt with the many interesting properties of the effect itself. However, SRS also holds promise as a research tool for special spectroscopic investigations; to name just a few examples, the study of fast chemical processes of various kinds (detection of intermediate reaction products), light scattering experiments in the atmosphere, and the study of other nonlinear effects which may require the use of an intense light source either of one specific frequency or containing several specific frequencies simultaneously. Many potential users of SRS in applications of this type might find it cumbersome to utilize the coherent Raman effect, however, because they are not especially familiar with Raman spectroscopy. The present paper was written for the benefit of this group of readers; it is intended to assist in choosing new Raman laser materials if an experiment requires specific frequencies which have not yet been produced coherently, and it also includes a table listing all materials which have exhibited SRS to date, together with the observed frequency shifts. A considerable number of references are given which may serve as a guide for deeper penetration into general Raman spectroscopy, as well as for an orientation among the current problems in the field of SRS.

The spectral range which has already been covered

by the excitation of SRS extends from 3231 Å in the near ultraviolet to 16600 Å in the near infrared [1]–[16]. More than 100 coherent lines have been observed to date from over 30 substances. This represents a considerable extension of the frequency range beyond the shift to be expected from the highest fundamental vibrational frequency of any molecule, i.e., 4160 cm^{-1} exhibited by H_2. This extension was possible because of 1) the occurrence of an iteration process [1], [2] (the Raman-shifted light acts as exciting light), 2) the occurrence of parametric effects [5], [7], and 3) the use of frequency doubling techniques [16], [17].

So far it has been found impossible to produce coherently the complete Raman spectrum of any substance. Rather, only some of the most intense lines of the normal Raman spectrum of a chosen substance appeared in the SRS spectrum. An increase in the power density of the exciting laser light only enhanced the number of multiples and combinations of a few of the strongest Raman lines [2], [5], [10].

According to the theory of SRS by Hellwarth [18], [19], the peak intensity of a Raman line is a measure of the threshold height for Raman laser action.[1] In addition, the degree of depolarization of the Raman-scattered light is important, since this quantity enters into the calculation of the cross section for polarized scattering in the forward direction. (For a survey on SRS theory, see Bloembergen [23].) Many investigators of Raman line intensities have measured the integrated intensities rather than the maximum differential intensities. Since the half-widths for vibrational lines vary between about 2 cm^{-1} and at least 40 cm^{-1}, it is necessary in these cases to know also the line width in order to calculate the relative threshold for SRS of a particular line. There are only very limited data available on line widths and on line intensities relative to an intensity standard, and the published information on the depolarization of Raman lines is somewhat sketchy. However, a number of rules have been established theoretically and/or experimentally which allow a qualitative prediction of the four most

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[1] In all cases where a comparison has been made between experimental and theoretical values of the exciting light power density necessary to reach threshold for SRS, the theoretical values were found to be considerably higher [20], [21]. (They were computed from the measured scattering cross sections for incoherent Raman effect.) The discrepancies cannot be expressed by a constant factor, but are different for different lines. Several mechanisms have been suggested as causes [21], [22], but while one of them [22] was subsequently shown to be irrelevant [20], the others have not been tested conclusively as yet. In spite of this situation, the peak intensity of an incoherent Raman line can still be considered as the essential guide for its expected SRS threshold, and in each case where data are available, the rule has been followed that for any particular substance the incoherent line with the highest peak intensity should exhibit the lowest SRS threshold.

important properties of Raman lines—frequencies, intensities, line widths, and depolarization— on the basis of 1) the influence of the chemical bond and 2) the influence of the symmetry of the molecule and of the vibrational mode [24]–[28]. A comparison of all coherent Raman spectra obtained to date with the normal Raman spectra of the same substances clearly shows the general validity of these rules and establishes their applicability as a guide in selecting Raman laser materials for a specific purpose.

II. Principles for Selecting Raman Laser Materials

A. Influence of the Chemical Bond on the Properties of Raman Lines

It has been determined by Raman and infrared spectroscopy that certain chemical bonds or groups of atoms exhibit characteristic vibrational frequencies which vary within a relatively small range when the group belongs to various molecules. Table I shows a number of groups of atoms and the characteristic frequency ranges of their stretching vibrations. The total range extends from 445 to 4160 cm^{-1}. A more detailed account of the characteristic frequencies is found in Brandmüller and Moser [27], Jones and Sandorfy [30], and Mizushima [31]. Table II shows more specifically the changes in frequency one can expect to obtain if, for example, a NO_2 group is attached to various structures [32]. In many cases solvents affect the vibrational frequencies of dissolved molecules, thus providing a convenient means for tuning a Raman laser frequency. These frequency shifts, ranging up to some tens of cm^{-1}, are caused by complex formations in the liquid; the large shifts are caused by hydrogen bonding.

When a certain group is part of similar molecules, and when it is sufficiently isolated from another group of the same kind, its Raman lines possess not only characteristic frequencies, but characteristic intensities as well [28], [29], [33]. The intensities depend strongly on the type of bonds between the vibrating atoms. They are usually much higher for covalent than for ionic bonds. This is caused by the fact that the Raman line intensity resulting from a vibration of a bond is dependent on the rate of variation of the polarizability during the vibration. In the case of a covalent bond, valence electrons are shared by the atoms, and a change of the distance between the nuclei will strongly affect the polarizability. In the case of ionic binding, where each electron is essentially under the influence of only one nucleus, the change of polarizability during a vibration will be small, and accordingly, the intensity of the Raman line will also be small.

Investigations of numerous organic compounds have shown that a great enhancement of the intensity of certain Raman lines takes place (for excitation with the commonly used visible or near ultraviolet mercury lines)

TABLE I
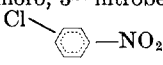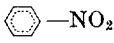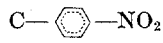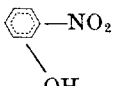### Characteristic Frequencies of Stretching Vibrations [27], [30], [31].

Frequency (cm^{-1})	Vibrating Group	Type of Compound
445–550	S—S	aliphatic disulfides
490–522	C—I	aliphatic comp.
510–594	C—Br	aliphatic comp.
570–650	C—Cl	aliphatic comp.
600–700	C—SH	mercaptans
630–705	C—S	aliphatic comp.
700–1100	C—C	aliphatic comp.
750–850	(benzene ring)	para derivatives of benzene
884–899	(cyclopentane ring)	cyclopentane and mono derivatives
939–1005	(cyclobutane ring)	cyclobutane and derivatives
990–1050	(benzene ring)	benzene and mono- to tri-subst. benzenes
1020–1075	C—O—C	aliphatic comp.
1085–1125	C—OH	aliphatic comp.
1120–1130	C=C=O	aliphatic comp.
1188–1207	(cyclopropane ring)	cyclopropane and derivatives
≈1190	SO_2	aliphatic comp.
1216–1230	—S=O	aliphatic comp.
≈1340	N(=O)(=O)	aromatic comp.
≈1380	N(=O)(=O)	aliphatic comp.
≈1380	(naphthalene rings)	naphthalene and derivatives
1590–1610	(benzene ring)	benzene derivatives
1610–1640	N=O	aliphatic comp.
1620–1680	C=C	aliphatic comp.
≈1630	C=N	aromatic comp.
1654–1670	C=N	aliphatic comp.
1650–1820	C=O	aliphatic comp.
1695–1715	C=O	aromatic comp.
1974–2260	C≡C	aliphatic comp.
2150–2245	C≡N	nitriles
≈2570	S—H	aliphatic comp.
2800–3000	C—H	aliphatic comp.
3000–3200	C—H	aromatic comp.
3150–3650	O—H	aliphatic comp.
3300–3400	N—H	aliphatic comp.
4160	H—H	H_2

when the molecule has conjugated bonds (i.e., alternating single and double bonds) or, more generally, when the molecule exhibits "resonance"[2] [28], [29]. Examples of the effect are presented in Table III. This shows the intensity of Raman lines from the NO_2 and the $C≡N$ groups, respectively, as part of 1) nonconjugated and 2) conjugated systems [29].

The following reason underlies this phenomenon. Conjugation causes a considerable change of the electronic energy states of a molecule compared with a similar one which has no conjugated bonds. It particularly affects the low-energy excited states which are frequently most important as intermediate states for the Raman
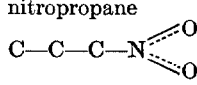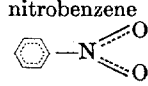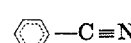
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[2] This term is used in chemistry to describe the delocalization of π electrons. The word "resonance" indicates that a molecule cannot be represented by a single classical structure with localized bonds or charges, but only by several such structures, and its true state is essentially a hybrid of these representations [34].

TABLE II

INFLUENCE OF VARIOUS RADICALS ON THE FREQUENCY OF THE SYMMETRIC NO_2 VIBRATION

Substance	Vibrational Frequency (cm⁻¹) [32]
1—chloro, 3—nitrobenzene Cl⟨○⟩—NO₂	1353
nitrobenzene ⟨○⟩—NO₂	1345
p—nitrotoluene C—⟨○⟩—NO₂	1340
o—nitrophenol ⟨○⟩—NO₂ \OH	1322*

* This large shift is due to intramolecular hydrogen bonding.

TABLE III

INTENSITY OF RAMAN LINES FROM 1) NONCONJUGATED AND 2) CONJUGATED SYSTEMS [29]

Group	Substance	Vibrational Frequency (cm⁻¹)	Peak Intensity*
NO₂	1) nitropropane C—C—C—N⟨O O	1382	25
	2) nitrobenzene ⟨○⟩—N⟨O O	1346	700
CN	1) acetonitrile C—C≡N	2250	29
	2) benzonitrile ⟨○⟩—C≡N	2230	200

* Relative to 1/100 of the peak intensity of the line CCl_4 313 cm⁻¹.

effect. A study of the electronic spectra of similar substances with and without conjugation demonstrated two consequences of the delocalization of π electrons very clearly: 1) The first electronic absorption band appears at lower frequencies, and 2) its oscillator strength is greatly increased. The explanation for these two effects can be found in the review articles by Förster [35] and Mulliken and Rieke [36]; it can be briefly stated as follows: The first allowed transition from the ground state to an excited state of a molecule is frequently due to a charge transfer (transition from a covalent ground state to an ionic excited state in atomic orbital approximation) or to charge exchange (transition from a symmetrical to a corresponding antisymmetrical state in atomic orbital approximation). Molecules with conjugated bonds, however, have strongly ionic excited states of especially low energy, since delocalized π electrons are more easily ionized than σ electrons. The energy of these excited states decreases with the number of π electrons and the length of the conjugated chain, while the transition moment increases with increasing chain length (the moment is proportional to the distance across which the charge is transferred or exchanged).

The effect of the changes in the excited electronic states on the intensity of the Raman lines can be seen by considering the mathematical expression for the intensity of the Raman process [24]. If a light wave with the electric vector

$$E = A^* e^{2\pi i \nu_0 t} + A e^{-2\pi i \nu_0 t} \qquad (1)$$

is incident on a molecule, a quantum mechanical treatment of the Raman process yields the following expression for the intensity of the scattered light per molecule:

$$I \propto (\nu_0 + \nu_{kn})^4 \, |C_{kn}|^2. \qquad (2)$$

Here ν_0 is the frequency of the exciting light; ν_{kn}, the frequency corresponding to the energy difference between initial state k and final state n; and C_{kn}, the complex amplitude of the induced dipole moment. The latter is a linear function of the amplitude of the exciting light:

$$C_{kn} = c_{kn} A. \qquad (3)$$

The tensor c_{kn} is called the scattering tensor, and its components in Cartesian coordinates are

$$(C_{\rho\sigma})_{kn} = \frac{1}{h} \sum_r \left(\frac{\langle k \, |M_\sigma| \, r \rangle \langle r \, |M_\rho| \, n \rangle}{\nu_{rk} - \nu_0} \right.$$
$$\left. + \frac{\langle k \, |M_\rho| \, r \rangle \langle r \, |M_\sigma| \, n \rangle}{\nu_{rn} + \nu_0} \right. \qquad (4)$$

The matrix elements $\langle k \, |M| \, r \rangle$ and $\langle r \, |M| \, n \rangle$ represent the amplitudes of the electric moment for the transitions $k \rightarrow r$ and $r \rightarrow n$, respectively, with r designating the intermediate states; for example,

$$\langle k \, |M| \, r \rangle = \int \psi_r^* M \psi_k \, d\tau.$$

The two changes of the electronic states produced by charge or binding resonance, namely, the shift of the lowest excited states toward lower energies and the increase of the transition moments, will cause an increase of the scattering tensor components (4) by decreasing in the denominator $\nu_{rk} - \nu_0$ for the lowest excited electronic states and by simultaneously increasing the magnitude of the corresponding matrix elements in the numerator. This explains the enhancement in the intensity of certain Raman lines from molecules with de-

localized π electrons as compared to other organic molecules exclusively containing σ electrons.[3]

The closer the frequency of the exciting light approaches that of the first electronic absorption band of any molecule, the more emphasized, in general, is the role of the approached states as intermediate states for Raman scattering. In the case of resonance, the corresponding frequency difference term in (4) will become very large[4] and only the approached electronic state needs to be considered.[5] Resonance Raman effect [27], [29] has been studied mainly on conjugated systems, and the intensity of certain Raman lines was found to increase by several orders of magnitude. The stimulated version of the resonance Raman effect has not been reported yet.

B. Influence of the Symmetries of Molecules and Molecular Vibrations on the Properties of Raman Lines

In general, the scattering tensor is complex and unsymmetric, and the sum which extends over all the excited electronic states and represents its components cannot be evaluated. An important simplification of this problem was found by Placzek [24]. He showed that for a nondegenerate electronic ground state and for a ν_0, which is essentially different from any electronic or vibrational eigenfrequency of the molecule, the scattering tensor is real and symmetric and is related to the polarizability tensor. Its components can then be expressed as sole functions of the vibrational coordinates q_i. By a Taylor expansion in these coordinates, Placzek derived expressions for the intensity and the degree of depolarization of Raman lines, which contain only two invariants of the polarizability derivative tensor $\boldsymbol{\alpha'}$: its "average" (or isotropic part) α_0' and its "anisotropy" γ'^2. Under these conditions, the Raman intensity due to scattering by a single molecule becomes

$$I = Q_{kn}I_0 = \frac{2^7\pi^5(\nu_0 + \nu_{kn})^4}{9c^4[1 - \exp(-h\nu_{kn}/kT)]}$$

[3] Since some of the terms in (4) may be negative, an "interference of probability amplitudes" can occur. For many of the molecules in question and the excitation frequencies as stated, the situation is much simplified, however, by the following findings: Experimental studies on polyenes and on nitro-compounds [29], as well as theoretical intensity calculations on polyenes and some aromatics [37], have shown that for the strongest Raman lines from these compounds only the lowest excited states are essential as intermediate states, thus eliminating the sum over all the other states in (4). For additional detailed theoretical treatments on this problem of the interference of probability amplitudes, see Behringer and Brandmüller [29], Behringer [38], and Albrecht [39].

[4] A damping correction must be added to (4) if resonance occurs [38].

[5] For some simple molecules or ions (e.g., CCl_4, SO_4^{2-}, CO_3^{2-}), all Raman lines were found to be enhanced in case of resonance with the first absorption bands [40]. However, this is not the case for all molecules. For conjugated molecules, mainly Raman lines due to totally symmetric vibrations have been enhanced in intensity when the first absorption bands were approached [27].

Experimental evidence was presented by Shen and Shaham and by Lallemand and Bloembergen that the anomalies in the SRS thresholds result form a self-focusing effect of the exciting laser beam in the Raman active liquid. (Y. R. Shen and Y. J. Shaham, "Beam deterioration and stimulated Raman effect," *Phys. Rev. Letters*, vol. 15, pp. 1008–1010, December 27, 1965; P. Lallemand and N. Bloembergen, "Self-focusing of laser beams and simulated Raman gain in liquids," *Phys. Rev. Letters*, vol. 15, pp. 1010–1012, December 27, 1965.)

$$\cdot b_{kn}^2(3\alpha_0'^2 + \tfrac{2}{3}\gamma'^2)I_0 \qquad (5)$$

for irradiation with a collimated beam, and the degree of depolarization for linearly polarized exciting light, observed perpendicularly to the direction of $\mathbf{E}$ and the direction of incidence, becomes

$$\rho_s = \frac{I_\perp}{I_\parallel} = \frac{3\gamma'^2}{45\alpha'^2 + 4\gamma'^2}. \qquad (6)$$

Here, Q_{kn} is the total scattering cross section, I_0 is the intensity of the exciting light,

$$b_{kn} = \left(\frac{h}{8\pi^2\nu_{kn}}\right)^{1/2}$$

$$\alpha_0' = \frac{1}{3}\left[\left(\frac{\partial\alpha_{xx}}{\partial q_i}\right)_0 + \left(\frac{\partial\alpha_{yy}}{\partial q_i}\right)_0 + \left(\frac{\partial\alpha_{zz}}{\partial q_i}\right)_0\right], \text{ and}$$

$$\gamma'^2 = \frac{1}{2}\left\{\left(\frac{\partial\alpha_{xx}}{\partial q_i} - \frac{\partial\alpha_{yy}}{\partial q_i}\right)_0^2 + \left(\frac{\partial\alpha_{yy}}{\partial q_i} - \frac{\partial\alpha_{zz}}{\partial q_i}\right)_0^2\right.$$
$$\left. + \left(\frac{\partial\alpha_{zz}}{\partial q_i} - \frac{\partial\alpha_{xx}}{\partial q_i}\right)_0^2 + 6\left[\left(\frac{\partial\alpha_{xy}}{\partial q_i}\right)_0^2 + \left(\frac{\partial\alpha_{yz}}{\partial q_i}\right)_0^2 + \left(\frac{\partial\alpha_{zx}}{\partial q_i}\right)_0^2\right]\right\}.$$

For molecules possessing the symmetry of one of the common point groups, certain components of the polarizability tensor vanish, as was determined with the aid of group theory. This results in some general rules concerning intensity and depolarization for lines of certain symmetries. It was found that for the totally symmetric vibrations α_0' does not vanish, but that it does vanish for all others (the rule is only approximately valid for degenerate vibrations). In general, therefore, the totally symmetric vibrations produce the most intense Raman lines.

For totally symmetric vibrations of all molecules of cubic symmetry (point groups O_h, T_h, O, T_d, T) $\gamma'^2 = 0$, and therefore, $\rho_s = 0$ according to (6). For all other symmetry groups ρ_s is not determined by symmetry and varies between 0 and $\tfrac{3}{4}$. For all nontotally symmetric vibrations $\rho = \tfrac{3}{4}$, since α_0' vanishes. The values for ρ which are quoted in the literature are in general too high for strongly polarized lines [41]. This results from the fact that they represent mean values because the depolarization of a Raman line varies as a function of frequency due to its rotational wings: The center part (Q branch), which contains all the light scattered on account of the isotropic part of the polarizability derivative tensor, is more strongly polarized.

In the case of crystals, it is customary to distinguish between internal and external (lattice) vibrations. The former are vibrations which take place within groups of atoms which are more tightly bound to each other than to other atoms or groups in the crystal, e.g., CO_3^{2-} in calcite or any molecule in a molecular crystal. The totally symmetric ones among these vibrations generally show little dependence of their properties on the phase of the material, provided that the compound exists in a free state. Very detailed calculations have been made on absolute intensities and depolarizations by Saksena [42]

for all modes of lattice vibrations in the 32 crystal classes for specified directions of irradiation.

The width of vibrational Raman lines is essentially determined by rotational motions of the molecule as a whole or some of its parts, by intermolecular interactions (in liquids and solids), by the occurrence of structurally similar, weakly coupled groups which are not located in equivalent positions within the molecule, and by isotope effects. The complexity of these effects explains the lack of a general theory for the width of Raman lines in liquids and solids.

It was found experimentally that totally symmetric vibrations usually produce the sharpest lines in any one spectrum. This can be understood by means of a detailed theoretical discussion of the rotational Raman effect [43]. According to this theory, only the anisotropy of the polarizability derivative tensor is responsible for the rotational structure (or the rotational wings) of vibrational lines. Consequently, lines with vanishing or small γ'^2 (totally symmetric vibrations) are usually very narrow.

The theory of the rotational Raman effect applies strictly only to gases, but it is still possible to make some qualitative statements for the case of a liquid or a solution. The following two effects have the most profound influence on the widths of Raman lines from liquids: the random fluctuations of the intermolecular forces and the formation or dissociation of complexes [44]. Both effects will change the rotational mobility of the molecules and can, therefore, increase as well as decrease the line width. Again, the influence will be most pronounced for nontotally symmetric vibrations and will hardly, or not at all, affect the totally symmetric vibrations for which γ'^2 is small or vanishes [45], [46]. However, if a group participates in a hydrogen bond, even its totally symmetric vibrational line may markedly change its width [45].

III. DISCUSSION OF MATERIALS AND VIBRATIONS EXHIBITING SRS

If one considers the substances and the participating vibrations which have been found to exhibit SRS to date (Table IV), one finds that there are representatives of a large variety of classes of materials among those listed: different kinds of aromatic compounds (e.g., benzene derivatives and naphthalene derivatives), saturated six-membered rings, different kinds of aliphatic compounds (e.g., ketones and dienes), inorganic compounds, and elements.

The organic compounds were used either as liquids, solutes, or gases, the inorganic compounds as crystals or liquids, and the elements as crystals, liquids, or gases. All vibrations which were found active in SRS are stretching vibrations, with the exception of one S_8 vibration (216 cm^{-1}) [32]. They are all of the totally symmetric kind. Many of the groups which participate in these vibrations are either complete conjugated systems (one aromatic ring or two condensed aromatic rings) or parts of conjugated systems $C=C$, $C\equiv N$, and NO_2. In a con-

siderable number of cases, CH_n ($n = 1, 2, 3, 4$) vibrations could be stimulated. These vibrations are known to produce intense lines because of their large zero-point amplitude which is due to the small mass of the H atom (this applies to H_2 as well) and also because of some proportionality existing between the intensity and number of participating bonds (for $n > 1$) [50]. In most of the listed organic compounds, several CH_n groups exist per molecule; however, since the groups are weakly coupled, they do not add to the peak as much as to the width of the line. The compounds CCl_4 and $CH Cl_3$ are weaker scatterers than those with a conjugated system, as can be seen from Table V. This table lists some of the SRS materials, together with relative intensity values of the strongest Raman line of each. The intensity is expressed by a scattering coefficient S (also called standard intensity) relative to the 459 cm^{-1} line of liquid CCl_4, as defined by Bernstein and Allen [51]:

$$S = \frac{(45\alpha'^2 + 7\gamma'^2)}{(45\alpha'^2 + 7\gamma'^2)_{459}}. \qquad (7)$$

The absolute scattering cross section for a Raman line can be calculated from the scattering coefficient S, since it has been determined that $(45\alpha'^2)_{459} = 13 \times 10^{-8}$ cm^{4}g^{-1} for CCl_4 vapor [60]. Using expressions from [24] and [23], together with (5) and (7), the following approximate relation between the scattering coefficient S and the total scattering cross section Q for forward scattering per molecule and per unit solid angle is obtained for irradiation with a linearly polarized collimated beam:[6]

$$Q = \frac{2^4\pi^4}{45} b^2 (\bar{\nu}_0 - \bar{\nu})^4 S$$

$$\cdot \frac{(45\alpha'^2 + 7\gamma'^2)_{459}}{1 - \exp(-hc\bar{\nu}/kT)} \left(\frac{n_0^2 + 2}{3}\right)^4 g. \qquad (8)$$

Here, $\bar{\nu}_0$ and $\bar{\nu}$ are the respective wavenumbers of the exciting light and molecular vibration, g is the degree of degeneracy of the Raman line; and n_0, the refractive index of the particular substance at the frequency of the exciting light. The factor $((n_0^2 + 2)/3)^4$ is a local field correction,

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[6] The absolute value of α'^2 for the 459 cm^{-1} Raman line of CCl_4 has been measured from the liquid [61] as well as from the vapor. The liquid value was determined by measuring relative to the Rayleigh line and the vapor value by measuring relative to the pure rotational line of hydrogen ($J = 1 \rightarrow 3$) [60]. The two values for α'^2 obtained in this manner differ by a factor 2.6. Since the theoretical formulas for Raman and Rayleigh scattering apply to a gas only, a number of corrections must be made when they are applied to scattering in a liquid. All corrections for the Raman line apply for the Rayleigh line as well and, therefore, are cancelled out in a comparative measurement. However, Rayleigh scattering intensities are affected in addition by interference effects and Tyndall scattering, and the corrections for these effects contain a large uncertainty [60]. Thus, the value for α'^2 obtained from the vapor can be considered as more accurate, and should, therefore, be used in (8). The use of an α'^2 value determined from vapor measurements ignores the influence of intermolecular interactions in the liquid. However, in most cases, this influence can be expected to be fairly small for totally symmetric vibrations, and scattering cross sections calculated in this way from scattering coefficients agree quite well with those quoted in Bret and Mayer [21] and McClung and Weiner [56].

TABLE IV

Substances Found to Exhibit SRS

Substance	Vibrating Group*	Observed Fundamental Frequency Shifts,** (cm⁻¹)	Reference	Substance	Vibrating Group*	Observed Fundamental Frequency Shifts,** (cm⁻¹)	Reference
α-sulfur	S_8	216	[7]	oxygen	O—O	1552	[9]
carbon tetrachloride	C—Cl	460	[6], [9]	cinnamaldehyde	C=C	1624	[12]
α-sulfur	S_8	470	[7]	styrene	C=C	1631	[10]
carbondisulfide	CS_2	655	[4]	3-methylbuta-diene-1, 3	C=C	1638	[14]
chloroform	C—Cl	663	[6]	pentadiene-1, 3	C=C	1655	[14]
orthoxylene	ring	730	[3]	benzonitrile	C≡N	2229	[15]
calcium tungstate	WO_4	911	[11]	nitrogen	N—N	2327	[9]
deuterated benzene	ring	944	[2]	tetrahydrofuran	CH_2	2849	[6]
benzene	ring	990	[2]	cyclohexane	CH_2	2852	[2]
pyridine	ring	992	[2]	cyclohexanone	CH_2	2863†	[3]
aniline	ring	997	[13]	orthoxylene	CH_3	2913†	[3]
styrene	ring	999	[10]	methane	CH_4	2916	[8]
bromobenzene	ring	1000	[13]	acetone	CH_3	2921	[3]
benzonitrile	ring	1002	[13], [15]	metaxylene	CH_3	2933	[3]
ethyl benzene	ring	1002	[3]	piperidine	CH_2	2933†	[3]
toluene	ring	1004	[2]	tetrahydrofuran	CH_2	2939	[6]
fluorobenzene	ring	1009	[13]	cyclohexanone	CH_2	2945	[3]
calcite	CO_3	1086	[7]	1, 1, 2, 2 tetra-chloroethane	C—H	2984	[3]
styrene	not known	1315	[10]	deuterium	D—D	2991	[8]
diamond	C—C	1332	[7]	paraxylene	C—H	2998	[3]
nitrobenzene	NO_2	1344	[2]	styrene	C—H	3056	[10]
1-bromo-napthalene		1363	[2]	benzene	C—H	3064	[2]
1-chloro-naphthalene		1368	[12]	hydrogen	H—H	4155	[8], [9]
naphthalene		1380	[6]	mesitylene			[66]

* The assignments are according to Landolt and Börnstein [32], except for pyridine [47], styrene [48], and all monoderivatives of benzene [49].

** The uncertainty of the frequency shifts can be as large as ±10 cm⁻¹. In some cases, the shifts quoted in the references were replaced by more accurate results obtained by the present author.

† These laser lines appeared as multiplet. Only the smallest shift is given [3].

TABLE V

Scattering Coefficient S, Degree of Depolarization ρ_s, and Linewidth δ for Some Incoherent Raman Lines, Which Have Been Produced Coherently

Substance	Vibrational Frequency (cm⁻¹)	S	Ref.*	ρ_s	Ref.	δ (cm⁻¹)	Ref.**
carbon tetra-chloride	459	1.00	[51]	0.0065	[41]	≈5	determined from [57]
chloroform	668	0.669	[53]	0.092	[41]	≈8	
benzene	992	4.470 / 4.406	[53] / [52]	0.028	[41]	1.8	[54]
d-benzene	945	4.04	[52]				
toluene	1004	2.816	[53]	0.01	[55]	1.5	[54]
nitrobenzene	1345	5.27	calc. from [56]	0.22	[56]	6.9	[54]
methane	2914	3.0	calc. from [50]	0.00	[50]		
hydrogen	4160	1.38					
deuterium	2993	1.16					

* Many scattering coefficients have been measured repeatedly. See also Brandmüller and Moser [27], Jesson and Thompson [58], and Marckmann et al. [59].

** The linewidths according to Brandmüller and Schrötter [54] are directly measured.

which accounts for the change of the applied radiation field when acting upon a molecule in a substance of refractive index n_0 [67].

Most substances which have shown SRS have been in the liquid phase, and only four crystals are among the listed SRS materials. The following reasons may be pointed out to explain the fact: There are very few crystal structures which are compatible with the demands of covalent compounds regarding valency and spatial configuration. The most important ones among these are the diamond, zincblende, and wurtzite structures, but only diamond-type crystals have purely covalent bonds. (The III–V compound semiconductors, for example, which crystallize in the zincblende lattice, and the II–VI compounds, which crystallize either in the zincblende or wurtzite lattice, have partially ionic bonds. Therefore, they can be expected to be weaker scatterers than diamond or silicon.) It follows from the above argument that, organic compounds form, in general, molecular crystals whose external (lattice) vibrations are not very strong because of the weakness of their intermolecular bonds. The internal vibrations of these crystals, on the other hand, are only slightly shifted in frequency and little altered in intensity by the transition from the liquid to the solid phase. Therefore, as long as one does not go to very low temperatures where the linewidths can be expected to decrease, little incentive exists to use molecular crystals for SRS, rather than the corresponding liquids. At power levels similar to those required to achieve SRS from internal vibrations of covalent complexes in calcite (CO_3^{2-}) and calcium tungstate (WO_4^{2-}), some other crystals containing covalent complexes should also exhibit SRS.

It has been observed that crystals show surface damage, damage tracks, or cleavage when subjected to a laser beam of a power density in the multi-MW/cm^2 range.[7] The damage has been ascribed to acoustical phonons generated by the laser beam [62], [63], but is not yet fully understood. (See also Hercher [64] and Chiao et al. [65].) Under the same circumstances, several organic liquids have shown evidence of some photochemical reactions, such as a change of color or the appearance of numerous small suspended particles. No investigations of these processes occurring in liquids have been reported as yet. The effects mentioned here may restrict considerably the number of suitable materials for any application requiring their repetitive use, and they also set an upper limit for the power density with which a particular liquid or solid can be irradiated repeatedly.

In conclusion, it can be stated that it is only a question of the achievable power level of the exciting laser and of the chemical stability and/or mechanical strength of the compound whether a Raman active substance can be stimulated to exhibit Raman laser action. However, for a high conversion efficiency at typical excitation power

levels (0.5–50 MW), one should choose compounds with strong absorption bands close to the exciting frequency, in particular conjugated compounds for excitation in the visible or near ultraviolet; also, for a restricted frequency range, compounds containing CH groups, and more generally, groups with strongly covalent bonds. One should anticipate the most success with the stimulation of totally symmetric stretching vibrations for any given compound.

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