

On the theory of collision-induced lines forbidden in Raman scattering

B. D. Fainberg

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The Raman scattering cross section for a molecule perturbed by collisions is determined within the framework of the impact theory of relaxation. It is shown that lines forbidden by the selection rules for a single molecule may appear in this case. Relaxation impact parameters, which describe the interference phenomena in molecular transitions (channels) due to their impact mixing, are responsible for the effect. In the case of nonresonant scattering, mixing of two-photon transitions of the Raman-scattering type between various vibrational sublevels of the electron ground state are of most importance. The mixing of channels corresponding to transitions to the intermediate states is appreciable only under resonance scattering conditions. The dependence of the forbidden line intensities of the fundamental frequencies in the SF₆ Raman spectrum on the gas density, which was previously observed experimentally, and the weak pressure dependence of the relative scattering cross sections corresponding to the Raman frequencies, can be explained by the theory.

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It was shown earlier^[1] that the action of noise excitation (such as appears, in particular, in the collisions of particles in a gas) on a quantum system leads to a decrease in its symmetry in the general case. This decrease is a consequence of the mixing of different transitions of the quantum system, due to their interaction with the surroundings. This effect should obviously violate the usual selection rules in many optical phenomena. Thus, the existence of quadratic polarization in centrally symmetric systems interacting with the surrounding medium was predicted in^[1]. It is also natural to expect violation of the selection rules under the considered conditions in the case of Raman scattering (RS). Interest in the latter has been significantly increased by the recent experimental observation and study of collision-induced lines in the gas SF₆^[2] forbidden to Raman scattering. The present work is devoted to the consideration of the phenomenon under discussion within the framework of the impact theory of relaxation.

The impact theory in its non-adiabatic variant, which was used early in the analysis of multiplet spectra,^[3-5] leads to the appearance of phase memory—the nonsecular terms of the relaxation matrix, which are due to the impact mixing of the various transitions (channels). It must be expected that these terms should lead to a significant redistribution of the line intensities in the Raman scattering spectrum and, in particular, to the appearance of forbidden bands, similar to what happens in the case of single-photon spectra^[3-5] (see also^[6]). Thus, the present work should be regarded as the first in vibrational spectroscopy, where the impact theory and the phenomenon of interference of transitions is employed for the investigation of the resolution of lines in Raman scattering.

We consider the main features of the effect under discussion. The Hamiltonian of the entire system (molecule perturbed by collisions and the quantum electromagnetic field) \hat{H} can be written in the form

$$\hat{H} = \hat{H}_M + \hat{F} + \hat{W} + \hat{V}, \quad (1)$$

where $\hat{H}_M = \hat{H}_0 + \hat{u}$ is the molecular Hamiltonian, \hat{H}_0 is the harmonic part of \hat{H}_M , \hat{u} the anharmonic correction, \hat{F} is the Hamiltonian operator of the electric dipole interaction of the molecule with the quantum electromag-

netic field;^[7] \hat{V} is the operator of perturbation of the molecule by the shock, which, we assume, does not affect the quantum electromagnetic field,¹⁾ i.e.,

$$V_{m\nu, n\mu} = V_{mn} \delta_{\nu\mu}, \quad (2)$$

where the indices m and n denote the molecular terms, ν and μ denote the states of the electromagnetic field, and $\delta_{\nu\mu}$ is the Kronecker symbol.

For the states of the entire system, we introduce the notation: $|i0\rangle$ —the initial state in the Raman scattering process, when the molecule is on the vibrational sublevel i of the electronic ground state in the presence of N photons, which represent the incident wave; $|j - \mathbf{k}_1 \cdot \mathbf{k}_2\rangle$ is the final state, when the molecule returns to the vibrational sublevel j of the electronic ground state, absorbing a photon from the incident wave with wave vector \mathbf{k}_1 , frequency ω_1 , polarization \mathbf{e}_1 and emitting a photon with the corresponding parameters $\mathbf{k}_2, \omega_2, \mathbf{e}_2$.

The probability of the transition $|i0\rangle \rightarrow |j - \mathbf{k}_1 \cdot \mathbf{k}_2\rangle$ per unit time is determined by the quantity $d \overline{|a_{j-\mathbf{k}_1 \cdot \mathbf{k}_2, i0}|^2} / dt$, where $\overline{|a_{j-\mathbf{k}_1 \cdot \mathbf{k}_2, i0}|^2}$ is the probability amplitude of the transition, the bar denotes averaging over all realizations of random perturbation of \hat{V} . The quantity $\overline{|a_{j-\mathbf{k}_1 \cdot \mathbf{k}_2, i0}|^2}$ is none other than the diagonal element $\rho_{j-\mathbf{k}_1 \cdot \mathbf{k}_2, j-\mathbf{k}_1 \cdot \mathbf{k}_2}$ of the density matrix, defined under the initial condition

$$\rho_{m\nu, n\mu}(t=0) = \delta_{mn} \delta_{\nu\mu} \delta_{i0}. \quad (3)$$

Consequently, the probability of scattering of the molecule in a definite direction with given polarization, averaged over all the initial states of the molecule $|i\rangle$, can be represented in the form

$$dw = \sum_{|\mathbf{k}_j|} \sum_i \rho_{ii}^{(0)} \sum_j \frac{d}{dt} \rho_{j-\mathbf{k}_1, \mathbf{k}_2, j-\mathbf{k}_1, \mathbf{k}_2}, \quad (4)$$

where $\rho_{ii}^{(0)}$ denotes the equilibrium density matrix of the molecule.

In the impact approximation, which is valid at moderate gas density, we can write the following equation for the density matrix of the entire system:

$$\dot{\rho}_{m\nu, n\mu} + i\hbar^{-1} [\hat{H}_M + \hat{F} + \hat{W}, \hat{\rho}]_{m\nu, n\mu} = - \sum_{m', n'} P_{m, n, m', n'} \rho_{m', n', m', n'}. \quad (5)$$

The latter is obtained by analogy with the equation introduced by Burshtein^[5] only for the density matrix of the molecule (without a quantum electro-magnetic field). This analogy is a consequence of the assumption (2). The relaxation parameters $P_{mn, m'n'}$ that enter in (5) do not depend on the time and are determined by the scattering matrix according to the formulas of ref. 5. It is important to emphasize that (5) is valid for both strong and weak interaction of the molecule with the medium.^[2]

We shall solve (5) by the method of successive approximations in the interaction energy of the molecule with the electromagnetic field under the initial condition (3). As a result, in the case of nonresonant Raman scattering, we obtain for the steady state by transforming in (4) from the probability dw to the scattering cross section $d\sigma$ and from summation over $|\mathbf{k}_2|$ to integration over ω_2 the following expression:

$$d\sigma = \int_{\omega_2} d\omega_2 d\sigma(\omega_2) = \int_{\omega_2} d\omega_2 \frac{\omega_2^2 \sqrt{\omega_1 \omega_2}}{2\pi^2 \hbar c^4} d\omega_2 L^3 \sum_i \rho_{ii}^{(0)} \sum_j \text{Im} \left(\sum_v \rho_{j-\mathbf{k}_1, \mathbf{k}_2, v0} A_{jv}'' \right), \quad (6)$$

where v denotes any vibrational sublevel in the electronic ground state, $\rho_{j-\mathbf{k}_1, \mathbf{k}_2, v0}$ satisfies the equation

$$\rho_{j-\mathbf{k}_1, \mathbf{k}_2, v0} = a_{j0}^{-1} \left[i\hbar^{-1} \delta_{v,0} 2\pi L^{-3} \sqrt{\omega_1 \omega_2} A_{ji}'' - i\hbar^{-1} \sum_{v'} (u_{jv'} \rho_{v'-\mathbf{k}_1, \mathbf{k}_2, v0} - \rho_{j-\mathbf{k}_1, \mathbf{k}_2, v'0} u_{jv'}) - \sum_{v'' \neq v} P_{jv, v''} \rho_{v''-\mathbf{k}_1, \mathbf{k}_2, v'0} \right], \quad (7)$$

$a_{jv} = i(\omega_{jv} - \omega_1 + \omega_2) + P_{jv, jv}$; ω_{jv} are the frequencies of the corresponding transitions, L^3 is the volume of the cube of quantization of the electromagnetic field, $d\omega_2$ is the element of solid angle for the directions \mathbf{k}_2 , A_{jv}' and A_{ji}'' are the components of the magnetic matrix elements for the transitions $v \rightarrow j$ and $i \rightarrow j$, respectively,

$$A_{jv}' = \sum_n \left[\frac{(\mathbf{e}_2 \mathbf{D}_{jn})(\mathbf{e}_1 \mathbf{D}_{nv})}{\omega - \omega} + \frac{(\mathbf{e}_1 \mathbf{D}_{jn})(\mathbf{e}_2 \mathbf{D}_{nv})}{\omega + \omega_1} \right], \quad (8a)$$

$$A_{ji}'' = \sum_n \left[\frac{(\mathbf{e}_2 \mathbf{D}_{jn})(\mathbf{e}_1 \mathbf{D}_{ni})}{\omega - \omega} + \frac{(\mathbf{e}_1 \mathbf{D}_{jn})(\mathbf{e}_2 \mathbf{D}_{ni})}{\omega + \omega_2} \right], \quad (8b)$$

$\hat{\mathbf{D}}$ is the dipole moment operator of the molecule. It is seen directly from (6) and (7) that thanks to the presence of nonsecular terms $P_{mn, m'n'}$ ($mn \neq m'n'$), which are due to collisions, lines appear that are absent in the radiation of an isolated molecule. The intensity of the latter depend on the pressure, since the parameters $P_{mn, m'n'}$ are proportional to the gas density,^[5] and the quantities $a_{jv}^{-1} P_{jv, v'v''}$ describe the impact mixing of two-photon transitions of the Raman scattering type between different vibrational sublevels of the electronic ground state. It can be shown that the mixing of channels corresponding to transitions to the intermediate state, in the case of nonresonant Raman scattering, is described by terms of the form $P_{mn, m'n'}(i\Delta\omega)^{-1}$, which are very small, since $\Delta\omega$ for them is of the order of the frequency of the allowed electron transition from the ground state. Therefore, we shall neglect the latter terms (they are important only in the case of resonant and preresonant Raman scattering).

In the general case, the solution of the system (7) is very cumbersome, in view of the large number of vibrational sublevels. However, if the frequency of the forbidden (or weakly allowed) line $\omega_1 - \omega_{\kappa 0}$ of interest to

us (the index 0 denotes the vibration-free state) is significantly different from all the other vibrational frequencies of the molecule, the use of the secular approximation^[8] is possible, according to which, in first order in (7), there can remain only terms with $\rho_{v' - \mathbf{k}_1, \mathbf{k}_2, v'0}$, for which $\omega_{jv'} = \omega_{v'v''}$ (such terms obviously appear in the case of a harmonic molecule). Then, by the method of successive approximation in the parameters

$$P_{jv, v''} [i(\omega_{jv'} - \omega_{v'v''})]^{-1} (\omega_{jv'} \neq \omega_{v'v''}),$$

$u_{jv'}(\hbar\omega_{jv'})^{-1}$, one can find the solution of (7) (in the next approximation and so on. But even the system of secular approximation contains in the general case a large number of equations. However, the system can be simplified, since: 1) the parameters $P_{jv, v''}, v'', v''''$ contained in it, which are the generalization of the corresponding transition probabilities $w_{v''v} = P_{jv, v''}, v'', v''''$, decrease significantly with increase in the energy difference between the lower (or upper) states of the considered pairs of levels with the same transition frequencies;^[5] 2) if the perturbing particles are in the state of thermodynamic equilibrium, then^[3]

$$P_{v', v''} = P_{v'', v'} \exp(\omega_{v'v''}/kT),$$

which leads to a strong decrease in the coupling of the considered pairs of levels at not too high temperatures with increase in the given energy difference. Consequently, we can take the solution

$$\rho_{j-\mathbf{k}_1, \mathbf{k}_2, v0}^{\text{sec}} = a_{j0}^{-1} i\hbar^{-1} L^{-3} 2\pi \sqrt{\omega_1 \omega_2} A_{j0}'' \quad (9)$$

as the secular approximation in the given case.

We now find the scattering cross section $d\sigma_v$ in the vicinity of the frequency $\omega_1 - \omega_{v0}$:

$$d\sigma_v = \int_{\omega_1 - \omega_{v0} - \delta\omega}^{\omega_1 - \omega_{v0} + \delta\omega} d\omega_2 d\sigma(\omega_2)$$

under the condition that (a) all the frequencies $|\omega_{v'v'}|$ ($v \neq v'$) greatly exceed the values of the relaxation parameters and $|u_{jv'}|$; (b) the scattered light is recorded in a frequency interval $2\delta\omega$ such that

$$\text{Re } P_{v0, v0} \ll \delta\omega \ll |\omega_{v'v'}|$$

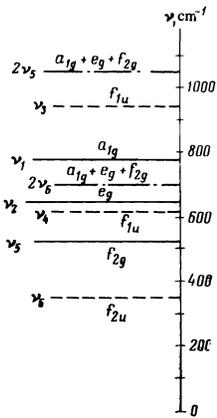
($\text{Re } P_{v0, v0}$ represents the relaxation halfwidth of the state $|v\rangle$). It is not difficult to see, keeping (6)–(8) in mind, that, in each case in which collisions are absent and we can neglect the anharmonicity, the expression for the quantity $d\sigma_v$ determined above goes over into the Kramers-Heisenberg formula.^[7]

In addition, we define the relative scattering cross section $\eta = (d\sigma_{\kappa} / d\sigma_{s'})$, where

$$d\sigma_{s'} = \omega_1 \omega_2^3 \hbar^{-2} c^{-4} d\omega_2 |A_{s0}|^2 (A_{v0} = A''_{v0} \text{ for } \omega_2 = \omega_1 - \omega_{v0})$$

represents the scattering cross section in the vicinity of some definite allowed frequency $\omega_2 = \omega_1 - \omega_{s'0}$ (in the following, we denote by the index s the vibrational sublevels to which the transition from the state $|0\rangle$ is allowed in Raman scattering). We assume that the distance between the neighboring $|\kappa\rangle$ and $|s\rangle$ levels of interest to us $|\omega_{s\kappa}| \ll \omega_{s0} + \omega_{\kappa 0}$ (this is achieved, in particular, in the SF₆ molecule (see the figure)). Then, solving (7) by the method of successive approximations with account of (9), we obtain at low temperatures ($\rho_{v0}^{(0)} \approx 1$) for the quantity η :^[4]

$$\eta = |A_{s'0}|^{-2} \text{Re} \left[\left(A_{s0} + i \sum_s \frac{A_{s0} (P_{s0, s0} + i\hbar^{-1} u_{ss})}{\omega_{ss}} \right) \times \left(A_{s0} + i \sum_s \frac{A_{s0} (P_{s0, s0} + i\hbar^{-1} u_{ss})}{\omega_{ss}} \right) \right] \quad (10)$$



Vibrational levels of the electronic ground state of the SF₆ molecule: solid lines—sublevels corresponding to transitions from the |0⟩ state that are allowed in Raman scattering; dashed lines—levels corresponding to the fundamental vibrational frequencies to which transitions from the |0⟩ level are forbidden in Raman scattering; dot-dash—sublevels corresponding to combination frequencies. The corresponding symmetry is shown around each level.

The arguments 1), 2) and the conditions a), b) were used in the derivation of (10).

Let us now consider the experiment of ref. 2 from the point of view of the developed theory.⁵⁾ For a change in the SF₆ gas pressure from 0 to 30 atm, an increase is observed in the relative scattering cross section of the forbidden fundamental ν₃ and ν₆ bands that is approximately linear with the density (see the drawing). The increase runs from 10⁻³ to 4 × 10⁻³ and 2 × 10⁻³, respectively. Furthermore, Raman bands have been recorded for which the value of the relative scattering cross section is almost unchanged with pressure (for them, η ~ 10⁻³ = 10⁻²).

Since the value of u_{SK} differs from zero, only if the states |s⟩ and |κ⟩ have the same symmetries,^[11] the sublevels corresponding to the combination frequencies 2ν₅ and 2ν₆ should be coupled by the anharmonic interaction with practically all the states corresponding to the allowed transitions in the Raman scattering. Consequently, a perceptible increase with pressure of the relative scattering cross section of the given frequencies can be observed, as follows from (10), only in the case in which the values of the relaxation terms P_{κ0,s0} are not less than the values of the parameters u_{KS}. At the same time, the sublevels, which correspond to the forbidden vibrations (ν₆, ν₄ and ν₃) are not connected with the anharmonic interaction with any of the levels on which the transition from the state |0⟩ is allowed in Raman scattering. Thus, for otherwise equal conditions, a preferential growth with pressure should be observed in the relative scattering cross section of the lines of the fundamental frequencies that are forbidden by symmetry, in comparison with the scattering cross section of the lines corresponding to the combination frequencies, which takes place in the experiment.^[2]

Further, both terms that are linear in the gas density (proportional to P_{κ0,s0}) and terms that are quadratic in the density (proportional to P_{κ0,s0}P_{S0,κ0}) are present in (10). Inasmuch as the quantity η in ref. 2 was changed by a small factor, the dependence of η on the pressure, which is determined by (10), can generally appear close to linear in the case considered, as was observed in ref. 2.

Using the experimental results given in Fig. 2 of ref. 2, we estimate the values of the relaxation parameters that define the dependence of η on the density, for a gas pressure of say 15 atm. Since the distance between the corresponding sublevels |κ⟩ and |s⟩ is

~ 100 cm⁻¹, we obtain the estimate |P_{VV'}, v''v'''| ~ 1–2 cm⁻¹.

It should be noted that if the interaction of the molecule with the surrounding medium is weak (i.e., the description of the relaxation process is possible within the framework of perturbation theory,^[5,9]) then the form of Eqs. (5) that we have used is practically unchanged for any relaxation mechanism. Consequently, the results obtained in the present work are valid also for the case of a molecule in a condensed medium (that is, if it interacts weakly with the surroundings). Therefore, the mechanism that we have considered can also serve, at least qualitatively, for the interpretation of the forbidden lines in Raman scattering, which have been observed in CO₂ gas at high pressure,^[12] and also in certain liquids.^[2,13]

In conclusion, we note that violation of the selection rules in the course of different processes can turn out to be a very sensitive indicator of the presence of perturbing fields in many cases. Therefore, both the experimental and the theoretical study of the given circle of phenomena should yield valuable information relative to the character of interatomic and intermolecular interactions.

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APPENDIX

We consider the case in which the sublevel |κ⟩ of interest to us is closest only to a single state |s⟩ so that only the corresponding transitions |0⟩ → |κ⟩ and |0⟩ → |s⟩ will mix most effectively. This situation is realized, for example, for states corresponding to the oscillations ν₄ and ν₂ in the SF₆ molecule (see the figure). Then, at low temperatures (ρ₀₀⁽⁰⁾ ≈ 1), we have from (6)–(8)

$$d\sigma(\omega_2) = \frac{\omega_1 \omega_2^3}{\pi \hbar^2 c^4} d\omega_2 \operatorname{Re} \frac{a_{s0}|A_{s0}|^2 + a_{s0}|A_{\kappa 0}|^2 - (A_{s0}^* A_{\kappa 0} f_{s\kappa} + A_{\kappa 0}^* A_{s0} f_{\kappa s})}{a_{s0} a_{\kappa 0} - f_{s\kappa} f_{\kappa s}}, \quad (\text{A.1})$$

where f_{VV'} = P_{V0,V'0} + iħ⁻¹u_{VV'}. It follows directly from (A.1) that the spectral dependence dσ(ω₂) is entirely analogous to the spectrum of absorption of an equilibrium three-level system with nearby excited states, which was considered in detail in^[6], if we make the substitution

$$\begin{aligned} a_{s0} &\rightarrow i(\omega_{s1} - \omega) + \gamma_{s1}, & a_{\kappa 0} &\rightarrow i(\omega_{\kappa 1} - \omega) + \gamma_{\kappa 1}, \\ A_{s0} &\rightarrow d_{s1}, & A_{\kappa 0} &\rightarrow d_{\kappa 1}, & f_{s\kappa} &\rightarrow \beta_{s1}, & f_{\kappa s} &\rightarrow \beta_{\kappa 1}. \end{aligned} \quad (\text{A.2})$$

All the undefined notation in (A.2) is the same as in^[6]. Thus, the conclusions of^[6] (see also^[3-5]) apply to the case investigated here, i.e., the effect of the parameters f_{SK} and f_{KS} on the frequency dependence of the scattering cross section dσ(ω₂) leads in the general case both to a change in the contours of the individual transitions |0⟩ → |κ⟩ and |0⟩ → |s⟩ and also to their mixing and to a significant redistribution of the intensities.

If the sublevels |κ⟩ and |s⟩ are well separated, then we obtain the special case of Eq. (10) by transforming to the quantity η in Eq. (A.2). Here summation over s is of course absent. In the case in which the operator \hat{V} has only the nondiagonal matrix elements different from zero, we have P_{κ0,s0} = -P_{S0,κ0}^{*},^[5] and consequently,

$$d\sigma_{\kappa} = \frac{\omega_1 \omega_2^3}{\hbar^2 c^4} d\omega_2 \left| A_{s0} + i \frac{A_{s0} f_{\kappa s}}{\omega_{s\kappa}} \right|^2, \quad (\text{A.3})$$

and the quantity $A_{\kappa 0} + iA_{S0}f_{\kappa S}(\omega_{S\kappa})^{-1}$ represents the amplitude of scattering in the vicinity of the frequency $\omega_2 = \omega_1 - \omega_{\kappa 0}$.

¹In other words, we neglect the effect exerted on the radiation field of the considered molecule by the radiation of exciting particles. For our purposes, this assumption is unimportant, since we are interested first of all in the appearance of scattered radiation at the forbidden frequency; furthermore, because of the incoherence of the spontaneous Raman scattering, there is practically no interference of the radiations of different molecules.

²We have used in the present work a representation in which $|m\rangle$ and $|n\rangle$ are the eigenstates of the Hamiltonian \hat{H}_0 .

³In the case of weak interaction with the medium, this relation can be proved with complete rigor. [^{1,9}] In the case of a strong interaction, this relation, at least for the transition probabilities, can be introduced phenomenologically, in accord with Boltzmann statistics. [⁵]

⁴In the second factor in the curly brackets on the right side of (10) we have omitted, for the reasons indicated above, the double sum

$$\sum_{v \neq 0}^i \sum_{j \neq i, \kappa}'' P_{jv, \kappa 0} A_{jv}^* (\omega_{jv} - \omega_{\kappa 0})^{-1},$$

where the frequencies ω_{jv} satisfy the condition $\omega_{jv} = \pm \omega_{S0}$. At not too low temperatures, possibly, the contribution of the latter cannot be neglected in view of the structure of the terms

$P_{jv, \kappa 0}$ ($j \neq \kappa$, $v \neq 0$) contained in it, a structure that is different from $P_{S0, \kappa 0}$ (or $P_{\kappa 0, S0}$). However, even when this sum is taken into consideration, the conclusions that follow undergo no change.

⁵The distance between neighboring vibrational sublevels in the electronic ground state of the SF_6 molecule amounts to ~ 10 - 100 cm^{-1} (see the figure). This does not exceed in order of magnitude the reciprocal of the duration of the individual collision τ_C^{-1} (in the cases of interest to us, τ_C is estimated at $(10^{-12} - 10^{-13})$ sec [^{2,10}]). Consequently, the conditions of nonadiabatic mixing of states and the appearance of nonsecular elements of the relaxation matrix are realized. However, the latter, by virtue of the different exclusions, can sometimes vanish (for example, in the case of a vector character of the interaction between particles [^{4,5}]). This fact lies outside the phenomenological framework. Nevertheless, we note that the analytic estimates of the values of the nonsecular terms entail considerable difficulties [⁵] and have been carried out at the present time only in the simplest cases. [^{4,5}] This state of affairs is also aggravated by the lack of necessary

information on the character of the intermolecular interactions in sulfur hexafluoride in view of the relative complexity of the SF_6 molecule (for this, see [¹⁰]).

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