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Abstract

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ON THE THEORY OF RAMAN SCATTERING OF LIGHT

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It is known that, under conditions of excitation of Raman scattering of light by frequencies ν that are much smaller than the frequencies of electronic-vibrational transitions of the substance ν_{ev}, the intensity of Raman lines I is approximately proportional to ν^4. At values of the difference $\nu_e - \nu$ (where ν_e is the frequency of the maximum of the absorption band) of the order of 10 000–30 000 cm^{-1}, deviations from proportionality between I and ν^4 are already readily observed. These deviations can be satisfactorily described both within the framework of classical theory (by the dependence on ν of the derivative of the molecular polarizability α with respect to the normal nuclear coordinate Q_n (derivatives with respect to Q_n at the equilibrium position of the nuclei are hereinafter denoted by a prime)), and in quantum theory (by the dependence on ν of the matrix element of polarizability α_{01}, corresponding to the vibrational transition $0 \to 1$ in the scattering of light). The intensity of the line $0 \to 1$ (I_1) is determined by the set of components of the tensor $|\alpha'|$, or, respectively, $|\alpha_{01}|$ (in the simplest case, by the square of the largest component).

Application of the classical theory leads to the formula

$$\alpha' = \frac{e^2}{m} \sum_e \left[\frac{f'_e}{\nu_e^2 - \nu^2 + i\nu\Gamma_e} - \frac{2 f_e \nu_e \nu'_e}{(\nu_e^2 - \nu^2 + i\nu\Gamma_e)^2} \right]; \tag{1}$$

in this case the second derivative, which determines the intensity of the overtone, I_2,

$$\alpha'' = \frac{e^2}{m} \sum_e \left[\frac{f''_e}{\nu_e^2 - \nu^2 + i\nu\Gamma_e} - \frac{4 f'_e \nu_e \nu'_e + 2 f_e \nu_e \nu''_e}{(\nu_e^2 - \nu^2 + i\nu\Gamma_e)^2} + \frac{2 f_e \nu_e'^2 (3\nu_e^2 + \nu^2 - i\nu\Gamma_e)}{(\nu_e^2 - \nu^2 + i\nu\Gamma_e)^3} \right]. \tag{2}$$

Here f_e is the oscillator strength corresponding to the electronic transition $0 \to e$. For a diatomic molecule, the quantity Γ_e is better set equal not to the damping constant, but to the real half-width of the absorption band,* which depends

both on the damping constant γ_e and on the width of the system of components of the vibrational structure.**

In quantum theory ([1])

$$\alpha_{0n} = \frac{1}{h}\sum_{e}{}'\sum_{v}\frac{\nu_{ev}}{\nu_{ev}^2 - \nu^2 + i\nu\gamma_{ev}} M_{0e}^2\, A_{0v}A_{vn}, \tag{3}$$

where A_{0v} is the overlap integral of the nuclear wave functions, $\int u_0^{(0)}(q)u_v^{(e)}(q)\,dq$ (the lower indices on u denote vibrational quantum numbers, the upper indices denote electronic states); ν_{ev} is the frequency of the electronic-

* The point is that the quantities $\mathrm{Re}\,\alpha(\nu)$ and $\mathrm{Im}\,\alpha(\nu)$ depend on the real contour of the absorption band, and not only on damping.

** For polyatomic molecules Γ_e must depend on the width of the system of components of the vibrational structure corresponding to the given normal nuclear coordinate.

of the vibrational transition $0, 0 \to e, v$, M_{0e} is the matrix element of the dipole moment of the transition $0 \to e$, formed from electronic functions.

If in formulas (1) and (2) the terms containing f_e' and f_e'' may be neglected (this is permissible near absorption bands and in the absorption region), then these formulas are simplified; when one electronic level is predominant, one may then write

$$|\alpha'| = k\frac{f_e\nu_e\nu_e'}{[(\nu_e^2 - \nu^2)^2 + \nu^2\Gamma_e^2]} = \frac{1}{k}|\alpha|^2\frac{\nu_e'}{f_e} \tag{4}$$

and, correspondingly,

$$|\alpha_{01}| = \frac{1}{h}M_{0e}^2\left|\sum_{v}\frac{\nu_{ev}}{\nu_{ev}^2 - \nu^2 + i\nu\gamma_{ev}}A_{0v}A_{v1}\right|; \tag{5}$$

where k is a constant.

If the terms containing the derivatives ν^e may be neglected (apparently, this is possible far from absorption bands)*, then

$$|\alpha'| = |\alpha|f_e'/f_e. \tag{6}$$

Calculations by the formulas of the classical and quantum theories, i.e., by formulas (1) and (3) (or, respectively, by formulas (4) and (5)), lead to approximately identical values of the intensities of the lines of the Raman-scattering spectrum in those cases where the difference $\nu_e - \nu$ is sufficiently large and

Fig. 1

Figure 1: Fig. 1

considerably (at least by a factor of $1^{1/2}$) greater than the half-width of the absorption band; in the region of smaller values of $\nu_e - \nu$, approximate agreement of the results of calculation by the formulas of the classical and quantum theories is obtained only for large damping constants (greater than $2Q_{01}\nu'_e$, where Q_{01} is the zero amplitude of nuclear vibrations). Obviously, for very large damping formulas (1), (2), and (4) are applicable over the entire frequency interval of the incident light. For smaller damping these formulas are applicable only outside the absorption region. In this case, to approximate the true relations in the absorption region in the classical model, one should take into account the contribution of the higher (odd) derivatives of α, primarily the third derivative α'''.**

Fig. 1

Formulas (1), (2), (4) correspond to the conditions under which the nuclear vibration frequency ω is considerably less than γ. For $\gamma < \omega$ it must be borne in mind that the depth of modulation of α should be the smaller, the larger ω is (an additional factor that is a function of γ/ω should be introduced).

Relation (1) may be illustrated by a graph (see Fig. 1), on which the parameters of the classical model of a diatomic molecule with a short lifetime of the excited state that are of interest to us are qualitatively represented: the contour of the absorption band $\varepsilon(\nu)$; the real part of the polarizability $\operatorname{Re}\alpha(\nu)$; vectors (dashed arrows) determining the values of the complex polarizability α in the complex plane for

* Under these conditions, in formula (3) the matrix element M_{10e} remains under the summation sign; it should be regarded as a function of the nuclear coordinate and of the vibrational quantum number v of the corresponding sublevel of the electronic excitation level.

** Thus, instead of $\alpha' Q_{01}$, for the calculation of I_1 one should take $\alpha' Q_{01} + \frac{1}{8}\alpha'''(Q_{01})^3 + \cdots$.

several values of the frequency of the incident light ν (the direction of the field vector of the light wave coincides with the abscissa axis); the vectors (solid arrows) represent the derivatives α with respect to the nuclear coordinate Q.

Outside the absorption band we are dealing with amplitude modulation of the oscillation of the induced moment, while at the center of the band the predominant role is played by phase modulation; when the phase modulation is of considerable depth, intense overtones inevitably appear in the spectrum.*

According to Fig. 1, for two values of ν (limiting the half-width of the absorption band) the values of α' are imaginary, while for $\nu = \nu_e$ they are real.

The quantum model gives analogous results.

In Fig. 2, along with the contour of the absorption band $\varepsilon(\nu)$, the values of α are given in the complex plane for the equilibrium value (vector AB) and for two extreme values of the oscillating nuclear coordinate (vectors AC and AD) for the case in which, in the equilibrium configuration, $\nu \simeq \nu_e$ (to simplify the interpretation of the diagram, one may here conventionally imagine that during the vibration of the nuclei it is not ν_e that changes, but ν).

Fig. 2 **Fig. 3**

The vector DC may be regarded as the doubled amplitude of modulation with frequency ω of the vector AB; roughly speaking, it is equivalent to the quantity $2\alpha' Q_{01}$, or, more correctly, to the difference $(\Delta\alpha)$ of the quantities α at the two extreme positions of the nuclei (this difference, in a better approximation than $2\alpha' Q_{01}$, determines the intensity of the Raman-scattering lines). The vector EB (the difference of the vectors BC and DB) is approximately equivalent to $\alpha''(Q_{01})^2$ and, roughly speaking, determines the intensity of the overtone.

Fig. 3 corresponds to the quantum model (equation (3)) for ν somewhat smaller than ν_{e0} and $\gamma \simeq\sim 2\omega$. The vectors in the complex plane determine the contributions of the vibrational sublevels v of the electronic excitation level to the quantity α_{01} (the absorption maximum corresponds to $v = 3$).

From the equations given above, both in the classical and in the quantum theory, it follows that under strong damping, even under resonance conditions $I_2 \ll I_1$ (especially if the change in the equilibrium value of the normal nuclear coordinate Q_n upon electronic excitation is small). However, as the damping decreases, the overtones must increase faster than the fundamental tone and, ultimately, may become close to it in intensity. Thus an approach will occur to that intensity distribution which is observed in resonance fluorescence.

Formulas (1)–(4) show that, as ν increases in the region $\nu < \nu_e$, the values I_1 and I_2 should increase, and with a further increase of ν (for $\nu > \nu_e$) should again decrease (while the positions of the maxima of $I(\nu)$ and $\varepsilon(\nu)$ may differ somewhat).

* As for resonance fluorescence, it may be associated with frequency-amplitude modulation of the natural vibration.

In the literature the opinion has been expressed that I_1 should vary in proportion to $\varepsilon(\nu)$. From formulas (3), as well as (1), (2), and (4), it follows that, generally speaking, proportionality should not be observed.*

Near and at the beginning of the absorption band, under very strong damping, I_2 may increase with increasing ν somewhat faster than I_1; under moderate damping I_1 increases faster, and I_2 much faster than under strong damping. The dependence of I on ν for different lines of one and the same substance may differ considerably in accordance with differences in the derivatives ν_e with

respect to different normal coordinates, even in the case where the intensity of these lines is determined by one and the same level of electronic excitation.

From the experimental data ([2]) on the dependence of the intensity of the fundamental-tone line I on the frequency ν, one can calculate Γ_e by formula (4). Using the data on the intensity of the nitro-group line of n-nitrodiethylaniline, obtained upon excitation by the green and blue, or, respectively, the blue and violet mercury lines, we obtain $\Gamma_e = 2300$ cm^{-1} and $\Gamma_e = 5000$ cm^{-1}.

The fact that these two figures differ substantially is evidently due not so much to the inaccuracy of the initial experimental data and to the simplification made in the calculation (neglect of terms containing derivatives f_e), as to the fact that the damping in this case is not very large, and formula (4) can give only semi-quantitative results in the absorption region. The actual value of the half-width of the absorption band is 4500 cm^{-1}. An approximate estimate by formula (3) of quantum theory gives $\gamma_e =\sim 2000$ cm^{-1}. Evidently the "half-width" of the system of components of the vibrational structure and the damping make quite comparable contributions here to the resulting half-width of the absorption band.

From the experimental data on the intensity coefficient $I_{\max}$ of the combination-scattering line at $\nu \cong \nu_e$ and on the degree of depolarization, one can make an approximate estimate of the Cartesian components $|\Delta\alpha|$. For n-nitrodiethylaniline, $I_{\max} = 2\,000\,000$ units corresponds to the largest value of $|\Delta\alpha|$ of the order of 600 Å^3. At the same time, the upper possible limit of $|\Delta\alpha|$ should be about $0.1\,\varepsilon_{\max}$**, i.e., in the present case** ~ 2000 **Å**^{3}**. The data on** $I_{\max}$**,** $\varepsilon_{\max}$**, and the observed half-width of the absorption band, and formula (3), lead to a value of** γ **of the order of** 3000 cm^{-1}**. This value and the values obtained above, as the results of rough orientational estimates, are in quite satisfactory agreement. However, naturally, they may differ very strongly from** γ **determined from fluorescence damping.***

The possibilities of observing the resonance Raman spectrum are limited to a considerable extent by losses of light due to absorption, which in practice may reach 99% and more. However, from formulas (1) and (3) there follows, it would seem, the paradoxical conclusion that in the region of the most intense absorption bands the conditions for observing resonance scattering are more favorable than in the region of weaker bands.

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* In liquids there should be appreciable variations in the values of ν_e for individual molecules, in accordance with variations in the orientations of neighboring molecules. This should lead to broadening of the absorption band and contribute approximately to proportionality between I and $\varepsilon(\nu)$.

** The coefficient ~ 0.1 (for an isotropic model ~ 0.03) is determined by universal constants; $\varepsilon_{\max}$ is the molar decimal absorption coefficient at the maximum of the band in the absence of preferential orientation of the molecules; the result is in $Å^3$.

*** In the latter case we are dealing with the lifetime of only the very lowest vibrational sublevels of the electronic excitation level.

Note: Figure translations are in progress. See original paper for figures.