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1964

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Abstract

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LIGHT SCATTERING, FLUORESCENCE, AND TRANSIENT PHENOMENA

(Presented by Academician A. N. Terenin, 30 VII 1963)

In considering the secondary emission of light by molecules as a function of conditions, it is more convenient to turn to the quantum or classical theory, or else reasonably to combine individual elements of them.

Outside resonance, to describe combinational scattering of light (Raman scattering), one may use the simplest classical model, in which the polarizability of the molecule α is considered a linear function of the nuclear coordinate q (owing to the dependence on q of the oscillator strength and the electronic frequency ν_e) ([1]). This model is also suitable under resonance conditions, if the damping constant of the electronic oscillator γ is considerably greater than the frequency of the nuclear vibrations ω, and $\gamma \gg \omega > \Gamma$, where Γ is the damping constant of the oscillator that is the source of the radiation incident on the molecule (adiabatic approximation; for each new value of q, the electron vibrations have time to reach a steady state).

For not very large γ, the expansion of $\alpha(q)$ in a power series in q even near resonance can no longer be limited to the linear term (in the resonance region the series then becomes divergent ([2])). At smaller values of γ, when $\omega > \gamma > \Gamma$, the electron vibrations for each new value of q do not reach a steady state. The separation of the "proper" and "forced" vibrations of the electron here becomes to a greater degree conventional. In a time sweep, during the action of the forcing force, vibrations which in essence might be called "proper" then arise in each cycle of modulation and create beats.

Under these conditions one must abandon the concept of the polarizability of the molecule as a function of the nuclear coordinate q; the amplitude of the displacement of the electron is no longer uniquely related to q and depends in a complicated way on time. Instead of "polarizability" one may introduce a more general function, depending on time t, similar to the "transfer function" $K(\nu, t)$ used in the theory of oscillations and in radio electronics. This function is determined by the solution of the equation of motion of the electron with the modulated oscillator frequency ν_e:

$$\ddot{x} + \gamma\dot{x} + \nu_e^2(q)x = F(t), \tag{1}$$

where x is the coordinate of the electron; F is the force with which the electric

Fig. 1 schematic spectra

Figure 1: Fig. 1 schematic spectra

field of the incident light wave acts; $\nu_e(q)$ is the frequency of the natural vibrations of the oscillator (radians/sec). Ultimately we arrive at a set of relative amplitudes of Fourier components, which are similar to the matrix elements of polarizability in the quantum theory.

For $\gamma < \Gamma$, even in the absence of modulation caused by the motions of the nuclei, the electron vibrations under resonance occur in an unsteady regime; the separation of the "forced vibration" becomes a pure convention and loses its meaning, as does the concept of a "spectrum" corresponding to a particular separate solution of the differential equation of electron motion (1). In the spectra of secondary emission for the model adopted, systems of bands should be observed that approximately coincide in position and width with the components of the vibrational structure $\nu_e(0) \pm m\omega$ in the absorption spectrum ($m = 0, 1, 2 ...$) (resonance fluorescence).

The refined classical model (equation (1)) correctly reflects not all aspects of the phenomenon (for example, the consequences of differences in ω in the ground and excited electronic states and the relative intensity of anti-Stokes lines) ([3]). However, the general form of the absorption spectrum (and also of emission) given by the classical and quantum theories becomes similar in many respects. The idea that in the classical theory

it is not quite correct to regard the transition frequencies as those between two continuous curves of potential energy, and, in the quantum theory, as those between discrete electron-vibrational sublevels. Both theories give a continuous spectrum for large γ, and a discrete one for small γ.

Turning to the quantum-mechanical theory, we shall use the expression for the matrix element of the polarizability ([1]):

$$\alpha_{0n} = \frac{2}{hc} \sum_e \sum_v \frac{\nu_{ev}}{\nu_{ev}^2 - \nu^2 + i\nu\gamma_{ev}} M_{0e}^2 A_{0v} A_{vn}, \tag{2}$$

where ν_{ev} is the frequency of the transition $0, 0 \to e, v$ (electronic transition $0 \to e$ with a change of the quantum number of nuclear vibrations $0 \to v$), in cm^{-1}; M_{0e} is the matrix element of the dipole moment of the electronic transition $0 \to e$, constructed from electronic wave functions; A_{0v} and A_{vn} are overlap integrals of nuclear wave functions; the indices 0, n, and v are the quantum numbers of nuclear vibrations in the initial, final, and electronically excited states. Let us first consider relation (2) in the aspect of the Condon approximation (M_{0e} does not depend on v or q).

Fig. 1. Form of the absorption band (dashed line) and of the scattering

spectrum (solid line) for $\gamma > \omega > \Gamma$ and for $\omega > \gamma > \Gamma$. Frequency of the incident light ν^*.

Resonance scattering of light at $\gamma \gg \omega > \Gamma$ differs from nonresonance scattering chiefly by its high intensity. As usual, the unshifted scattering is much more intense than the shifted scattering, while the overtone lines are much weaker than the Raman lines of the fundamental tones; thus the total "width" of the spectrum $\nu \pm m\omega$ is small (however, the ratio of the intensities of lines of different orders depends strongly on γ). Along with this, other characteristic features of scattering are retained: the dependence of the positions of the lines on the frequency of the incident light ν; the approximate reproduction, in each component of the series $\nu \pm m\omega$, of the contour of the incident-light line; the fraction of afterglow in the secondary radiation is very small.

At smaller values of γ ($\omega > \gamma > \Gamma$), when the individual components of the vibrational structure of the absorption band no longer overlap one another, but are still appreciably broader than the line of the exciting light, the first of the features of scattering (the sharp predominance of the component of unshifted scattering, the small "width" of the spectrum) is lost to a considerable degree (see Fig. 1). In formula (2) the resonance denominator, as a function of ν, sharply singles out the contribution to the matrix elements α_{0n} of one or another vibrational sublevel v of the electronic excitation level (the "resonant sublevel"). The ratio of the intensities of lines of different orders now depends little on γ, but instead depends strongly on ν and on the quantum number v of the "resonant sublevel." In resonance with a Franck–Condon sublevel, α_{00}, α_{02} must be large (with $\alpha_{00} > \alpha_{02}$) and α_{01}, α_{03} small. In resonance with other sublevels, for a sufficiently large difference Δ between the equilibrium values of the nuclear coordinate in the ground and excited electronic states, the overtone lines in the Raman spectrum may prove to be considerably more intense than the fundamental-tone lines, and the fundamental-tone lines more intense than the unshifted-scattering line. With respect to the distribution of intensity among the components, the secondary radiation approaches resonance fluorescence (transient phenomena of the first kind). Spectra of this type have been observed ([4]).

Fig. 2 gives a qualitative idea of how the quantities $|\alpha_{0n}|^2$, and thereby the relative intensity of the lines in the spectrum of secondary radiation, may vary if the frequency ν falls into one or another region of the struc-

the contour of the absorption band (in the spectral region from the beginning to the middle of such a band).

As γ is further decreased ($\omega > \gamma \simeq \Gamma$), a gradual transition should be observed in the spectrum of the secondary resonant radiation (transient phenomena of the second kind), from an approximate reproduction in each

Fig. 2. Relative values $|\alpha_{0n}|^2$ at different frequencies of the incident light ν according to formula (2) (model of a diatomic molecule; $\omega = 1000$ cm^{-1}; frequency of the transition $0,0 \to e,0$, $\nu_{e0} = 27\,000$ cm^{-1}; frequency of the

Fig. 2

Figure 2: Fig. 2

"Franck-Condon" transition $\nu_{e3} = 30\,000$ cm^{-1}, $\gamma = 350$ cm^{-1}). The maxima of $|\alpha_{0n}|^2$ are located near the maxima of the components of the vibrational structure of the absorption band. The index $0 \to 0$ corresponds to unshifted scattering, $0 \to 1$ to first-order combination scattering, $0 \to 2$ to the first overtone, etc.

component of the contour of the exciting line (the specificity of scattering) to an approximate reproduction of the contours of the oscillator' s own lines, with attenuation, and then to a loss of the dependence of the position of the emission line on the position of the incident-light band (the specificity of resonance fluorescence).

Thus, resonant secondary radiation occurring without intermediate transitions in the excited state*, may have the character of resonant scattering (for $\gamma \gg \Gamma$), resonant fluorescence (for $\gamma \ll \Gamma$), and peculiar transient phenomena, in which two types may be distinguished: when $\gamma \simeq \omega > \Gamma$ and when $\omega > \gamma \simeq \Gamma$.

Let us note that if the quasi-line fluorescence spectrum of a frozen solution is excited in the region of the component of the absorption band $0,0 \to e,0$, and if the half-width of this component is $s \simeq \Gamma$, then the secondary radiation can, generally speaking, be called both resonance fluorescence, ordinary fluorescence, and combination scattering.

* The distinction, proposed by B. I. Stepanov and P. A. Apanasevich [6], between resonant radiation and secondary radiation involving intermediate transitions in the excited state (ordinary fluorescence) is quite expedient, but not always definite, since cases of an intermediate type are possible—redistribution between states close in energy, $\delta E \lesssim \Gamma$ (for example, differing in the orientation of neighboring molecules).

Taking afterglow into account in classifying the kinds of secondary radiation is not without meaning. The fraction of afterglow in secondary radiation is, roughly speaking, $\Gamma/(\Gamma+\gamma)$, and in resonance fluorescence ($\gamma \ll \Gamma$) it approaches unity, whereas in light scattering ($\gamma \gg \Gamma$) it is close to zero.

Let us suppose that in a liquid the frequency ν_{ev} is modulated by a rather broad spectrum with a small mean frequency Ω, owing to the rotational and vibrational motions of neighboring molecules ($\omega > \gamma_{ev} > \Omega, \Gamma$).

Since the mean lifetime of the corresponding states of motion of molecules in a liquid is very short (almost chaotic motions), and since usually $\gamma_{ev} > \Omega$, the probability of a combination of the frequencies $\nu \pm m\omega$ with the frequencies Ω in the forced vibrations of the electronic oscillator is correspondingly small. Within the framework of the quantum model this can be explained by analogy with the contributions of vibrational sublevels of the electronic excitation level

to α_{0n} (as is known, for $\gamma \gg \omega$ the contributions of different vibrational sublevels to all matrix elements α_{0n} except α_{00}, owing to the difference in signs, largely compensate one another, and in the spectrum the unshifted component with frequency ν sharply predominates ([1,5])).

Thus, for $\gamma > \Gamma$ the width of the lines in the scattering spectrum is comparatively little affected by intermolecular interaction, whereas lines caused by intrinsic vibrations may broaden strongly in accordance with the depth of modulation of the frequencies ν_{ev}.

A large relative intensity of overtones is quite possible in resonance Raman scattering if it is connected with differences in the resonant denominators of the contributions of different vibrational sublevels v to α_{0n} (see formula (2)), and is extremely improbable if Raman scattering is due to the dependence of M_{0e} on q.

In connection with this, and with the fact that upon rotation of the molecule the frequencies ν_{ev} do not change, whereas the Cartesian components M_{0e} (with respect to the coordinate system fixed in space) do change, or, in other words, the amplitude of the force acting on the oscillator changes, it is easy to understand why in rotational and rotation–vibrational Raman scattering under resonant excitation the rotational quantum number changes, as usual, only by ± 2.

The relation between the total intensity of the lines in the scattering spectrum I and the molar absorption coefficient of a substance $\varepsilon(\nu)$ at a given frequency of the incident light ν can be established on the basis of formula (2). Bearing in mind that $\sum_v A_{0v}A_{v0} = 1$ and $\sum_v A_{0v}A_{vn} = 0$, we obtain from (2) the equality, which we give here in approximate form:

$$\sum_n |\alpha_{0n}|^2 = \frac{3c^3}{2\nu^3} \operatorname{Im} \alpha_{00}, \tag{3}$$

where c is the velocity of light (the frequency ν is in radians/sec).

Taking into account the role of nonradiative transitions and redistribution among levels in the excited state in the real damping constant γ (with the radiative damping constant γ), the relative intensity of radiation by one molecule (an isotropic oscillator) is

$$\frac{I}{I} \simeq \frac{8\pi\nu^4}{3c^4} \sum_n |\alpha_{0n}|^2 \simeq \frac{\gamma}{\gamma} \frac{4\pi\nu}{c} \operatorname{Im} \alpha_{00} = \frac{\gamma}{\gamma} \operatorname{const} \cdot \varepsilon(\nu).$$

It follows from this that proportionality between the intensity of individual lines $I_n(\nu)$ and $\varepsilon(\nu)$ is more probable in those cases when Raman scattering is due to the dependence $M_{0e}(q)$, and not $\nu_e(q)$, and when the ratios between the intensities of lines of different orders, as well as γ /γ, do not depend on ν.

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Received
10 VII 1963

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