Raman scattering of light near and far from resonance

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The review deals with various variants of classification of the types of secondary emission of light by molecules; cases are distinguished in which the secondary emission occurs without additional processes that find their way between photon emission and absorption; the advisability of differentiating between the cases of resonance fluorescence and resonance scattering is noted. Reference is made to papers that have made contributions to the development of quantum-mechanical and classical theory of Raman scattering and to the development of the concepts of the relations between electron-vibrational absorption spectra, fluorescence spectra, and scattering excitation near and near and far resonance. Conditions are considered of excitation of the spectrum at different relations between the electronic-oscillator damping constant, the atom vibration frequency, the rotational frequencies, and the difference between the frequency of the incident light and the frequency of the electronic transition. The conditions for the excitation of typical light scattering, typical resonance fluorescence, and certain intermediate types, in which individual features of scattering are combined with certain features of fluorescence (phenomena of the transition type) are noted. The results of investigations of different models of the scattering centers, their advantages, shortcomings, and limits of applicability are compared. The most interesting results of the experimental investigations of resonant scattering of light by molecules and crystals are noted.

CONTENTS

1. INTRODUCTION

Raman scattering (RS) of light by molecules is one of the forms of light transformation by matter wherein the frequency change is determined by the difference between the molecule energy in the initial and final states. The most thoroughly investigated are those cases in which the change of the frequency of the incident light involves a change in the quantum numbers of the intramolecular vibrations of the atoms and in which relatively weak light fluxes are used to excite the spectra. The study of RS spectra obtained under such conditions (including resonance-scattering spectra) has yielded much useful information on different aspects of the interaction of light with molecules, and also on the structure of simple and polyatomic molecules. The technical capabilities of RS spectroscopy have by now been greatly expanded, particularly in connection with the use of lasers (see the reviews[1-4]. Accordingly, interest in the principles of Raman scattering itself has also increased.

The increase in the number of investigated objects and excitation conditions, and further development of the theory, have contributed to the discovery of new interesting phenomena, and have made it possible to establish important relations between different forms of molecular-optics phenomena and to uncover greater prospects for the study of secondary emission.

Most information on RS spectra has been obtained in experiments with solutions or pure liquids, where no rotational structure of the line is usually observed, and

the rotary motion of the molecules is manifest only in the form of line broadening. Therefore in the study of these spectra one usually deals with the frequency at the maximum of the line (band), with the integrated intensity, and with the averaged degree of depolarization ρ. Much experience has been gained in the use of these quantities to relate lines to definite forms of atom vibrations and to solve various spectrochemical problems, using empirically established laws and correlations (see the reviews[5-8]). Depending on the methods and purposes of the investigations, RS lines have been described in terms of intensity coefficients[8], the "coefficients of activity in scattering"[9], the values of the transition probability (see below), the quantum yield, or the scattering cross section[7,10].

The problem of RS line intensity is closely connected with the problem of the very origin of Raman scattering; it is of interest both from the point of view of applications of the spectra and from the point of view of determining the nature of the phenomenon. Although the principles of the phenomenon are by now well known, in concrete cases we are still unable to identify the factors determining the appearance of the RS.

Different variants of both classical and quantum-mechanical theories were used to describe molecular scattering. When using various models, which had frequently led to contradictory conclusions, it was important to establish the true relations between them and the regions of applicability of each. As usual, different

simplified models have narrower regions of applicability, but in definite cases they lead to satisfactory solutions that are compact and contain no unnecessary details.

2. TYPES OF SECONDARY EMISSION OF LIGHT BY MOLECULES; CLASSIFICATION

Secondary emission comes in a great variety of forms which must be described and classified separately. A rational classification and terminology should contribute to a shorter and practically more convenient description of the aggregate of molecular-optics phenomenon. At present, however, there are still no established traditions, and different authors use greatly differing procedures, so that it is difficult to compare and to generalize the results of the experimental and theoretical research. The types of secondary emissions are characterized by using spectral and temporal characteristics, polarization, indicatrices, and reactions to additional perturbations.

Stepanov and Apanasevich ([11], Sec. 25) believe that secondary-emission mechanisms can differ only in whether the annihilation and creation of the photon follow each other ("light scattering") or whether additional transitions take place between them and modify the intermediate excited state of the molecule and by the same token the energy or the polarization of the secondary-emission photon ("photoluminescence"). This proposed differentiation is quite useful, although not always definite, since cases are possible in which only a small change in the molecule energy, $\Delta E \leq \Gamma$, takes place between the emission and absorption (Γ is half the bandwidth of the incident light), for example as a result of a change in the orientation of neighboring molecules or as a result of other time-dependent perturbations. Additional processes in the intermediate state can be considered in some cases as transitions between sublevels of the excited state, and in other cases as irregular evolutions of some additional elements of the field, which lead only to a broadening of the excitation level, and under certain conditions to a secondary-emission line.

When a classical theory is used, simultaneity of the absorption, emission, and of the additional (intermediate) processes is not excluded; in quantum electrodynamics this corresponds only to simultaneous changes in the probability amplitudes $b_n(t)$ of the initial, final, and various intermediate states of the "molecule + radiation field" system.

The subdivision of the photon conversion process into a number of stages is usually used in the analysis of photoluminescence, and in some papers also in the analysis of scattering (see, e.g., [12-14]; cf., [15, 16]). In [17], resonant Raman scattering was represented as a sequence of three separate stages: 1) absorption of photon $\hbar\nu$, 2) production of quantum $\hbar\omega$, 3) emission of photon $\hbar(\nu - \omega)$. This representation, however, does not agree with the fact that the frequency ω and the half-width of the RS lines correspond to parameters of vibrational sublevels of the electronic ground state, and not of the excited (intermediate) state, and also with the absence of "rotational depolarization" of typical scattering lines.

Secondary emission can contain simultaneously different forms, for example scattering and photoluminescence, which are connected with the same level of the electronic excitation of the molecules [18, 19]. In the exposition that follows we shall not concern ourselves with photoluminescence and consider only those forms of secondary emission which occur without intermediate processes in the excited state. In complicated systems, in the case of rapid vibrational relaxation, they amount to a smaller fraction of the radiation [20, 21] but in spite of this they may turn out to be the only noticeable emission element (cf. [21]).

In most papers, a distinction is made between resonance scattering and resonance fluorescence ([15, 16], [21-25] and others). In [11], to the contrary, it is assumed that these forms of emission do not differ in nature and should should be regarded as "scattering"; at the same time, some authors define any resonant emission as fluorescence. Rebane [26] includes resonance fluorescence in the more general concept of "hot luminescence." On the other hand, the authors of [11] consider it necessary to differentiate between afterglow and emission in the stationary illumination regime ("scattering") even if the spectra are the same; the possible identity of the spectra is regarded only as an outward similarity of the phenomena.

The duration of the afterglow can vary in a very wide range (cf. [11]), in accordance with the variations of the damping constant γ_e of the electronic oscillator. The fraction of the afterglow in the secondary resonant emission of a simple oscillator illuminated by a damped light wave (with a damping constant Γ) is roughly speaking, $\Gamma/(\Gamma + \gamma_e)$, and approaches unity if $\Gamma \gg \gamma_e$ or zero if $\gamma_e \gg \Gamma$ [22]. From this point of view, the secondary emission has clearly the character of fluorescence at $\Gamma \gg \gamma_e$ and the character of scattering at $\gamma_e \gg \Gamma$. In the former case the emission spectrum practically duplicates the natural spectrum of the medium (within certain limits, also independently of the frequency of the maximum band of the incident light), and in the latter case it duplicates the line contour of the incident light. These and other characteristic differences justify the use of a terminology that distinguishes between resonance scattering and resonance fluorescence, and is acceptable both for illumination with a damped light wave and for stationary illumination of matter by a light band half-width Γ (at least in those cases when the components are mainly separated in the spectrum or in time).

In order to accentuate the important factors in the classification, we turn first to a simple model of an oscillator with two energy levels, the lower of which has very large lifetime τ_0; the frequency of the maximum of the absorption band will be designated ν_e. Figure 1 shows the irradiation conditions near resonance at $\Gamma < \gamma_e$, if the probability that the molecule converts one photon $\hbar\omega$ (without changing its energy) in a time Δt
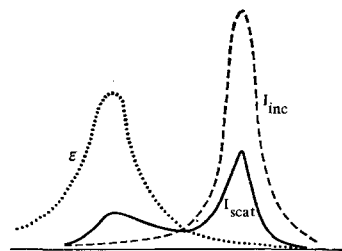

FIG. 1. Absorption spectrum (dotted line), incident-light spectrum (dashed line), and secondary-emission spectrum (solid line) for the model of an oscillator with two energy levels.

P. P. Shorygin

is proportional to the absorption coefficient $\epsilon(\nu)$ and to the number of the corresponding photons. Since $\nu_e - \nu > \Gamma$, γ_e in this case, two maxima are observed in the emission spectrum. One lies in the region of the incident-light frequency ν and should be attributed to scattering, and the other lies in the region of ν_e and should be attributed to fluorescence (see, for example,[27,28]). We see that the intensity of the secondary radiation is concentrated predominantly in the narrower component.

If the regions $\nu \pm \Gamma$ and $\nu_e \pm \gamma_e$ overlap little, then we can confine ourselves in the estimate of the scattering line (band) intensity or of the fluorescence intensity to integration in the first or in the second of the two indicated regions (cf.[15]). In the overlap region, the demarcation between the two is ambiguous. In one of the demarcation variants, the scattering intensity is approximately proportional to $\gamma_e[(\nu_e^2 - \nu^2)^2 + \nu^2(\Gamma + \gamma_e)^2]^{-1}$. The total resonance-emission energy is approximately proportional to $(\Gamma + \gamma_e)^{-1}$, the fraction of the fluorescence in it is close to $\Gamma/(\Gamma + \gamma_e)$, and the fraction of the scattering is close to $\gamma_e/(\Gamma + \gamma_e)$.

According to[7], the amplitude of the probability of photon conversion by the molecule is divided at least into two parts, one of which determines scattering and the other resonance fluorescence; the conversion can be effected via three channels, "scattering," "fluorescence," and "a mixed process" (see Chap. 4). At $\Gamma = \gamma_e$ and $\nu = \nu_e$, the last mentioned channel should account for half the energy of the secondary emission. Under such conditions, according to[21,26], an "interference" takes place between hot luminescence and light scattering, which can be distinguished perhaps only by their polarization properties. The word "interference" can mean here not more than superposition of two hypothetically separable contributions to the amplitude.

In those cases when no distinct demarcation of different forms of resonance emission in the spectrum can be made, it is most important to obtain a general description of the emission. According to[22,23], the emission exhibits typical scattering attributes under certain conditions, fluorescence attributes under others, and intermediate-type attributes in still other cases. Combination of different types of emission elements in different bands of the spectrum is possible[18,19] (cf.[16], where only typical scattering or fluorescence phenomena are recognized).

According to[15], a comparison of the possibilities of determining the probability secondary emission in terms of the product of the probabilities of absorption and spontaneous emission shows that the resonance and non-resonance scattering (unlike resonance fluorescence) is a two-photon process and cannot be interpreted as a sequence of one-photon absorption and emission processes (cf.[12,13])[1]. We can point out in this connection that the "quantum yield" of the secondary emission depends on the intensity of the competing (nonradiative) processes and on the real constant γ_e, but depends little on Γ; in the resonance region at $\gamma_e \ll \Gamma$, when the secondary emission has the character of resonance fluorescence, and at $\gamma_e \gg \Gamma$, when it has the character of scattering, the quantum yields at a fixed value of Γ are approximately the same. Thus, the probability of conversion of the absorbed photons can be regarded in both cases as equal to the probability of spontaneous emission. However, the very possibility of representing the photon scattering probability in terms of the product of the ab-

sorption and spontaneous-emission probabilities (see[7,28,29]) is not directly connected with the answer to the question whether scattering takes place in the form of a single act.

In the investigation of complicated oscillators (molecules), one introduces in addition the probability that photons from secondary-emission (for example, scattering) will ultimately make up one of the lines (bands) of a progression $\nu - n\omega$. In such a series, the probability distribution may correspond to the distribution of the probabilities in spontaneous emission if resonance or near-resonance occurs with one individual component ν_{ev} of the absorption spectrum (see, for example,[28] and formula (35) in that review).

It is customary to distinguish between different forms of RS, depending on the degrees of freedom to which a fraction of the incident-light energy is transferred. Thus, in scattering of light, changes can take place in the energies of the electrons, the atom vibrations, the rotational motions of the molecule, the diamagnetic and spin states, and the crystal-lattice element vibrations (in pure, combined, and mixed forms). In addition, two-, three-, and many-photon processes are possible, as well as stimulated and inverted processes. Each of these forms can be a source of varied valuable information.

3. DEVELOPMENT OF QUANTUM MECHANICAL THEORY OF RAMAN SCATTERING OF LIGHT

The most investigated were the possibilities of a theory in which the quantum-mechanical description of the light-scattering molecule is combined, on the basis of the correspondence principle, with the classical description of radiation. The interaction of light with molecules was usually considered in second order of time-dependent perturbation theory. When choosing the perturbation operator, most studies confined themselves to the dipole approximation (the "dipole-length" operator). The components of the polarizability tensor were determined in this manner.

The intensity (I_{0k}) of the RS line corresponding to a change $0 \to k$ in the quantum number of the atom vibrations, for molecules that can be freely oriented in space, is proportional to $(\nu - \omega)^4 \sum_\rho |\sum_\sigma (\alpha_{\rho\sigma})_{0k}|^2$, where $(\alpha_{\rho\sigma})_{0k}$ is the Cartesian ($\rho\sigma$) coordinate of the matrix element of the polarizability. The Kramers-Heisenberg-Weisskopf formula represents $(\alpha_{\rho\sigma})_{0k}$ as a sum of contributions of the electron-vibrational excitation levels. These contributions are determined primarily by the matrix elements of the dipole moment $\tilde{M}$, which are made up of the molecular wave functions:

$$(\alpha_{\rho\sigma})_{0k} = \frac{1}{\hbar} \sum_e \sum_v \left[\frac{(\tilde{M}_\sigma)_{ev}^{00} (\tilde{M}_\rho)_{ev}^{0k}}{\nu_{ev}^{00} - \nu + (1/2)\, i\gamma_{ev}} + \frac{(\tilde{M}_\sigma)_{ev}^{0k} (\tilde{M}_\rho)_{ev}^{00}}{\nu_{ev}^{0k} + \nu + (1/2)\, i\gamma_{ev}} \right]. \quad (1)$$

The type of electron-vibrational transition in (1) is determined by the indices of the electronic level and of the quantum number of the atom vibrations in the initial (00), intermediate (ev), and final (0k) states; ν_{ev}^{00} is the frequency of the $00 \to ev$ transition and will henceforth be written about the superscripts, ν is the frequency of the incident (quasimonochromatic) light, γ_{ev} is the damping constant, and ω is the frequency of the vibration of the atoms.

In the practice of molecular spectroscopy one usually deals with systems in which nonradiative transitions from the excited state ev patently predominate. In these

cases, the formulas that take only radiative damping into account are not suitable for the description of resonance emission, but the introduction of a damping constant corresponding to the real width of the absorption band can lead to perfectly satisfactory results if the damping is exponential. In[20, 21] are considered separately the radiative-damping constants γ_{rad} of the electronic oscillator and the damping constant γ_{at} of the vibrations of the nuclei in the electron-excited state (vibrational relaxation).

The authors of[30], examining the time dependence of the induced moment and using the Bogolyubov averaging method, modified the expressions for α_{0k} and excluded the damping constant completely. Under resonance conditions, the contribution of the resonant level was not included in this case in α_{0k}. However, the proof of the modified formula is of doubtful validity.

Formulas similar to (1) can be obtained in different ways, including methods of classical theory, quantum mechanics, and quantum electrodynamics; see, for example,[7,29,31,32], and also[30] (the resolvent method). In one of the variants, unlike in (1), momentum matrix elements replace the dipole-moment matrix elements under the summation sign[33]. The common factor $1/\nu(\nu - \omega)$, which is not present in (1), can then create the impression that the new form determines a different dependence of the RS line intensity on the frequency of the incident light (see, e.g.,[34]). The new form, however, can be reduced to (1) by a simple identity transformation[35,36], provided only one does not omit the summation over e. It is important that the transformation of (1) into a new form is accompanied by a modification of the contributions of different levels e of the electronic excitation. The relative contribution of the "remote" e levels becomes more appreciable, and the possibility of simplifications resulting from taking into account only one neighboring e level is practically lost.

Formula (1) corresponds to conditions when the incident-light intensity is not very large (both far from resonance and colse to it) and $\gamma_{ev} > \gamma_{00}$, γ_{0k}; the value of γ_{ev} can be larger or smaller than the atom vibration frequency ω. The limitations connected with the interaction between the excitation levels will be discussed later; the possibilities of using (1) for polar and non-polar molecules are discussed in[37], p. 35.

Formula (1) can be used directly to determine the integrated line intensity in the scattering spectrum, referred to the integrated intensity of the excited light, not only in the case of quasimonochromatic excitation, but also in the case of excitation with a rather broad band, provided that $\Gamma \ll \nu_e - \nu$. When $\Gamma \geq \gamma_e$ and $\Gamma \geq \nu_e - \nu$ (when the contours of the incident-light band and the oscillator absorption band overlap appreciably), the separation of the light described by the polarizability matrix element from the total flux of secondary emission of the "scattering" becomes formal and to a certain degree arbitrary. Under these conditions, however, one can use formula (1) to describe individual sections of the spectrum or the entire secondary emission that occurs without intermediate transitions in the excited state[2]. To determine the intensity in the simplest variant, without allowance for phase correlations, it suffices to introduce integration with respect to ν; a rigorous solution (using the entire set of matrix elements α_{0k}) does not exclude the possibility of describing the resonance emission, including the afterglow, by means of a time scan. The

scattering of light (but not resonance fluorescence) can be described, by Breit's formula[39], which differs from (1) in that it contains the differences $\gamma_e - \Gamma$ in place of γ_e. This formula does not offer great new possibilities, for when $\Gamma \ll \gamma_e$ it reduces in practice to (1), and when $\Gamma \geq \gamma_e$ the separation of the "scattering" of light has little meaning in most cases. When $\Gamma = \gamma_e$, the matrix element of the polarizability can become infinite and can become physically meaningless even close to this condition.

Direct utilization of (1) for practical estimates of α and of the character of the secondary emission is made difficult by the insufficient knowledge of the molecular wave function. The abundance of difficult-to-calculate parameters has stimulated searches for acceptable simplifications and modifications of the formula, which describe various particular cases in a simpler form.

One simplification that has been fully justified is based on subdivision, in the adiabatic approximation, of the complete molecular wave functions Ψ into electronic (φ) and nuclear (u) functions. The interaction of the electrons and the nuclei is taken into account in limited form. Thus,

$$\Psi_{ev} = \varphi_e(\xi, Q) u_{ev}(Q); \tag{2}$$

another form, $\Psi_{ev} = \varphi_e^{(v)}(\xi) u_{ev}(Q)$, is also possible. The subscripts e and v determine here the electronic state and the quantum number of the atomic vibrations, ξ is the coordinate of the electron, and Q is the nuclear normal coordinate.

On the basis of (2), the dipole-moment matrix element (the component $\sigma\sigma$) is represented as follows:

$$(\tilde{M}_\sigma)_{ev}^{00} = \int u_{ev} \mathcal{M}_{\sigma e}(Q) u_{00} dQ;$$

here $M_{\sigma e}$ is constructed on the basis of the electronic wave functions and is regarded as a function of the nuclear coordinates (but not of v); the following series expansion is customarily used:

$$\mathcal{M}_{\sigma e}(Q) = M_{\sigma e}(1 + \eta_e Q + \zeta_e Q^2 + \ldots). \tag{3}$$

In principle we need not introduce the dependence of M_e on Q, but merely supplement M_e with a correcting factor $D^{(e)}$ that takes into account in general the rather weakly pronounced individual features of each vibrational sublevel ev (see below).

In any of these variants it is possible to separate two factors that determine the contribution of each electronic excitation level e in α_{01}: 1) the $M_{\sigma e}(Q)$ dependence, or in other words the dependence of $D^{(e)}$ on v; 2) the dependence of the resonant denominator in (1) on v, which in the semiclassical theory is taken into account in the form of the $\nu_e(Q)$ dependence.

These two factors were considered in different forms, starting with[40,41], in numerous papers, in which the main regularities and tendencies were described. It was established that the second factor is due principally to the change (Δ_e) of the equilibrium value of the nuclear coordinates in electronic excitation, and that its role increases when the resonance region is approached. The contributions of both factors to α_{01} can be represented in first approximation in the form of two individual terms; for α_{02}, α_{03}, and other α_{0k}, mixed terms are also obtained even in the first approximation.

When the linear approximation is used within the framework of (3), formula (1) as applied to one diagonal element $\sigma\sigma$ takes the form

$$\alpha_{0k} = \frac{1}{\hbar} \sum_e \mathrm{M}_e^2 \sum_v F(v,v) [A_{v0}^{(e)} + \eta_e B_{v0}^{(e)}] [A_{vk}^{(e)} + \eta_e B_{vk}^{(e)}]; \qquad (4)$$

here

$$A_{vk}^{(e)} = \int u_{ev} u_{0k} \, dQ, \qquad (5)$$

$$B_{vk}^{(e)} = \int u_{ev} Q u_{0k} \, dQ \qquad (6)$$

etc.,

$$F(v,v) = \frac{2\nu_{ev} - k\omega + i\gamma_{ev}}{\nu_{ev}^2 - \nu^2 + i\nu_{ev}\gamma_{ev} - k\omega\,(\nu_{ev} - \nu + i\gamma_{ev}) - (1/4)\gamma_{ev}^2}. \qquad (7)$$

Under ordinary conditions, $k\omega \ll \nu_{ev}$ and

$$F(v,v) \approx 2\nu_{ev}/(\nu_{ev}^2 - \nu^2 + i\nu_{ev}\gamma_{ev}). \qquad (8)$$

In a somewhat different variant[42,43],

$$\alpha_{0k} \approx \frac{2}{\hbar} \sum_e \mathrm{M}_e^2 \sum_v \frac{\nu_{ev}}{\nu_{ev}^2 - \nu^2 + i\nu_{ev}\gamma_{ev}} A_{0v}^{(e)} A_{vk}^{(e)} D_{0v}^{(e)} D_{vk}^{(e)}. \qquad (9)$$

Expressions for the off-diagonal elements ($\rho\sigma$) are obtained in the same manner.

Formulas (4) and (9) give a general idea of the role of different levels e of the electronic excitations, of the role of the vibrational structure (latent or explicit) or the 0 → e absorption bands, and of the contribution of individual e sublevels to the matrix elements α_{0k} for different "vibrational" transitions 0 → k to the RS. Formula (9) makes obvious the connection between the UV absorption spectra and the intensity of the RS lines; the more intense the UV absorption band the closer it lies to the exciting line, and the broader the system of components ev of the vibrational structure of this band the larger the role it plays in the intensity I_{0k} of the RS line. The 0 → e electronic transitions and the corresponding levels e, which make an appreciable contribution to α_{0k}, were called "effective" or "actual"[44] (cf.[36]).

The overlap integrals $A_{0v}^{(e)}$ and $A_{vk}^{(e)}$ are rather easy to calculate, if the nuclear vibration frequency in the ground state ($\omega^{(0)}$) and in the electron-excited state ($\omega^{(e)}$) is approximately the same ($\omega^{(0)} = \omega^{(e)} = \omega$). Then, for a harmonic oscillator at $v \geq k$ (omitting the indices e)

$$A_{vk} = (k!/v!)^{1/2} \exp(-d^2)(-2d)^{v-k} L_v^{v-k}(2d^2), \qquad (10)$$

where $d = \Delta/2\sqrt{2}Q_z$, Q_z is the zero-point amplitude of the atom vibrations, and L is a Laguerre polynomial (cf. the formulas in[45] for transitions with phonon excitation in crystals). The quantity $2\sqrt{2}d = \Delta/Q_z$ for a diatomic molecule determines the number of components of the vibrational structure of the 0 → e absorption band within the "half-width" of the system of components ev (and depends, naturally, on e). The conditions $v < k$ and $\omega^{(0)} \neq \omega^{(e)}$ were considered in[42], and the influence of the anharmonicity was considered in[38,42,46,47a].

An important circumstance is that the signs of the products $A_{0v}A_{vk}$ for different sublevels v are not the same, provided only that $k \neq 0$[40]. This determines the distinguishing features of the dependence of the intensities $I_{0k}(\nu)$ of lines of different order on the frequency of the incident light. The alternations of the signs of $A_{0v}A_{vk}$ in the sequence of sublevels v are the cause of the particularly small intensity of the overtones of nonresonant RS.

The overlap integrals form an orthonormal system and

$$\sum_v A_{0v} A_{vk} = \begin{cases} 1 & \text{if } k = 0, \\ 0 & \text{if } k \neq 0. \end{cases} \qquad (11)$$

Therefore neglect of the differences in the resonant denominators in (9) for different sublevels v (their averaging) at $\eta_e = 0$ means reduction of all the matrix elements α_{0k} except α_{00} to zero (cf.[47b]).

Among the sublevels v of one electronic level, the largest contribution to α_{00} and α_{ee} far from resonance is made by the "Franck-Condon" sublevel $v^* \approx 2d^2 = \Delta^2/4Q_z^2$; the largest contributions to α_{01} are made by certain sublevels v_a and v_b, with $v_a < v^* < v_b$ and $v_a - v_b \approx (\Delta/Q_z)(\omega^{(e)}/\omega^{(0)})$. The general character of the distribution of the contributions in excitation far and near the resonance can be estimated from Figs. 2 and 3.

Integrals of the type B_{vk}, which are contained in (4), take, according to[42], the following form at $\omega^{(0)} = \omega^{(e)}$:

$$B_{vk} = [(\Delta/2) + (2Q_z^2/\Delta)(k - v)] A_{vk}.$$

The dependence of M_e on Q results in certain changes in the contributions of the ev sublevels to α_{0k} (see the example in Fig. 2d). In this case the expression $\sum_v (A_{0v} + \eta B_{0v})(A_{vk} + \eta B_{vk})$, unlike $\sum_v A_{0v} A_{vk}$, is no longer equal to zero. If the signs of η_e and Δ_e are not equal, the influence of these parameters on the contribution of the electronic level in α_{0k} can be mutually cancelled out to one degree or another (up to the vanishing of α_{0k} at a certain value of ν).

If η plays the predominant role, then the contributions of all the sublevels v of the electronic level e can have equal signs. In the case of nonresonant excitation, regardless of the presence or absence of a vibrational structure of the absorption band, the electronic excitation level can then be regarded as a single level e:

$$\alpha_{01} = (4/\hbar) \sum_e [\nu_e^*/(\nu_e^{*2} - \nu^2)] M_e^2 \eta_e Q_z,$$
$$\alpha_{02} = (2\sqrt{2}/\hbar) \sum_e [\nu_e^*/(\nu_e^{*2} - \nu^2)] M_e^2 (\eta_e + 2\zeta_e) Q_z^2, \qquad (12)$$

where ν_e^* is the frequency of the maximum of the zero 0 → e absorption band; $\nu_e^* \approx \nu_{ev}*$. These formulas correspond approximately to Placzek's theory of polarizability (neglect of the presence of the vibrational structure of the absorption band, when the "electronic transition can be replaced by the center of gravity"[3], which is permissible at a large distance from resonance). In this approximation, the contributions of the electronic level e to all α_{0k}, including α_{00} (and possibly
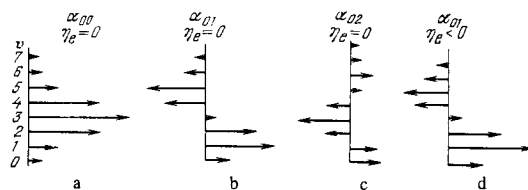

FIG. 2. Distribution of the contributions made to α_{00}, α_{01}, and α_{02} by the sublevels v at $\eta_e = 0$ (a – c) and to α_{01} at $\eta_e < 0$ (d) are from resonance [58] ($v^* = 3$).
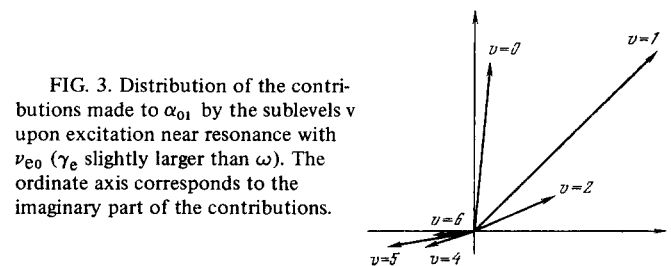

FIG. 3. Distribution of the contributions made to α_{01} by the sublevels v upon excitation near resonance with ν_{e0} (γ_e slightly larger than ω). The ordinate axis corresponds to the imaginary part of the contributions.

also to all I_{0k}) increase all in similar fashion and relatively slowly with increasing ν.

An interesting property of the aggregate of coefficients is reflected in accordance with[49] by the relation

$$\sum_e v_e^* M_e^2 \eta_e = 0,$$

from which it follows that the signs of the coefficients η_e are not the same. The difference between the signs of η_e, like the difference between the signs of the contributions of individual vibrational sublevels v in (4) and (9), leads to a stronger dependence of α_{01} and I_{01} on the frequency ν of the exciting light. The electronic levels, however, are usually not numerous and differ more in energy, so that a significant influence of the signs of η_e on $I(\nu)$ is less probable[49].

One of the ways of investigating the $M_e(Q)$ dependence is expansion of the wave functions, in the adiabatic approximation, in a Taylor series in Q by the method of Herzberg and Teller; within the framework of the first order of perturbation theory, according to[50],

$$\mathcal{M}_e(Q) = \mathbf{M}_e + (1/\hbar) \sum_{s \neq e} [h_{es} \mathbf{M}_s Q/(\nu_e - \nu_s)], \tag{13}$$

where s and e are the electronic excitation levels (see[37,46,51,52,179]). Formula (13) contains off-diagonal matrix elements a_{es}, which determine (when Q is shifted by unity) the interaction energy due to the mixing of the states e and s referred to Q = 0:

$$h_{es} = \langle \varphi_e(\xi) \mid (\partial H_e/\partial Q)_0 \mid \varphi_s(\xi) \rangle, \tag{14}$$

where H_e is the Hamiltonian of the electrons of the molecule (at a definite position of the nuclei), and φ_e and φ_s are the eigenfunctions of this Hamiltonian at Q = 0. In the opinion of the authors of[48], the denominators in (13) should be regarded as functions of Q; in this connection, they criticize the results in[46,47a], although they themselves use (in a different form) only the first-order approximation.

The connection of h_{es} with the quantities η_e follows already from the simple relation[49]

$$\eta_e = (1/\hbar) \sum_{s \neq e} [h_{es}/(\nu_e - \nu_s)] (M_s/M_e).$$

In[49] (see also[37]) it is emphasized that in Raman scattering the role of Δ_e, or in other words the role of the aggregate of vibrational sublevels v, is connected with the diagonal elements $h_{ee} = K_e \Delta_e = h(\partial \nu_e/\partial Q)_0$, whereas the values of η_e are connected with the off-diagonal elements. The letter K above denotes the force constant of the chemical bond (diatomic-molecule model); the subscript labels the electronic state.

In[37,46], on the basis of (13) and (14), sufficiently general formulas are obtained in the form of three terms

$$A^* + B^* + C^* = (\alpha_{\rho\sigma})_{01}, \tag{15}$$

which reflect the role of the vibrational structure of the absorption band connected with Δ (term A*, which contains A_{ee}), and the roles of the interactions of the electronic excitation levels with one another (term B*, containing the off-diagonal elements h_{es}) and with the ground state (term C*, which includes coefficients of the type h_{e0}). These formulas differ in essence from (9) in that the contribution of the coefficients η to the terms B* and C* are defined concretely. Allowance for the latter corresponds to the Placzek polarizability-theory approximation (cf.[37,48]). As to the term A*, it is equivalent to expression (9) if we put all D = 1.

Off resonance we have[37]

$$B_{\rho\sigma}^* = \frac{1}{\hbar^2} \sum_{e \neq 0} \sum_{s \neq 0} \frac{1}{\nu_e - \nu_s} \sum_v \Big[\Big(\frac{M_{\sigma 0 e} h_{es} M_{\rho s 0}}{\nu_{ev} - \nu} + \frac{M_{\rho 0 e} h_{es} M_{\sigma s e}}{\nu_{ev} + \nu} \Big) A_{0v} B_{vk} $$
$$+ \Big(\frac{M_{\sigma 0 s} h_{se} M_{\rho e 0}}{\nu_{ev} - \nu} + \frac{M_{\rho 0 s} h_{se} M_{\sigma e 0}}{\nu_{ev} + \nu} \Big) A_{vk} B_{0v} \Big], \tag{16}$$

where $\mathbf{M}_\rho$ and $\mathbf{M}_\sigma$ are labeled by the indices of both combining electronic levels. According to[37,52], the term B* should be particularly important if the molecule has a weak long-wave 0 → e absorption band and an intense short-wave s → 0 band.

According to[37], the term C* is less significant than B*, and corresponds to levels s for which the transitions 0 → s are forbidden, whereas B* includes h_{es} of the combining levels.

Damping is taken into account near resonance[46] and summation over v is retained in all terms of (15). Far from resonance, the summation over v drops out and the expression A* + B* + C* becomes close to the formulas of the simple semiclassical theory.

Peticolas and co-workers[51] obtained an expression corresponding to (15) and (16), using third-order perturbation theory and assuming

$$\Psi_{\mathrm{I}}(t) = U_{\mathrm{I}}(t, t_0) \Psi_{\mathrm{I}}(t_0),$$

where the operator U_{I} is expressed in terms of the interaction Hamiltonian for the "molecule + field" system; this Hamiltonian is subdivided into the Hamiltonians of the interaction of the field with the electrons and of the electrons with the nuclei. The problem is solved, with insignificant differences, also within the framework of second-order perturbation theory with an expansion of the type (13). In the second variant, the probability of the 0 → 1 transition for molecules oriented in a definite manner becomes, after some simplifications,

$$W_{01} = \text{const} \cdot \frac{\nu(\nu - \omega)}{\omega} \Big| \sum_{e,s} \Big[\frac{M_{\rho 0 e} h_{es} M_{\sigma s 0}}{(\nu_e - \nu)(\nu_s - \nu)} + \frac{M_{\sigma 0 e} h_{es} M_{\rho s 0}}{(\nu_e - \omega + \nu)(\nu_s - \omega + \nu)} $$
$$+ \frac{h_{0e} M_{\rho e s} M_{\sigma s 0}}{\nu_e(\nu_s - \nu)} + \frac{h_{0e} M_{\sigma e s} M_{\rho s 0}}{\nu_e(\nu_s - \omega + \nu)} + \frac{M_{\rho 0 e} M_{\sigma e s} h_{s0}}{\nu_s(\nu_e - \nu)} + \frac{M_{\sigma 0 e} M_{\rho e s} h_{s0}}{\nu_s(\nu_e - \omega + \nu)} \Big] \Big|^2, \tag{17}$$

where $\nu_e = \nu_e^*$ and $\nu_s = \nu_s^*$. Neglect of the vibrational ev structure in both variants is partly offset by inclusion of the diagonal elements (e = s), which makes possible (at least far from resonance) to represent in unified form the terms of the type A*, B*, and C*. In the first variant, unlike in (17), the resonant denominators contain $\nu_e + \omega$ instead of ν_e; the diagonal element (e = s) therefore yields two resonance points for one e level; these points are interpreted in[53,54] as resonances "with the incident" photon and "with the scattered photon." It suffices, to note, however, that under conditions when the diagonal element predominates neglect of the vibrational structure near resonance is permissible only if $\gamma_e \gg \omega$, when the $I(\gamma)$ curve has one maximum. If $\gamma_e < \omega$, an entire series of maxima should be observed, as shown in Fig. 6 below.

Formulas of the type (17) are genetically connected with Loudon's formula[55] for crystals. The latter takes into account the electron-phonon interaction in the form of a deformation potential that corresponds to the matrix elements h_{ee} and h_{es}.

In[47a], unlike in the previously noted papers, account is taken of the differences between the systems of the normal coordinates and the ground and excited states e; the electronic wave functions are expanded in the normal coordinates $Q^{(0)}$ and $Q^{(e)}$ of the ground and excited states, and the coordinates that transform in accordance

with one and the same irreducible representation are included. Then

$$M_{\sigma 0e} = \int \varphi_0 (\xi, Q^{(0)} = 0) \hat{M}_\sigma (\xi) \varphi_e (\xi, Q^{(e)} = 0) \, d\xi,$$

However, no sufficient justification is given for this form.

The representation of $(\alpha_{\rho\sigma})_{0k}$ in the form of three terms $A^* + B^* + C^*$ facilitates the analysis of the general formulas, but becomes rather unrealistic in higher approximations.

In the cited papers, in which the expansion (13) was used, no estimate was made of the extent that the results are valid if only the linear terms are retained; yet in a number of cases, particularly for antisymmetrical oscillations, one can expect nontrivial relations, particularly at small h_{es}, owing to the inversion of the contributions of the interacting electron levels in the case of oscillation of Q_{as}. The linear terms are known to be insufficient for a determination of the intensity of the overtones, and even for the $1 \to 2$ transitions.

Koningstein[56] continued the expansion and obtained expressions for the overtones and for the composite tones in the case of regions far from resonance. A formula of the type (17) for arbitrary $0 \to k$ transitions in resonant interaction was obtained in[17]; in place of the sum over e and s, there is in this case only one term

$$M_{\sigma 0e} h_{ee}^k M_{\rho e 0} \left[\prod_{m=0}^{k} (\nu_e + m\omega - \nu + (1/2) \, i\gamma_e) \right]^{-1}.$$

Introduction of the damping, however, does not eliminate the disparities noted above. In[17], as in[57], provision is made for a successive appearance of k quanta $\hbar\omega$ in the intermediate electron-excited state of the molecule (cf. page 100).

The use of formulas of the type (16), (17), or (4) calls for knowledge of the electron wave functions. If these are known, one can subsequently choose any variant. It can be noted that to calculate the contribution of the electronic e level to $(\alpha_{\rho\sigma})_{01}$ on the basis of formulas of the type (4), it suffices in practice to know the wave function φ_e, and also φ_σ at two values of Q; the use of formulas (14), (16), etc. calls for knowledge of the wave functions of an entire <u>assembly</u> of levels and a set of h_{es} (i.e., no less an amount of information).

Summation over v in (4), (9), and (16) entails certain difficulties, since it becomes necessary to take into account the contributions of a rather large number of sublevels. This has induced searches for more convenient methods of calculation, with the sum over v replaced by simpler expressions, or at least by other more advantageous series. The proposed variants provide for definite restrictions on the conditions and in most cases are not suitable for resonance excitation.

One of the possible procedures is to substitute a certain "center of gravity" for an entire group of sublevels that are arranged in sequence and produce contributions of the same sign to α_{0k}. For the RS line of the principal tone ($0 \to 1$) there are usually two such groups; thus, we obtain two terms of opposite signs in place of an infinite series; they can be regarded as quantities proportional to the polarizabilities of the molecule at two extremal positions of the vibrating atoms[58]. This procedure has limited capabilities and cannot be used for excitation near resonance at not too large a damping (γ_e), and also at small Δ_e.

Another method is to expand the tensor α_{0k} (or its part $\alpha_{0k}^{(1)}$ which is connected with Δ) in powers of $(\nu_{ev} - \nu_{e0})$[46,47a,52,59] or $(\nu_{ev} - \nu_{ev*})$[21,33,37]. The matter reduces to an expansion of a frequency multiplier of each sublevel v followed by summation (in first order in v); then according to[46], taking one electron level into account, we have

$$\alpha_{0k}^{(1)} = \text{const} \cdot \sum_{n=0}^{\infty} (-1)^n \left[\frac{1}{(\nu_{e0} - \nu)^{n+1}} + \frac{1}{(\nu_{e0} + \nu)^{n+1}} \right] \sum_v (\nu_{ev} - \nu_{e0})^n A_{0v} A_{vk}. \tag{18}$$

The expansion for the RS lines $0 \to 1$ is limited in[46] to the term with n = 1 (which corresponds approximately to the use of the first method), and for the RS lines $0 \to 2$ it is limited to the term with n = 2.

In some simplest cases, the sum over v in (18) are quite easy to obtain. Thus, for a harmonic oscillator, taking into account only one excitation level e and at $\omega^{(0)} = \omega^{(c)}$ we have from[46] for the RS lines $0 \to 1$ and $0 \to 2$

$$\sum_v (\nu_{ev} - \nu_{e0}) A_{0v} A_{v1} = \omega\Delta/2Q_z = \sqrt{2} \, d\omega,$$

$$\sum_v (\nu_{ev} - \nu_{e0})^2 A_{0v} A_{v2} = \omega^2\Delta^2/2 \sqrt{2} \, Q_z^2 = 2 \sqrt{2} \, \omega^2 d^2.$$

The analogous sum for the $1 \to 2$ line differs from the sum for $0 \to 1$ by an additional factor $\sqrt{2}$.[52] This method yields ultimately in[46] expressions that are similar, as suggested by the author, to the formulas of the simplest variant of the semiclassical theory. Similar expressions were obtained in[47a] (formula (21a)). The conditions $\omega^{(e)} \neq \omega^{(0)}$ are considered in[60].

According to[47a], the series (18) converges if $v^*\omega^{(e)}/(\nu_{e0} - \nu) < 0.5$. According to[46], it converges only if the atom oscillations are anharmonic in the electron-excited state (when the sublevels come closer together progressively with increasing v). It is therefore concluded in[46] that the convergence of the classical-theory power-law series

$$\alpha (Q) = \alpha_0 + (\partial\alpha/\partial Q)_0 Q + (1/2) (\partial^2\alpha/\partial Q^2)_0 Q^2 + \ldots, \tag{19}$$

is also determined by the anharmonicity in the excited state. Actually the series (19) converges much more rapidly than (18); the reason is that $\alpha(Q)$ is expanded about Q = 0, and this value corresponds to ν_{ev*} and not to ν_{e0}.

An expansion of the type (18) about the value ν_{ev*} yields a rapidly converging series that agrees better with the semiclassical theory. To determine α_{01} far from resonance it suffices then to have one term with n = 1 (or at most two terms with n = 1 and n = 3). To attain such an accuracy with an expansion about ν_{e0} it would be necessary to have at least four terms.

A series expansion about ν_{ev*} was used in earlier papers (see[33]), but the convergence was not considered. According to[33,61]

$$(\alpha_{\rho\sigma})_{0k} = \sum_{n, q, s, e} \left\{ \frac{(-1)^n (M_{\sigma e})_q (M_{\rho e})_s}{\hbar^{n+1} (\nu_{ev*} - \nu)^{n+1}} [Q^q (H_e + E_0 - \hbar\nu_{ev*})^n Q^s]_{0k} + G_{nqse} \right\}. \tag{20}$$

Here $(M_{\sigma e})_q$ and $(M_{\rho e})_s$ are the q-th and s-th of the coefficients of an expansion of type (3) of the functions $M_e(Q)$ and $M_e(Q)$ in powers of Q, H_e is the operator of nuclear motion in the electronic state e, and G_{nqse} corresponds to the second term in the square brackets of (1).

The retention of only three terms (n = q = 0, s = 1; n = s = 0, q = 1; s = q = 0, n = 1) in the sum over n, s,

and q in (20) transforms (20) into an expression equivalent to the simplest formula of the semiclassical theory, in which the first derivatives of M_e and ν_e are retained (see Chap. 5). Allowance for the next higher terms of the series (20) corresponds to allowance for the higher derivatives of M_e and ν_e.

An expression similar to (20), based on matrix elements of the momentum S_e (see page 102 above and[33]), is also connected definitely with the semiclassical-theory formula containing M_e, but this connection is more complicated. The latter is due to the fact that there is no simple proportionality between the terms in the aggregates of S_e and M_e, there is no simple term-by-term correspondence in the expansions of $S_e(Q)$ and $M_e(Q)$, and the distribution of the contributions of the electronic levels to $\alpha_{\rho\sigma}$ is quite different in the two variants.

Another way of eliminating the summation over v was used in[49]. For the case of harmonic vibrations of the nuclei and $\omega^{(0)} = \omega^{(e)}$, with allowance for the $M_e(Q)$ dependence for one level e, we have

$$\alpha_{00} = \frac{1}{\hbar\omega} M_e^2 \sum_{n=1,2} \left(\frac{1}{Z_n} + \eta_e \frac{\sqrt{2} Q_H}{d} \right) {}_1F_1(1, Z_n+1; -2d^2),$$

$$\alpha_{01} = \frac{1}{\hbar\omega} M_e^2 \sum_{n=1,2} \frac{\sqrt{2} d + 2\eta_e Q_H (Z_n+1/2)}{Z_n^2 + Z_n} {}_1F_1(2, Z_n+2; -2d^2) \text{ etc;}$$

here

$$Z_1 = \omega^{-1} [\nu_{e0} - \nu + (1/2) i\gamma_e], \quad Z_2 = \omega^{-1} (\nu_{e0} + \nu),$$

${}_1F_1$ is a confluent hypergeometric function. It should be noted that as a result of such transformations one infinite series is replaced by other no less complicated ones; furthermore, the convergence has not been thoroughly investigated.

Tang and Albrecht[37,62] have considered ways of eliminating the summation with respect to e and proposed to expand the resonant denominators (1) for each electronic level e (without allowance for the sublevels v) in a power series about a certain mean value of the electronic-excitation energy, E_{av}, in analogy with the procedure used in[33] for individual v sublevels. They propose that a successful choice of E_{av} makes it possible to separate a small number of dominant terms in the resultant series. In this variant the matrix elements of the polarizability are constructed by using electronic wave functions of only the ground state (φ_0). However, the convergence of the series is limited by very stringent conditions, including the condition of very large distance from resonance (larger than required for the convergence of the series obtained for the frequency multipliers of individual vibrational sublevels ev). The entire series can be transformed in the adiabatic approximation into a series that corresponds in general to the matrix element $\langle u_{00} | \alpha_{\rho\sigma}(Q) | u_{0k} \rangle$. If only the first two terms are retained in the series, it is possible to change over to the derivative of the polarizability referred to the value $\nu = 0$:

$$(\partial\alpha_{\rho\sigma}/\partial Q)_0 \approx 2 (\alpha_{\rho\sigma})_0 [(\partial/\partial Q) (\varphi_0 | \hat{M}_\rho \hat{M}_\sigma | \varphi_0)]_0 ([\varphi_0 | \hat{M}_\rho \hat{M}_\sigma | \varphi_0)_0]^{-1}.$$

At $\nu > 0$, the possibility of limiting the series to two terms becomes smaller even far from resonance.

It is obvious that the use of wave functions of only the ground state cannot suffice for a description of the aggregate of the experimental data on the intensity. Other ways of simplifying formula (1) lead likewise to loss of information in one form or another.

To facilitate the description of the polarizability tensor, it was subdivided into isotropic, anisotropic, and antisymmetrical parts (for example, in[47a, 62]), it was separated into a part that can be described in the adiabatic approximation and a remainder part (not specified concretely by the authors)[13], or was subdivided in accordance with the contributions of the σ and π electrons[50,63]. For polyatomic molecules one frequently uses an arbitrary subdivision of the polarizability tensor into contributions of individual chemical bonds. This is physically justified if the coupling between the electron shells of individual fragments of the molecules is very weak (cf.[64]); the opposite case (strong coupling) was treated on the basis of the model of a free electron in a potential box.

Sushchinskiĭ[7] separates from the polarizability matrix element a component satisfying the condition of Placzek's "polarizability theory" (the remainder is subsequently designated $\bar{R}$). The diagonal element is represented in the form

$$(\alpha_{\sigma\sigma})_{0k} = \frac{1}{\hbar} \int u_{0k}^* \left[\sum_e \frac{\mathscr{M}_{\sigma e}^2(Q)}{\bar{\nu}_e - \nu + (1/2) i\bar{\gamma}_e} + \frac{\mathscr{M}_{\sigma e}^2(Q)}{\bar{\nu}_e - k\omega + \nu + (1/2) i\bar{\gamma}_e} \right] u_{00} dQ + \bar{R}$$

$$= \int u_{0k}^* \alpha_{\sigma\sigma}(Q) u_{00} dQ + \bar{R},$$

where $\bar{\nu}_e$ and $\bar{\gamma}_e$ are quantities averaged within the assembly of sublevels v of one electron level. The remainder $\bar{R}$ reflects the influence of the existing differences in ν_{ev} and γ_{ev}, which are not taken into account in the principal part of the expression; at large distance from resonance we have $\bar{R} \approx 0$.

In the general case $\bar{R}$ is not concretely specified, but in the case of sharp resonance with participation of only one sublevel ev = er we have from[7]

$$\bar{R} = \frac{1}{\hbar} \frac{\int u_{er} \mathscr{M}_{\sigma e}(Q) u_{0k}^* dQ \int u_{er}^* \mathscr{M}_{\sigma e}(Q) u_{00} dQ}{\nu_{er} - \nu - (1/2) i\gamma_{er}}.$$

The contribution of the remaining ev sublevels is assumed to satisfy the polarizability-theory conditions and is taken into account by the function $\alpha_{\sigma\sigma}(Q)$. However, recognizing that a possible difference can exist in the signs of the resonant denominators for different ev, we can say that the value of $\bar{\nu}_e$ at which the polarizability-theory formula gives acceptable solutions depends strongly on the frequency ν of the incident light and can go far beyond the limits of the real absorption band.

Concrete calculations of α_{01} and $\alpha(Q)$ for certain very simple molecules far from resonance were performed many times; some comparisons are contained in[37,62]. The semiempirical calculations for complicated molecules were based mainly on the classical theory (Chap. 5).

Allowance for the rotational sublevels of the initial (J_0), the intermediate (J_{int}), and the final (J_f) states (including also the situation when $\Omega > \gamma_e$, where Ω is the rotational frequency), makes it possible to estimate the intensities of the components of the rotational structure of the RS lines. Morozov[65] notes that the contribution of the sublevel ev of a diatomic molecule to α_{0k} consists of contributions (of equal sign) of two or three rotational sublevels evJ_{int}. According to[65], Placzek's theorem stating that total RS line intensity is independent of J_0 cannot be extended to the resonance region. The Kramers-Heisenberg-Weisskopf formula is valid at resonance for the O and S branches, since one intermediate sublevel J_{int} takes part here, but in the case of the Q branch there are possible limitations if the off-diag-

onal elements of the damping matrix are appreciable[66]. Under ordinary conditions, the intensity of the light scattered in the perpendicular direction, when the sample is illuminated with monochromatic natural light of frequency ν, is determined for the Q, O, or S branch by the formula

$$I = \text{const} \cdot \exp\left(-\frac{BJ_0(J_0+1)}{kT}\right) \sum_{m_0, \, m_f} [3 \mid (\alpha_{\rho\sigma})^{kJf \, m_f}_{0J_0m_0} \mid^2 + \mid (\alpha_{\sigma\sigma})^{\sigma J \, m_f}_{0J_0m_0} \mid^2];$$

here B is the rotational constant (in cm^{-1}); the indices 0, J_0, and m_0 determine the initial vibrational, rotational, and magnetic quantum numbers, while k, J_f, and m_f are the same for the final state. The formula describes scattering by diatomic molecules that are freely oriented in space. The detailed data on the polarizability matrix elements for the resonance region are given in the original paper[66].

The degree of depolarization as a function of J_0 was considered in[65,67]. According to the semiclassical theory under the conditions $\Gamma < \gamma_{ev} < \Omega$, "rotational depolarization" is possible as the result of afterglow elements in each cycle of molecule rotation (the unsteady state of the electronic oscillator)[24]. The quantum and semiclassical theories are generally in agreement in the comparison of the selection rules for ΔJ outside and inside the resonance region[24,65].

In considering light scattering by isolated molecules, we have confined ourselves to cases in which the initial (0) and final (f) electron states of the molecule coincide (f = 0). In the absolute case, the transitions from (1) to (4), (9), (16), etc. cannot be realized; similar procedures and an expansion of the type (13), but without allowance for the v sublevels, lead in accordance with[68] to an expression that, omitting certain details, is of the form

$$\hbar(\alpha_{\rho\sigma})_{00 \to fk} = \langle u_{ik} \mid u_{00} \rangle \sum_e \frac{M_{\rho0e}M_{\sigma e0}}{\bar{\nu}_e - \nu} + \langle u_{fk} \mid Q \mid u_{00} \rangle \sum_e \frac{M_{\rho es}(M_{\sigma es}h_{s0} + M_{\sigma s0}h_{se})}{\bar{\nu}_e - \nu};$$

here $\bar{\nu}_e$ is the average frequency of the electronic transition $0 \to e$. The second term determines the scattering intensity at f $\neq$ 0 and k $\neq$ 0. The principal part of the "electronic Raman scattering," corresponding to f $\neq$ 0, is, however, not accompanied by a change in the vibrational quantum number (k = 0), and is described by the first term. Experience shows that electronic Raman scattering is much less intense than ordinary RS (f = 0, k = 1), and the scattering cross section is smaller by one or two orders of magnitude. Cases have been noted in which the scattering tensor $(\alpha_{\rho\sigma})_{00 \to fk}$ is antisymmetrical even far from resonance[68].

Interesting data on the influence of the magnetic field, which leads to a splitting of the 0 and f levels and of the electronic RS lines (the "Zeeman-Raman effect") were obtained in[69].

The two-photon RS process relates electronic states 0 and f of like parity; this cannot be said of the three-photon process and of scattering of the dipole-quadrupole type (see[70]).

In this case, if the intensity of the incident light is very large, lines of frequency $2\nu \pm n\omega$ can appear in the spectrum of the scattered light (the hyper-Raman effect—HRE). Under ordinary conditions, their intensity is exceedingly low (but proportional to the square of the intensity of the incident light). It can be described with the aid of a hyperpolarizability tensor (of third rank). In the region where Placzek's theory is applicable, the hyperpolarizability β of the molecule is regarded as a

function of the nuclear coordinate Q; then the matrix element β_{0k}, which determines the intensity of the $2\nu-k\omega$ emission line (the 00 $\to$ 0k transition) is

$$\beta_{0k} = \langle u_{00} \mid \beta(Q) \mid u_{0k} \rangle.$$

Here $\beta(Q)$ is expressed in terms of the matrix elements of the moments of the electronic transitions, constructed from the electronic wave functions φ[71,72].

A more general expression for the components of the hyperpolarizability tensor can be obtained within the framework of perturbation theory, when the wave function of the perturbations of the system is

$$\Psi_n^{\text{pert}} = \Psi_n + \sum_e (a_{en}^{(1)} + a_{en}^{(2)}) \Psi_e,$$

and $a_{en}^{(1)}$ reflects only the linear dependence on the amplitude of the incident light wave, while $a_{en}^{(2)}$ reflects the quadratic dependence. In final analysis, according to[71] we have (without the indices $\rho\sigma$, and with the radiative damping constants γ)

$$\beta_{0k} = \frac{2}{\hbar^2} \sum_{r, \, s} \left[\frac{\tilde{M}_{0s}\tilde{M}_{se}\tilde{M}_{ek}}{(\nu_{0s} - \nu - i\gamma_{0s})(\nu_{0e} + \nu - i\gamma_{0e})} \right.$$
$$\left. + \frac{\tilde{M}_{0s}\tilde{M}_{se}\tilde{M}_{ek}}{(\nu_{0s} + 2\nu - i\gamma_{0s})(\nu_{ek} + \nu - i\gamma_{ek})} + \frac{\tilde{M}_{0e}\tilde{M}_{es}\tilde{M}_{sk}}{(\nu_{0s} - 2\nu - i\gamma_{0s})(\nu_{0e} - \nu - i\gamma_{0e})} \right].$$

In this formula $\tilde{M}$, γ, and ν are labeled by the two indices of the combining levels. Unlike formula (1) for α_{0k}, we have here double summation over the levels of the electronic excitation (e, s); appreciable contributions are made to β_{0k} only by those e and s levels which are coupled to each other and to the initial and final states by nonzero transition moments.

Further transformations of β_{0k} with allowance for the ev sublevels in the Born-Oppenheimer approximation are effected in the same manner as the α_{0k} transformations (see[71]). In[51], β_{0k} was determined on the basis of an expansion of the type (13); a formula similar in structure to (17) was obtained.

The selection rules for the change of the vibrational quantum number in the HRE off resonance are the same as in ordinary RS and $I_{2\nu-2\omega} \ll I_{2\nu-\omega} \ll I_{2\nu} \ll I_\nu$. However, the selection rules connected with symmetry are essentially different[71,72], and in HRE there is no possibility of registering frequencies ω_p that are not observed either in the RS or in the IR spectra.

4. USE OF QUANTUM-ELECTRODYNAMICS METHODS

A consistent application of the methods of quantum mechanics to the analysis of the transformation of light by molecules includes quantization of the radiation field. When the nonstationary processes of photon absorption and emission are considered, one usually starts with a system of equations for the time variation of the probability amplitudes b_n of the state ψ_n (m and n are quantum numbers of the system):

$$i\hbar\dot{b}_n(t) = \sum_m b_m(t) V_{nm}e^{i\nu_{nm}t}, \qquad (21)$$

where V is the operator of the field-molecule interaction energy. Solution of the system of equations by perturbation theory (without allowance for damping) under the initial conditions $b_0(0) = 1$ and $b_m(0) = 0$ (at all m $\neq$ 0) makes it possible to determine in general form the probability of absorption and emission of light by the molecule (but not the radiative width).

A solution of the system (21) with the cited initial conditions which is valid also when $t > \tau_e$, was given at one time by Weisskopf. It was obtained more rigorously by Heitler and Ma by representing the nonstationary solution of the Schrödinger equation in terms of a superposition of stationary solutions. Thus, the transformation of light by a molecule with two energy levels was considered in a closed system at $t = \infty$ (the last condition determines the possibility of describing the line contour, but not the intensity). The solution was extended in[73] to the model of a molecule with three energy levels, and in[7] to a system with an arbitrary number of levels. In different variants, the problem was considered also in[15,16,74,75], and also in[33] and[47a], which were cited in Chap. 3.

Apanasevich[76] considered the stationary regime of transformation of light in an unclosed system, which has a less artificial character (although it has not yet been fully developed); it was assumed that the state of the radiation field and the probabilities of finding a molecule in some particular state did not depend on the time, and that the number of photons transformed by the molecule is proportional to the time. A constant field of the incident light is ensured by using an extraneous light source. The behavior of such an "unclosed" system is described by a system of equations that differ somewhat from (21); the probability amplitudes for the state of the incident light and of the molecule in the ground state are assumed to be constant. The principal results of[76] agree with Weisskopf's formula.

The solution given by Weisskopf corresponds to conditions when different excitation levels are not coupled by the radiation field[29]. In the presence of such a coupling between quantum-system states that decay at different rates (or coupling between differently damped vibrations of the classical system), the subdivision of the overall process into independent decays of individual levels (or vibrations) is impossible. Diagonalization of the Hamiltonian of the molecule (or separation of the normal vibrations) then leads to the appearance of off-diagonal elements of the damping matrix. The decay of the system differs in this case from exponential, and the corresponding spectral lines have an anomalous form, which may affect also the dependence of the intensity $I(\nu)$ of the secondary-emission line on the frequency of the exciting light in the resonance region (see[77-79], and also Chap. 7).

The introduction of off-diagonal elements γ extends the possibilities of investigating the transformation of light in systems in which the energy levels are coupled by external forces (anticrossing of levels; coupled vibrations) or an external field[80]. It is no less interesting to describe the secondary-emission intensity beats[81], the appearance of a gap in the absorption band (transparency lines) due to mixing of states in vibronic, Coriolis, or spin-orbit coupling.

In those cases when the excitation-level interaction mechanism is known, the method of Heitler and Ma with allowance for the off-diagonal elements of γ leads to the same result as the Fano method of configuration mixing[77] and a few other procedures.

The solution of system (21) is expressed in terms of matrix elements V, which determine the probability of the transition of the "molecule + radiation field" system from one state to another. By starting from a system of equations that determine V, we can obtain $b_n(t)$ for any

time t. The most interesting are the solutions for t in the range $\hbar/(E_n - E_0) \ll t \ll \tau_0$, where τ_0 is the lifetime of the initial state of the system. The probability of the transition $0 \to n$ per unit time is in this case

$$(d/dt) \mid b_n(t) \mid^2 = (2\pi/\hbar) \mid \mathscr{V}_n \mid^2 \delta (\widetilde{E}_n - \widetilde{E}_0), \qquad (22)$$

where $\widetilde{E}$ is the energy of the entire system and E is the energy of the molecule.

Formulas such as (22) lead to solutions that can be regarded as generalizations of the expressions obtained on the basis of the Kramers-Heisenberg-Weisskopf formula (1) to include the case when off-diagonal elements of the damping matrix, which are important in the resonance region, are taken into account. If the latter are small (and in any case off resonance), it suffices to use in place of the complete system of equations for V only a set, corresponding to formula (1), of independent equations for individual intermediate levels e. In this case, for example, $V_{0 \to 1}$ reflects the absorption of virtual photons that appear as a result of $1 \to 0$ transitions, whereas in the complete system $V_{0 \to 1}$ reflects absorption of the photons that appear in the transitions $1 \to 0$ and $2 \to 0$[29].

The description of the transformation of light by the method of Heitler and Ma at $\tau_e \ll t \ll \tau_0$ is equivalent to describing the processes in the unclosed system in accordance with[76]. The solution of the problem at $\tau_e \ll t \ll \tau_0$ and at $t = \infty$ leads to identical results with respect to the contours, accurate to γ_0. There are simple relations between the solutions of the two variants. Thus, the probability of the appearance of a secondary photon σ per unit time at $t \ll \tau_0$ is determined by the probability of absorption of a photon of incident light λ during the same time, multiplied by the probability that the secondary-emission photon is of the type σ if it is certain that transformation of one photon of type λ has taken place (i.e., at $t = \infty$).

The complete expressions for the displaced and undisplaced scattering line intensities for the model of a molecule with one intermediate level e are given in[29,76]. When two intermediate levels are taken into account (e = 1 and 2), and if their interaction is in accordance with[29], we have

$$\mid (\alpha_{\rho\sigma})_{0h} \mid^2 = F \mid (\widetilde{M}_\rho)_{2h} \mid^2 [(ab + 1) x - 1]^2, \qquad (23)$$

where

$$F^{-1} = \frac{\hbar^2}{16} (\nu_2 - \nu_1)^2 \left\{ \left[4x^2 - 4x - \frac{\gamma_{2 \to 0} - \gamma_{2 \to k}}{(\nu_2 - \nu_1)^2} (a - b)^2 \right]^2 \right.$$
$$\left. + [(x - 1)(\gamma_{2 \to 0} + \gamma_{2 \to k}) + x(\gamma_{1 \to 0} + \gamma_{1 \to k})]^2 \right\},$$
$$x = (\nu_2 - \nu)/(\nu_2 - \nu_1), \quad a = (\widetilde{M}_\sigma)_{02}/(\widetilde{M}_\sigma)_{01}, \quad b = (\widetilde{M}_\rho)_{1h}/(\widetilde{M}_\rho)_{2h};$$

$\gamma_{e \to 0}$ and $\gamma_{e \to k}$ correspond to the half-widths of the lines of the spontaneous transitions $e \to 0$ and $e \to k$, while ν_e and ω are the frequencies of the transition $e \to 0$ and $k \to 0$.

Formula (23) near resonance gives a larger deviation from the Kramers-Heisenberg-Weisskopf formula the closer ν is to the resonance point, the more the overlap of the intermediate levels, and the larger the quantity $a\gamma_{2 \to k} + b\gamma_{2 \to 0}$.

In connection with the foregoing, we call attention to the fact that most experimental data on the $I(\nu)$ dependence pertain to systems with continuous absorption bands, $0 \to e$, in which the components of the vibrational and rotational sublevels overlap to a large degree; in this case it may not be possible to satisfy in the reson-

ance region the conditions under which the Kramers-Heisenberg-Weisskopf formula and all the variants that reduce to it or contain additional assumptions or simplifications can be used.

In[66], the scheme described above is extended to include systems in which nonradiative transitions are possible, particularly transitions of the type of predissociation from the electron-excited state e to another state (j) characterized by a larger energy-level width (under conditions when two e sublevels overlap the level j). In place of the radiative-damping constant, the solutions contain resultant constants that reflect the probabilities of the nonradiative transitions.

Sushchinskiĭ[7] has considered the scattering of light by a molecule with any number of intermediate levels, using the notion of quasistationary energy levels and basing himself on perturbation theory for the transitions between degenerate states of the "molecule + radiation field" system. The damping was taken into account by introducing into the Hamiltonian an additional non-Hermitian "damping operator" (without off-diagonal elements). The dependence of the perturbation operator on the time was practically disregarded.

According to[7], the probability amplitude for finding the system in the state k is

$$b_h(t) = b_h^{\text{dir}}(t) + b_h^{\text{RS}}(t) + b_h^{\text{RF}}(t); \qquad (24)$$

$b_k^{\text{dir}}(t)$ is determined by the direct transitions $0 \to k$, $b_k^{\text{RS}}(t)$ is determined by transitions via intermediate states e in scattering, and $b_k^{\text{RF}}(t)$ is the same for resonance fluorescence. The squares of the moduli of each of the three function in the right-hand side of (24) are regarded as probabilities of the transitions $0 \to k$ after a time t via the corresponding mode (this is possible when $\tau_e \ll t \ll \tau_k$); cf. formula (22). The function $|b_k(t)|^2$ contains also mixed terms, including $b_k^{\text{RS}}(t) b_k^{\text{RF}}(t)$, which according to (7) should describe simultaneous excitation of RS and resonance fluorescence. Since, however, the function $|b_k(t)|^2$ are connected with the transformation of one photon, the mixed term can be interpreted more readily as a correction to the description of the secondary emission in the form of a combination of typical "RS" and "resonance fluorescence."

The general formula for the transition probability[7] reflects the correlations in the distribution of the photons of the incident and scattered radiation over the frequencies, angles, and polarizations. The time dependence of the probability of conversion of the photon λ into a scattered-light photon σ' in the frequency interval $d\nu_\sigma'$ in a closed system is expressed by the factor $F_k(t)$. When $\gamma_e > \gamma_k \gg \Gamma > \gamma_0$ we have

$$F_h(t) = \frac{1 + \exp(-\gamma_h t) - 2 \exp[-(1/2)\gamma_h t - (1/2)\Gamma t] \cos at}{a^2 + (1/4)\gamma_h^2},$$

where a characterizes a point on the contour of the Stokes RS line (a = 0 at the maximum). The factor $F_k(t)$ contains terms that attenuate with time and oscillate. To calculate the real intensity, the conditions τ_k, $\tau_e \ll t \ll \tau_0$ are considered (this is not equivalent to the aforementioned conditions for $b_k(t)$!). Then $\exp(-\gamma_k t) \approx 0$ and $F_k(t)$ no longer depends on t (see the interpretation in[82]), and when $\gamma_k \gtrsim \Gamma$ it reduces to a convolution of the contours of the exciting line and of the "true" contour of the RS line (which depends in final analysis on $\gamma_k + \gamma_0$).

The probability W^{RF} of the $0 \to e \to k$ transition via an intermediate resonant level e in resonance fluorescence was considered in[7] assuming arbitrary γ_e ($\gtrsim \Gamma$) (cf.[22]). If ν is close to ν_e^* at $\gamma_e \gg \gamma_k$, we have in the time interval from 0 to t (t $\ll \tau_k$) and in the frequency interval $d\nu_\sigma'$

$$W^{\text{RF}} = \text{const} \cdot |\tilde{M}_{0e}|^2 |\tilde{M}_{ek}|^2 S \frac{\exp(-\gamma_k t) + \exp(-\gamma_e t) - 2\exp(-\gamma_e t/2) \cos zt}{z^2 - (1/4)\gamma_e^2},$$

where S is the convolution of the contours of the exciting line and of the absorption line $0 \to e$ (it is maximal if $\nu = \nu_e^*$); the quantity z characterizes a point on the contour of the fluorescence band (z = 0 at the maximum).

In most studies, no allowance was made for the field-component phase correlations. Allowance for these correlations is of great importance, for example, in the study of intensity beats of spontaneous-emission (on going from a superposition excited state) and of secondary emission (when a field with definite phase correlations acts). An exposition within the framework of quantum electrodynamics is given, in particular, in[81]. In the simplest case, the secondary-emission photons are described by superposition wave functions with the same initial-phase difference as the exciting-light photons; a correspondence is observed with the description of the phenomenon in classical theory[81].

On the whole, it can be noted that the analysis of secondary emission on the basis of quantum electrodynamics is more consistent. It extends the possibility of studying line contours and can be regarded as a further justification of the simpler methods of studying the intensity.

5. DEVELOPMENT OF THE CLASSICAL THEORY OF RAMAN SCATTERING

The usual conditions for the excitation of RS far from resonance have made it possible to make extensive use of the simplest variant of classical theory. This variant regards oscillations $\mu(t)$ of the dipole, produced by polarization of the electron shell of the molecule by the field of a monochromatic light wave as the steady-state oscillations (see[22]). The oscillation amplitude $\mu(t)$ is modulated by the vibrations of the atoms (without a phase shift). The line intensity of the first-order RS is determined by the modulation depth, which is proportional to $(\partial \alpha / \partial Q_p) Q_{a,p}$; here α is the polarizability of the molecule, Q_p is the p-th normal coordinate describing the vibration of the atoms, and $Q_{a,p}$ is the corresponding amplitude.

In the semiclassical theory, the derivative $\partial \alpha / \partial q$ of the polarizability is determined by the sum of the contributions of the electronic-excitation levels[40,41]. These contributions depend on the dipole-moment matrix elements M_{0e} of the transitions $0 \to e$, or, in another variant[83], on the corresponding Cartesian component of the oscillator strength f_e. The second variant leads to more compact expressions, which will be presented below. The component f_e represents all the components of the vibrational structure of the $0 \to e$ absorption band; $f_e(Q)$ is assumed to be proportional to $\nu_e(Q) M_e^2(Q)$, but the possibility of imitating $f_e(Q)$ by an arbitrary dependence of f_e on Δ_e is not excluded (integration with respect to Q is also implied).

We then have for one Cartesian component[58,64]

$$\frac{\partial \alpha}{\partial Q} = \frac{e_{\text{el}}^2}{2\pi m_{\text{el}}} \sum_e \left[\frac{f_e'}{\nu_e^2 - \nu^2 + i\nu\gamma_e} - \frac{2f_e\nu_e\nu_e'}{(\nu_e^2 - \nu^2 + i\nu\gamma_e)^2} \right], \qquad (25)$$

$$\frac{\partial^2 \alpha}{\partial Q^2} = \frac{e_{el}^2}{2\pi m_{el}} \sum_e \left[\frac{f_e''}{v_e^2 - v^2 + iv\gamma_e} + \frac{4f_e'v_e v_e' + 2f_e v_e v_e''}{(v_e^2 - v^2 + iv\gamma_e)^2} + \frac{2f_e v_e'^2 (3v_e^2 + v^2 - iv\gamma_e)}{(v_e^2 - v^2 + iv\gamma_e)^3} \right].$$

(26)

The primes denote derivatives with respect to Q at $Q = 0$; $v_e = v_e^*$ corresponds to the maximum of the absorption band (cf.[34], where a correspondence to the $00 \to e0$ frequency is proposed, and also[85]).

Similar expressions are obtained if the procedure is based on separating terms containing the derivatives of M_e and v_e. The contribution of each electronic level to $\partial \alpha / \partial Q$ does not depend on the choice between these two variants, but the relative role of the two terms (of which each such contribution in (25) is made up) depends to a certain degree on this choice[43]. The off-diagonal elements can be expressed by the same methods (see, for example, formula (7) in[61]). Different ways of justifying (25) are described in[49,61,85].

The role of the vibrational sublevels (ev) in semi-classical theory is represented not as the summation of the contributions with the corresponding resonance denominators, but as differentiation of v_e with respect to Q. The latter corresponds to the known simplifications of the ev system and to a replacement of definite groups of neighboring sublevels by certain "centers of gravity," which is permissible far from resonance (see Chap. 3). The derivative v_e' depends on the change (Δ_e) of the equilibrium value of Q following electronic excitation[40].

According to (25) and (26), the existence of Raman scattering is determined by two factors: the dependence on the nuclear coordinate M_e (or f_e), and v_e (cf. Chap. 3). Most authors are of the opinion that the dependence of v_e on Q is of primary significance for RS lines of fully-symmetrical vibrations in the case of excitation not too far from resonance[8,20,35,40,86]; this is confirmed, in particular, by experimental data on the function $I(v)$[43,83,87,88] and by an analysis of the vibrational structure of the absorption band of the $0 \to e$ transitions[18,89] (cf., however,[7,36,90-92,179]); calculation data for H_2^+ far from resonance are given in[59].

For antisymmetrical vibrations we have $(\partial v_e / \partial Q_{as})_0 = 0$ (cf.[93]). This holds true in the presence of a coupling between the electron shells of identical fragments of a symmetrical molecule. If the coupling is very weak, then each of these fragments can be assigned its own local electronic transition frequency v_e. Mixing of the electronic wave functions of the fragments can then be admitted only at $Q_{as} \approx 0$. Under definite conditions, one can introduce derivatives of v_e with respect to the local nuclear coordinates (within the limits of the fragment).

Ting[52], assuming $M_e(Q) = const$ and $\partial v_e / \partial Q_{as} = 0$, reached the conclusion that the as-vibration lines in the Born-Oppenheimer approximation should be excluded completely by the selection rules. Observation of these lines in experiments is attributed to the influence of the intermolecular interaction and to the coupling between the electron-excitation level, which depends on the nuclear coordinates (h_{es}; see Chap. 3).

It was noted in[94] that these conclusions are incorrect. The assumption $h_{es} \neq 0$, generally speaking, contradicts the assumption $M_e(Q) = const$. Further, even a simple additive scheme using the concept of anisotropic polarizability of chemical bonds points to an appreciable intensity of the as-vibration lines, say of molecules with C_{2v} symmetry (although not for all orientations of the molecule relative to the polarization plane of the incident light). Additivity of the increments

of the polarizability (α') of chemical bonds presupposes independence of the electron shells of the individual chemical bonds in a polyatomic molecule; under these conditions, additivity makes it possible to estimate (in qualitative agreement with experiment) the intensity ratio of the antisymmetrical and symmetrical vibration RS lines, I_{as}/I_s, as a function of the mutual spatial arrangement of the fragments (cf.[47a, 62]). The source of the derivatives of the polarizability is not specified concretely; it may be connected either with $M_e(Q)$ or with $v_e(Q)$.

If the electronic oscillators ascribed to symmetrical-molecule fragments of the same type are coupled, and if it can be assumed that $(\partial v_e / \partial Q_{as})_0 = 0$ for the nonlocal levels of the electronic excitations (for the splitting com-components of the "local" levels), then the Q_{as} oscillation at $h_{es} \neq 0$ (see formula (13)) can lead to inversion of the contributions made to the polarizability by the indicated fragments and to oscillations of the polarization of the possible electronic transition. We then have $\partial \alpha_{\rho\sigma} / \partial Q_{as} \neq 0$ for definite off-diagonal elements (cf.[95]). In general one cannot exclude $I_{as} \neq 0$ both in the absence and in the presence of a coupling between the molecule fragments. As a rule, however, $I_{as} \ll I_s$ (but this can still not be regarded as proof that the factor $\partial v_e / \partial Q$ predominates; cf.[47a]). According to[47a, 93], the change of symmetry of the molecule following electronic excitation and the lifting of the degeneracy of the electronic states by the Q_{as} oscillations should favor an increase of I_{as}, particularly in the resonance region[74].

An analysis of formulas (25) and (26) leads to the conclusion that only _amplitude_ modulation of the $\mu(t)$ oscillations takes place off resonance, and in the resonance region there is also _phase_ modulation[84]. Figure 4 illustrates the changes in the complex polarizability for nuclear vibrations following excitation in the region of the center of the continuous absorption band at $\gamma_e \gg \omega$ and $\Delta_e \neq 0$. The figure shows in the complex plane the values of α for the equilibrium value ($\overline{AB}$) and for the two extremal values of the oscillating coordinate Q ($\overline{AC}$ and $\overline{AD}$). The vector $\overline{DC}$ is the difference between the values of α at the two extremal positions of the nuclei, and determines I_{01}. The vector $\overline{EB}$, roughly speaking, corresponds to the quantity $\alpha'' Q_a^2$ and determines the intensity I_{02} of the first overtone[58].

In the general case, the spectrum of the oscillations of the induced moment is determined by a series that describes the undisplaced scattering and a sequence of Stokes (St) and anti-Stokes (A) components:

$$\mu(t) = \mu_0(t) + \mu_{st1}(t) + \mu_{A1}(t) + \mu_{st2}(t) + \ldots$$

In the adiabatic approximation at $\gamma_e \gg \omega$ we have

$$\left. \begin{array}{l} \frac{\mu_0(t)}{\mathscr{E}_a} = |\alpha| \cos(vt - \varphi_0) + \frac{1}{4} |\alpha''| Q_a^2 \cos(vt - \varphi_2) + \ldots, \\[2mm] \frac{\mu_{st}(t)}{\mathscr{E}_a} = \frac{1}{2} |\alpha'| Q_a \cos[(v - \omega)t - \varphi_1] + \\[2mm] \qquad + \frac{1}{16} |\alpha'''| Q_a^3 \cos[(v - \omega)t - \varphi_3] + \ldots, \\[2mm] \frac{\mu_{st2}(t)}{\mathscr{E}_a} = \frac{1}{8} |\alpha''| Q_a^2 \cos[(v - 2\omega)t - \varphi_2] + \ldots; \end{array} \right\}$$

(27)

here E_a is the incident-light electric-field intensity oscillation amplitude. Under resonance conditions $\varphi_0 = \varphi_2 = \pi/2$ and $\varphi_1 = \pi$; far from resonance all the φ are equal to zero[96].

The intensity of the undisplaced line in the scattering spectrum (for a single molecule) is thus determined by
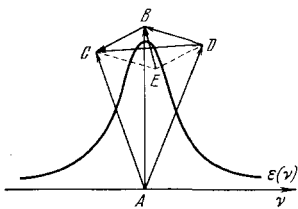
FIG. 4. Complex values of α at equilibrium and at the two extremal positions of vibrating nuclei at $\nu = \nu_e^*$ and $\gamma_e \gg \omega$.

the polarizability at Q = 0 and by the even derivatives of α, the intensity of the first-order RS line is determined by the aggregate of the other derivatives, etc.[84,96]. The contribution of the higher derivatives increases when resonance is approached.

If we assume $Q_a = 2Q_z$, then $(\partial\alpha/\partial Q)Q_z = \alpha_{01}$ far from resonance, and both the classical and quantum theories lead to the same values of the RS Stokes line intensity, although some discrepancy is obtained in the values of the summary intensity $I_\nu + I_{\nu-\omega} + I_{\nu+\omega}$[32].

The validity of the aforementioned variant of the classical theory is restricted by the requirement that the nuclear vibration amplitude not exceed the convergence radius R of the series (19). For a diatomic molecule at $\omega^{(0)} \approx \omega^{(e)}$ we have

$$R = (\hbar/k|\Delta_e|)[(v_e^* - v)^2 + (1/4)\gamma_e^2]^{1/2} \div (1/2)|\Delta_e|.$$

At $|\Delta_e| \geq Q_a$, the series (19) converges at any frequency of the incident light outside the absorption band. The convergence radius decreases, however, as resonance is approached and reaches a minimum at $\nu = \nu_e^*$; in this case R is proportional to $\gamma_e|\Delta_e|^{-1}$, and the series (19) converges (albeit relatively slowly) if $\gamma_e > 2\kappa\omega$. In the opposite case, the series diverges and the simplest model of the classical theory is certainly unsuitable[96]. See also[32,97] concerning limitations that arise in the estimate of the overtone intensity.

The limitations on the use of a power-series expansion of $\alpha(Q)$ have stimulated the use of a direct expansion of the induced moment $\mu(t)$ in a Fourier series in harmonics with frequencies $\nu \pm n\omega$, which is possible in principle, even if the power series diverges.

Assuming that the frequency $\nu_e(Q)$ of the electronic oscillator is modulated by the vibrations of the atoms and that $|\alpha(t)| = \alpha_0 + \sum_{n=1}^{\infty} a_n \cos n\omega t$, Krushinskii[49,96] obtained, on the basis of the dispersion formula for the polarizability, expressions for the coefficients a_n of the Fourier expansion of $\alpha(t)$; these coefficients reflect the elements of the amplitude and phase modulation of $\mu(t)$. The squares of the coefficients determine the intensities of the corresponding lines in the scattering spectrum. In nonresonant region, each such coefficient corresponds to a sum of terms obtained from the power series in formulas (27), and consequently includes the contributions of the higher terms of the expansion of $\alpha(Q)$ (which become more appreciable as the resonance region is approached). Off resonance, at $f_e(Q) = $ const and $\omega^{(e)} = \omega^{(0)}$ we have

$$a_1 = \frac{e_0 f_e}{2m_3 v\kappa\omega} \left\{ \frac{|v_e - v|}{[(v_e - v)^2 - \kappa^2\omega^2]^{1/2}} - \frac{v_e + v}{[(v_e + v)^2 - \kappa^2\omega^2]^{1/2}} \right\};$$

$\kappa\omega$ characterizes the depth of modulation of ν_e; for a diatomic molecule (nuclear coordinate q, amplitude q_a) we have

$$\kappa\omega = \hbar^{-1}K\Delta q_a = (\partial v_e/\partial q) q_a.$$

The cited formulas of the classical theory are based in one form or another on a "quasistatic approximation"

(adiabatic slow variation of the parameters of the electronic oscillator and vibrations in the steady state), when the polarizability is regarded as a function of Q. In the resonance region, this approximation is suitable only at very large damping γ_e[22].

In the general case, account is taken also of the transient processes occurring when the parameters of the oscillator are altered through a change of Q. This can be done in accordance with[31] in the solution of Hill's equation; for a one-dimensional oscillator we have

$$\ddot{x} + \gamma_e(t)\dot{x} + v_e^2(t) x = (e_{el}/m_{el})\mathscr{E}_a \cos vt, \quad (28)$$

where x is the electron coordinate and $\nu_e(t)$ is the instantaneous value of the electron natural-oscillation frequency.

Equation (28) contains one frequency ν_e; generalization to other cases entails no difficulty. In the region of stable solutions of (28), the particular integral used to describe the induced oscillations of the oscillator is a bounded periodic function of the second kind; it can be represented in the form of a product of two factors, one of which varies in time with frequency ν, and the other contains an aggregate of harmonic components with frequencies $n\omega$.

If $\Delta_e \neq 0$ and $\nu_e(t) \approx \nu_e^* - \kappa\omega \cos \omega t$, then a solution of (28) is obtained in a rather simple form if $\gamma_e(q) = $ const, $f_e(q) = $ const, and $\omega^{(e)} = \omega^{(0)} = \omega$. These conditions are not obligatory in principle, but they do simplify the solutions and make it possible to focus attention on the most interesting aspects. In this case the amplitude of the induced oscillations corresponding to the lines $\nu - n\omega$ is

$$a_n = \frac{e_3^2 f_e}{2m_3 v v_e^*} \sum_{m=-\infty}^{\infty} \left[\frac{J_m(\kappa)J_{m+n}(\kappa)}{(v_e^* - m\omega) - v - (1/2) i\gamma_e} + \frac{J_m(\kappa)J_{m-n}(\kappa)}{(v_e^* - m\omega) + v + (1/2) i\gamma_e} \right], \quad (29)$$

where $J_z(\kappa)$ is a Bessel function of the first kind of order z, and κ (see above) is the index of the modulation of the frequency ν_e. Roughly speaking, κ determines the number of components of the vibrational structure of the $0 \to e$ absorption band within the limits of the "half-width" of the ev component system (cf. Chap. 3). As shown in[49], the sums over m in (29) can be replaced by certain integral representations.

Formulas of the type (29) are similar to the quantum-theory formulas of type (9). The Bessel functions are here the analogs of the overlap integrals of the nuclear wave functions (at least at small values of κ); for example,

$$\sum_{m=-\infty}^{\infty} J_m^2(\kappa) = 1, \qquad \sum_{m=-\infty}^{\infty} J_m(\kappa)J_{m+1}(\kappa) = 0$$

in analogy with formulas (11)[49]. The product of the overlap integrals $A_{0v}A_{vk}$ and the product $J_m(\kappa)J_{m+n}(\kappa)$ of the Bessel functions, in accordance with[32], can be represented in the form of very similar series. The most complete correspondence between these series and the estimates of the Stokes-line intensity I_{01} is obtained if one assumes $Q_a = 2Q_z$. This requires, however, a different normalization for the overtones, one dependent on the order of the overtone. It should also be added that the summation over m in (29) corresponds to summation over v in (9).

Formula (29) is sufficient in practice for a description of secondary emission following excitation with quasimonochromatic light. In[32] they consider a more general case and the action of the field of a time-damped

light wave, obtained solutions that include both natural oscillations $x_0(t)$ and induced oscillations $x_1(t)$ and determined the conditions under which partial or complete separation of these oscillations is meaningful. In addition, the problem is extended to include polyatomic molecules with several degrees of freedom for the vibrating atoms, and also to systems with anharmonic vibrations of the nuclei and with a linear dependence of $\nu_e(Q)$. A characteristic feature of the obtained solutions is the presence in the resonance denominators of terms of the type $i(\gamma_e - \Gamma)$. This results in a similarity with the Breit formula (see page 102), but the general solution of the equation of motion of the electron $x(t) = x_0(t) + x_1(t)$ describes a larger group of optical phenomena.

An analysis of the obtained solutions shows that in the absence of external forces the emission spectrum should represent a series of bands of almost dispersion shape, of width γ, with maxima near the frequencies $\nu_e^* + \sum_p m_p \omega_p$, where m_p are series of integers; the amplitudes of the corresponding Fourier components are proportional to $\prod_p J_{m_p}(\kappa_p)$. When an external field is applied, the motion of the electron is described by the function $x(t) = x_0(t) + x_1(t)$, and the emission spectrum is determined by the squares of the modulus of the Fourier integral $\int_0^\infty x(t)e^{iut}dt$ for all frequencies u. Off resonance, the spectrum $x(t)$ can be regarded approximately as the sum of the spectra $x_0(t) + x_1(t)$. The spectrum $x_1(t)$ consists of a number of bands (including overtones and compound tones), which duplicate approximately the form of the exciting line. Their maxima lie approximately near the frequencies $\nu + \sum_p n_p \omega_p$, and the Fourier-component amplitudes off resonance decrease rapidly with increasing n_p. The overtones and the composite tones can appear in the spectra even if ν_e varies sinusoidally. The intensity of each line is proportional to the initial amplitude of the corresponding Fourier component of the electron oscillation. The initial oscillation amplitude corresponding to a composite tone is proportional to the product of the initial oscillation amplitudes corresponding to the fundamental tones whose frequencies make up the frequency of the composite tone.

The condition $\Gamma \gg \gamma_e$ or $\Gamma \ll \gamma_e$ usually makes it possible to restrict the analysis to either $x_0(t)$ or $x_1(t)$. This cannot be done, however, if Γ and γ_e are commensurate, and particularly in the resonance region. A separate analysis of the spectra of the "natural" and "induced" oscillations is meaningful in those cases (in those frequency regions) where these spectra do not overlap.

If the incident-light frequency ν is close to the frequency of one of the components of the vibrational structure of the $0 \rightarrow e$ absorption band (we shall denote it by $\nu_e^* + r\omega$, where the integer r is the "number" of the resonance sublevel), then $x_0(t)$ predominates in general in the sum $x_0(t) + x_1(t)$ at $\Gamma > \omega > \gamma_e$ and small $|r|$, but the share of $x_0(t)$ differs strongly in different bands of the emission structure spectrum. If $|r|$ and $|\gamma_e - \Gamma|$ are sufficiently large, then the spectra $x_0(t)$ and $x_1(t)$ do not overlap in practice, but when $\Gamma \approx \gamma_e$ their separation is meaningless in most cases.

At $\Gamma \approx \gamma_e$ and at minimal values of $|r|$, the secondary emission is close in its character to resonance fluorescence and includes the afterglow. At larger $|r|$ it be-

comes more similar to the nonresonant scattering, and at $r \gg \kappa(\omega/\gamma_e)^{1/2}$ the component $\nu_e^* + r\omega = \nu$ predominates strongly. When $\Gamma \approx \gamma_e \gg \omega$ the spectrum of the resonant radiation should have the form of a broad structureless band in the region of the frequencies of the incident light. At $\Gamma \approx \gamma_e \ll \omega$ and small $|r|$, it should have a vibrational structure similar to that of the absorption band[23].

If γ_e and Γ differ strongly, then the spectra $x_0(t)$ and $x_1(t)$ can be separated in the emission spectrum. In the particular case when ω exceeds γ_e and Γ, the spectrum $x_1(t)$ can contain a series of lines (bands) $\nu + n\omega$, among which the undisplaced component ν predominates, while the spectrum $x_0(t)$ can contain a series of lines $\nu_e^* + m\omega$. The larger Γ, γ_e, $|r|$, and κ, the less intense the secondary emission and all its components. The larger γ_e/ω, γ_e/Γ, and $|r|$, the larger the fraction of the undisplaced component with frequency ν in the spectrum $x_1(t)$ (this component should predominate strongly at large γ_e/ω). In the spectrum $x_0(t)$, the intensity distribution among the components depends, naturally, only on the parameters of the oscillator itself, primarily on the modulation index κ; at small κ, the most intense component is ν_e^*.[23]

The half-width of the components is close to Γ in the spectrum x_1 and close to γ_e in the spectrum x_0. Accordingly, the absorption and natural emission spectra have a pronounced vibrational structure $\nu_e^* + m\omega$ at $\gamma_e < \omega$ and have the form of a broad structureless band at $\gamma_e > \omega$. The spectrum of the induced emission has a structure at $\omega > \Gamma$ and its structureless at $\omega < \gamma_e$, Γ. Cases when one part of the emission spectrum (for example, the part corresponding to x_1) has a vibrational structure while the other is structureless are perfectly feasible.

Thus, depending on the spectral composition of the incident light and on the properties of the oscillator, the secondary emission can have typical features of the scattering of light, of resonance fluorescence, of emission of the intermediate type, or else combine one of these types in one part of the spectrum with another type in another part of the spectrum.

Within the framework of the description of the behavior of a compound oscillator in a time scan at $\omega > \gamma_e > \Gamma$, the frequency ν_e is modulated by the vibrations of the nuclei and approaches periodically the frequency ν of the incident light. During the time when the frequency ν_e is closest to resonance, the amplitude of the electron oscillation increases, and during the succeeding period of time it again decreases (but unevenly, with beats). In the repeated approach to resonance, the amplitude is still large enough. Depending on the frequency ν, the new period of excitation can give rise to oscillations that coincide in phase with those remaining from the preceding period of the excitation (and then the amplitude continues to grow), or quenching of the oscillations can occur. These circumstances cause the appearance of maxima and minima, i.e., the vibrational structure of the absorption band and of the natural emission band. If $\gamma_e \gg \omega$, then the electron oscillations have time to be almost completely damped during one period of the nuclear vibration, and no superposition of the "excitation waves" occurs[23].

According to[23], the intensity of the entire emission spectrum, recorded for a large number of molecules under stationary illumination at resonance with any of

the components $\nu_e^* + m\omega$, is proportional to the absorbed energy and to the fraction of energy lost in the form of secondary emission, i.e., γ_{rad}/γ_e. The absorbed and emitted energies are larger the smaller the values of Γ/γ_e, γ_e/ω, and $|r|$. At $r = 0$ this energy is smaller the larger the depth of modulation $\nu_e(t)$, and the opposite holds true at $r \neq 0$.

The cited data and conclusions show that if one forgoes some of the simplifications of the model, the classical theory yields rather abundant and interesting information on the character of the secondary emission in the spectral and time scans, on the phase correlations between the oscillations in different parts of the emission-band contour, on the energy balance, etc. The qualitative conclusions concerning the energy distribution in the spectrum are in agreement with the conclusions of the quantum theory; certain discrepancies in the quantitative estimates are due partly to the remaining elements of the simplifications and partly to fundamental limitations.

The model of an oscillator with periodically varying rigidity is adequate under certain conditions for the analysis of electron-vibrational motion in a molecule in the quasiclassical approximation of quantum mechanics. The motion of the electron along a trajectory in an effective field with a potential that depends parametrically on q can be described as a nonstationary state made up of a superposition of stationary states. Then the equation describing the motion of the "center of gravity" of the electronic wave packet takes the form

$$(d^2\xi_{av}/dt^2) + v_c^2(q)\,\xi_{av} = 0, \tag{30}$$

where ξ_{av} is the average value of the electron coordinate[49]. If it is assumed that the nuclei execute harmonic oscillations, i.e., are in a superposition state constructed of stationary wave functions of the harmonic oscillator, then (30) coincides with the classical equation for free parametric oscillations of the coordinate ξ.

The classical theory of RS developed in the present chapter does not provide for energy transfer from one degree of freedom to another. Such a transfer can be considered within the framework of the system of equations determining the motion of the electron and of the nuclei:

$$\ddot{x} + \gamma_e\dot{x} + v_c^2(q)\,x = (e_{el}/m_{el})\,\mathscr{E}(t), \quad \ddot{q} + \gamma_{at}\dot{q} + \omega^2(x)\,q = F(x), \tag{31}$$

where $\nu_e(q)$, $\omega(x)$, and $F(x)$ are functions that determine the connection between the motions of the nuclei (q) and of the electron (x). It is possible to represent in this manner the excitation of nuclear vibrations in which the average value of the nuclear coordinate is changed by the action of the light-wave field on the electronic oscillator, the subsequent loss of the nuclear vibration energy, and a transition to free damped oscillations of the electron (i.e., to fluorescence)[23].

Lugovoĭ[98] uses for the description of the RS phenomenon the equation of motion of nuclei acted upon by an external force due to the field of the incident light, under conditions when the polarizability of the molecule depends on q; the equation for a diatomic molecule is

$$\ddot{q} + \gamma_{at}\dot{q} + \omega^2 q = 1/\mu_{at}\,(\partial\alpha/\partial q)\,\mathscr{E}^2, \tag{32}$$

where μ_{at} is the reduced mass of the vibrating atoms, E is the intensity of the external field, and γ_{at} is the damping constant of the atom vibrations. The additional dipole moment induced in the molecule by the external

field when the nuclei are displaced from the equilibrium position is given in the linear approximation in q by

$$P = (\partial\alpha/\partial q)\,q\mathscr{E}. \tag{33}$$

Lugovoĭ[98] considers the action of a biharmonic field, one component of which (with frequency ν) is produced by an external light source, and the other (with frequency $\nu - \omega$) is produced by surrounding molecules of the same type or has the character of zero-point oscillations in space. The former case corresponds to conditions when stimulated RS occurs, and the second corresponds according to[98] to the onset of ordinary RS. In accordance with the material equation (32), the molecule absorbs field energy of frequency ν and produces secondary emission containing the frequency $\nu - \omega$. It should be noted that the resultant oscillation of the indicated biharmonic field (and of the external force in the right-hand side of (32)) can be described as an oscillation with beats of frequency ω; it is therefore capable, in accordance with (32), of giving rise to vibrations of the atoms.

According to (32) and (33), the steady-state energy of radiation with frequency $\nu - \omega$ is proportional to the squares of the amplitudes of the field oscillations of both modes (ν and $\nu - \omega$). By determining the amplitude E_ν in terms of the intensity of the incident light and the amplitude $E_{\nu-\omega}$ in terms of the energy of the zero-point field oscillations, Lugovoĭ[98] obtained for I_{01} an expression equivalent to Placzek's formula. Thus, allowance for the component of the external field $\nu - \omega$ in the considered approximation does not change the results and has a formal character. However, the entire scheme as a whole is of interest, since it brings closer together the methods of describing ordinary and stimulated RS.

A model of two oscillators (electronic and nuclear) coupled via a purely anharmonic element of the type $(x + q)^3$ was proposed in[99]. The oscillations of q at a given temperature are described on the basis of the fluctuation-dissipation theorem. Solution of a system of equations similar to (31) determines the response of the scattering system; resonance points at $\nu = \nu_e$ and $\nu = \nu_e + \omega$ are obtained for the Stokes RS line, just as in accordance with the Loudon formula.

In concluding this section we note that the simplest variant of the classical theory was used extensively to analyze data on the intensity of the RS lines of polyatomic molecules, on the basis of an additive scheme in which individual chemical bonds were ascribed definite polarizability increments. Details concerning the calculation methods, together with examples, are contained, in particular in the book[6] (Secs. 48—49) and in the[100,101,180]. The indicated increments have an arbitrary character, since in real polyatomic molecules the electronic excitation is usually nonlocal[8,102]. In[8] (Sec. 5) it is noted that the derivative of the polarizability of the molecule with respect to the normal coordinate ($\partial\alpha/\partial Q$) can be resolved in terms of the derivatives with respect to the natural coordinates ($\partial\alpha/\partial q_i$) without further separation of the polarizability with respect to the individual chemical bonds.

The relations between the derivatives $\partial\alpha/\partial q$ and the character of the chemical bond are discussed in[8,101]. A comparison of the derivatives $\partial\alpha/\partial q$ for different types of chemical bonds, calculated from the experimental data (far from resonance) for numerous simple molecules, can be found in[8,9,87,101], and a comparison with

the conjugation conditions can be found in[8,91,103]; see also[180].

For practical experimental determination of the derivatives $\partial\alpha_{\rho\sigma}/\partial Q$ and the symmetry of the scattering tensor, one uses suitable intensity standards. Measurements of the intensity and polarization of the lines can be supplemented in this case by information on the scattering indicatrix[104] and the line contours (see, for example,[44]). In individual cases, data were used on the RS energy yield[105] (cf., however,[106]), on the influence of the constant electric field on the intensity of the IR absorption bands[107], on the photoelasticity constants[108], and on the influence of the intermolecular interaction[109].

In addition to the polarizability, vibrations of the atoms can modify also the optical activity; in such a case, differences in the RS line intensities are possible following excitation with right- and left-circularly polarized light. Such differences under the action of a constant or modulated magnetic field make it possible to study the relation between Raman scattering and the Faraday effect[110].

6. SCATTERING OF LIGHT BY CYRSTAL IMPURITY CENTERS

Problems involved in secondary emission by impurity centers in a crystal were considered in[20,21,28] and elsewhere with allowance for the interaction between the electronic excitation of the impurity center with the lattice vibrations and with one of the local vibrations of the impurity-molecule atoms. In such systems, rapid vibrational relaxation (small τ_{ev}) are made possible by the "anharmonic" coupling of the local vibration with the lattice vibrations.

The RS spectra have revealed intensive lines or bands of transitions (predominantly single-phonon) with a change in the lattice-vibration energy and the energy of the impurity-center atom local-vibration line[111,125]. The local-vibration line intensity off resonance is determined, according to[21], mainly by a dependence of the type $M_e(Q)$. For this case, the transformation $(\alpha_{\rho\sigma})_{0k}$ was used, with expansion in powers of the difference of the vibrational Hamiltonians (see Chap. 3); under conditions close to resonance, it was assumed that $M_e(Q)$ is constant at $\Delta_e \neq 0$.

The probability $W(\nu_{em}, \nu)$ of a transition with production of a photon $\hbar\omega$ was described in[21,28] on the basis of a formula of type (1), which included the electronic-oscillator radiative-damping constant γ_{rad}. In another variant, a modified Kubo method was used (method of linear response to a time-dependent perturbation). For resonant excitation and with account taken of one electronic-excitation level e, the somewhat simplified form is obtained

$$W(\nu_{em},\nu) = \text{const} \cdot \nu^4 |M_e|^4 \int_{-\infty}^{\infty} \exp(i\mu\nu_{em} - i\nu\mu)d\mu$$

$$\times \int_0^\infty \exp\left[i(\nu-\nu_{e0})(t-t') - \frac{1}{2}\gamma_{rad}(t+t')\right] A(tt'\mu)\,dt\,dt',$$

$$A(t, t', \mu) \tag{34}$$

$$= \left\langle \exp\left(\frac{it'H_e}{\hbar}\right) \exp\left(\frac{i\mu H_0}{\hbar}\right) \exp\left(\frac{-itH_e}{\hbar}\right) \exp\left[-iH_0(\mu+t'-t)\frac{1}{\hbar}\right]\right\rangle_1,$$

where ν_{em} is the secondary-emission frequency, H_0 and H_e are the vibrational Hamiltonians for the electronic states 0 and e of the molecule, the symbol $\langle...\rangle_1$ denotes temperature averaging over the 0v sublevels. The two

variants are equivalent according to[21] and describe scattering and photoluminescence.

When calculating the correlator $A(t, t', \mu)$, it is possible to take into account the anharmonicity and the damping (γ_{at}) of the atom vibrations in the electronically-excited state (which is introduced in[28] independently of γ_e), and also Δ_e and $\omega^{(e)} \neq \omega^{(0)}$. In[21,28], a small anharmonicity was assumed and the pair-correlation approximation was used. After expanding $A(t, t', \mu)$ in a series and after certain simplifications, formula (34) was used to describe the secondary emission under different excitation conditions. In the case of excitation with monochromatic light near resonance with one ev sublevel, if $\Gamma, \gamma_e \ll \gamma_{at} \ll (\omega^{(e)} - \omega^{(0)}) \ll \omega$, the integration of $W(\nu_{em}, \nu)$ with respect to $d\nu_{em}$ leads to the following expression for the total integrated intensities of the ev $\rightarrow$ 0k resonance-fluorescence line and the 00 $\rightarrow$ 0k Raman-scattering line:

$$I_{0\to v\to k}(\nu) = \frac{\text{const} \cdot \nu^4 |M_e|^4}{(\nu_{ev}-\nu)^2 + \nu^2\gamma_{at}^2} S^{2v+k}$$

$$\times \sum_{n=0}^{k} \sum_{l=0}^{n} \sum_{m}^{n-l} \frac{(-1)^{l+m}S^{-(2k+2n+l+m)}}{(k-n)!\,l!\,m!\,(k-l-m-n)!\,(v-l-k+n)!\,(v-m-n)!} \tag{35}$$

$$= \frac{1}{2v\gamma_{at}}\gamma_{rad}W_{abs}(\nu)\,|A_{vk}|^2;$$

here $W_{abs}(\nu)$ is the absorption probability for the frequency ν, while S is the dimensionless Stokes loss and depends on Δ_e; the subscripts of I denote the successive changes in the quantum numbers of the lattice vibrations. Other cases were also considered ($\Gamma \gg \gamma_{at}$), when only resonance fluorescence is excited, etc.). In all cases, it was assumed that $\gamma_{nonrad} = 0$, when the intensity of the entire secondary emission is close to the intensity of the absorbed light.

The density matrix method was used in[113]; the matrix elements were determined on the basis of perturbation theory by the Perel'-Konstantinov diagram method. It is concluded in[20,21,113] that at $\Gamma \approx 0$, the secondary emission includes only scattering if $\nu < \nu_{e0}$, and the luminescence is γ_{at}/γ_{rad} times more intense than the scattering if $\nu > \nu_{e0}$ (see Chap. 2).

7. EXCITATION OF SPECTRA IN THE REGION OF THE ABSORPTION BAND; EXPERIMENTAL DATA

Resonant Raman scattering of light was first observed in experiments with solutions of p-nitrodiethyl aniline and p-nitrophenolates[41,114a] with excitation in the center of an intense broad structureless absorption b and 0 $\rightarrow$ e, at $\gamma_{ev} > \omega > \Gamma$; it was established that the molar intensity coefficients of certain RS lines are larger by hundreds of thousands of times than under ordinary conditions of excitation far from resonance. According to tentative estimates, τ_{ev} is less than 10^{-12} sec, and the quantum yield (relative to the absorbed light) is of the order of 10^{-6}.

The RS spectra retained the characteristic features of scattering. Thus, the line position was determined by the frequency ν of the incident light, and the half-width did not exceed the usual values (<15 cm^{-1}); the intensity decreased rapidly in the series of lines ν, $\nu - \omega$, $\nu - 2\omega$... From formulas (4), (9), (25), and (26), however, it follows that the resonance RS line intensity, especially the intensities of the overtones, should increase with decreasing γ_{ev} and γ_{ev}/ω; the overtones can constitute an

appreciable fraction of the scattered-light intensity even when γ_{ev} and ω are commensurate (at $\Delta_e \neq 0$).

A dependence of the intensity on γ_{ev} does not mean that the RS should be strongly influenced by the "photoluminescence-quenching" molecules (cf. [27]), since the values of γ_{ev} (unlike γ_{e0}) are in our case still quite large and it is difficult to increase them further. Thus, the quenching molecules can practically eliminate the usual photoluminescence without affecting the RS lines [18,25,114b].

It can be stated that the molecular interaction affects the intensity of the resonance RS lines much less than the fluorescence intensity, but much more than the nonresonant scattering. In the latter case, the lines are usually intensified by 1.3—4 times on going from the gas to the liquid [115,181]. In solutions, when the refractive index of the solvent is increased from 1.2 to 1.6, a 10—60% increase of the intensity was observed [116a] and was ascribed mainly to modification of the incident light-wave field [116b, 181]. Transition to molecular crystals is accompanied by a further increase of the intensity [115b, 117a], which is connected, according to [117b] with phase correlations of the radiating molecules. In the case of resonant excitation of RS, no distinct connection with the refractive index was observed; the predominant factors were the variations of the frequencies ν_{ev}, which can lead to intensity changes by a factor 10—100 and more [18,44,114a]. In the gas → liquid transition, at large values of τ_{ev}, the primary role is assumed by the decrease of τ, which contributes to a decrease of I_{0k}.

The influence of the medium on the line width is much less pronounced in resonance RS than in ordinary and resonance fluorescence. This can be easily explained within the framework of classical and quantum theory. One can use an oscillator model in which the frequency ν_{ev} is modulated by a broad spectrum with average frequency Ω_{MM} as a result of rotation of neighboring dipole molecules and vibrations of the molecules relative to one another. Since the averate lifetime of the corresponding rotational and vibrational states of the molecules in a liquid is very small (almost random motion), and since usually $\gamma_{ev} > \Omega_{MM}$, the probability of combination of the frequencies $\nu \pm k\omega$ with the frequencies Ω_{MM} in induced oscillations of the electronic oscillator is accordingly small [24]. This can be explained within the framework of the quantum model by the analogy with the contributions of the vibrational sublevels ev to the matrix elements of the polarizability α_{0k}. As noted in Chap. 3, the entire ensemble of ev sublevels is effective when $\gamma_e \gg \omega$; in view of the difference in the signs of the contributions of the individual sublevels to all the α_{0k}, with the exception of α_{00}, these contributions cancel each other to a considerable degree when $k \neq 0$, and the unshifted component predominates strongly in the $\nu \pm k\omega$ spectrum.

Later investigations yielded the spectra of resonance scattering of numerous organic and inorganic compounds in solutions [18,19,25,114b, 118-120], spectra of vapors [121], crystals, crystalline powders [122-124,182], amorphous products (glass) [112], impurity centers of crystals [111,126], adsorbed substances [114b, 124b] including those adsorbed in a monomolecular layer [127], compounds in saps and living tissues of plants [128]. Usually (see, however, [123], and also [129], where incidentally the identification of the lines is not reliable), lines were ob-

served only for fully symmetrical vibrations of the atoms (essentially polarized). This agreed with the predictions of the theory, from which it follows that the resonant excitation favors predominance of the factor $\partial\nu_e/\partial Q_p$ (in other words, Δ_{ep})[40], which is significant for fully-symmetrical vibrations. The degree of depolarization ρ for linear and elongated molecules near resonance [41,114b, 130,131] and in the resonance region [119a, 121a, 135b, 138b, 144] reflects the predominant role played by one polarized electron of the electronic transition. The degree of depolarization following excitation near and far from resonance is practically the same according to [73,136]. For the 656 cm^{-1} line of CS_2 according to [137] and for the butadiene line according to [138a], the depolarization following short-wave excitation turned out to be much larger, although it did not exceed 0.5. In the resonance region, a value $\rho > 0.5$ was noted for the ion S_3', [125] and $\rho \approx 0$ was observed for the MnO_4' line [122,123]. Measurements of the polarization and of the intensities of the Q, O, and S branches of the lines of I_2 were made in [138b, 139]. The polarization measurements of the spectra of polyene compounds are taken in [140a] to indicate that the resonance-scattering tensor has a certain asymmetry.

Almost all the compounds investigated in the cited studies have structureless absorption bands. This pertains also to the I_2 molecules in solutions. An interesting feature of the resonance RS spectra of iodine and some other simple molecules and ions is the large relative intensity of the overtones [132-134, 140b], which form a progression $\sim n\omega$. Excitation of the iodine-vapor spectrum in the region of the continuum of the absorption band of the type $^1\Sigma_g^+ \rightarrow ^3\Pi_{0u}$ revealed a progression $\sim n \cdot 213$ cm^{-1} up to the thirteenth overtone [121] (Fig. 5); all the lines were polarized and their width in the $n\omega$ series increased progressively. According to [133], when the excitation is in the fine-structure zone of the same absorption band, the observed secondary-emission lines are depolarized and ascribed to resonance fluorescence; with increasing pressure of the extraneous gas, the depolarization ρ of these lines decreased gradually from 6/7 to 1/2, thus indicating a smooth transition to scattering. Similar observations are described in [141a]; it is noted there that the selection rules for the vibrational quantum number (k) are altered, with a gradual transition from a smooth decrease of the intensity in the series $\nu - k\omega$ (as in Fig. 5) to a typical Franck-Condon distribution of the resonance-fluorescence line intensities (when individual lines of the progression drop out completely under the experimental conditions). In addition, a modification of the rotational structure of the lines was observed when the R branch of the fluorescence line agreed and coincided with the Q branch of the RS line.

The interpretation of the foregoing results and the discrimination between fluorescence and scattering was based in [141b] on whether the contributions to α_{0k} are

FIG. 5. Resonance RS spectrum of iodine vapor excited in the continuum region of the $^1\Sigma_g^+ \rightarrow ^3\Pi_{0u}^+$ band ($\nu = 20,487$ cm^{-1}) [121a].

made by one or several ev sublevels; the value of Γ and its relation with γ_{ev}, ω, Ω, and $\nu_{ev} - \nu$ were not considered (see the exposition in Chap. 2 and following).

A unique picture was observed for bromine vapor. Excitation in the fine-structure zone of the absorption band ($\nu = 14{,}400$ cm^{-1}) revealed a series of doublets; the doublet components $\sim n \cdot 315$ cm^{-1} are polarized and are attributed to resonant RS, while the components $\sim n \cdot 308$ cm^{-1} are depolarized and pertain to resonance fluorescence[142]. It should be noted that depolarization produced when resonance is approached is not a unique criterion for distinguishing between scattering and fluorescence; the depolarization is more readily connected with the quantity Ω/γ_e, where Ω is the rotational frequency, rather than Γ/γ_e.

The high intensity of the overtones in the RS spectra of iodine and bromine when excited in the region of the continuum is explained in[15] on the basis of the assumption that there is no "interference" of the contributions of different excitation levels and that there exists only one level e (having no vibrational sublevels). The frequency factor in the general formula for the intensity I_{0k} of the $0 \to k$ line was integrated in[15,135a] with respect to $d\nu_e$ within the limits of the continuum; in[135a], I_{01} was more readily similar to I_{00}, and in no form did it represent the differences in the signs of $u_{01}(Q)$ in the bands $Q > 0$ and $Q < 0$ (yet these differences are very important and have a bearing on the signs of the contributions of different regions of the continuum); this pertains also to a certain degree to[143]. In this case one cannot exclude the possibility of using classical theory and involving higher derivatives of ν_e and α. In[143], the matrix element of the polarizability (when the density matrix was used) was subdivided into a continuum-band contribution that coincided with the line of the incident light (imaginary part) and the contributions of the remaining bands of the continuum and of the discrete (long-wave) part of the absorption band. In the opinion of the authors of[143,144], the last part is quite important in this case.

An analysis of formulas (4), (9), and (29) has shown that on going from $\gamma_e > \omega > \Gamma$ to $\omega > \gamma_e > \Gamma$ the energy distribution in the series of lines $\nu - k\omega$ (where k = 0, 1, 2, ...) can change and approach to one degree or another the characteristic distribution for the spontaneous emission ev $\to$ 0k. Under these conditions, the energy distribution no longer depends strongly on γ_e, but on the other hand is strongly dependent on the frequency ν of the incident light and on the quantum number v of the corresponding "resonance sublevel," the contribution of which to the polarizability matrix elements is strongly pronounced because of the smallness of the resonance denominator. At resonance with the "Franck-Condon" sublevels v*, the elements $|\alpha_{00}|$ and $|\alpha_{02}|$ should be large (at $|\alpha_{00}| > |\alpha_{02}| > ...$) and the elements $|\alpha_{01}|$ and $|\alpha_{03}|$ should be small. At resonance with other sublevels at large Δ_e, one cannot exclude the possibility that the lines of the RS overtones will turn out to be more intense than the lines of the fundamental tone, and that the line of the fundamental tone is more intense than the line of the undisplaced scattering. Thus, we lose one of the characteristic features of scattering, the progressive and rapid decrease of the intensity in the $\nu - k\omega$ series. The line contours, however, still retain the specific features of scattering and remain independent of γ_{ev} (spectrum of type-I transition)[24].

A qualitative idea concerning the relative values of $|\alpha_{0k}|^2$ and the secondary-emission line intensity $I_{0k}(\nu)$ (i.e., concerning the "excitation spectra" of the RS lines) under conditions when the frequency ν falls in some particular region of the structured absorption band can be gained from Fig. 6.

Excitation of the spectra in the region of the structured absorption band was realized in experiments with solutions of polyene compounds[19,19b,145-147]. Whereas the molar intensity coefficient I^S of the strongest line of nitrodiethyl aniline, when excited at the maximum of the structureless absorption band reaches 4 million units (I^S of the 313 cm^{-1} CCl$_4$ line at $\nu = 22{,}938$ cm^{-1} is assumed equal to 100 units; see[8], Chap. 6), an intensity up to 10^9 was observed in this case, and up to 10^8 units in the case of overtones and composite tones[19,145]; under similar conditions, lines of intensity $\sim 3 \times 10^8$ units were observed in the spectrum of β-carotene[147].

Wtih further decrease of γ_e ($\omega > \gamma_e \geq \Gamma$), a gradual transition should be observed in the resonance-emission spectra ("transition-phenomena of the second kind"), from approximate duplicate of each exciting-line contour component (a distinguishing feature of scattering at $\Gamma > \gamma_{0k}$) to duplicates of the line contours of spontaneous-emission ev $\to$ 0k with weakening and subsequent loss of the dependence of the emission-line positions on the position of the incident-light band (a distinguishing feature of resonance fluorescence). The sensitivity of the emission spectrum to the influence of "quenchers" then increases.

The situation is somewhat more complicated with the lines of the vibrational-rotational RS. The character of the rotational structure of the lines can change already on going from $\gamma_e > \Omega > \Gamma$ to $\Omega > \gamma_e > \Gamma$ (where Ω is the rotational frequency), and the degree of depolarization can increase. When $\Gamma > \Omega > \gamma_e$, the rotational motion of the molecules contributes to complete depolarization of the resonant emission. At the same time, the emission of the atoms at $\Gamma - \gamma_e$ can retain in part the polarization and coherence even in the case of resonant excitation-energy transfer between the atoms atoms[148].

Thus, in the study of secondary emission that occurs without intermediate transitions in the excited state, one can observe, in addition to the characteristic cases of resonant scattering ($\gamma_e \gg \Gamma$, ω, Ω) and resonance fluorescence ($\gamma_e \ll \Gamma$), also some unique transition phenomena, including emission at $\omega > \gamma_e > \Gamma$, Ω and at $\omega > \Omega > \gamma_e > \Gamma$, where some of the features of typical scattering are lost.

Scattering in crystals has certain distinguishing features connected with the possibilities of nonlocal excitations. In experiments with semiconducting and nonconducting crystals, resonance scattering was observed with excitation of phonons[149-153], plasmons, and mixed modes[153,154]. Proximity to resonance greatly favored multiphonon transitions (with excitation of longitudinal optical phonons) and turned out in some cases to be more probable than single-phonon transitions[155,156]. According to[45,157], two-phonon transitions are connected with the simultaneous excitation of two phonons (in one act), and according to[158] they are connected with two successive acts in one intermediate state or in similar states of two successive scattering processes; the second variant, in the form described in[57], is similar
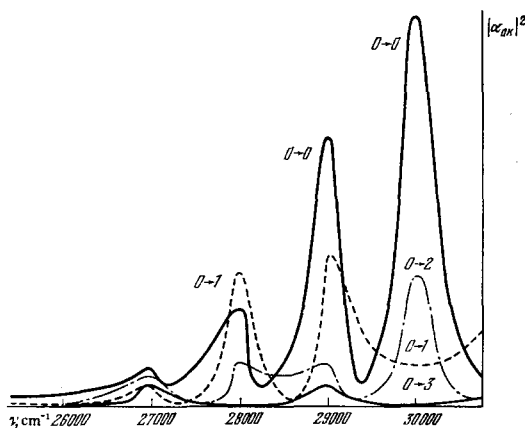
FIG. 6. Relative values of $|\alpha_{0k}|^2$, which determines the "excitation spectra of the RS lines" in the region $\nu \lesssim \nu_{ev*}$ in accordance with formula (9). Diatomic-molecule model, $\omega = 1000$ cm^{-1}, $\nu_{ev*} = 30{,}000$ cm^{-1}, $\gamma_e = 350$ cm^{-1}, $\eta_e = 0$. The maxima of $|\alpha_{0k}|^2$ lie near the maxima of the components of the vibrational structure of the absorption band. The labels on the curves denote the transitions $0 \to k$.

FIG. 7. Spectrum of resonant emission of CdS crystal. $\nu = 18{,}360$ cm^{-1}; LO and 2LO–phonon lines, L$^+$ and L$^-$—mixed unstable phonon-plasmon modes [153].

to hot luminescence. Intermediate states may be free [53,159] and bound excitons [150,158,160], and according to [161] also "exciton polaritons," the wave functions of which are close to the exciton wave functions; the role of the exciton + phonon combined levels (see, for example, [162]) was hardly considered. Scattering is treated as polariton conversion in [54,163]. The RS intensity is connected predominantly with the lattice deformation potential according to [164-165] and with the electron-optical constants [167b] according to [163,167a] (non-symmetrical modes of LO phonons).
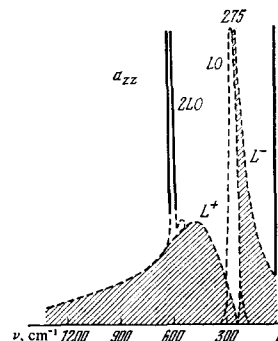
In some cases the semiconductor scattering spectra contained broad asymmetrical bands, which were attributed to transitions to mixed states that decay rapidly (for example, with transition of a plasmon into a single-electron excitation) (see the treatment in Chap. 4 and the example in Fig. 7).

The scattering cross section for the single-phonon transition should have, according to [53,99], two resonance points in the region of one excitation level (when ν or $\nu - \omega$ coincides with the frequency of the transition to the discrete exciton level or with $E_{gap}/\hbar$), which agrees with experiment according to [150]; cf., however, the experimental data in [168-170]. Discrepancies between the maxima of $I(\nu)$ and $\epsilon(\nu)$ were noted in [169,171]. In individual cases, a decrease of the intensity with increasing ν in the pre-resonance region (antiresonance points) were observed [164,172]; it is attributed to cancellation of terms, of which one depends little on ν and the other, of opposite sign, has a resonance denominator in the form $(\nu_e - \nu)^2$.

Proximity to resonance favors an increase of the sensitivity of the intensity to the influence of additional perturbations that modify the positions of the excitation levels. Large changes in the intensity of the CdS lines were observed in [173a] following application of an external magnetic field that caused separation of the Landau sublevels; there are certain data pointing to the influence of electric fields [173b].

Transitions with spin flip due to participation of the conduction electrons were observed near resonance conditions in [174]; the difference between the frequencies of the displaced and undisplaced scattering was de-

termined, naturally, by the intensity of the external magnetic field. A general description of the scattering cross section, including scattering with excitation of magnons and with transitions between Landau levels, is given in [175a] (see also [175b].

RS spectra of metals and metallic compounds were observed in most cases in the region of strong absorption of light [176].

Interesting results of resonance excitation of electronic RS were obtained in experiments with ions of rare-earth elements and solutions [177] and with silicate crystals [170]. The excitation was in the region of very weak absorption bands, but the resonance effect was quite appreciable. In principle it can be sharply pronounced, but "superposition" of contributions of other excitation levels, which favors a smoothing of the $I(\nu)$ dependence, plays an important role.

Different variants of obtaining the resonant hyper-Raman effect were discussed in [71], including the conditions when ν or 2ν coincides with one of the frequencies ν_e, or when ν and 2ν coincide simultaneously with the frequencies of two electronic transitions (double resonance). In the latter case the line intensity can be quite large and comparable with the line intensity of the usual (two-photon) RS.

Excitation of the spectra of stimulated RS in the region of the absorption band could be realized only with accompanying participation of fluorescence emission, which produced a sufficient emission density in the frequency region $\nu - \omega$, but did not interfere significantly with the observation of the narrower RS lines [5,178]. Population inversion of the electronic-excitation level was obtained in experiments where the spectrum of cryptocyanine was excited with a ruby laser, as proposed in [5] (cf., however, [178]); the level in question was regarded as the initial and final state, while the electronic ground state was regarded as intermediate.

* * *

Recent studies have made a large contribution to the development of Raman-scattering spectroscopy. Much progress was made in the measurement techniques. The volume of information obtained from the experiments has increased greatly and its accuracy was improved; new interesting phenomena were described; clearer and more complete ideas were gained concerning the origin of shifted scattering, concerning the relation between scattering and other molecular-optical phenomena, the correlations between different methods of description, and concerning the possibilities and applicability limits of various models of the scattering centers; premises were created for a more effective utilization of scatter-

ing centers; premises were created for a more effective utilization of scattering spectra for molecular-structure analysis and other practical problems.

[1)]The authors of [[28]] classify also photoluminescence as a two-photon process. It should be noted, however, that the demarcations between single-photon and two-photon processes and between real and virtual transitions (as well as between different variants of the chronology of the two-photon process) are all arbitrary.

[2)]It is assumed in [[38]] that the Kramers-Heisenberg-Weisskopf formula describes also photoluminescence.

[3)]However, the interpretation of the "polarizability theory" in [[48]] does not correspond at all to these conditions.

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[1] T. R. Gilson and P. J. Hendra, Laser Raman Spectroscopy, L., Wiley-Interscience, 1970.

[2] Ya. S. Bobovich, Usp. Fiz. Nauk 97, 37 (1969); 108, 401 (1972) [Sov. Phys.-Uspekhi 12, 20 (1969); 15, 671 (1973)].

[3] Advances in Laser Raman Spectroscopy, v. 1 (Proc. of the 3rd Intern. Conference on Raman Spectroscopy, Reims, 1972), L., Heyden and Son, 1972.

[4] R. E. Hester and J. H. Clarke, Raman Spectroscopy, N. Y., W. Benjamin, 1972.

[5] Ya. S. Bobovich and A. V. Bortkevich, Usp. Fiz. Nauk 103, 3 (1971) [Sov. Phys.-Uspekhi 14, 1 (1971)].

[6] J. Brandmuller and H. Moser, Moscow, Mir, 1964.

[7] M. M. Sushchinskiĭ, Spektry kombinatsionnogo rasseyaniya molekul i kristallov (Raman Spectra of Molecules and Crystals), Nauka, 1969.

[8] P. P. Shorygin, Uspekhi khim. 40, 694 (1971).

[9] W. F. Murphy, W. Holzer and H. J. Bernstein, Appl. Spectr. 23, 211 (1969).

[10] G. Eckhardt and W. G. Wagner, J. Mol. Spectr. 19, 407 (1966).

[11] B. I. Stepanov and V. P. Gribkovskiĭ, Vvedenie v teoriyu lyuminestsentsii (Introduction to Luminescence Theory), Minsk, AN BSSR, 1963.

[12] E. W. Small and W. L. Peticolas, Biopolymers 10, 69 (1971).

[13] A. F. Lubchenko and B. M. Pavlik, Fiz. Tverd. Tela 5, 1714 (1963) [Sov. Phys.-Solid State 5, 1246 (1963)].

[14] V. V. Leonov, Zh. Prikl. Spektr. 14, 488 (1971).

[15] J. Behringer, Zs. Phys. 229, 206 (1969).

[16] J. Behringer, Theorie der molekularen Lichtstreuung, München, Universität, 1967.

[17] L. A. Nafie, P. Stein, and W. L. Peticolas, Chem. Phys. Lett. 12, 131 (1971). QD 1.C56

[18] P. P. Shorygin and T. M. Ivanova, Dokl. Akad. Nauk SSSR 121, 70 (1958) [Sov. Phys.-Doklady 3, 764 (1958)].

[19] P. P. Shorygin and T. M. Ivanova, Opt. i spektr. 15, 176 (1963).

[20] E. D. Trifonov and K. Poiker, Fiz. Tverd. Tela 7, 2345 (1965) [Sov. Phys.-Solid State 7, 1897 (1966)].

[21] K. Rebane, V. Hizhnyakov and I. Tehver, AN SSSR 16, 207 (1967).

[22] P. P. Shorygin and L. L. Krushinskiĭ, Opt. i spektr. 17, 551 (1964).

[23] P. P. Shorygin and N. S. Andreev, ibid. 23, 687 (1967).

[24] P. Schorygin and L. Kruschinskiĭ, Ber. Bunsenges. phys. Chem. 72, 495 (1968).

[25] J. Behringer, Zs. Elektrochem. 62, 544 (1958).

[26] K. Rebane, Vtorichnoe svechenie primesnogo tsentra kristalla (Secondary Luminescence of Crystal Impurity Center), Tartu, IFA AN ESSR, 1970.

[27] L. N. Ovander, Opt. i spektr. 4, 555; 5, 10 (1958); 10, 420 (1961).

[28] V. Hizhnyakov and I. Tehver, Phys. Stat. Sol. 39, 67 (1970).

[29] V. A. Morozov and P. P. Shorygin, Opt. i spektr. 20, 214 (1966).

[30] M. Jacon, M. Berjot and L. Bernard, J. de Phys. 30, 850 (1969); 32, 517 (1971); C. R. Ac. Sci. B274, 344 (1972).

[31] L. L. Krushinskiĭ and P. P. Shorygin, Opt. i spektr. 16, 30 (1964).

[32] N. S. Andreev and P. P. Shorygin, ibid. 22, 714 (1967).

[33] I. I. Kondilenko, P. A. Korotkov, and V. L. Strizhevskiĭ, ibid. 9, 26 (1960); 29, 1070 (1970).

[34] M. Ya. Tsenter and Ya. S. Bobovich, ibid. 16, 246, 417 (1964).

[35] I. I. Kondilenko and V. E. Pogorelov, ibid. 19, 41 (1965).

[36] H. Buyken, K. Klauss and H. Moser, Ber. Bunsenges. phys. Chem. 71, 578 (1967).

[37] J. Tang and A. C. Albrecht, in: Raman Spectroscopy, v. 2, N.Y., Plenum Press, 1970.

[38] V. Hizhnyakov and I. Tehver, Phys. Stat. Sol. 21, 755 (1967).

[39] G. Breit, Rev. Mod. Phys. 5, 91 (1933).

[40] P. P. Shorygin, Zh. Fiz. Khim. 25, 341 (1951).

[41] P. P. Shorygin, Zh. Fiz. Khim. 21, 1125 (1947); Dokl. Akad. Nauk SSSR 78, 469 (1951).

[42] L. L. Drushinskiĭ and P. P. Shorygin, Opt. i spektr. 11, 24, 151 (1961).

[43] P. P. Shorygin and T. M. Ivanova, ibid. 25, 200 (1968).

[44] P. P. Shorygin, Izv. Akad. Nauk SSSR, ser. fiz. 12, 576 (1948); 13, 328 (1949).

[45] M. L. Williams and J. Smit, Sol. State Comm. 8, 2009 (1970).

[46] F. A. Savin, Opt. i spektr. 19, 555 (1965); 20, 989 (1966).

[47] a) E. M. Verlan, ibid., p. 605, 802; b) L. Rimai and M. E. Heyde, Chem. Phys. Lett. 10, 207 (1971).

[48] J. I. Musher and J. M. Schulman, Intern. J. Quantum Chem., No. 5, 183 (1971).

[49] L. L. Krushinskiĭ and P. P. Shorygin, Opt. i spektr. 19, 562 (1965).

[50] A. C. Albrecht, J. Chem. Phys. 34, 1476 (1961).

[51] W. L. Peticolas, L. Nafie and P. Stein, ibid. 52, 1576 (1970).

[52] C. H. Ting, Spectrochim. Acta A24, 1177 (1968).

[53] B. Bendow and J. L. Birman, ibid. B1, 1678 (1970); B4, 552 (1971).

[55] R. Loudon, Adv. Phys. 13, 423 (1964); J. de Phys. et Rad. 26, 677 (1965).

[56] J. A. Koningstein, J. Mol. Spectr. 28, 309 (1968).

[57] R. M. Martin and C. M. Varma, Phys. Rev. Lett. 26, 1241 (1971).

[58] P. Shorygin, Pure and Appl. Chem. 4, 87 (1962).

[59] J. M. Schulman, R. Detrano, and J. I. Musher, Phys. Rev. A5, 1125 (1972).

[60] A. J. Sadlej, Spectrochim. Acta A26, 421 (1970).

[61] I. K. Kondilenko and V. E. Pogorelov, Opt. i spektr. 26, 203 (1969).

[62] J. Tang and A. C. Albrecht, J. Chem. Phys. 49, 1144 (1968).

[63] F. A. Savin, Opt. i spektr. 15, 42 (1963); 19, 743 (1965).

[64] H. Hacker, Dissertation (Universität München, 1968).

[65] V. A. Morozov, Opt. i spektr. 18, 198; 19, 35 (1965).

[66] V. A. Morozov, ibid. 21, 145 (1966).

[67] O. S. Moretnsen, Chem. Phys. Lett. 5, 515 (1970).

[68] J. A. Koningstein, in: Spectroscopy in Inorganic Chemistry, v. 2, N.Y., Academic Press, 1971, p. 79.

[69] J. A. Koningstein and G. Mace, Chem. Phys. Lett. 3, 443 (1969).

[70] Ying-Nan Chiu, J. Chem. Phys. 52, 3641, 4950 (1970).

[71] D. A. Long and L. Stanton, Proc. Roy. Soc. A318, 441 (1970).

[72] L. Stanton, Mol. Phys. 23, 601 (1972).

[73] M. M. Sushchinskiĭ and V. A. Zubov, Opt. i spektr. 13, 766 (1962).

[74] E. M. Verlan, ibid. 20, 1003 (1966); 26, 899 (1969).

[75] D. F. Walls, Zs. Phys. 224, 117 (1971).

[76] P. A. Apanasevich, Opt. i spektr. 5, 99 (1958).

[77] V. Fano and J. W. Cooper, Phys. Rev. A137, 1364 (1965).

[78] V. A. Morozov, Opt. i spektr. 22, 971 (1967).

[79] V. A. Morozov and P. P. Shorygin, ibid. 19, 289 (1965).

[80] M. Bixon and J. Jorther, Mol. Phys. 17, 109 (1969).

[81] V. A. Morozov, Opt. i spektr. 20, 491 (1966); 23, 3 (1967).

[82] I. I. Kondilenko and V. E. Pogorelov, ibid. 31, 380 (1971).

[83] P. Schorygin and L. Kruschinskij, Zs. Phys. 150, 332 (1958).

[84] P. P. Shorygin and L. L. Krushinskii, Dokl. Akad. Nauk SSSR 133, 337 (1960) [Sov. Phys.-Doklady 5] Fizicheskie problemy spektroskopii, materialy XIII soveshchaniya (Physical Problems of Spectroscopy, Proc. 13th Conf.), Leningrad, 4 July 1960, Vol. 1, AN SSSR, 1962, p. 346.

[85] M. Jacon and L. Bernard, C. R. Ac. Sci. B274, 344 (1972).

[86] Y. Kato and H. Takuma, J. Chem. Phys. 54, 5398 (1971); R. J. Clark and C. J. Willis, J. Chem. Soc. A, 838 (1971).

[87] R. J. Clark and C. J. Willis, Inorg. Chem. 10, 1118 (1971).

[88] R. J. Clark, B. K. Hunter and P. D. Mitchell, J. Chem. Soc. Farad. Trans., ser. II, 68, 476 (1972).

[89] J. Behringer, in Raman Spectroscopy, v. 1, N.Y., Plenum Press, 1967, p. 168.

[90] J. Brandmüller and H. Hacker, Zs. Phys. 184, 14 (1965); A. C. Albrecht and M. C. Hutley, J. Chem. Phys. 55, 4438 (1971).

[91] E. D. Schmid and B. Brosa, ibid. 56, 6267 (1972); Preprint, 1972.

[92] B. Brosa, Dissertation (Universität Freiburg, 1972).

[93] W. Hofmann and H. Moser, Ber. Bunsenges. Phys. Chem. 64, 310 (1960); 68, 129 (1964).

[94] J. Behringer, J. Brandmüller and K. Klauss, Zs. Naturforsch. 23a, 2121 (1968).

[95] B. L. Tomlinson and W. L. Peticolas, J. Chem. Phys. 52, 2154 (1970).

[96] L. L. Krushinskii, Opt. i spektr. 14, 767; 15, 747 (1963).

[97] L. N. Ovander, Fiz. Tverd. Tela 4, 1471 (1962) [Sov. Phys.-Solid State 4, 1081 (1962)]; Opt. i spektr. 26, 519 (1969).

[98] V. N. Lugovoi, Vvedenie v teoriyu vynuzhedennogo kombinatsionnogo rasseyaniya (Introduction to Theory of Stimulated Raman Scattering), Nauka, 1968.

[99] A. S. Barker and R. Loudon, Rev. Mod. Phys. 44, 18 (1972).

[100] L. M. Sverdlov, M. A. Kovner, and E. P. Kraĭnov, Kolebatel'nye spektry mnogoatomnykh molekul (Vibrational Spectra of Polyatomic Molecules), Nauka, 1970.

[101] M. Wahl, Spectrochim. Acta A26, 1963 (1970).

[102] L. S. Mayants and B. S. Averbukh, Teoriya i raschet intensivnosteĭ v kolebatel'nykh spektrakh molekul (Theory and Calculation of Intensities in Vibrational Spectra of Molecules), Nauka, 1971.

[103] E. D. Schmid, G. Berthold and B. Brosa, Ber. Bunsenges. phys. Chemie 75, 1334 (1971).

[104] T. C. Damen, R. C. Leite and S. P. Porto, Phys. Rev. Lett. 14, 9 (1965); L. Nafie, P. Stein and W. Peticolas, J. Chem. Phys. 52, 1584 (1970).

[105] I. I. Kondilenko and P. A. Korotkov, Opt. i spektr. 17, 457 (1964); 23, 894 (1967).

[106] N. K. Sidorov, ibid. 26, 104 (1969).

[107] E. Anastassakis and E. Burstein, Phys. Rev. B2, 1952 (1970).

[108] A. M. Maradudin and E. Burstein, ibid. 164, 1081 (1968).

[109] O. I. Arkhangel'skaya and N. G. Bakhshiev, Opt. i spektr. 31, 53 (1971).

[110] L. D. Barron and A. D. Buckingham, Mol. Phys. 20, 1111 (1971); 23, 145 (1972).

[111] I. R. Nair and C. E. Hathaway, Phys. Lett. A30, 253 (1969).

[112] R. J. Kobliska and S. A. Solin, Sol. Stat. Comm. 10, 231 (1972).

[113] K. Poiker and E. D. Trifonov, Fiz. Tverd. Tela 10, 1705 (1968) [Sov. Phys.-Solid State 10, 1346 (1968)].

[114] a) P. P. Shorygin, Dokl. Akad. Nauk SSSR 87, 201 (1952); Izv. AN SSSR, ser. fiz. 17, 581 (1953) b) L. Rimai, D. Gill, and J. L. Parsons, J. Am. Chem. Soc. 93, 1353 (1971).

[115] a) G. A. Vorob'eva and I. I. Kondilenko, Ukr. Fiz. Zh. 13, 193 (1968). b) F. Perzl and H. Moser, J. Mol. Spectr. 26, 237 (1968).

[116] a) G. Fini, P. Mirone, and P. Patella, ibid. 28, 144; L. P. Kalashnikova and N. K. Sidorov, Opt. i spektr. 28, 260; 29, 421 (1970); b) R. Hornischer and H. Moser, Zs. Phys. Chem. 73, 118 (1970); N. K. Sidorov, L. S. Stal'makhova, and N. V. Bogachev, Opt. i spektr. 30, 693 (1971); V. S. Libov and N. G. Bakhsheiv, ibid. 31, 48.

[117] a) V. S. Ryazanov and M. M. Sushchinskiĭ, Zh. Eksp. Teor. Fiz. 54, 1099 (1968) [Sov. Phys.-JETP 27, 589 (1968)]; b) L. A. Shelepin, ibid., p. 1463 [784].

[118] H. W. Schrötter, Zs. Elektrochem. 64, 853 (1960); W. Maier and F. Dörr, Appl. Spectr. 14, 1 (1960); W. Krasser, H. W. Nürnberg, Naturwiss. 54, 134 (1967); R. J. Gillespie and M. J. Morton, Chem. Comm Comm., 1565 (1968); W. Krasser and H. W. Nürnberg, Zs. Naturofrsch. A25, 1394 (1970).

[119] a) H. W. Schrötter and J. Brandmüller, in: Advances in Molecular Spectroscopy, N. Y., Pergamon Press, 1962, p. 1128; b) L. Rimai, R. G. Kilponen and D. Gill, J. Am. Chem. Soc. 92, 3824 (1970).

[120] M. E. Heyde, L. Rimai and R. G. Kilponen, ibid. 94, 5222 (1972).

[121] a) W. Holzer, W. F. Murphy and H. J. Bernstein, J. Chem. Phys. 52, 399 (1970); b) W. Kiefer and H. J. Bernstein, ibid. 57, 3017 (1972).

[122] W. Kiefer and H. J. Bernstein, Chem. Phys. Lett. 8, 381 (1971); Preprint, 1972.

[123] W. Kiefer and H. J. Bernstein, Mol. Phys. 23, 835 (1972).

[124] a) Ya. S. Bobovich and Ya. A. Éĭdus, Opt. i spektr. 16, 424 (1964); b) P. C. Li, J. P. Devlin, and H. A. Pohl, J. Phys. Chem. 76, 1026 (1972).

[125] W. Holzer, W. F. Murphy and H. J. Bernstein, J. Mol. Spectr. 32, 13 (1969); Chem. Phys. Lett. 4, 641 (1970).

[126] J. M. Worlock and S. P. Porto, Phys. Rev. Lett. 15, 697 (1969).

[127] P. J. Hendra and P. M. Stratton, Chem. Rev. 69, 342 (1959); P. J. Hendra and E. Loader, Trans. Farad. Soc. 67, 828 (1971).

[128] D. Gill, R. G. Kilponen and L. Rimai, Nature 227 (5259), 743 (1970).

[129] M. Tasumi, Chem. Lett. 1 (1), 75 (1972).

[130] D. G. Rea, J. Mol. Spectr. 4, 499 (1960).

[131] Ya. S. Bobovich and N. M. Belyaevskaya, Opt. i spektr. 19, 198 (1965); 22, 315 (1967).

[132] R. J. Gillespie and M. J. Morton, J. Mol. Spectr. 30, 178 (1969).

[133] I. R. Beattie, G. A. Ozin and R. O. Perry, J. Chem. Soc. A, 2071 (1970).

[134] O. S. Mortensen, J. Mol. Spectr. 39, 48 (1971).

[135] a) O. S. Mortensen, Mol. Phys. 22, 179 (1971); b) W. Kiefer and J. J. Bernstein, Chem. Phys. Lett. 16, 5 (1972).

[136] M. Ya. Tsenter and Ya. S. Bobovich, Opt. i spektr. 12, 54 (1962).

[137] L. Bernard and R. Dupeyrat, J. de Chim. Phys. 65, 410 (1968).

[138] a) V. A. Zubov, Tr. FIAN 30, 3 (1964); b) M. Berjot, M. Jacon, and L. Bernard, C. R. Ac. Sci. B274, 404 (1972).

[139] W. Kiefer and H. J. Bernstein, J. Mol. Spectr. 43, 366 (1972).

[140] a) D. Gill, R. G. Kilponen and L. Rimai, Chem. Phys. Lett. 8, 634 (1971); b) W. Kiefer and H. J. Bernstein, Appl. Spectr. 25, 500, 609 (1971).

[141] a) M. Berjot, M. Jacon and L. Bernard, Canad. J. Spectr. 17, 60 (1972); b) M. Jacon, M. Berjot and L. Bernard, C.R. Ac. Sci. B273, 956 (1971).

[142] W. Kiefer and H. W. Schrötter, J. Chem. Phys. 53, 1612 (1970).

[143] M. Jacon, M. Berjot and L. Bernard, C. R. Ac. Sci. B273, 595 (1971).

[144] M. Berjot, M. Jacon and L. Bernard, Opt. Comm. 4, 117, 246 (1971); 5, 94 (1972).

[145] T. M. Ivanova, L. A. Yanovskaya, P. P. Shorygin, Opt. i spektr. 18, 206 (1965).

[146] M. C. Hutley and D. J. Jacobs, Chem. Phys. Lett. 3, 711 (1969).

[147] M. C. Hutley and D. J. Jacobs, ibid. 6, 269 (1970).

[148] L. Chiu, J. Chem. Phys. 52, 366 (1970).

[149] J. F. Scott, T. C. Damen and R. C. Leite, Sol. State Comm. 7, 953 (1969).

[150] R. C. Leite and J. F. Scott, Phys. Rev. Lett. 22, 130, 780 (1969).

[151] A. Pinczuk and E. Burstein, ibid. 21, 1073 (1968).

[152] R. M. Martin and T. C. Damen, ibid. 26, 86 (1971).

[153] J. F. Scott, Sol. State Comm. 9, 759 (1971).

[154] A. Pinczuk, L. Brillson and E. Burstein, Phys. Rev. Lett. 27, 317 (1971).

[155] J. F. Scott, Phys. Rev. B2, 1209 (1970).

[156] J. F. Scott and T. C. Damen, ibid. B3, 1295 (1971).

[157] M. V. Klein and S. P. Porto, Phys. Rev. Lett. 22, 782 (1969).

[158] J. F. Soctt, R. C. Leite and T. C. Damen, Phys. Rev. 188, 1285 (1969).

[159] A. K. Ganguly and J. L. Birman, ibid. 162, 806 (1967).

[160] P. J. Colwell and M. V. Klein, Sol. State Comm. 8, 2095 (1970).

[161] J. J. Hopfield, Phys. Rev. 182, 945 (1969).

[162] M. P. Fontana and E. Mulazzi, Phys. Rev. Lett. 25, 1102 (1970).

[163] E. Burstein, D. L. Mills and A. Pinczuk, ibid. 22, 348 (1969).

[164] J. M. Ralston, R. L. Wadsack and R. K. Chang, ibid. 25, 814 (1970).

[165] E. Anastassakis and C. H. Perry, Phys. Rev. B4, 1251 (1971).

[166] R. M. Martin, ibid., p. 3676.

[167] a) W. G. Nilsen, ibid. 182, 838 (1969); b) J. D. Masso, C. Y. She and D. Edwards, Phys. Rev. B1, 4179 (1970); W. D. Johnston, ibid., p. 3494.

[168] E. F. Gorss, A. G. Plyukhin and L. G. Suslina, ZhETF Pis. Red. 15, 312 (1972) [JETP Lett. 15, 220 (1972)].

[169] F. Cerdeira, W. Dreybrodt and M. Cardona, Sol. State Comm. 10, 591 (1972).

[170] R. L. Wadsack and R. K. Chang, ibid., p. 45.

[171] J. B. Renucci, M. A. Renucci and M. Cardona, ibid. 9, 1235 (1971).

[172] T. C. Damen and J. F. Scott, ibid., p. 383.

[173] a) T. C. Damen and J. Shah, Phys. Rev. Lett. 26, 249 (1971); b) L. Brillson and E. Burstein, ibid. 27, 808.

[174] C. K. Patel and R. E. Slusher, Phys. Rev. 167, 413 (1968); 177, 1200 (1969); P. A. Fleury and J. F. Scott, ibid. B3, 1979 (1971); S. R. Brueck and A. Mooradian, Phys. Rev. Lett. 28, 161 (1972).

[175] a) F. A. Blum, Phys. Rev. B1, 1125 (1970); b) V. P. Makarov, Zh. Eksp. Teor. Fiz. 55, 704 (1968) [Sov. Phys.-JETP 28, 366 (1969)].

[176] J. F. Scott, R. F. Leheny and J. P. Remeika, Phys. Rev. B2, 3883 (1970); W. J. Brya, Sol. State Comm. 9, 2271 (1971); R. Srivastava and L. L. Chase, Phys. Rev. Lett. 27, 727 (1971).

[177] A. Kiel and J. F. Scott, Phys. Rev. B2, 2033 (1970); P. Grünberg and J. A. Koningstein, J. Chem. Phys. 53, 4584 (1970).

[178] M. B. Melishchuk, E. A. Tikhonov and M. T. Shpak, Zh. Prikl. Spektr. 16, 642 (1972).

[179] A. H. Kalantar, E. S. Franzosa and K. K. Innes, Chem. Phys. Lett. 17, 335 (1972).

[180] M. E. Koenig and M. Bigorne, Spectrochim. Acta A28, 1693 (1972).

[181] W. Rohman and E. Welsch, Zs. phys. Chem. 250, 237 (1972).

[182] T. Fukumoto, H. Yoshida and S. Nakashima, J. Phys. Soc. Japan 32, 1674 (1972).

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