

Optical properties of molecules in the field of resonant low-frequency laser radiation

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We investigate the singularities of the optical spectra of light absorption and emission by a molecule in the field of a low-frequency laser at resonance with the frequency of the dipole-active molecular vibration. The optical characteristics of the molecule are calculated by solving the kinetic equation for the density matrix of the vibrational subsystem in an external electromagnetic field. The effect of enhancement of the red (long-wave) wing of the laser radiation is theoretically interpreted. A dependence of the optical effects on the intensity and duration of the laser pulse is indicated.

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1. Turning-on a low-frequency laser that emits at resonance with the dipole-active molecule vibrations should lead to a substantial transformation of the bands of light absorption and scattering by the molecule, owing to the effects of the electron-vibrational interaction with participation of "hot" vibrations. If the excited electronic state lies below the dissociation threshold (see, e.g., Ref. 1), then a unique manifestation of electron-vibrational effects is made possible by the selective excitation of these states. In particular, anti-Stokes luminescence can appear as a result of multiphoton absorption of infrared (IR) radiation and ensure a nonadiabatic transition of the electron from the ground to the excited state ("inverse nonradiative transition") with subsequent emission of a short-wave photon (see also experiments on the so-called instantaneous luminescence²). Another interesting fact is the experimental observation of the effect of enhancement of the red (long-wave) absorption wing of the probing radiation, due to the participation of vibrations excited by the laser radiation in the light-absorption process.^{3,4} In addition, the shapes of the absorption and emission bands turn out to be dependent on the intensity of the laser radiation.³ (Under definite conditions,³ the effects depend also on the laser-pulse energy.)

The present paper is devoted to the development of a consistent theory of the optical properties of molecules in a low-frequency resonant laser field. We consider separately the cases of noncentrosymmetric (NSC) and centrosymmetric (CS) molecules. In the former case the dipole-active vibration excited by the laser radiation interacts directly with the electron. In the latter case this interaction is due to anharmonic coupling of the vibrations [for example, the dipole-active (q) and the fully symmetrical (Q) vibrations of the molecule].

The mathematical description of the problem reduces to a solution of the equation for the density matrix of the vibrational system in an external electromagnetic field, with account taken of the interaction of this system with the dissipative subsystem. The latter may constitute vibrations having a sufficiently dense vibrational-rotational spectrum, or else radiation fields. The expression obtained for the density matrix is used to calculate the cross sections of various optical processes

(absorption, secondary emission, optical luminescence of a two-term molecule), as well as to calculate the average vibrational occupation numbers $\bar{n}(t)$ in the IR field. In particular, the formula obtained for $n(t)$ [see (16)] takes for times $t \lesssim \Gamma^{-1}$ (is the effective width of the excited electronic term) the form

$$\bar{n}(t) = n + \Delta n(t), \quad (1)$$

where

$$\Delta n(t) \approx (ft/2\hbar)^2, \quad t \lesssim \Gamma^{-1} \ll \gamma^{-1}, \\ f = 2\hbar\omega \frac{F}{F_0}, \quad F_0 = e_0 \frac{\hbar\omega}{\mu^2} \left(\frac{\hbar}{M\omega} \right)^{1/2}.$$

Here n is the Planck occupation number, M , μ , and ω are the mass, dipole moment, and frequency corresponding to the q -vibration, e is the electron charge, F is the amplitude of the resonant IR radiation, and γ is the damping constant of the q -vibration. Heating effects are apparently significant if the inequality $\Delta n \geq n$ holds for times $t \sim \Gamma^{-1}$. This inequality limits the amplitude of the external electromagnetic field:

$$F \geq F^* = \frac{F_0 \Gamma}{\omega} n^{1/2}. \quad (2)$$

At $T = 300$ K, $\hbar\omega \sim 0.12$ eV, $M \sim 10^{-23}$ g, $\mu \sim 0.1$ D, and $\Gamma \sim 10^9$ sec⁻¹ we have $F^* \sim 10^3$ V/cm. Thus, the heating effects become appreciable at relatively low values of the electromagnetic field intensity. We note that if the laser pulse duration is $\tau_0 < \Gamma^{-1}$, then the heating effects are practically negligible, so that only the pulses of duration $\tau_0 > \Gamma^{-1}$ are important. A dependence of the optical effects on the laser-pulse energy should then be expected at $\tau_0 \lesssim \gamma^{-1}$. At $\tau_0 > \gamma^{-1}$ a stationary case is realized and the optical effects should depend only on the laser-radiation power.

2a. We obtain now a kinetic equation for the density matrix of the system in the case of a noncentrosymmetric molecule, when the dipole-active q -vibration excited by the laser radiation interacts directly with the electron. In the weak-anharmonicity model, account should be taken of the width of the vibrational level. For molecules with few atoms, as is well known, it is necessary to take the vibrational-rotational interactions into account.⁵ For polyatomic molecules the constant of the vibrational-rotational interaction is small

(because of the large moment of inertia), and a greater role is assumed by the vibrational-rotational interactions. To be definite, we shall consider hereafter the latter case.

We choose the interaction of the q -vibrations with the dissipative subsystem in the form

$$V_{\beta\tau} = \sum_{j_1, \dots, j_n} f_{j_1, \dots, j_n} \beta_{j_1, \dots, j_n}^+ t_{j_1, \dots, j_n}^+ + \text{H.c.}$$

[Here β^+ , t_j^+ (β , t_j) are the creation (annihilation) operators of the dipole-active q -vibrations and of the dissipative-subsystem vibrations, respectively]. The term $V_{\beta\tau}$ contains contributions from 2, 3, and more vibrational interactions, defined by the anharmonic-coupling coefficient functions $f_{j_1}, f_{j_1 j_2}, \dots$. Using the Zwanzig's projection method,⁶ and making the usual assumption that where dealing with a Markov process,⁷ we can obtain for the reduced density matrix $\sigma = \text{sp}_{\mathcal{T}} \rho$ the following kinetic equation ($\text{sp}_{\mathcal{T}}$ denotes summation over the variables of the dissipative subsystem):

$$\dot{\sigma}(t) = \frac{1}{i\hbar} [V_{\beta}(t), \sigma(t)] - \frac{\gamma}{2} \{ (1+n) (\beta^+ \beta \sigma - 2\beta \sigma \beta^+ + \sigma \beta \beta^+) + n (\beta \beta^+ \sigma - 2\beta^+ \sigma \beta + \sigma \beta \beta^+) \}. \quad (3)$$

Here

$$\frac{\gamma}{2} = \frac{\pi}{\hbar^2} \sum_{j_1, \dots, j_n} |f_{j_1, \dots, j_n}|^2 n! [(1+n_{j_1}) \dots (1+n_{j_n}) - n_{j_1} \dots n_{j_n}] \delta(\omega - \omega_{j_1} - \dots - \omega_{j_n}), \quad (4)$$

ω_j and n_j are the frequency and Planck occupation number of the j -th vibration of the dissipative subsystem;

$$V_{\beta}(t) = g(t) \beta + g^*(t) \beta^+ \quad (5)$$

describes the interaction of the q -vibrations with the IR laser radiation [$g(t) = f(t) \sin \omega_l t e^{-i\omega_l t}$, and the form of the function $f(t)$ is determined by the shape of the laser pulse]. If $\sigma(t)$ is specified in normal form, then in the basis of the coherent states it is easy to obtain for the normal (N) form of the density matrix $\sigma^{(N)}(\alpha, \alpha^*; t) = \langle \alpha | \sigma(t) | \alpha \rangle$ the following solution of Eq. (3) (see Ref. 8, p. 170):

$$\sigma^{(N)}(\alpha, \alpha^*; t) = \frac{1}{1+n} \exp \left\{ \frac{-|\alpha|^2 + \beta(t) \alpha + \beta^*(t) \alpha^* - |\beta(t)|^2}{1+n} \right\}, \quad (6)$$

$$\beta(t) = \frac{i}{\hbar} \int_0^t dt' g(t') \exp \left\{ -\frac{\gamma}{2} (t-t') \right\}. \quad (7)$$

2b. We consider next the case of a centrosymmetric molecule. We choose for simplicity the interaction between the q - and Q -vibrations in the form

$$V_{\beta b} = w(b^+ \beta + \text{H.c.})$$

[b^+ (b) is the operator of the creation (annihilation) of the Q -vibration, and w is the constant of the anharmonic coupling of the q - and Q -vibrations].

If we change over to new Bose operators A and B :

$$b = A \cos \psi + B \sin \psi, \quad \beta = B \cos \psi - A \sin \psi \quad (8)$$

[here $\text{tg} 2\psi = 2w/(\omega_2 - \omega_1)$, ω_1, ω_2 are respectively the frequencies of the Q - and q -vibrations], then the reduced density matrix $\sigma(t)$ of the vibrational subsystem of the centrosymmetric molecule satisfies, in second order in the interaction with the dissipative subsystem, the

kinetic equation

$$\dot{\sigma}(t) = \frac{1}{i\hbar} [V_{\beta}(t), \sigma(t)] - \frac{\tilde{\gamma}_B}{2} \{ (1+n_B) (B^+ B \sigma - 2B \sigma B^+ + \sigma B^+ B) + n_B (B B^+ \sigma - 2B^+ \sigma B + \sigma B B^+) \} - \frac{\tilde{\gamma}_A}{2} \{ (1+n_A) (A^+ A \sigma - 2A \sigma A^+ + \sigma A^+ A) + n_A (A A^+ \sigma - 2A^+ \sigma A + \sigma A A^+) \}. \quad (9)$$

Here $n_{A,B}$ is the Planck distribution of the vibrations of frequency $\omega_{A,B} = \omega_{1,2} \cos^2 \psi + \omega_{2,1} \sin^2 \psi \mp w \sin 2\psi$; $\tilde{\gamma}_A$ is the damping constant:

$$\frac{\tilde{\gamma}_A}{2} = \frac{\pi}{\hbar^2} \sum_{j_1, \dots, j_n} |f_{j_1, \dots, j_n}|^2 n! [(1+n_{j_1}) \dots (1+n_{j_n}) - n_{j_1} \dots n_{j_n}] \times \delta(\omega_A - \omega_{j_1} - \dots - \omega_{j_n}) \sin^2 \psi = \frac{\gamma_A}{2} \sin^2 \psi; \quad (10)$$

$\tilde{\gamma}_B$ is obtained from $\tilde{\gamma}_A$ by replacing ω_A with ω_B and $\sin \psi$ with $\cos \psi$. We have retained in Eq. (9) the non-oscillating terms and neglected the terms proportional to $\exp[\pm i(\omega_A - \omega_B)t]$, inasmuch as we shall be interested hereafter in the behavior of $\sigma(t)$ at $t \sim \Gamma^{-1}$ (it is assumed that $|\omega_A - \omega_B| \Gamma^{-1} \gg 1$).

We seek the solution of (9) in the form $\sigma(t) = \sigma_A \sigma_B$. In this case $\sigma_B(t)$ satisfies the equation

$$\dot{\sigma}_B(t) = \frac{1}{i\hbar} [V_B(t), \sigma_B(t)] - \frac{\tilde{\gamma}_B}{2} \{ (1+n_B) (B^+ B \sigma_B - 2B \sigma_B B^+ + \sigma_B B^+ B) + n_B (B B^+ \sigma_B - 2B^+ \sigma_B B + \sigma_B B B^+) \}. \quad (11)$$

Here $\tilde{V}_B(t)$ is that part of the operator $\tilde{V}_{\beta}(t)$ which contains the operators B and B^+ . The equation for $\sigma_A(t)$ is obtained accordingly by replacing B with A and $\tilde{\gamma}_B$ with $\tilde{\gamma}_A$. The solution of Eq. (9) for the normal forms of $\sigma_{A,B}$ is similar to (6).

3. We consider now the expression for the average dissipative power of probing optical radiation of frequency Ω with field intensity $\mathbf{E}(t)$, absorbed by a gas of two-term molecules. The change of the average energy U of the system per unit time can be connected with the average value of the dipole-moment operator d in the following manner⁹:

$$\frac{dU}{dt} = -\langle \mathbf{E}(t) \langle d \rangle_t \rangle, \quad \langle d \rangle_t = \text{Sp} \{ \rho(t) \}, \quad (12)$$

where $\rho(t)$ is the complete density matrix of the system in question. The quantity

$$K_t^F(\Omega) = \frac{8\pi}{c n_0 E^2 V} \frac{dU}{dt}$$

over a time t greatly exceeding the characteristic relaxation time in the system, has the meaning of the coefficient of absorption of light of frequency (c is the speed of light in vacuum, n_0 is the refractive index in the medium, and V is the volume of the system). In the general case, for a measurement time T , it is meaningful to introduce the averaged characteristic

$$K^F(\Omega) = \frac{1}{T} \int_{-T/2}^{T/2} dt K_t^F(\Omega).$$

The light absorption coefficient $K^F(\Omega)$ averaged over the detector measurement time coincides with the "instantaneous" value of the light absorption coefficient $K_t^F(\Omega)$, if $K_t^F(\Omega)$ is practically independent of t during the detector measurement time T .

In the analysis of the optical processes in an electron-

vibrational system, we shall confine ourselves to the adiabatic approximation, inasmuch as for a nondegenerate electronic state the nonadiabatic terms of the electron-vibrational interaction are significant only in the case of nonradiative transitions. The corresponding level widths, governed by nonadiabatic effects can be taken into account phenomenologically by introducing the damping constant Γ . We confine ourselves, as usual, to the lowest order in the interaction of the electron with the probing light of frequency Ω . Under these approximations, the expression for the absorption coefficient $K_i^F(\Omega)$ takes the form

$$K_i^F(\Omega) = \frac{2\pi\Omega}{\hbar c n_0 V} |d_{12}|^2 \operatorname{Re} \int_0^\infty d\tau \exp\left[-i(\Omega - \epsilon)\tau - \Gamma \frac{\tau}{2}\right] \times \langle U_1(t, t-\tau) U_2(t-\tau, t) \rangle. \quad (13)$$

Here $U_{1,2}(t, t_0)$ are the evolution operators determined by the total vibrational Hamiltonians in the ground (1) and in the excited (2) electronic states of the system.

We neglect for simplicity in the evolution operators $U_{1,2}(t, t_0)$ the interaction with the dissipative subsystem. We assume that the time of measurement of the absorption coefficient of the probing light with the detector is short enough, so that the observed value of the absorption coefficient practically coincides with $K_i^F(\Omega)$. It is convenient to carry out the subsequent calculations in a coherent-state basis.⁶ Omitting the details of the calculation, we present the expression for $K_i^F(\Omega)$ in the case of a noncentrosymmetric molecule in the field of absolutely coherent (δ) laser radiation (we neglect for simplicity the frequency effect):

$$K_i^F(\Omega, \delta) = \frac{2\pi\Omega}{\hbar c n_0 V} |d_{12}|^2 e^{-a(1+2n)} \times \sum_{p,s=-\infty}^{+\infty} J_p^2(\rho) I_s(z) \left(\frac{1+n}{n}\right)^{s/2} \frac{\Gamma/2}{[\epsilon - \Omega + (p+s)\omega]^2 + \Gamma^2/4}. \quad (14)$$

Here $J_p(x)$, $I_s(x)$ are respectively Bessel functions of real and imaginary argument, a is the heat-release parameter,

$$z = 2a[n(1+n)]^{1/2}, \quad \rho = 2a^{1/2} |\beta(t)|.$$

In the case of multimode laser radiation, the absorption coefficient is obtained from (14) by averaging this expression with a Gaussian (g) weighting function¹⁰:

$$K_i^F(\Omega, g) = \frac{2\pi\Omega}{\hbar c n_0 V} |d_{12}|^2 \exp\{-a[1+2\bar{n}(t)]\} \times \sum_{p=-\infty}^{+\infty} J_p(\bar{z}_t) \left(\frac{1+\bar{n}(t)}{\bar{n}(t)}\right)^{p/2} \frac{\Gamma/2}{(\epsilon - \Omega + p\omega)^2 + \Gamma^2/4}. \quad (15)$$

The vibrational occupation numbers $\bar{n}(t)$ in the field of a laser radiation are given by

$$\bar{n}(t) = n + |\beta(t)|^2 \quad (16)$$

($\bar{z}_t = 2a[\bar{n}(t)(1+\bar{n}(t))]^{1/2}$). Unlike Eq. (14) for a coherent source of laser radiation, the structure of (15) is the same as that of the well known formulas of the theory of multiphonon processes,¹¹ the only difference being that the equilibrium occupation numbers n of the vibrations are replaced by the occupation numbers $\bar{n}(t)$ of the vibrations in the laser-radiation field. The concrete form of the occupation numbers $\bar{n}(t)$ depends on the

form and duration of the laser radiation.

In the steady state we obtain for the absorption coefficient of light of frequency Ω in the case of a centrosymmetric molecule with allowance for the interaction of the dipole-active q -vibrations with fully symmetrical Q -vibration,

$$K^F(\Omega, \delta) = \frac{2\pi\Omega}{\hbar c n_0 V} |d_{12}|^2 \exp[-a_A(1+2n_A)] \times \exp[-a_B(1+2n_B)] \sum_{m,k=-\infty}^{+\infty} J_m^2(\rho_B) J_k^2(\rho_A) \times \sum_{p,s=-\infty}^{+\infty} I_p(z_B \sin^2 \psi) I_s(z_A \cos^2 \psi) \frac{\Gamma/2}{[\epsilon - \Omega + (p+m)\omega_B + (s+k)\omega_A]^2 + \Gamma^2/4}. \quad (17)$$

Let the condition $|\omega(\omega_2 - \omega_1)^{-1}| \ll 1$ be satisfied (this inequality frequently holds for many molecular systems⁴). Then $\sin\psi \sim \psi$, $\cos\psi \sim 1$. Assuming t to be much longer than all the characteristic times in this system, and that the laser radiation frequency $\omega_l \approx \omega_A$, $|\omega_B - \omega_l| \gg \gamma$, we readily obtain $\rho_A \gg \rho_B$ ($\rho_A = 2a_A^{1/2} f\psi/\hbar\gamma_A$, $\rho_B = a_B^{1/2} f/\hbar|\omega_B - \omega_l|$). Under the assumed approximations, the light absorption coefficient is described by relation (14) in which the following substitutions must be made

$$\rho_i \rightarrow \rho_A, \quad \bar{z}_i \rightarrow \bar{z}_A = 2a_A[\bar{n}_A(1+\bar{n}_A)]^{1/2},$$

where $\bar{n}_A = n(\omega_A) + (f\psi/\hbar\gamma_A)^2$.

In the case of small heat release ($a \ll 1$, $I_0(\bar{z}) \sim 1$) the absorption coefficient at the frequency of the 0-0 transition, which is proportional to the intensity of the zero-phonon line (ZPL) is of the form

$$K_{ZPL}^F(\Omega, t) = K_{ZPL}^0 \exp\{-2a|\beta(t)|^2\} \quad (18)$$

for NCS molecules and

$$K_{ZPL}^F(\Omega) \approx K_{ZPL}^0 \exp\{-2a_A(f\psi/\hbar\gamma_A)^2\} \quad (19)$$

for CS molecules (K_{ZPL}^0 is the absorption coefficient in the absence of laser radiation). Thus, it follows from (18) that the ZPL intensity decreases exponentially with increasing laser-radiation field intensity. In the case of centrosymmetric molecules, at $\psi \ll 1$, it follows from (19) that the intensity of the ZPL decreases insignificantly with increasing intensity of the field.

The time dependence of $\bar{n}(t)$ allows us to investigate the absorption bands using the shape and duration (τ_0) of an IR laser radiation pulse. Borisevich⁴ investigated experimentally the dependence of the ZPL on the duration of a laser pulse for acrolein molecules, in which a CO₂ laser excited the strain vibration of the CH₂ group of the acrolein, which transferred its energy to the vibrations active in the electronic transition. If we choose for simplicity a pulse waveform

$$f(t) = f e^{-t/\tau_0} \quad (t > 0),$$

then we find from Eq. (7), in which we replace $\beta(t)$ by $\beta(t)\psi^2$, that

$$\beta(t) = \frac{f(\tau_0/2)}{\hbar(1-\gamma\tau_0/2)} \{e^{-t/2} - e^{-t/\tau_0}\} \psi^2.$$

The time dependence of the ratio $\chi_F^{ZPL} = K_{ZPL}^F/K_{ZPL}^0$, calculated from formula (18) in which (for CS molecules)

$\beta(t) \rightarrow \beta(t)\psi^2$ (see Fig. 1), describes qualitatively the evolution of the ZPL intensity observed in Ref. 4. At low temperatures, the long-wave wing of the absorption band usually "freezes out" in the absence of laser radiation. Turning on laser radiation that is at resonance with the dipole-active vibrations should lead, in accordance with (15), to enhancement of the red wing of the band, as was in fact observed in Refs. 3 and 12.

In the absence of laser radiation, the long-wave wing of the band is well described by the Urbach formula,¹³ so that

$$K^0(\Omega) \sim \exp\left\{-\frac{\sigma}{kT}(\varepsilon - \Omega)\right\},$$

where $\sigma \leq 1$. When the vibrations are enhanced by laser, the maximum of the absorption band shifts, as usual, into the long-wave region, and its half-width increases with the field intensity. The shape of the band is then sufficiently accurately approximated by a Gaussian curve

$$K^F(\Omega) \sim \exp\{-(\Omega_1 - \Omega)^2/2\Omega_2\}$$

($\bar{\Omega}_1$ is the position of the maximum and $\bar{\Omega}_2$ is connected with the half-width of the band) in the frequency region corresponding to the red wing of the initial unperturbed absorption band. It is easily seen that in this case the ratio $\kappa_F(\Omega) = K^F(\Omega)/K^0(\Omega)$ as a function of the frequency has a characteristic maximum. It appears that this maximum is observed in the electron-absorption spectrum of OsO_4 molecules¹² excited by a resonant CO_2 laser (the dipole active ν_3 vibration with frequency 960 cm^{-1} was excited).

4. Using the calculation procedure employed in the derivation of (13) for the light-absorption coefficient, we can obtain the following expression for the spectrum of the resonant secondary emission (RSE) in the field of a coherent laser source:

$$dW^F(\Omega_0, \Omega) = B e^{-2a(1+2\bar{n})} 2 \text{Re} \int_0^{\infty} d\mu e^{i(\varepsilon - \Omega_0)\mu} \int_0^{\infty} d\tau d\tau' J_0(R) \exp\{i(\varepsilon - \Omega_0)(\tau' - \tau)\} \\ \times \exp\left\{-\frac{\Gamma}{2}(\tau + \tau')\right\} \exp\{z[\cos(\omega\tau + \varphi) + \cos(\omega\tau' - \varphi)]\} \\ \times \exp\left\{4z \sin \frac{\omega\tau}{2} \sin \frac{\omega\tau'}{2} \cos\left(\frac{\omega\tau - \omega\tau'}{2} - \omega\mu - \varphi\right)\right\}. \quad (20)$$

Here Ω_0 is the frequency of the incident light with wave vector \mathbf{k}_0 and polarization λ_0 ; \mathbf{k} and λ are the corres-

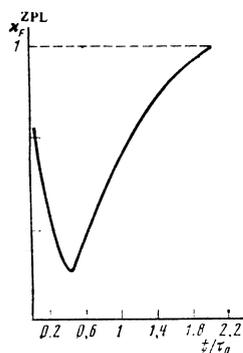


FIG. 1. Temporal evolution of the ZPL intensity (one division on the ordinate axis corresponds to 0.1).

ponding characteristics of the scattered light, $B = N^0 \hbar^{-4} |W_{12}^{k_0 \lambda_0} W_{21}^{k \lambda}|^2$, is the matrix element of the dipole interaction, $N^0(\Omega_0)$ is the distribution of the incident-light photons; $\tan 2\varphi = i(1 + 2\bar{n})^{-1}$;

$$R^2 = 4\varphi^2 \left[\sin^2 \frac{\omega\tau}{2} + \sin^2 \frac{\omega\tau'}{2} - 2 \sin \frac{\omega\tau}{2} \sin \frac{\omega\tau'}{2} \cos\left(\frac{\omega\tau - \omega\tau'}{2} - \omega\mu\right) \right]. \quad (21)$$

In the case of multimode laser radiation, the RSE spectrum is obtained from (20) by averaging the latter, as usual, with a Gaussian wave function. The expression obtained in this case for the RSE spectrum coincides with the corresponding expressions of Refs. 14 and 15, except that the occupation numbers n are replaced by the occupation numbers $\bar{n}(t)$ in the IR laser field. We note that the integral intensity of the secondary emission $I^F(\Omega_0)$ is given by

$$I^F(\Omega_0) = \int d\Omega dW^F(\Omega, \Omega_0) = \frac{B\pi}{\Gamma} \exp\{-a(1+2\bar{n})\} \\ \times 2 \text{Re} \int_0^{\infty} d\tau \exp\left[-\frac{\Gamma\tau}{2} + i(\varepsilon - \Omega)\tau + z_i \cos(\omega\tau - \varphi)\right], \quad (22)$$

where $I^F(\Omega_0)$ is proportional to the absorption coefficient of the incident light. In the region of the frequency of a pure electronic transition we obtain

$$I^F(\Omega) \approx B\pi \frac{\exp[-a(1+2\bar{n}(t))]}{(\varepsilon - \Omega_0)^2 + \Gamma^2/4}. \quad (23)$$

The ratio $\kappa_F = I^F(\Omega_0)/I^0(\Omega_0)$ (I^0 is the integral intensity in the absence of laser radiation), which is equal to

$$\kappa_F = \exp[-2a(f/\hbar\gamma)^2] = \exp(-2a\xi_0 F^2),$$

depends strongly on the intensity of the electric field of the laser radiation and decreases exponentially. For low intensities

$$\kappa_F = 1 - 2a\xi_0 F^2 + \dots \quad (24)$$

Figure 2 shows the theoretical (2) and experimental¹⁶ (1) plots of the ratio κ_F of the integral intensities on the IR-laser emission density for anthracene vapor.

According to the general expressions for K^F and dW^F , the intensity of the vibrational satellites with $\nu > \nu_{\text{ZPL}}$ decreases with increasing IR intensity, and their half-width, determined by Γ , remains unchanged. Thus, if the frequency of the incident light is close to the frequency of the pure electronic transitions, then the RSE intensity, and the structure of the spectrum remains unchanged, in agreement with experiment.¹⁶ It is possible to obtain similarly an expression for the RSE in the case of CS molecules.

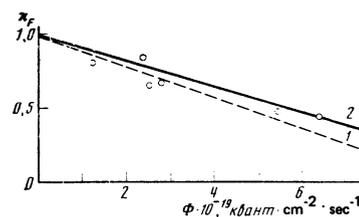


FIG. 2. Dependence of the light extinction on the density of the infrared radiation. The points and curve 1 were taken from Ref. 16, curve 2 was calculated at $a = 7$, $\mu = 0.1 D$, $M = 10^{23} \Gamma$, $\gamma^{-1} = 3 \times 10^{-8}$ sec, and $\hbar\omega_l = 0.12$ eV.

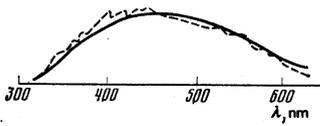


FIG. 3. Spectrum of "instantaneous" luminescence. The dashed line shows the experimental curve from Ref. 2.

5. We consider now the spectrum of the instantaneous luminescence dW_L^F . This process corresponds to n -photon excitation of an electron from the ground state (1) to the excited state (2), followed by emission of a luminescence photon to level (3) located lower than level (2). A distinction must be made between two cases: a) $\gamma \gg \Gamma$, b) $\gamma \leq \Gamma$. In case (a) it is easy to verify that the instantaneous-luminescence spectrum is given by

$$dW_L^F(\Omega) \sim W_{12}^F W_{23}^F(\Omega). \quad (25)$$

Here W_{12}^F is the probability of n -photon excitation $1 \rightarrow 2$, $W_{23}^F(\Omega)$ the probability of the luminescence $2 \rightarrow 3$ in the absence of resonant IR. In case (b) the expression for the probability of the instantaneous luminescence cannot be factored out. The spectrum of the instantaneous luminescence can be calculated in this case by the procedure described above. Since the expression for this spectrum cannot be represented in simple analytic form, it is not cited here. In luminescence experiments¹ the case (a) was realized, and the shape of the luminescence band was described by formula (25) (broad electron-vibrational bands). It appears that the case (a) realized also in the experiments of Ref. 2. In the case of large heat-release parameters

$$dW_L^F(\Omega) \sim \exp\{-(\bar{\Omega}_1 - \Omega)^2 / 2\delta\Omega\}$$

($\bar{\Omega}_1$ is position of the maximum, $\delta\Omega = 2(2\Omega_2 \ln 2)^{1/2}$ is the half-width of the emission line). At $\hbar\bar{\Omega}_1 \sim 2.78$ eV and $\delta\Omega \sim 1.2$ eV, the quantity dW_L^F describes well the instantaneous-luminescence line shape observed in Ref. 2 (see Fig. 3).

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