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TWO-PHOTON ABSORPTION BY CENTRALLY SYMMETRIC ORGANIC MOLECULES

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A theory of the structure of electron-vibrational bands in two-quantum transitions in centrally symmetric molecules is developed. Polarization characteristics of two-quantum absorption of molecules in solutions are considered. The spectrum of the cross section for two-quantum absorption of linearly polarized light and the frequency dependence of the ratio of the absorption cross sections for circularly and linearly polarized light are investigated experimentally for an anthracene solution. The theory and experiment are compared.

1. INTRODUCTION

TWO-PHOTON absorption, which comes into play at large radiation powers, can serve as an important source of information on the properties of matter, for example on the spectrum, on the symmetry of different states, etc. Thus, observation of a symmetrically excited electronic state in chloronaphthalene was reported in [1]. Considerable interest attaches to a study of two-quantum absorption in centrally-symmetrical organic molecules, where intense two-quantum transitions were observed between electronic states of different parity, which are symmetry-forbidden in the electric dipole approximation.[2] At present there are sufficient grounds, both theoretical and experimental,[3-6] for treating these two-quantum transitions as electron-vibrational ones.[1)]

Indeed, in the adiabatic approximation the stationary wave function corresponding to the s electronic and j_s vibrational states can be represented in the form of the product[7]

$$\Psi_{s,j_s}(r,R)=\Theta_s(r,R)\varphi_{j_s}(R), \tag{1}$$

where r and R are the coordinates of the electrons and of the nuclei, $\Theta_S(r, R)$ is the eigenfunction of the Hamiltonian of the molecule for fixed nuclei, and $\varphi_{j_S}(R)$ is the wave function of the nuclei in the s-th electronic state. For centrally-symmetrical molecules, the parity of the state $\Psi_{S,\,j_S}$ is determined by the symmetry of the functions Θ_S and φ_{j_S}. For odd functions Θ_S and φ_{j_S}, the state $\Psi_{S,\,j_S}$ is even and therefore the two-quantum transitions to an odd electronic state with excitation of odd vibrations are allowed. As to the intensity of such transitions, the estimates given below (see also [8]) are in accord with the experimentally observed quantities.[9]

The decisive role of the asymmetrical oscillations of the excited state should be reflected in the spectrum of two-photon absorption. Indeed, under the experimental conditions one always deals with a two-photon transition into a definite electron-vibrational state, since the spectrum of the absorbed radiation is much narrower than the width of the electron-vibrational band.

In the present paper we discuss in detail the spectral and polarization properties of the cross section of two-photon absorption for electron-vibrational transitions. We present experimental results on the frequency dependence of the cross section of two-photon transitions at different polarizations of the absorbed light for anthracene molecules in solution. The experiment was compared with the theory.

2. THEORY

A. The general expression for the probability of two-photon transitions is well known, and in the dipole approximation it takes the form[10]

$$W=\frac{1}{\hbar}\chi''_{1221}(\omega_1,\omega_2)\varepsilon_1\varepsilon_2\varepsilon_2\varepsilon_1|E_1|^2|E_2|^2, \tag{2}$$

where $E_{1,\,2}$, $\epsilon_{1,\,2}$, and $\omega_{1,\,2}$ are the amplitude, polarization vector, and frequency of the electric field of the light wave,

$$\chi''_{1221}=\frac{\pi}{\hbar^3}\sum\rho_l\left|\sum_m\frac{d^{(1)}_{lm}\,d^{(2)}_{mk}}{\omega_2-\omega_{ml}}+\frac{d^{(2)}_{lm}\,d^{(1)}_{mk}}{\omega_1-\omega_{ml}}\right|^2\delta(\omega_{kl}-\omega_1-\omega_2), \tag{3}$$

χ''_{1221} is the imaginary part of the cross-susceptibility tensor.[11] [2)] The Latin letters in (3) number the states of the molecular system, $d^{(1),(2)}_{lm}$ is the matrix element of the dipole moment (projection on the direction (1) or (2)), ω_{lm} are the eigenfrequencies of the system, and ρ_l is the equilibrium density matrix.

The rest of problem reduces to finding the matrix elements of the dipole moment of the molecule

$$\hat{\mathbf{d}}=\sum_i e\hat{\mathbf{r}}_i+\sum_j g_j\hat{\mathbf{R}}_j \tag{4}$$

[1)] An analogous situation (the allowing of symmetry-forbidden electronic transitions by vibrations) is well known in ordinary single-photon spectroscopy, for example, forbidden transitions in benzene[7].

[2)] In the derivation of formulas (2) and (3), the interaction with the field was represented in the form **d** · **E**. The use of an interaction in the form **p** · **A** in the approximate calculations with allowance for only a few of the lower states can sometimes lead to incorrect results[12,13].

(g_j is the ion charge). In the adiabatic approximation we have

$$\langle sj_s|\mathbf{d}|s'j_{s'}'\rangle = \langle j_s|\mathbf{d}_{ss'}|j_{s'}'\rangle(1-\delta_{ss'}) + \mathbf{D}^s_{j'_s, j_s}\delta_{ss'}, \tag{5}$$

$\langle \mathbf{d}_{ss'}(R) = \langle s|\mathbf{d}|s'\rangle$ is the matrix element of the dipole moment of the electron system, and $\mathbf{D}^s_{j'_s, j_s}$ is the matrix element of the dipole moment of the molecule, which determines the intensity of the infrared transitions in the s-th electronic state. We change over to the normal coordinates of the nuclei of the molecules $\mathbf{Q}^s_\alpha$ for the s-th electronic state. Representing $\mathbf{d}$ in the form of a series in $\mathbf{Q}^s_\alpha$ and retaining only the linear terms, in analogy with [14], we obtain

$$\langle sj_j|\mathbf{d}|mj_m'\rangle = \mathbf{d}_{sm}(0)\langle j_s|j_m'\rangle + \sum_\alpha \lambda_{sm}{}^\alpha\langle j_s|Q_\alpha{}^s|j_m'\rangle$$
$$\times(1-\delta_{sm}) + \sum_\alpha g_{\alpha s}\langle j_s|Q_\alpha{}^s|j_m'\rangle \mathbf{e}_\alpha{}^s\delta_{sm}. \tag{6}$$

Here $\mathbf{e}^s_\alpha$ are the unit vectors of the polarization of the normal vibrations,

$$\lambda_{sm}{}^\alpha = \sum_k\left\{\frac{\mathbf{d}_{km}}{\hbar\omega_{sk}}\left\langle \Theta_s{}^0\left|\frac{\partial H}{\partial Q_\alpha}\right|\Theta_k{}^0\right\rangle + \frac{\mathbf{d}_{sk}}{\hbar\omega_{mk}}\left\langle \Theta_k{}^0\left|\frac{\partial H}{\partial Q_\alpha}\right|\Theta_m{}^0\right\rangle\right., \tag{7}$$

and the matrix elements in (7) are defined with the aid of the functions $\Theta^0_m = \Theta_m(r, R^0_j)$, where R^0_j are the coordinates of the nuclei in the equilibrium configuration of the s-th electronic state;

$$g_{\alpha s} = \sum_j g_j(\mathbf{R}_j\mathbf{e}_\alpha{}^s) + \lambda_{ss}\mathbf{e}_\alpha{}^s; \tag{8}$$

$g_{\alpha s}$ is the effective charge and determines the intensity of the infrared transitions.

It should be noted that the first term in (6) is larger than the other two, the order of magnitude of which relative to the first can be estimated from (7) and (8). A tentative comparison can be carried out by putting $\hbar\omega_{sk} \sim e^2/R_0$, where R_0 is the characteristic distance between nuclei; then the second and third terms are of the order of $\Delta R/R_0$, where ΔR is the amplitude of the oscillations of the nuclei.

B. We now proceed directly to consider the spectrum of the two-photon transitions. We consider first allowed transitions (transitions between electronic levels of equal parity). We assume for simplicity that the molecule is in the ground state ($s = 0$ and $j_s = 0$). We then have for the probability of the two-quantum transition

$$W(\omega_1, \omega_2) = A(\boldsymbol{\varepsilon}_1, \boldsymbol{\varepsilon}_2)|E_1|^2|E_2|^2\langle 0|j_{s'}\rangle\delta(\omega_{s'j_{s'}, 00} - \omega_1 - \omega_2), \tag{9}$$

where $\omega_{s'j'_{s'}00}$ are the molecule eigenfrequencies corresponding to transitions from the ground state to the electron-vibrational states $s'j_{s'}$. The quantity

$$A = \frac{\pi}{\hbar^4}\left|\sum_m \frac{(\mathbf{d}_{0m}\boldsymbol{\varepsilon}_1)(\mathbf{d}_{ms'}\boldsymbol{\varepsilon}_2)}{\omega_2 - \omega_{m0}} + \frac{(\mathbf{d}_{0m}\boldsymbol{\varepsilon}_2)(\mathbf{d}_{ms'}\boldsymbol{\varepsilon}_1)}{\omega_1 - \omega_{m0}}\right|^2 \tag{10}$$

depends little on the frequency and describes only the polarization properties of the two-quantum absorption; from (10) we see that within the limits of one electronic band there is no frequency dependence of the two-quantum absorption on the polarization of the absorbed light. It follows from (9) that the two-quantum absorption spectrum contains a set of frequencies corresponding to transitions to vibrational sublevels of the excited electronic state. The relative line intensity is determined by the overlap integral $\langle 0|j_{s'}\rangle^2$, which differs from zero for oscillations with symmetry A_{1g}. This corresponds to the appearance of fully-symmetrical vibrations of the excited electronic state in the spectrum.

C. For electronic states of different parity (forbidden transitions) we have from Eqs. (2), (3), and (6)

$$W(\omega_1, \omega_2) = \frac{\pi}{\hbar^4}|E_1|^2|E_2|^2\sum_{j_s j_{s'}}\rho_{j_s}\delta(\omega_{sj_s, s'j_{s'}} - \omega_1 - \omega_2) \tag{11}$$

$$\left|\sum_\alpha \langle j_s|Q_\alpha|j_s'\rangle\left\{\sum_m\left[\frac{(\mathbf{d}_{sm}\boldsymbol{\varepsilon}_1)(\overset{\alpha}{\lambda}_{ms'}\boldsymbol{\varepsilon}_2) + (\overset{\alpha}{\lambda}_{sm}\boldsymbol{\varepsilon}_1)(\mathbf{d}_{ms'}\boldsymbol{\varepsilon}_2)}{\omega_2 - \omega_{ms}}\right.\right.\right.$$
$$\left. + \frac{(\mathbf{d}_{sm}\boldsymbol{\varepsilon}_2)(\overset{\alpha}{\lambda}_{ms'}\boldsymbol{\varepsilon}_1) + (\overset{\alpha}{\lambda}_{sm}\boldsymbol{\varepsilon}_2)(\mathbf{d}_{ms'}\boldsymbol{\varepsilon}_1)}{\omega_1 - \omega_{ms}}\right]$$
$$\left.\left. + \left[\frac{(\mathbf{d}_{ss'}\boldsymbol{\varepsilon}_1)(\mathbf{e}_\alpha\boldsymbol{\varepsilon}_2)}{\omega_1} + \frac{(\mathbf{d}_{ss'}\boldsymbol{\varepsilon}_2)(\mathbf{e}_\alpha\boldsymbol{\varepsilon}_1)}{\omega_2}\right](g_{\alpha s} - g_{\alpha s'})\right\}\right|^2.$$

To simplify the subsequent analysis of expression (11) we put, just as in the preceding case, $s = 0$ and $j_s = 0$. In addition, we assume vibrations of different types to be nondegenerate, and the frequencies of the two absorbed photons to be equal. Taking these assumptions into account, we obtain from (11)

$$W(\omega) = 4\frac{\pi}{\hbar^4}|E|^4\delta(\omega_{s'j';0} - 2\omega)\langle 0|Q_\alpha|1_0{}^\alpha\rangle^2\langle 1_0{}^2|j_{s'}\rangle^2 \tag{12}$$
$$\times\left|\sum_m(\omega - \omega_{m0})^{-1}[(\mathbf{d}_{0m}\boldsymbol{\varepsilon})(\overset{\alpha}{\lambda}_{ms'}\boldsymbol{\varepsilon}) + (\overset{\alpha}{\lambda}_{0m}\boldsymbol{\varepsilon})(\mathbf{d}_{ms'}\boldsymbol{\varepsilon})]\right.$$
$$\left. + \omega^{-1}(\mathbf{d}_{0s'}\boldsymbol{\varepsilon})(\mathbf{e}_\alpha\boldsymbol{\varepsilon})(\lambda_{00} - \lambda_{s's'})\right|^2.$$

Let us consider the dependence of W on the frequency of the light (the spectrum of W). The main frequency dependence is connected with the delta function that separates the frequencies corresponding to transitions to different electron-vibrational states. The gross structure of the spectrum within the limits of the electron vibrational band constitutes a number of lines corresponding to excitation of vibrations of different types.

The expression under the absolute-value sign determines the types of the possible electron-vibrational transitions and their intensity. This expression differs from zero only for odd oscillations. Indeed, $d_{0m} \neq 0$ for odd states m, and then m and s′ have the same parity and $\lambda^\alpha_{ms'} \neq 0$ only for asymmetrical vibrations α (see formula (7)); in the case when m are even states ($d_{ms'} \neq 0$) we have $\lambda^\alpha_{0m} \neq 0$ again only for asymmetrical vibrations; the same pertains to λ_{00} and $\lambda_{s's'}$. The intensity of any particular line in the spectrum is determined also by the overlap integral $\langle 1^\alpha_0 j_{s'}\rangle^2$ of the vibrational functions 1^α_0 (excitation of one quantum of odd vibration of type α) and $j_{s'}$ (vibrational wave function of the final state). Representing these functions in the form of a product of wave functions of the individual vibrations, we obtain

$$\langle 1_0{}^\alpha|j_{s'}\rangle^2 = \langle 1_0{}^\alpha|1_{s'}{}^\alpha\rangle^2\prod_\beta\langle 0|j_{s'}{}^\beta\rangle^2 \approx \prod_\beta\langle 0|j_{s'}{}^\beta\rangle^2, \tag{13}$$

where β numbers the fully-symmetrical vibrations. We have taken into account here the fact[7] that for asymmetrical vibrations the overlap integral is close to unity only for states with identical quantum numbers. The quantity $\prod_\beta\langle 0|j^\beta_{s'}\rangle$ determines the progression over the fully-symmetrical vibrations (an analogous quantity determines the vibrational structure of the spectrum of a single-quantum transition). The analysis presented implies the following characteristic of the electron-vibrational spectrum that is forbidden with respect to the symmetry of two-photon absorption. Within the limits of one electron band, the spectrum consists of a set of series, the first of which is shifted to the short-wave side of the 0–0 transition by an amount equal to the frequency of the lowest-frequency asymmetrical vibration. Each of the series consists of peaks corresponding to the excitation of asymmetrical vibrations of different types. The relative magnitude of the peaks remains the same on going from series to series. The distance between the series is determined by the frequencies of the fully-symmetrical vibrations, which are active in the single-quantum transitions.

The foregoing picture of the spectrum is tentative, since it is constructed without allowance for the finite width of the electron-vibrational states. Under the experimental conditions, this broadening is appreciable (with the exception of the case of the Shpol'skii effect), and different electron-vibrational states overlap.

D. It should be noted that in the experiment one is usually interested not in the probability of the two-quantum absorption, which depends on the intensity of the light, but in the so-called cross section of two-quantum absorption, which is determined only by the properties of the molecules,

$$\delta(\omega)=W(\omega)\,/\,F^2, \tag{14}$$

where F is the quantum flux density. Naturally, the frequency dependences $W(\omega)$ and $\delta(\omega)$ are the same. For convenience in comparison with experiment, let us estimate the absolute value of δ. Using (14) jointly with (9) and (10), we obtain for the transition between the levels of identical parity the standard estimating formula

$$\delta=\frac{(2\pi)^3}{\hbar^2}\frac{1}{\Delta\omega}\left(\frac{\omega}{cn(\omega)}\right)^2\left|\frac{d_{1m}d_{m2}}{\omega_{2m}-\omega}\right|^2. \tag{15}$$

On going from (10) to (15), we confined ourselves in the sum (10) to a single intermediate state m and replaced the delta function by the quantity $(\Delta\omega)^{-1}$, which describes the broadening of the level. Assuming for the quantities in (15) values that are typical of polycyclic aromatic compounds (dipole moments on the order of the Debye value, $\Delta\omega \sim 300\ \text{cm}^{-1}$, and $\omega \sim \omega_{2m}-\omega \sim 1.5\times10^4\ \text{cm}^{-1}$), we have $\delta \sim (10^{-49}\text{–}10^{-50})\ \text{cm}^4$ sec/photon.

To estimate the two-quantum transitions between electronic states of different parity, it is necessary to consider (14) in conjunction with (12). As already noted above, both terms under the absolute-value sign in (12) have a relative magnitude $\Delta R/R$ compared with the corresponding term in (10). Consequently, a general rough estimate can be obtained by using (15). The ratio of the displacement ΔR of the nuclei as a result of the vibrations to the equilibrium distance R is of the order of

$$(\Delta R\,/\,R)^2 \approx \omega_{\text{vib}}\,/\,\omega_{0m}, \tag{16}$$

where ω_{vib} is the vibration frequency. The parameter (16) indeed determines the relative smallness of the probability of the transitions between levels of different parity, and its value for typical cases is $\sim(30\text{–}100)^{-1}$. A somewhat more accurate estimate can be obtained, at any rate, for the second term under the absolute-value sign in (12). We assume that the difference between the charges is $\lambda_{S'S'}-\lambda_{00}\sim\lambda_{00}$, and we have in analogy with (15)

$$\delta=\frac{(2\pi)^3}{\hbar^2}\frac{1}{\Delta\omega}\left(\frac{\omega}{cn(\omega)}\right)\frac{|d_{0s'}|^2|D_{01}|^2}{\omega^2}, \tag{17}$$

where D_{01} is the dipole moment of the vibrations of the molecule. For anthracene, for example, $d_{0S'} \sim 0.7$ D (transition to the level B_{2u}), $D_{01} \sim 0.3$D, and $\Delta\omega \sim 300\ \text{cm}^{-1}$, and for δ we have in this case $\delta \approx 10^{-51}$.

E. Let us discuss one more feature of two-quantum absorption, namely the dependence of the transition probability on the character of the polarization of the absorbed light and on the mutual orientation of the dipole moments that enter in the composite matrix element. We introduce, just as in [5], the quantity Ω equal to the ratio of the probabilities of the two-quantum absorption of light of circular and linear polarization. In two-photon transitions, unlike single-photon transitions, Ω is not equal to unity even for a system of randomly oriented molecules (gas, solution). The magnitude of this ratio depends on the mutual orientation of the dipole moments,[5, 15, 16] and this pertains to an equal degree both to the probability of the symmetry-allowed two-photon transition (10) and to the probability of the symmetry-forbidden transition (12). However, whereas for the allowed two-photon transition Ω does not depend on the frequency within the limits of one electron band, this is not the case for an electron-vibrational two-quantum transition.

As follows from (14), the orientation of the dipole moments depends on the symmetry of the vibration excited during the transition, and accordingly the value of Ω is likewise independent of the symmetry of the vibration, and as a result is independent of the frequency. The latter is an important characteristic of electron-vibrational transitions. Let us consider in greater detail the dependence of Ω on the type of the excited vibration, using as an example two-quantum transitions between the electronic levels A_{1g} and B_{2u} in a molecule of symmetry D_{2h} (a case corresponding to two-quantum absorption of anthracene at a frequency on the order of 14,000 cm^{-1}). We confine ourselves here to a consideration of the electronic transitions in the plane of the molecule. In a molecule of symmetry D_{2h}, excitation of asymmetrical vibrations of the type b_{1u}, b_{2u}, and b_{3u} is possible.

Excitation of b_{1u} vibration. In this case the probability of the transition is determined by the terms in (12) with the factor $(\lambda_{00}-\lambda_{S'S'})$:

$$W=4\frac{\pi}{\hbar^4}|E|^4\langle 0|Q_{b_{1u}}|1^0_{b_{1u}}\rangle^2\prod_{\beta}\langle 0|j_{s'}{}^{\beta}\rangle^2|\omega^{-1}(\mathbf{d}_{0s'}\boldsymbol{\varepsilon})(\mathbf{e}_{b_{1u}}\boldsymbol{\varepsilon})(\lambda_{00}-\lambda_{ss'})|^2. \tag{18}$$

The dipole moment of the electronic transition $\mathbf{d}_{0S'}$ is directed along the y axis, and the dipole moment of the vibrations (unit vector $\mathbf{e}_{b_{1u}}$) is directed along the z axis. Averaging (18) over the directions of the randomly oriented molecules yields

$$\Omega=W_{yz}{}^{c}\,/\,W_{yz}{}^{L}=1.5.$$

Excitation of vibration b_{2u}. In this case the intermediate states can be levels with symmetry B_{2u}, A_{1g}, B_{3g}, and B_{1g}. In the first two cases, the dipole moments of the transitions are parallel and directed along the y axis, and the two other cases they are likewise parallel but directed along x. As to the last term in (12), the dipole moments for it are also parallel and directed along y. Combining all the terms corresponding to dipole moments in the x and y directions, and denoting them by W_{xx} and W_{yy}, we obtain for the polarization ratio

$$\Omega = \frac{4W_{yy}^2 + 4W_{xx}^2 - 4W_{xx}W_{yy}}{6W_{yy}^2 + 6W_{xx}^2 + 4W_{xx}W_{yy}}. \qquad (19)$$

Depending on the ratio of W_{xx} to W_{yy}, the polarization ratio varies from 0.25 to 0.67.

Vibrations of type b_{3u}. Just as in the preceding case, two-quantum transitions with excitation of vibrations b_{3u} are possible with participation of intermediate states of symmetry B_{3u}, B_{1g}, B_{2u}, and A_{1g}. In this case, however, unlike the b_{2u} vibrations, the dipole moments in the composite matrix element are mutually perpendicular (W_{xy} and W_{yx} for the first and second pairs of intermediate states, respectively). In the third term the dipole moment is determined by the diagonal quantities λ and is directed along the x axis, while the electronic transition $d_{0s'}$ is directed along the y axis.

The results of the averaging in this situation yield $\Omega = 1.5$. Thus, depending on the type of the final vibrational state, the polarization ratio can range from 0.25 to 1.5.

3. EXPERIMENT

In the experiment, we investigated the dependence of the probability of two-photon absorption for linear polarization of the exciting radiation and of the polarization ratio Ω on the frequency of the exciting light. The measurements were made for a solution of anthracene in cyclohexane in the wavelength region 7200–7600 Å.

An experimental investigation of the spectrum of two-quantum absorption was reported earlier,[6] and we shall therefore describe here in detail the measurement of the Ω(ω) dependence.

A block diagram of the experiment is shown in Fig. 1. The variable-frequency source of powerful radiation 1 was a dye-solution laser (cryptocyanine and others). The excitation was by a single pulse of a ruby laser. Narrowing of the generation band (to 5 Å) and smooth variation of the wavelength in the range 100–150 Å were accomplished by using a diffraction grating in place of the dye-laser mirrors. Coarser tuning was by using different dyes and by varying their concentrations in the solutions. The laser radiation was linearly polarized; this was ensured both by the geometry of the laser itself and by using Glan prism 2 as a polarizer.

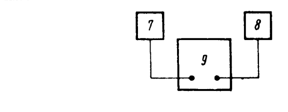

FIG. 1. Block diagram of the setup used to measure the Ω(ω) spectrum. 1–Variable-frequency dye laser, 2–Glan psim, 3–cell with "standard" substance, 4–cell with investigated substance, 5–quarter-wave "plate," 6–spectrograph, 7 and 8–photomultipliers, 9–two-beam oscilloscope.

In the experiment we measured the relative intensity of the luminescence of the anthracene (cell 4), excited by two-quantum transitions at linear and circular polarization. Since the measurements at linear and circular polarization were carried out in different flashes, it was necessary to monitor the intensity of the laser radiation. This was done by means of two-photon absorption in another, "standard," solution 3 (in this case it was a similar solution of anthracene), the fluorescence of which was excited only by linearly polarized light. Such a measurement method greatly reduces the errors due to fluctuations of the laser radiation.

The polarization converter was a tunable quarter-wave "plate" 5, consisting of two quartz wedges. Tuning of the "plate" was by displacing the wedges relative to each other. Depending on the angle between the polarization of the radiation and the optical axis of the "plate" (0 or 45°), the polarization of the light in cell 4 was either linear or circular. Tuning of the "plate" to λ/4 was by means of a procedure analogous to that described in [5].

The wavelength of the exciting radiation was monitored by an ISP-51 spectrograph 6, with camera UF-84.

The luminescence of the investigated solution and of the "standard" was received with the aid of photomultipliers (8 and 7 in the block diagram, respectively). The pulses from the photomultipliers (I_1 and I_2) were fed to a two-beam oscilloscope 9. The sought quantity Ω was determined from two series of measurements (at different polarizations) and was determined from the simple relation

$$\Omega = \left(\frac{I_2'}{I_1'}\right)_{\text{av}} \left(\frac{I_1''}{I_2''}\right)_{\text{av}}, \qquad (20)$$

where the single-primed and double-primed quantities correspond to circular and linear polarization, respectively.

4. EXPERIMENTAL RESULTS. DISCUSSION

A. Figure 2 shows the Ω(ω) dependence together with the two-quantum absorption spectrum δ(ω). The dashed line in the figure denotes the 0–0 transition. The verti-

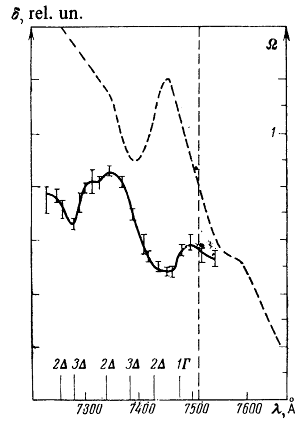

FIG. 2. Spectrum of the cross section of two-photon absorption δ(ω) (dashed) and spectrum of the polarization ratio Ω(ω) (solid line). The vertical dashed line marks the 0-0 transition; the vertical lines on the abscissa axis mark the frequencies of the asymmetrical vibrations of the ground state, reckoned from the 0-0 transition; the designations of the types of vibrations are in accord with [17].

cal lines on the abscissa axis mark the frequency bands of the asymmetrical vibrations of anthracene in the ground state, relative to 0–0, taken from papers on infrared absorption.[17, 18] The corresponding vibrations of the excited state should be active in two-quantum transitions. Indeed, a vibrational structure appears in the spectrum of the two-quantum absorption, and a shift towards the short-wave side relative to the 0–0 transition is clearly seen. The vibrational structure includes two peaks shifted by approximately 200 cm^{-1}, on both sides of the 0–0 transition (λ = 7450 and 7580 Å). The peak shifted to the short-wave side is connected with a transition to the vibrational sublevel of the excited state B_{2u}, and the peak in the long-wave region corresponds to a transition from the vibrational sublevel of the ground state A_{1g}. The population of the vibrational sublevel of frequency $\sim 200\ \mathrm{cm}^{-1}$ is smaller by a factor $\exp \omega/kt \sim 3$ ($\omega \sim 200\ \mathrm{cm}^{-1}$, $T = 300\,^{\circ}\mathrm{K}$) than the population of the ground state, corresponding approximately to the ratio of the peaks on Fig. 2. A confirmation of the temperature origin of the absorption in the long-wave region of the spectrum, and in particular of the maximum of absorption at λ = 7580 Å, may be the temperature dependence of the absorption at λ = 7670 Å in an alcohol solution of anthracene, which we investigated. The measurements have shown that the absorption decreases with decreasing temperature approximately like $\exp -\Delta/kT$, $\Delta = \Delta E + b(T - T_0)$, where $\Delta E = 530\ \mathrm{cm}^{-1}$ is the difference between the energy of the purely electronic transition at $T = 300^{\circ}$ and the energy of the light quantum, and $b = 0.73\ \mathrm{cm}^{-1}/\mathrm{deg}$ describes the change of the energy of the purely electronic transition with changing temperature. Such a relation corresponds simply to a decrease in the populations of the corresponding vibration sublevels with decreasing temperature.

The spectrum also exhibits an inflection in the short-wave region, located 600 cm^{-1} away from the 0–0 transition (λ = 7350 Å) (this inflection is apparently connected with a vibration with frequency on the order of 600 cm^{-1}, which appears in the infrared spectra.[17, 18]

B. The dependence of the polarization ratio Ω on the frequency within the electron-vibrational band, shown in Fig. 2, confirms the electron-vibrational nature of the two-quantum transitions in anthracene. In addition, the $\Omega(\omega)$ dependence, together with the $\delta(\omega)$ spectrum, makes it possible to obtain additional information, for example, concerning the symmetry of the vibrations taking part in the transitions. Thus, a clear-cut correspondence is observed between the maximum of the $\delta(\omega)$ curve and the minimum of $\Omega(\omega)$ at λ = 7450 Å. This indicates (see Sec. 2E) that the 200 cm^{-1} vibration has a symmetry b_{2u}. The inflection of the function $\delta(\omega)$ corresponds to a maximum of the Ω curve, pointing to a symmetry b_{3u} of the $\sim 600\ \mathrm{cm}^{-1}$ vibration (this agrees with data on infrared measurements[18]). We note that a certain asymmetry of this maximum of Ω is possibly connected with the overlap of the zeroth and first series, based on the fully-symmetrical vibration at 390 cm^{-1}. In addition, the function $\Omega(\omega)$ has a minimum (λ = 7280 Å), which has no analog on the $\delta(\omega)$ curve. This minimum is due to the b_{2u} vibration of frequency $\sim 840\ \mathrm{cm}^{-1}$ of the excited electronic state.

This example shows that the polarization spectrum Ω offers certain advantages in the study of the role of different vibrations in forbidden two-photon transitions.

Thus, the experimental results of a study of the properties of forbidden two-quantum transitions in centrally-symmetrical molecules are in good agreement with the theory of electron-vibrational transitions and are completely explained by this theory.

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