

Two-photon absorption and spectroscopy

V. I. Bredikhin, M. D. Galanin, and V. N. Genkin

Radiophysics Scientific Research Institute, Gor'kii, and P. N. Lebedev Physics
Institute of the USSR Academy of Sciences

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1. INTRODUCTION

The creation of powerful light sources—optical quantum generators (lasers)—has led to the development of nonlinear optics, and in particular to nonlinear spectroscopy. In the last ten years, a large number of papers has been devoted to the questions of two-quantum absorption and its connection with the energy structure of matter. The purpose of this review is to discuss the information which has been or can be obtained from data on two-photon absorption in different substances. By a two-photon transition we shall mean a transition between energy levels with energy difference equal to the sum of the energies of the two absorbed quanta. Here it is assumed that ordinary resonance absorption is absent.

In ordinary absorption spectra, we are concerned with the absorption coefficient as a function of the frequency of the field. For crystals, with the polarization taken into account, this can be three functions. In two-quantum spectroscopy, we are concerned with the absorption as a function of two frequencies, i.e., instead of a plane curve, the spectrum is a two-dimensional surface. The dependence on the polarization for two-photon absorption is more complicated, and in particular, even for isotropic media, the mutual orientation of the electric vectors of the absorbed fields is important. Thus, the information which can be obtained from a two-photon spectrum is greater than that given by a one-photon spectrum. It must be noted that, sometimes, two-photon and one-photon spectra contain different information. Thus, e.g., in the dipole approximation, two-photon transitions are allowed between states of the same parity, whereas one-photon transitions are allowed between states of different parity. In the theoretical treatment, we shall always assume the field of the electromagnetic waves to be given. In analyzing the experiments, wherever it is necessary we shall take into account the effects of propagation, which, in the cases considered, reduce to attenuation of the waves and change of their polarization.

It is pertinent to note that two-photon processes can be used not only to study matter, but also to study the coherent properties of radiation, and also in a whole series of applications (the measurement of the duration of pico-second pulses, two-photon excitation of lasers, two-photon tunable lasers, power limiters, and so on). These questions are not considered below.

In Sec. 2, a general analysis of an approximate description (with two or a few levels or bands taken into account) of two-quantum transitions is given. It is shown

that, in the study of two-quantum absorption (and, incidentally, of Raman scattering), it is more convenient to use the energy of interaction with the field \mathbf{E} in the form $(\mathbf{d} \cdot \mathbf{E})$, where \mathbf{d} is the dipole moment. In Sec. 3, the features of experiments on two-photon absorption in different media are analyzed. Section 4 is devoted to the study of two-quantum transitions in molecules and molecular crystals. A detailed comparison with experiment is performed. Finally, in Sec. 5, two-photon absorption in semiconductors and ionic crystals is discussed. The theory is compared with experiment. It is shown on the basis of the experimental data that two-photon absorption in $A_{II}B_{VI}$, $A_{III}B_{V}$ and $A_{IV}B_{IV}$ semiconductors can, in its principal features, be described in a unified way in a two-band model.

2. GENERAL RELATIONS FOR TWO-PHOTON TRANSITIONS

a) Two-photon transition probability. The general properties of two-quantum absorption were studied back in the 1930's^[1,2] and have been adequately discussed in reviews and monographs^[3-8]. Here, therefore, we write out the expression for the probability of two-photon transitions per unit time, omitting its derivation:

$$W_{21}^{ab} = (2\pi)^2 \omega_a \omega_b |M_{21}^{ab}|^2 \{[\epsilon_{aa}(\omega_a) \epsilon_{bb}(\omega_b)]^{1/2} c^2 \hbar^2\}^{-1} F_a F_b \delta(\omega_{21} - \omega_a - \omega_b). \quad (2.1)$$

The expression (2.1) describes the transition of a system from state 1 to state 2 under the action of two (a and b) monochromatic fields (with frequency ω_a , polarization direction \mathbf{e}_a , and quantum flux F_a); $\epsilon_{aa}(\omega_a)$ is the diagonal component of the dielectric-permittivity tensor in the direction of \mathbf{e}_a ; M_{21}^{ab} is the composite matrix element. For the following, we shall need the explicit form of the composite matrix element in the dipole approximation for the one-electron problem. As is well known^[1,2]

$$M_{21} = \frac{e^2}{m^2 \omega_a \omega_b} \sum_l \left(\frac{p_{21}^a p_{l1}^b}{\omega_{l1} - \omega_b} + \frac{p_{21}^b p_{l1}^a}{\omega_{l1} - \omega_a} \right), \quad (2.2)$$

where e is the charge and m the mass of the electron, and p_{21}^a is the matrix element of the component of the momentum operator in the direction of \mathbf{e}_a ; l labels the stationary states of the system.

Expression (2.2) is obtained using perturbation theory, if the interaction of the system with the field is chosen in the form

$$V = - (e/c) \mathbf{A}(t) \hat{p}, \quad (2.3)$$

where $\mathbf{A}(t)$ is the vector potential of the electromagnetic

field. We note that the form (2.2) of the composite matrix element is not unique, although it is very common in the literature. In fact, using a canonical transformation^[9-11], we can reduce the expression (2.2) in the case of a discrete spectrum (an electron in a molecule) to the form

$$M_{21}^{ab} = e^2 \sum_l \left(\frac{r_{21}^a r_{l1}^b}{\omega_{l1} - \omega_a} + \frac{r_{21}^b r_{l1}^a}{\omega_{l1} - \omega_b} \right), \quad (2.4)$$

where $r_{ll'}$ is a matrix element of the coordinate operator^[12]:

$$r_{ll'} = -ip_{ll'}/m\omega_{ll'}. \quad (2.5)$$

If the spectrum of the energy eigenvalues has a band structure (an electron in a crystal lattice), then we can write in place of (2.2)^[10,13]

$$M_{21}^{ab} = e^2 \left[\frac{\partial}{\partial k_a} \frac{\Omega_{21}^b(k)}{\omega_{21}(k) - \omega_b} + \frac{\partial}{\partial k_b} \frac{\Omega_{21}^a(k)}{\omega_{21}(k) - \omega_a} + \sum_l \left(\frac{\Omega_{21}^a \Omega_{l1}^b}{\omega_{l1}(k) - \omega_b} + \frac{\Omega_{21}^b \Omega_{l1}^a}{\omega_{l1}(k) - \omega_a} \right) \right]. \quad (2.6)$$

In (2.6), l is the band index and $\hbar\mathbf{k}$ is the quasi-momentum in the band;

$$\begin{aligned} \Omega_{ll'}(\mathbf{k}) &= -i r_{ll'}(\mathbf{k}) - \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}') \delta_{ll'}, \\ \dot{\Omega}_{ll'}(\mathbf{k}) &= i\omega_{ll'} \Omega_{ll'} = -(i p_{ll'}/m) + i \nabla_{\mathbf{k}} \mathcal{E}_l(\mathbf{k}) \delta_{ll'}(\hbar). \end{aligned} \quad (2.7)$$

$\mathcal{E}_l(\mathbf{k})$ is the dispersion law of the electrons in the band^[14]. The expressions (2.4) and (2.6) can also be obtained directly from perturbation theory, if we represent the energy of the interaction of the system with an electric field $\mathbf{E}(t)$ in the form

$$V = e\mathbf{r}\mathbf{E}(t).$$

Naturally, the expressions (2.2) and (2.4), (2.6) for the composite matrix element are completely equivalent.

b) Approximate expressions for the composite matrix element when not all the levels (bands) are taken into account. It is often found to be impossible to determine the composite matrix element from the formulas (2.2) or (2.4), (2.6), since for specific substances the characteristics of far from all the states are known. This forces us in describing two-quantum absorption to use some or other approximation for the composite matrix element M_{21} . It is usually assumed that the principal contribution to the probability of a two-quantum transition is associated with those intermediate states i which lie close to the levels 1 and 2:

$$\hbar |\omega_{i1}|, \hbar |\omega_{21}| \ll \hbar\omega_a, \hbar\omega_b.$$

The contribution of distant states j , i.e., of states for which

$$\eta = |(\omega_a + \omega_b)/\omega_{ij}| \ll 1, \quad (2.8)$$

is assumed to be negligibly small.

In this approximate approach, the expressions (2.2) and (2.4), (2.6) for the composite matrix element are no longer equivalent. The form (2.4), (2.6) of the composite matrix element turns out to be preferable, since the terms discarded in the summation over l contain an extra factor η^2 compared with the corresponding terms in (2.2). Moreover, the few-band approximation in (2.2) may turn out to be incorrect, while the approximate expressions following from (2.4) or (2.6) will describe two-quantum transitions sufficiently accurately. To see this, we consider the commutation relations between the coordinate and momentum^[12]

$$[p^a, r^b]_{21} = \sum_l [(p_{21}^a p_{l1}^b / \omega_{l1}) + (p_{21}^b p_{l1}^a / \omega_{l2})] = 0. \quad (2.9)$$

Comparing the expression (2.9) with (2.2), we find that

the contribution of states satisfying the inequality (2.8) is

$$\tilde{M}_{21} = (e^2/m^2\omega_a\omega_b) \sum_{i \neq j} [(p_{21}^a p_{i1}^b / \omega_{i1}) + (p_{21}^b p_{i1}^a / \omega_{21})]. \quad (2.10)$$

The expression (2.10) is obtained by summation of the zeroth-order and first-order terms in η for each j . It can be seen from (2.10) that the contribution of the high-lying states to (2.2) can be expressed in terms of the characteristics of the states i close to the levels 2 and 1. This contribution is not necessarily small. We add that it is precisely the term (2.10) which distinguishes the approximate (with not all the levels taken into account) expressions following from (2.2) and (2.4). In the case of a band spectrum, the contribution of the upper bands can be represented, using (2.7), in the form

$$\begin{aligned} \tilde{M}_{21}(k) &= (e^2/\omega_a\omega_b) \left[\sum_{i \neq j} (\omega_{21} \Omega_{21}^a \Omega_{i1}^b + \omega_{i1} \Omega_{21}^b \Omega_{i1}^a) - \right. \\ &\quad \left. - (\partial/\partial k_b) (\omega_{21}(k) \Omega_{21}^a) - \Omega_{21}^b \partial \omega_{21}(k) / \partial k_a \right]. \end{aligned} \quad (2.11)$$

We can see by comparing the expression (2.2) for the composite matrix element with (2.10) and (2.11) that the three-level (three-band) approximation^[10,11] in (2.10), (2.11) of the other levels (bands) to the composite matrix element is of the same order. The expression following from (2.2) in the two-band approximation is also found to be incorrect. Naturally, to obtain a correct result in approximate calculations, it is necessary to combine the contribution obtained from (2.2) when the levels i are taken into account, with (2.10) or (2.11). We emphasize that the approximate expressions following from (2.2), when combined with (2.10) or (2.11), are equivalent to those which can be obtained from (2.4) or (2.6) directly.

To conclude this section, it is appropriate to add that all the relations concerning approximate expressions for the composite matrix element are also valid in the description of Raman scattering.

c) Polarization dependence of two-photon transitions. Two-photon absorption depends essentially on the polarization of the electric fields. This dependence differs sharply from the polarization dependence of one-photon absorption, in that two-photon absorption depends on the polarization even in an isotropic medium. For spectroscopic purposes, the polarization dependence of W_{21}^{ab} is of special interest, since it enables us to obtain information on the symmetry of the states participating in the two-photon transition. In isotropic media and media with cubic symmetry, this dependence is determined by the polarization properties of the composite matrix element M_{21}^{ab} . In media with lower symmetry, the dependence of the two-photon transition probability W_{21}^{ab} on the polarization of the electric fields is determined also by the properties of the dielectric permittivity $\epsilon_{ab}(\omega)$. As can be seen from (2.1), $\epsilon_{ab}(\omega)$ appears directly in the expression for the two-photon transition probability and, in addition, the difference between the field acting on the electron and the macroscopic field occurring in the Maxwell equations is also related to $\epsilon_{ab}(\omega)$. The relation between the effective and macroscopic fields for nonlinear problems is discussed in^[15].

The polarization properties of two-photon absorption that arise from the polarization properties of the composite matrix element M_{21} will be discussed in Sec. 4 for isotropic media (vapors, liquids and solutions) and in Sec. 5 for crystals.

3. EXPERIMENTAL TECHNIQUE

Two-photon transitions in matter lead to attenuation of the incident fluxes of quanta. This attenuation depends both on the properties of the substance and on the magnitude of the quantum flux. We can introduce, e.g., the cross-section for absorption of quanta of type *a* in the presence of a field *b*:

$$\sigma = W_{21}^{ab}/F_b = \gamma_{21}^{ab} F_a.$$

The properties of the substance are characterized by the quantity γ_{21}^{ab} . For solutions, it is convenient to divide this quantity by the number of absorbing particles, introducing the two-quantum absorption "cross-section" per molecule:

$$\delta_{21}^{ab}(\omega_a, \omega_b) = W_{21}^{ab}/NF_a F_b \text{ for } a \neq b \text{ and } \delta_{aa} = W_{21}^{aa}/4NF_a^2,$$

where *N* is the density of absorbing particles. This quantity has the dimensions $\text{cm}^4 \text{sec}$.

For condensed media, it is more convenient to use the imaginary part of the nonlinear-susceptibility tensor^[5]

$$\chi_{aabb}^{\prime\prime}(\omega_a, \omega_b) = [c^2(\epsilon_{aa}\epsilon_{bb})^{1/2}/8\pi^2\hbar\omega_a\omega_b] W_{21}^{ab}/F_a F_b.$$

to characterize two-photon absorption.

a) One source. The features of the experimental technique for measuring two-photon absorption are associated primarily with the fact that, to obtain a measurable effect, large light fluxes, which can be obtained at present only from pulsed lasers, are necessary. The magnitude of the light flux is limited by the stability to light of the material being studied. For the fluxes applicable in practice $F \sim 10^{25} - 10^{26} \text{ cm}^{-2} \text{ sec}^{-1}$, the effective two-photon absorption cross-section $F\delta$ is found to be rather small. Nevertheless, in the fundamental-absorption region of condensed media, a direct measurement of the absorption is still possible, although near the absorption-band edge and for solutions or gases it is necessary to turn to indirect methods. We must keep in mind that, in the case of two-photon absorption of light from one source, the law of exponential decrease of the flux, $F(x) = F_0 \exp(-k_1x)$, is replaced by the hyperbolic law:

$$F(x) = F_0/(1 + k_2x),$$

where $k_2 = \delta NF_0$, i.e., depends on F_0 . However, the absorption is often so small that we can use the linear approximation $F(x) \approx F_0(1 - k_2x)$, where $k_2x \ll 1$, and we may speak of a two-photon "absorption exponent" for a light flux of given magnitude.

We also note that a direct measurement of the attenuation in semiconductors can be made difficult because of the linear absorption, e.g., by the free carriers formed in considerable quantities under the action of the powerful radiation^[16].

To measure small absorption, indirect methods are used. Of these methods, the most common is the measurement of the intensity of the luminescence excited in the two-photon absorption¹⁾. The luminescence method of measuring two-photon absorption has been applied in a large number of experiments, especially for solutions of organic substances, where it is, apparently, the only possible method. Most measurements have been performed at ruby-laser frequency ($\lambda = 694 \text{ nm}$). By measuring the luminescence intensity, it is especially easy to determine the relative values of δ . Absolute measurements are more difficult.

Values differing by more than an order of magnitude for the same substance have been given in the literature (see Sec. 4(d)).

In^[17], to determine the absolute values of δ a comparison of the luminescence intensity for two- and one-photon excitation was used, and in^[18], comparison with the radiation of a photometric lamp was used. The principal errors in the determination of the absolute value of δ are connected with the fact that, with a quadratic dependence of the luminescence intensity on the exciting flux, it is difficult to perform the averaging over the (transverse) space and time distributions of the laser intensity. To obtain a more exact absolute value of δ for a solution of anthracene, a ruby laser working in the single-mode regime was used in^[19]. Here, a comparison was made of the luminescence excited in the two-photon absorption of the laser radiation and the luminescence excited in the one-photon absorption of the second harmonic from the same laser. The results of these measurements are described in Sec. 4 (d).

An important stride in the development of the technique for measuring two-photon absorption has been the application of dye lasers with tunable frequency^{[20,21]2)}. This has made it possible to obtain two-photon absorption spectra even with one source. In^[20,21], the spectra of the absorption $\delta(\omega)$ and of the polarization ratio $\Omega(\omega)$ have been obtained by this method for a solution of anthracene in cyclohexane in the region of wavelengths 720–760 nm. A laser on solutions of polymethylene dyes, excited by a giant ruby-laser pulse, was used. A narrowing of the generation band to 5 Å was achieved by applying a diffraction grating as one of the resonator mirrors. Rough frequency tuning was effected by choosing different dyes and by changing the concentration of the solutions, and fine tuning by rotating the grating. The two-photon absorption was measured by the luminescence intensity. The laser intensity was monitored by the two-photon absorption in a standard solution. In addition to the two-photon absorption for linearly polarized light, the absorption for circularly polarized light was measured. A quarter-wave plate, tunable in accordance with the laser frequency and consisting of two quartz wedges able to move relative to each other, was used.

Along with the luminescence method, the photo-conductivity arising in the two-quantum photo-conductive effect is also used in the measurement of two-photon absorption in crystals. Indirect measurements by means of comparison with one-quantum absorption in semiconductors are complicated by the large difference in the conditions of two-quantum and one-quantum excitation to the interior of the band, this difference being connected with the strong influence of the state of the surface on the luminescence and conductivity for one-quantum excitation^[125]. Another difficulty of the indirect measurements in semiconductors arises from the complicated kinetics of the nonequilibrium carriers.

b) Two sources. The application of two independent sources for the measurement of two-photon absorption laid the foundations of two-photon spectroscopy. For one of the sources a pulse laser is used, as before, and for the other an ordinary pulsed xenon lamp is used. As a rule, the substance investigated is practically transparent for each of the sources separately. By cutting out a narrow portion from the continuous spectrum of the lamp by means of a monochromator, one can plot the two-photon absorption spectrum. The laser pulse and the

lamp flash are synchronized in order that their maxima occur at the same time. Usually, the lamp pulse is considerably longer than the laser pulse. Therefore, the phenomenon of two-photon absorption is observed experimentally as a decrease of the transmission of the light from the lamp at the moment the laser pulse acts on the substance. In the two-source method, it is possible to change the direction of polarization in the two beams independently, and this further increases the information obtainable.

In this method, only one of the sources should be strong, i.e., the laser source. The intensity of the second source is determined only by the practical requirements of the experiment. The two-photon absorption of the laser light induced by the presence of the light from the second source is, of course, negligibly small, and the observable effect of the absorption of the light from the second source at the time of action of the laser depends linearly on the intensity of the latter. This makes it considerably easier to determine the absolute magnitude of the absorption corresponding to a given flux from the laser, since in the calculations one can use the laser-intensity value averaged over the time and transverse cross-section of the beam.

The two-source method was first applied in the pioneering work of^[24], in which the laser operated in the free regime. In subsequent work, solid Q-pulsed lasers have been used. The experimental setups of the different authors differ only in technical details, such as, e.g., the directions of the two beams. They can be mutually perpendicular, directed at an angle to each other, or arranged in opposition. This does not play an important role, since the absorption depends on the direction of the electric vectors.

In measurements of the polarization angular dependences, it is necessary to pay attention to the mutual orientation of the electric vectors, and also, in the case of crystals, to their direction relative to the crystallographic axes. For birefringent crystals, it is also necessary to take into account that the state of polarization changes as the light propagates in the crystal.

Figure 1 shows the scheme of the experimental setup. For fluxes of about 10^{25} cm⁻² sec⁻¹, the two-photon absorption "exponent" usually amounts to a few hundredths of a cm⁻¹ and the decrease of transmission at the time of the laser pulse correspondingly reaches, at best, a few per cent. Therefore, the accuracy of the measurements and the sensitivity of the method are essentially limited by noise. In this respect, measurements of two-photon absorption have certain special features. A characteristic of these measurements is that, because of the single-pulse character of the experiment, it is difficult to use a

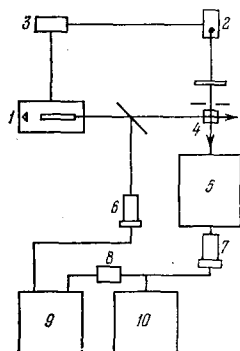


FIG. 1. Block diagram of the setup for two-photon spectroscopy with two sources: 1—laser, 2—pulsed lamp, 3—synchronization circuit, 4—sample, 5—monochromator, 6, 7—photomultiplier, 8—RC-filter, 9, 10—oscillographs.

differential method and, moreover, it is necessary to determine a small and rather short-duration change of signal against the background of a longer pulse. This places the photo-multiplier in a disadvantageous regime. Usually, one works in such a way that the pulse from the photo-multiplier goes simultaneously to two oscillographs, one of which (this can be a comparatively low-frequency one) detects the long (e.g., 20 μ sec) pulse of the lamp, and the other detects—through a differentiating ladder network—the short (20 nsec) pulse of the increase in absorption at the time of action of the laser. The magnitude of the laser pulse is monitored simultaneously.

The sensitivity of the method depends mainly on the shot noise of the photo-multiplier. For a crude estimate of the noise, we can take into account the fluctuations determined by the number of photo-electrons emitted from the cathode of the photo-multiplier (PM) in the resolving time of the apparatus, and neglect the other sources of noise, e.g., the effect of the PM diodes. If this number of photo-electrons is equal to n , the relative mean fluctuation of the signal is equal to $\Delta V/V = 1/n^{1/2}$. The number n of photo-electrons can be related to the amplitude V of the pulse at the load resistance of the PM. If τ is the time characterizing the width of the amplification band of the detecting apparatus, α is the gain of the PM, and R is the load resistance, then

$$n = V\tau/\alpha eR,$$

where e is the electron charge. Taking $V = 10$ V, $\tau = 10^{-7}$ sec, $\alpha = 10^6$, and $R = 75$ ohm, we find $\Delta V/V = 0.003$. The precision of the measurements obtained in practice is somewhat better, as a result of averaging over many pulses.

In^[25], an automatic "two-photon spectrometer" is described, in which the pulse amplitude is measured by a digital voltmeter and displayed on a printing device. The work of the whole apparatus is completely automated, and, because of this, high stability and good accuracy of the data obtained are achieved.

4. TWO-QUANTUM TRANSITIONS IN MOLECULES AND MOLECULAR CRYSTALS

a) Nature of Two-quantum Transitions in Organic Molecules. A fairly extensive literature has been devoted to the study of two-quantum absorption in molecules and molecular crystals. Organic aromatic compounds have been the object of study in the overwhelming majority of cases. This is due, firstly, to the fact that the spectra of these compounds are convenient for study, and, secondly, to the large probability of two-quantum transitions in them.

A considerable number of papers are associated with the study of anthracene^[18-23,26-61]. Using this compound as an example, the nature of the experimentally detected two-quantum transitions between electronic levels of different parity has been elucidated. Two-photon transitions between states of different parity are forbidden by symmetry in the dipole approximation. Many authors have assumed that the observable transitions between electronic levels of different parity in organic compounds are due to quadrupole and magnetic-dipole interactions^[34,40,51,62,63]. However, the probability of such multipole transitions is smaller than for dipole transitions by a factor of $(a/\lambda)^2$ (a is the size of the molecule and λ is the wavelength). For optics, this ratio is 10^{-6} — 10^{-7} . Estimates suggest that, generally speaking,

multipole transitions can be observed, but the first measurements of the absolute magnitude of the two-quantum absorption cross-section in organic molecules have already demonstrated the untenability of this explanation.³⁾ The investigations in [20,21,44,50,54,56,59,64] have made it possible to establish that two-quantum transitions in molecules have an electronic-vibrational character. But transitions between electronic levels of different parity are due, in the final analysis, to distortion of the symmetry of the molecules by asymmetric vibrations. The relative intensity of such transitions is equal to $\omega_{\text{vib}}/\omega_{\text{el}}$ (ω_{vib} and ω_{el} are the characteristic frequencies of the intra-molecular vibrations and of the electronic transitions respectively).

b) Structure of the spectrum of two-photon electronic-vibrational transitions^[21]. 1) Two-photon transitions in a molecule are characterized conveniently by the two-quantum absorption cross-section, which is determined by the properties of the molecule and does not depend on the quantum fluxes:

$$\delta = \frac{(2\pi)^3 \omega_a \omega_b}{\epsilon c^2 \hbar^2} |M_{21}^{ab}|^2 \delta(\omega_{21} - \omega_a - \omega_b) \quad (4.1)$$

$$= \frac{(2\pi)^3 \omega_a \omega_b}{\epsilon c^2 \hbar^2} \left| \sum_l \left(\frac{d_{1l}^a d_{l2}^b}{\omega_b - \omega_{l1}} + \frac{d_{1l}^b d_{l2}^a}{\omega_a - \omega_{l1}} \right) \right|^2 \delta(\omega_{21} - \omega_a - \omega_b);$$

Here \hat{d} is the operator of the dipole moment of the molecule:

$$\hat{d} = \sum_i e_i \hat{r}_i + \sum_j g_j \mathbf{R}_j, \quad (4.2)$$

where \mathbf{r}_i are the coordinates of the electrons, and g_j and \mathbf{R}_j are respectively the charges and coordinates of the nuclei. For the subsequent analysis, it is necessary to know the matrix elements of the dipole moment. We shall treat these in the adiabatic approximation, by representing the wavefunction ψ of a stationary state in the form^[65,66]

$$\Psi_{s_j}(\mathbf{r}, \mathbf{R}) = \theta_s(\mathbf{r}, \mathbf{R}) \varphi_{j_s}(\mathbf{R}) = \langle s | j_s \rangle, \quad (4.3)$$

where $\theta_s(\mathbf{r}, \mathbf{R})$ is an eigenfunction of the Hamiltonian of the molecule with the nuclei fixed, and $\varphi_{j_s}(\mathbf{R})$ is the wavefunction of the nuclei in the s -th electronic state.

If we use (4.3), the matrix element of the operator (4.2) can be written as follows:

$$\langle s_j_s | \hat{d} | m_j_m \rangle = \langle j_s | \mathbf{d}_{sm} | j_m \rangle (1 - \delta_{sm}) + D_{j_s j_s}^s \delta_{sm}; \quad (4.4)$$

$\mathbf{d}_{sm}(\mathbf{R}) = \langle s | \mathbf{d} | m \rangle$ is the matrix element of the dipole moment of the electronic part of the system and depends parametrically on the positions of the nuclei, and $D_{j_s j_s}^s$ is the matrix element of the dipole moment of the molecule, which determines the intensity of transitions between the vibrational sub-levels j and j' of the s -th electron state.

We change from the Cartesian coordinates \mathbf{R}_j of the nuclei to normal coordinates Q_α^s in the electronic state s (the index α labels the normal coordinates) and represent $\langle s_j_s | \hat{d} | m_j_m \rangle$ in the form of a series in the normal coordinates. Confining ourselves to the terms linear in Q_α , in place of (4.4) we have

$$\langle s_j_s | \hat{d} | m_j_m \rangle = \mathbf{d}_{sm}(0) \langle j_s | j_m \rangle + \sum_\alpha \lambda_{sm}^\alpha \langle j_s | Q_\alpha^s | j_m \rangle (1 - \delta_{sm}) + \sum_\alpha g_{\alpha s} \langle j_s | Q_\alpha^s | j_s \rangle e_\alpha^s \delta_{sm}; \quad (4.5)$$

here, \mathbf{e}_α^s are the units vectors of the polarization of the normal vibrations, and

$$\lambda_{sm}^\alpha = \sum_j \left\{ \frac{d_{jm}}{\hbar \omega_{jk}} \left\langle Q_\alpha^{(m)} \left| \frac{\partial H}{\partial Q_\alpha} \right| \theta_k^{(m)} \right\rangle + \frac{d_{sk}}{\hbar \omega_{mk}} \left\langle \theta_k^{(m)} \left| \frac{\partial H}{\partial Q_\alpha} \right| \theta_m^{(m)} \right\rangle \right\}. \quad (4.6)$$

The matrix elements in (4.6) are defined by means of the function $\theta_m^{(0)}(\mathbf{r}) = \theta_m(\mathbf{r}, \mathbf{R}_j^{(0)})$, where $\mathbf{R}_j^{(0)}$ are the coordinates of the nuclei in the equilibrium configuration of the s -th electronic state;

$$g_{\alpha s} = \sum_j g_j (\mathbf{R}_j \mathbf{e}_\alpha^s) + (\lambda_{ss} \mathbf{e}_\alpha^s) \quad (4.7)$$

is the effective charge determining the intensity of the vibrational transitions.

Below we shall need the relative magnitude of the different terms. An approximate comparison can be made by putting $\hbar \omega_{\text{sk}} \approx e^2/R_0$, where R_0 is the characteristic distance between the nuclei. Then the second and third terms will be of order $\Delta R/R_0$ relative to the first, where ΔR is the amplitude of vibrations of the nuclei.

2) We can now proceed directly to the analysis of the spectrum of the two-photon transitions. First of all, we consider the allowed transitions, i.e., transitions between electronic levels of the same parity. By substituting (4.5) into (4.1), we obtain for the absorption cross-section in zeroth order in $\Delta R/R$

$$\delta^{ab}(\omega_a, \omega_b) = \frac{(2\pi)^3 \omega_a \omega_b}{\epsilon \hbar^2 c^2} \times \sum_{j_l, j_s} \rho_{j_l}(j_l | j_s)^2 \delta(\omega_{s_j_s}; j_l - \omega_a - \omega_b) \left| \sum_m \frac{(d_{lm} \mathbf{e}_a)(d_{ms} \mathbf{e}_b)}{\omega_b - \omega_{ml}} + \frac{(d_{lm} \mathbf{e}_b)(d_{ms} \mathbf{e}_a)}{\omega_a - \omega_{ml}} \right|^2, \quad (4.8)$$

where $\omega_{s_j_s}; j_l$ are the molecular eigenfrequencies

corresponding to electronic-vibrational transitions, $\langle j_l | j_s \rangle$ is the overlap integral between the vibrational functions of the initial and final states, and ρ_{j_l} is the

equilibrium density matrix^[14] describing the population distribution of the vibrational sublevels of the initial state of the molecule. The expression (4.8) represents the total probability, averaged over the initial vibrational states and summed over the final vibrational states, of a two-photon transition between electronic levels. In going from (4.1) to (4.8), we have used the equality

$$\sum_m \langle j_l | j_m \rangle \langle j_m | j_s \rangle = \langle j_l | j_s \rangle, \quad (4.9)$$

which follows from the completeness and orthonormalization of the eigenfunctions of the vibrational problem for an arbitrary electronic state^[12].

We shall be interested in the structure of two-quantum transitions within the limits of one electronic band. We note that the factor inside the modulus sign in (4.8) does not depend on the parameters of the vibrational motion. If in addition we assume that, for all intermediate states m , the difference between the frequencies ω_{ml} of the electronic transitions and the field frequencies ω_a and ω_b are large compared with the width of the vibrational band, then this factor can be assumed to be constant inside the electronic band. We should add that this factor characterizes the total probability of a transition between the electronic states l and s ^[4].

Roughly speaking, the structure of the spectrum inside an electronic-vibrational band is determined by the δ -function in (4.8) and is a set of peaks corresponding to the different electronic-vibrational transitions. The intensity of the individual peaks depends on the overlap integral $\langle j_l | j_s \rangle$. If, e.g., the initial state is the ground state, $\rho_{j_l} = \delta_{j_l 0}$ (the ground-state symmetry is A_{1g}), then the overlap integral in (4.8) is non-zero only for fully symmetric vibrations of the final state⁵⁾.

Thus, the vibrational structure of a two-quantum transition depends principally on $\omega_a + \omega_b$. When the sum

$\omega_a + \omega_b$ is fixed, the absorption intensity, as can be seen from (4.8), depends on the product $\omega_a \omega_b$ and reaches a maximum when $\omega_a = \omega_b$. In practice, this dependence is of little importance, since, in experiments, we are most often concerned with close frequencies.

To conclude this examination of allowed transitions, we shall find estimates of the two-quantum absorption cross-section. The standard estimate formula has the form

$$\delta = [(2\pi)^3/\varepsilon\hbar^2c^2] (\omega^2/\Delta\omega) |d_{1m}d_{m2}/(\omega_{2m} - \omega)|^2. \quad (4.10)$$

To obtain (4.10) from (4.1), we have confined ourselves to taking one intermediate state m into account and have replaced the δ -function by the quantity $(\Delta\omega)^{-1}$ describing the broadening of the level. Substituting, for the quantities appearing in (4.10), values typical for polycyclic aromatic compounds (dipole moments of the order of a Debye, $\Delta\omega \sim 300 \text{ cm}^{-1}$, $\omega \sim \omega_{2m} \sim \omega_{m1} \sim 1.5 \times 10^4 \text{ cm}^{-1}$), we have $\delta \sim 10^{-48} - 10^{-50} \text{ cm}^4 \text{ sec photon}^{-1}$.

We note that this estimate is in agreement with the results of numerical calculation for a number of compounds^[64,67].

3) For electronic states of different parity (forbidden transitions), the two-quantum absorption cross-section, as follows from (4.1), (4.5), (4.6) and (4.9), is non-zero in first order in $\Delta R/R$:

$$\delta^{ab} = \frac{\omega_a \omega_b}{\varepsilon\hbar^2c^2} \sum_{j_l, j_s} \rho_{j_l} \delta(\omega_{j_l j_s} - \omega_a - \omega_b) \left| \sum_{\alpha} \langle j_l | Q_{\alpha} | j_s \rangle \right. \quad (4.11)$$

$$\times \left\{ \sum_m \frac{(d_{1m}e_a)(\lambda_{m_s}^{\alpha}e_b) + (\lambda_{1m}^{\alpha}e_a)(d_{m_s}e_b)}{\omega_b - \omega_{m1}} + \frac{(d_{1m}e_b)(\lambda_{m_s}^{\alpha}e_a) + (\lambda_{1m}^{\alpha}e_b)(d_{m_s}e_a)}{\omega_a - \omega_{m1}} \right.$$

$$\left. + \left[\frac{(d_{1s}e_a)(e_l^{\alpha}e_b)}{\omega_a} + \frac{(d_{1s}e_b)(e_l^{\alpha}e_a)}{\omega_b} \right] (g_{\alpha s} - g_{\alpha l}) \right\}^2.$$

In obtaining (4.11) from (4.1), the relation

$$\sum_{j_m} \langle j_l | Q_l^{\alpha} | j_m \rangle \langle j_m | j_s \rangle = \langle j_l | Q_l^{\alpha} | j_s \rangle. \quad (4.12)$$

was used. The equality (4.12), like (4.9), follows from the completeness and orthonormalization of the vibrational functions $|j_m\rangle$. In the expression (4.11), unlike (4.8), it is no longer possible to separate a factor depending only on the electronic coordinates of the molecule. In order to simplify the analysis of (4.11), we shall further assume that the molecule is in the ground state ($l=0, j_l=0$), that the vibrations of different types are harmonic and non-degenerate, and that the frequencies of both quanta are the same:

$$\omega_a = \omega_b = \omega, \quad e_a = e_b = e. \quad (4.13)$$

With these assumptions, the expression (4.11) for the cross-section can be simplified:

$$\delta(\omega) = (\omega^2/\varepsilon\hbar^2c^2) \delta(\omega_{s,00} - 2\omega) \langle 0 | Q_0^{\alpha} | 1_0^{\alpha} \rangle \langle 1_0^{\alpha} | j_s \rangle^2 \quad (4.14)$$

$$\times \left| \sum_m \{ (\omega - \omega_{m0})^{-1} [(d_{0m}e)(\lambda_{m_s}^{\alpha}e) + (\lambda_{0m}^{\alpha}e)(d_{m_s}e)] \} \right.$$

$$\left. + \omega^{-1} (d_{0s}e)(e_0^{\alpha}e) (\lambda_{00}^{\alpha} - \lambda_{0s}^{\alpha}) \right|^2.$$

In going from (4.11) to (4.14), we have used the fact that, in the harmonic approximation, for a transition from the ground state only the one matrix element $\langle 0 | Q_0^{\alpha} | 1_0^{\alpha} \rangle \neq 0$, and that^[12]

$$\langle 0 | Q^{\alpha} | j_s \rangle = \sum_{j_0} \langle 0 | Q_0^{\alpha} | j_0 \rangle \langle j_0 | j_s \rangle = \langle 0 | Q_0^{\alpha} | 1_0^{\alpha} \dots \rangle \langle 1_0^{\alpha} \dots | j_s \rangle. \quad (4.15)$$

We shall examine the frequency dependence of (4.14), which represents the intersection of the surface $\delta^{ab}(\omega_a, \omega_b)$ by the plane $\omega_a = \omega_b$. If we again confine ourselves to investigations of one electronic band, then, as in the preceding case, the spectrum is basically com-

posed of the electronic-vibrational transitions selected by the δ -function in (4.14). In contrast to (4.8), for forbidden transitions the cross-section is non-zero only for excitation of asymmetric vibrations. In fact, the possible types of electronic-vibrational transitions and their intensities are determined by the expression inside the modulus sign in (4.14). This expression is non-zero only for asymmetric vibrations. If, say, the state m is odd ($d_{0m} \neq 0$), then the levels m and s have the same parity, and then (cf. (4.6)) λ_{sm}^{α} is non-zero only for odd vibrations. The same can also be said of λ_{0m} for even states m .

The intensity of any given line in the spectrum is determined also by the overlap integral $\langle 1_0^{\alpha} | j_s \rangle$ of the vibrational function of the ground electronic state with excitation of one quantum of asymmetric vibration of type α , and the vibrational function of the final state j_s . Representing these functions in the form of products of functions referring to different vibrations, we find

$$\langle 1_0^{\alpha} \dots | j_s \rangle^2 = \langle 1_0^{\alpha} | 1_0^{\alpha} \rangle^2 \prod_{\beta} \langle 0 | j_s^{\beta} \rangle \approx \prod_{\beta} \langle 0 | j_s \rangle; \quad (4.16)$$

β in (4.16) labels the fully symmetric vibrations. In writing (4.16), we have taken into account that the equilibrium position is not displaced for asymmetric vibrations of excited states, and, consequently, the overlap integral is large (approximately equal to unity) only for vibrational states with the same quantum numbers. The quantity $\prod \langle 0 | j_s^{\beta} \rangle$ defines a progression over the fully symmetric vibrations (this quantity also determines the vibrational structure of a one-quantum transition).

The following characteristic feature of the two-quantum absorption spectrum for transitions between electronic levels of different parity arises from the above analysis. Within an electronic-vibrational band, the spectrum consists of a set of series, the first of which is shifted into the short-wave region from the 0-0 transition by the frequency of the asymmetric vibration of lowest frequency. Each series consists of peaks corresponding to the excitation of asymmetric vibrations of different types. The different series differ in the excitation not only of asymmetric vibrations but also of a fully symmetric vibration of one type or another. The spacings between the series are determined by the frequencies of the fully symmetric vibrations. The relative intensities of the peaks in a series remain the same on going from one series to another. The spectral pattern described here is shown in Fig. 2. It should be noted that this picture is only a guide, inasmuch as it does not take into account the finite width of the electronic-vibrational states. Under experimental conditions, this broadening is large (excluding the case of the Shpol'skiĭ effect^[68]) and the different electronic-vibrational levels can overlap. We note that the analysis given is easily extended to the case $\omega_a \neq \omega_b$. If we exclude resonance with an intermediate state, then the absorption cross-section for fixed $\omega_a + \omega_b$ falls by a factor of $4\omega_a\omega_b/(\omega_a + \omega_b)^2$ for $\omega_a \neq \omega_b$. As regards estimates, one can obtain from (4.14) in the corresponding approximations an estimate formula of the type (4.10):

$$\delta = [(2\pi)^3/\varepsilon\hbar^2] (\omega^2/\Delta\omega c^2) |d_{1m}d_{m2}/(\omega_{2m} - \omega)|^2 (\Delta R/R_0)^2. \quad (4.17)$$

The square of the ratio of the displacement of the nuclei in vibrations to the equilibrium distance is, in order of magnitude,

$$|\Delta R/R_0|^2 \approx \omega_{vib}/\omega_{0m}. \quad (4.18)$$

The parameter (4.18) determines the degree of forbid-

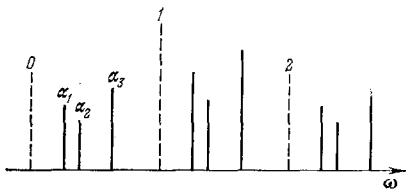


FIG. 2. Scheme of the two-photon absorption spectrum in centrosymmetric molecules in transitions between electronic levels of different parity. The dashed lines 0-2 show the progression based on the fully symmetric vibration (0 denotes the purely electronic transition). The solid lines show electronic-vibrational transitions corresponding to different (α_1 , α_2 and α_3) asymmetric vibrations.

denness of transitions between electronic states of different parity. For typical cases in polycyclic aromatic molecules, its value is 30^{-1} – 300^{-1} . A more accurate estimate can also be performed, at least for the second term inside the modulus sign in (4.14). Assuming that the difference $\lambda_{SS} - \lambda_{00} \sim \lambda_{00}$, we have, analogously to (4.17),

$$\delta = \{(2\pi)^3/\hbar^2\} |d_{0s}|^2 |D_{01}|^2/c^2\Delta\omega,$$

where D_{01} is the dipole moment of the molecular vibrations. For anthracene, e.g., $d_{0s} \sim 0.7D$ (transition to the B_{2u} level), $D_{01} \sim 0.3D$, $\Delta\omega \sim 300 \text{ cm}^{-1}$, and for δ we have in this case $\delta \sim 10^{-51} \text{ cm}^4 \text{ sec photon}^{-1}$.

4) In concluding our examination of the structure of the spectrum of two-quantum transitions in molecules, we must add that, in the approximation described (neglect of the broadening of the electronic-vibrational transitions), the principal features of the spectrum remain the same for molecular crystals. Naturally, in crystals it is necessary to take into account the shift and Davydov splitting of the electronic-vibrational bands. As regards estimates, in crystals it is necessary to take into account the difference between the effective and macroscopic fields. This difference can lead to an increase of the cross-section. Thus, if both fields are directed along a symmetry axis (say, along the z-axis), the increase of the cross-section per molecule can reach the value $[(\epsilon_z + 2)/3]^4$. If we take into account that, for organic crystals, the π -electrons (and it is precisely these which take part in transitions in the visible and near ultraviolet part of the spectrum) are spread out over the cells, the quantity $[(\epsilon_{zz} + 2)/3]^4$ must be regarded as an upper bound on the possible increase of the cross-section in crystals.

c) Polarization properties of two-quantum transitions in molecules. 1) As can be seen from (4.1), the two-quantum transition probability in a molecule depends on the mutual orientation of the fields and the dipole moments appearing in the composite matrix element. Since in a gas or solution the molecules are randomly oriented, in measurements we obtain the magnitude of the two-quantum absorption cross-section averaged over all possible orientations of the molecule relative to specified directions (the directions of polarization of the fields). This averaging of the cross-section can depend only on the mutual orientation of the fields and on the mutual orientation of the dipole moments appearing in the composite matrix element^[17,54,69]. Thus, if the dipole moments are parallel, then δ for $\mathbf{e}_a \parallel \mathbf{e}_b$ exceeds δ for $\mathbf{e}_a \perp \mathbf{e}_b$ by a factor of 3^[53]. For the case of one field, different δ are also obtained, the value depending on whether the absorbed quanta are linearly or circularly polarized.

The polarization dependence of the cross-section of two-quantum transitions contains information on the symmetry of the intermediate and final states taking part in the transitions. We shall illustrate this with the example of molecules with D_{2h} symmetry (the symmetry of the anthracene molecule), by considering the dependence of the absorption cross-section of the molecule on the degree of ellipticity of the light.

2) For allowed two-quantum transitions, for D_{2h} symmetry the final states in (4.8) (the ground state is A_{1g}) can be electronic states of the type B_{1g} , B_{2g} , B_{3g} and A_{1g} . It is easy to see that for states of the type B_{1g} the possible intermediate states have symmetry B_{2u} and B_{3u} . For either intermediate state, the dipole moments in the composite matrix element are mutually perpendicular. Averaging over the orientations of the molecules gives for the relative magnitude of the cross-section as a function of the ellipticity parameter of the light

$$\delta(a) = C[1 + 2a^2(1 + a^2)^{-2}], \quad (4.19)$$

where $a = 0$ for linearly polarized light and $a = 1$ for circularly polarized light. Of greatest interest is the ratio^[54]

$$\Omega = \delta(1)/\delta(0),$$

which is often measured experimentally. We note that, near $a = 0$ and $a = 1$, the function (4.19) depends weakly (in second order) on the ellipticity parameter a , and this makes it easier to find Ω . The polarization dependence (4.19) is also obtained for the final states B_{2g} and B_{3g} . In all the cases considered, $\Omega = 1.5$. For a final state of A_{1g} symmetry, intermediate states of three types are possible: B_{1u} , B_{2u} and B_{3u} . The dipole moments in the composite matrix element are parallel and directed along the x, y or z axis, if the intermediate states are of symmetry B_{1u} , B_{2u} or B_{3u} respectively. Neglecting, for simplicity, dipole moments aligned along the z-axis (the π -electron approximation for plane molecules), we find after averaging over the orientations of the molecules

$$\delta(a) = C(1 + a^2)^{-2}[(3a^4 + 2a^2 + 3)(1 + \gamma^2) + (\gamma/8)(21a^4 + 101a^2 + 16)]; \quad (4.20)$$

γ in (4.20) is the ratio of the terms in the composite matrix element with dipole moments aligned along the x-axis and the terms with dipole moments aligned along the y-axis:

$$\Omega = \delta(1)/\delta(0) = 2(1 - \gamma + \gamma^2)/(3 + 2\gamma + 3\gamma^2). \quad (4.21)$$

Depending on the magnitude of γ , the values of Ω in (4.21) are found to be in the range 0.67–0.25.

Thus, by polarization measurements, we can distinguish the final states of B_g and A_g symmetry in a molecule of D_{2h} symmetry. As follows from the results of Sec. 4 (b) (cf. (4.8)), the polarization characteristics within one electronic-vibrational band do not depend on the frequency and are determined by the symmetry of the purely electronic state.

3) For forbidden transitions, the situation is somewhat more complicated. We shall confine ourselves, for illustration, to examining transitions to the electronic state B_{2u} . It follows from (4.14) that such transitions are possible with excitation of b_{1u} , b_{2u} and b_{3u} vibrations. For a final state with excitation of b_{1u} vibrations, the intensity of two-photon transitions in plane molecules is determined by the term with $(\lambda_{00} - \lambda_{SS})$ in (4.14). The dipole moments are mutually perpendicular and $\Omega = 1.5$. For the final state with excitation of b_{3u} vibrations, as

intermediate electronic states it is necessary to take into account states of symmetry B_{3u} , B_{1g} , B_{2u} and A_{1g} . As in the case of b_{1u} vibrations, the dipole moments are mutually perpendicular and $\Omega = 1.5$.

If the final state corresponds to excitation of b_{2u} vibrations, then the intermediate states can be the electronic states B_{2u} , A_{1g} , B_{3g} and B_{1g} . In the first two cases the dipole moments are parallel and aligned along the x-axis, and in the others they lie along the y-axis; Ω for transitions with excitation of b_{2u} vibrations is described by the expression (4.21).

Thus, within one electronic-vibrational band, Ω depends on the frequency and can vary from 0.25 to 1.5, inasmuch as transitions corresponding to the excitation of different vibrations can overlap.

To conclude our examination of the polarization properties, we shall discuss the polarization of the luminescence excited in a two-quantum transition^[56b,69]. We again discuss a molecule of D_{2h} symmetry and assume that the two-quantum transition is to the B_{2u} electronic state. The luminescence from the B_{2u} state is polarized along the y-axis of the molecule. Suppose that the excitation occurs as a result of two-quantum absorption of linearly polarized light, and the luminescence is observed in a direction perpendicular to the direction of the incident light. Averaging over the orientations of the molecules, we find for the ratio of the luminescence fluxes I_{\parallel} and I_{\perp} with polarizations parallel and perpendicular respectively to the polarization of the incident light

$$R = \frac{I_{\perp}}{I_{\parallel}} = \begin{cases} \frac{2}{3} & \text{— excitation due to } b_{1u} \text{ and } b_{3u} \\ & \text{vibrations} \\ \frac{9 + 3\gamma^2 + 4\gamma^4}{3 + 15\gamma^2 + 6\gamma^4} & \text{— excitation due to } b_{2u} \text{ vibrations} \end{cases}$$

Thus, the luminescence polarization R also contains information on the symmetry of the vibrations. Measurement of Ω and R together makes it possible to determine γ in the case when vibrations of different symmetry overlap.

d) Principal experimental results on two-quantum absorption in molecules. 1) A considerable proportion of the experimental work has been devoted to obtaining the two-quantum absorption effect in different molecules (in solutions), mainly by means of a ruby laser ($\lambda = 694$ nm). Because of the small absorption coefficient ($\lesssim 10^{-4}$ cm $^{-1}$), the fact of two-quantum absorption has been established by the appearance of luminescence that is quadratically dependent on the pumping power. Multi-stage absorption either was absent or was monitored. Two-quantum transitions have been detected in the following molecules: anthracene, phenanthrene, pyrene, 3, 4-benzopyrene, naphthalene, chrysene, perylene, fluorene, triphenylene, 9,10-dichloroanthracene, fluoranthrene, benzanthracene, dibenzanthracene^[18,29,30,37,54,58,59,70], chloronaphthalene^[71,72], carbon disulfide^[73,74], nitrobenzene^[53], benzoquinone, naphthoquinone, anthraquinone, N-ethylacridone^[75], europium benzoylacetate^[18,59], europium thenoyl-trifluoroacetylacetate^[18,59], stilbene^[57], 3-dimethylamino-6-aminophthalimide, 3,6-tetramethyldiaminomethylphthalimide, 4-benzoylamino-N-methylphthalimide, 4-formylamino-N-methylphthalimide, 3-amino-N-phenylphthalimide, 4-toluy-p-sulphamino-N-methylphthalimide^[76], rhodamine-6G, rhodamine-C, eosin-Na, erythrosine and certain imido-carbocyanines^[77].

2) Measurements of the absolute magnitude of the two-quantum absorption cross-section in molecules have turned out to be a fairly complicated matter. The main difficulties are associated with the space-time inhomogeneity of the laser radiation, which is poorly controlled. The results of different authors therefore diverge widely. As an example, we give the values obtained by different authors for the cross-section of the anthracene molecule in units of 10^{-51} cm 4 sec photon $^{-1}$: 5×10^{-2} ^[23], 9×10^{-1} ^[38], 1.6 ± 0.5 ^[19], 4.3 ^[51], 4.8 ^[33], 6 ^[18], and 35 ^[17]. The results of^[19], in which special measures were taken to stabilize the space-time characteristics of the laser radiation (in the regime of one longitudinal and one transverse zeroth mode with giant-pulse generation), must be regarded as the most accurate. Measurements of the absolute cross-section performed at other frequencies using SRS^[34,74] should be regarded as giving a rough guide, inasmuch as the space-time inhomogeneities of the radiation of the driving laser in SRS are only reinforced. Polarization measurements have also been carried out for the frequency of a ruby laser^[48,54]. The values of Ω obtained in^[48] (0.7) and^[54] (0.87) are close. The measurements of^[40], where $\Omega = 0$ was found, must be regarded as erroneous. The polarization properties of the luminescence have also been measured^[38,54]. The values of R obtained in these papers are 1 and 0.8 respectively. From the polarization characteristics, it is possible, in principle, to establish the relative contribution of given vibrations to the cross-section of a two-quantum transition, although the existing results are insufficiently accurate for this. For exhibiting the vibrations effective in a two-quantum transition, relative measurements of the cross-section and polarization properties in a broad frequency range are of great value. Such measurements exist for α -chloronaphthalene^[72,75], nitrobenzene^[53], and anthracene^[20,23]. First we shall discuss the results of^[20,23], in which a sharply defined electronic-vibrational structure was observed. The investigations of^[20,23] were carried out by the luminescence method, using one source. The data obtained are shown in Fig. 3. The spectrum does indeed have vibrational structure, and the shift of the maximum in the two-quantum absorption relative to the 0-0 transition is clearly visible. The first peak on the short-wave side corresponds to a transition with excitation of a b_{2u} vibration Γ with frequency 200 cm $^{-1}$ in the B_{2u} electronic state. The peak in the long-wave part is due to population of the vibrational sublevel 1Γ ($\omega \sim 200$ cm $^{-1}$) of the ground electronic state A_{1g} (the transition $A_{1g}b_{2u} \rightarrow B_{2u}$). The relative intensity of the peaks symmetrically displaced from the 0-0 transition is determined by the

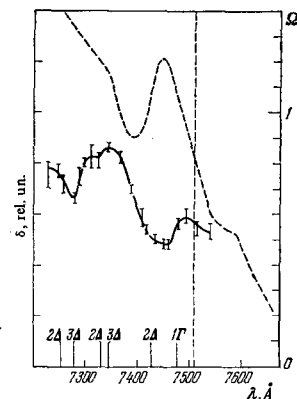


FIG. 3. Two-photon absorption spectrum $\delta(\lambda)$ (dashed curve) and polarization-ratio spectrum $\Omega(\lambda)$ (solid curve). The vertical dashed line denotes the 0-0 transition. The vertical lines along the abscissa denote the frequencies of the ground-state asymmetric vibrations, plotted relative to the 0-0 transition. The notation for the types of vibration corresponds to that in [78].

relative population of the ground state and of the asymmetric-vibrational sublevels. For the vibration considered, this ratio equals 3 at 300°K and grows exponentially with increasing temperature.

Also visible in the spectrum is an inflection in the short-wave region, 600 cm⁻¹ away from the 0-0 transition ($\lambda = 738$ nm); this inflection is evidently associated with the vibration of frequency of order 600 cm⁻¹ appearing in the infrared spectra^[78,79a].

The dependence, shown in Fig. 3, of the polarization ratio Ω on the frequency within the electronic-vibrational band confirms the electronic-vibrational character of the two-quantum transitions in anthracene. In addition, the dependence $\Omega(\omega)$, together with the spectrum $\delta(\omega)$, enables us to obtain additional information, e.g., on the symmetry of the vibrations taking part in the transitions. Thus, a clear correspondence can be seen between the maximum of the curve $\delta(\omega)$ and the minimum of $\Omega(\omega)$ at $\lambda = 745$ nm. This tells us (subsection (c)) that the vibration of frequency 200 cm⁻¹ has symmetry b_{2u} . The inflection of the function $\delta(\omega)$ corresponds to a maximum of the curve $\Omega(\omega)$, indicating the b_{3u} symmetry of the vibration ~ 600 cm⁻¹ (this agrees with the data of infrared measurements^[79a]). We note that there is a certain asymmetry of this maximum of Ω , possibly associated with the overlap of the zeroth series with the first series based on the fully symmetric vibration 399 cm⁻¹. In addition, the function $\Omega(\omega)$ has a minimum ($\lambda = 728$ nm) which has no analog in the curve $\delta(\omega)$. The b_{2u} vibration, of frequency ~ 840 cm⁻¹, of the excited electronic state is responsible for this minimum.

Thus, the experimental results in the study of the properties of forbidden two-quantum transitions in centro-symmetric molecules are in good agreement with the theory of electronic-vibrational transitions and are completely explained by this theory.

In α -chloronaphthalene^[72,75], the two-quantum absorption spectrum differs from the spectrum of the one-photon transitions (Fig. 4). The maximum observed at 42,000 cm⁻¹ in the two-photon absorption is associated by the authors with the presence of even electronic states (α -chloronaphthalene does not possess a center of inversion, but parity is a good quantum number for it). This explanation corresponds to an absolute magnitude of the cross-section of 3×10^{-50} cm⁴ sec/photon. In nitrobenzene, the spectra of the one- and two-photon transitions coincide (Fig. 5), and the cross-section 10^{-50} cm⁴ sec/photon corresponds to allowed electronic transitions, as we should expect for molecules with no center of symmetry.

e) Principal experimental results on two-photon absorption in organic crystals. As was noted above (b), the two-photon spectrum of molecular crystals should retain the principal features of the two-photon spectrum of molecules. In the case of crystals, however, there can be specific features associated with intermolecular interaction—in particular, with exciton effects.

The luminescence of organic crystals of phenanthrene, pyrene, anthracene and 3,4-benzopyrene, excited by two-photon absorption of radiation from a ruby laser (working in the free regime, i.e., with fluxes of the order of 10^{23} cm⁻² sec⁻¹), had already been observed in early work^[26,27]. Later, attempts were made to determine, by the luminescence method, the cross-section of two-photon absorption of ruby-laser radiation for crystals

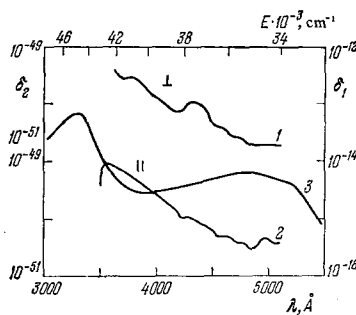


FIG. 4

FIG. 4. Two-photon absorption spectrum δ for longitudinally (1) and transversely (2) polarized photons in α -chloronaphthalene and the one-photon absorption spectrum (3).

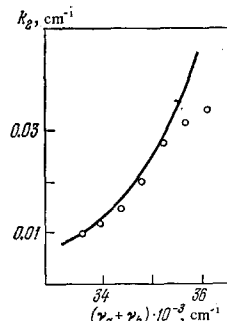


FIG. 5

FIG. 5. Two-photon absorption spectrum (circles) and one-photon absorption spectrum (solid curve, relative units) in nitrobenzene. The two-photon absorption spectrum was obtained with a ruby-laser radiation flux of 7×10^{25} cm⁻² sec⁻¹ and with $e_a \parallel e_b$ ^[53].

and to compare this with the cross-section for solutions. The ratios obtained for anthracene ($\delta_{\text{cryst}}/\delta_{\text{sol}} = 15$ ^[37], 8^[17], 55^[23]) differ rather widely, this being associated, apparently, with the experimental difficulties noted above.

Features specific to the crystal appear in the sharp anisotropy of the two-photon absorption. In the papers^[57,70], the polarization dependences were investigated for crystals of stilbene, anthracene and naphthalene. These crystals belong to the monoclinic system (the point group C_{2h}) and possess strong birefringence. Consequently, the state of polarization of the light changes as the light passes through the crystal. Therefore, a direct comparison with the theory of polarization dependences (see Sec. 5(c)) is possible only in the case when the light propagates along the direction of one of the optical axes or when the directions e_a and e_b of the electric vectors coincide with the principal axes of the crystal. In the general case, when e_a (or e_b) is at a certain angle α to one of the principal directions, the light in the crystal will be elliptically polarized. As the light passes through the crystal, the orientation of the ellipse will change, but the ellipse will always be confined in a rectangle with sides $e_x = |e \cos \alpha|$ and $e_y = |e \sin \alpha|$. Since the birefringence is large, an effect averaged over all such states of elliptical polarization will be observed in experiments.

As a result, the symmetry of the angular dependences will be increased—symmetry with respect to the principal planes will appear, even in those cases when it is absent in the original angular dependence. This increase in symmetry is associated with the fact that the expressions of the form $(e \cdot d)^2 = (e_x d_x + e_y d_y)^2$ appearing in the composite matrix element (2.4) will be transformed in the above averaging to $(e_x d_x)^2 + (e_y d_y)^2$.

For the C_{2h} group, the final states of an allowed two-photon transition can have the symmetry A_g or B_g . According to^[79b,102], the angular dependences have the following form:

$$A_g: [l_1 l_2 + \lambda_1 m_1 m_2 + \lambda_2 n_1 n_2 + \lambda_3 (l_1 m_2 + m_1 l_2) + \lambda_4 (l_1 m_2 - m_1 l_2)]^2, \\ B_g: [(m_1 n_2 + n_1 m_2) + \lambda_5 (m_1 n_2 - n_1 m_2) + \lambda_6 (n_1 l_2 + l_1 n_2) + \lambda_7 (n_1 l_2 - l_1 n_2)]^2,$$

where l_i , m_i and n_i are the cosines of the angles between e_a (or e_b) and the coordinate axes, and λ_i are parameters that are not determined by the symmetry.

We shall assume, e.g., that a crystal plate is cut out along the crystallographic planes a, b, i.e., the monoclinic axis b lies in the plane of the plate, while the light propagates along the normal to the plate and $\mathbf{e}_a \parallel \mathbf{e}_b$. Then $m_1 = m_2 = 0$, $n_1 = n_2 = \sin \theta$, $l_1 = l_2 = \cos \theta$ (θ is the angle between \mathbf{e} and the axis a), and we obtain the following angular dependences:

$$\begin{aligned} \text{for } A_g: & (\cos^2 \theta + \lambda_2 \sin^2 \theta)^2, \\ \text{for } B_g: & \sin^2 \theta \cdot \cos^2 \theta. \end{aligned} \quad (4.22)$$

Since in the present case the principal directions coincide with the axes a and b, and the angular dependences are even in θ , the arguments given above concerning birefringence do not affect the results.⁶⁾

The angular dependences obtained experimentally make it possible to establish unambiguously that they agree with the calculated dependences for A_g and disagree with those for B_g . Thus, e.g., for stilbene with the above orientation, the dependence $\cos^4 \theta$ was obtained. This dependence follows from (4.22) if we put $\lambda_2 = 0$ ^[57,70].

Establishing the symmetry of the final state in a two-photon transition is not sufficient to determine its nature. The question of the interpretation of the spectrum has been discussed intensively in connection with the two-photon spectrum of the anthracene crystal.

In^[44], the two-photon spectrum of an anthracene crystal was obtained by a two-source method (Fig. 6). The two-photon absorption cross-section (at 3.85 eV) was $\delta = 2 \times 10^{-49} \text{ cm}^4 \text{ sec}$. As can be seen from Fig. 6, the two-photon spectrum has a well defined vibrational structure. The magnitude of the absorption depends on the polarization, in agreement with the work^[57].

One of the assumptions that have been discussed^[21,44] is that the spectrum of the crystal, like the spectrum of the molecules, corresponds to the forbidden transition $A_g \rightarrow B_{2u}$; the forbiddenness is partially lifted owing to the non-fully-symmetric vibrations. According to another assumption^[50], in this spectrum an even exciton doublet A_g, B_g appears, which, in accordance with the calculation of^[80], arises from the even excited state B_g of the molecule, which lies at about 4.9 eV and is lowered in the crystal to 3.5–3.8 eV.

In^[22] the two-photon absorption cross-section in an anthracene crystal was measured for the anti-Stokes

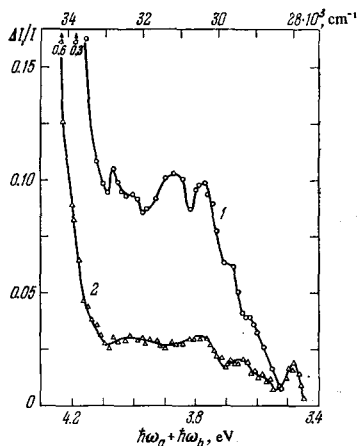


FIG. 6. Two-photon absorption spectrum of an anthracene crystal^[44]. 1— $T = 10^\circ \text{K}$, polarization along the b-axis; 2— $T = 77^\circ \text{K}$, polarization along the a-axis.

components of the stimulated Raman scattering for frequencies of 4.15, 5.3 and 4.7 eV. The values obtained are considerably higher than in the range 3.5–3.6 eV, and amount to 7.6×10^{-50} , 3.7×10^{-48} and $1.2 \times 10^{-48} \text{ cm}^4 \text{ sec}$. The analogous luminescence method was applied in the paper^[23] for the Stokes components, cross-sections being obtained in the range 3.1–3.56 eV. An analysis of all the existing data is performed in^[23]. In Fig. 7, taken from this article, the data of various authors are given. In it, the following interpretation of the spectrum of the anthracene crystal is proposed:

1) In the region 3.2–3.5 eV, we have the electronic-vibrational transition ${}^1A_{1g} \rightarrow {}^1B_{2u}$, which is allowed by the non-fully-symmetric vibrations. This interpretation is analogous to that of the molecular spectrum.

2) As regards the transition in the region 3.5–3.6 eV, in^[23] a new possibility is suggested—a transition to an even (g) state with transfer of charge. Thus, it is assumed that this is a specific crystalline state. From estimates, the cross-section of this transition can be of the order of 10^{-2} of that of the allowed electronic transition, in agreement with the experimental data.

3) In the region 4.2–4.8 eV, we have an allowed transition to the states A_{1g} and B_{1g} , which, according to^[80], lie at about 4.9 eV in the anthracene molecule. This agrees with the high value of δ ($\sim 10^{-48} \text{ cm}^4 \text{ sec}$) in this region.

4) Finally, the very weak absorption observed both in solution and in the crystal in the region of the 0–0 transition in the ${}^1B_{2u}$ state is possibly associated with a two-proton quadrupole transition. This interpretation requires further corroboration.

5. TWO-PHOTON ABSORPTION IN SEMI-CONDUCTORS AND IONIC CRYSTALS

Two-photon absorption in semiconductors has been studied especially intensively. This is due, firstly, to the wide investigations of semiconducting materials and, secondly, to the great diversity of the properties of semiconductors. Transitions into the interior of the conduction band have been studied theoretically and experimentally^[81].

Much attention has also been given to the spectra of two-quantum absorption near the band edge (transitions to exciton states^[82]). Below, the theory of two-quantum transitions in the one-electron approximation with allowance for exciton states is described, and an analysis,

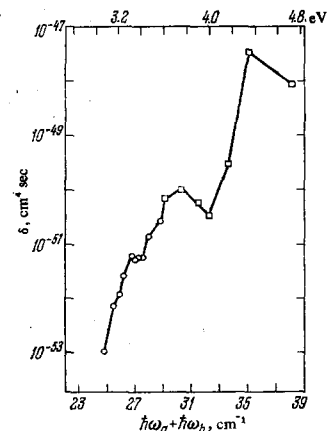


FIG. 7. Two-photon absorption spectrum of an anthracene crystal^[23].

and comparison with the theory, of the experimental data for A_{IV} , $A_{III}B_{V}$ and $A_{II}B_{VI}$ semiconductors, and also for ionic crystals, is carried out. Nonlinear effects in crystals are customarily described by means of cross-susceptibility tensors, which are the coefficients in the expansion of the polarization in a series in the field. Two-quantum transitions are described by the imaginary part χ''_{aabb} of the cross-susceptibility tensor of rank four. We can convince ourselves that for two⁷⁾ monochromatic fields polarized along the directions of a and b respectively,

$$W = 8\pi^2\omega_a\omega_b\hbar\chi''_{aabb}(\omega_a, \omega_b) F_a F_b / c^2 [e_{aa}(\omega_a) e_{bb}(\omega_b)]^{1/2}. \quad (5.1)$$

Comparing (5.1) with (5.2), we find⁸⁾

$$\chi''_{aabb}(\omega_a, \omega_b) = (\pi/\hbar^3 V) |M_{21}^{ab}|^2 \delta(\omega_a + \omega_b - \omega_{21}). \quad (5.2)$$

a) **Two-photon transitions in the one-electron approximation.** 1) We shall consider a two-photon transition between a filled valence band (1) and the conduction band (2) of a crystal, neglecting the electron-electron and electron-phonon interactions⁹⁾. It follows from the form of the composite matrix element (2.6) that transitions are possible only with conservation of the quasi-momentum $\hbar\mathbf{k}$. Substituting (2.6) into (5.2) and summing over all states \mathbf{k} for which

$$\omega_{21}(\mathbf{k}) - \omega_a - \omega_b = 0, \quad (5.3)$$

we obtain

$$\chi''_{aabb}(\omega_a, \omega_b) = \frac{e^4}{4\hbar^3\pi^2 V} \int \frac{dS}{|\nabla_{\mathbf{k}}\omega_{21}(\mathbf{k})|} \left| \sum_i \left(\frac{\Omega_{2i}^a \Omega_{1i}^b}{\omega_{1i} - \omega_b} + \frac{\Omega_{2i}^b \Omega_{1i}^a}{\omega_{1i} - \omega_a} \right) + \left(\frac{\partial}{\partial k_a} \frac{\Omega_{21}^a}{\omega_{21} - \omega_b} + \frac{\partial}{\partial k_b} \frac{\Omega_{21}^b}{\omega_{21} - \omega_a} \right) \right|^2. \quad (5.4)$$

The integration in (5.4) is performed in \mathbf{k} -space over the surface defined by Eq. (5.3)¹⁰⁾.

Here, it is pertinent to note that the terms in the first and second brackets inside the modulus sign in (5.1) have different structure. The first part of the composite matrix element contains the characteristics of the intermediate states, whereas the second is expressed only in terms of the characteristics of the bands taking part directly in the transition. In order to perform a comparative estimate of these terms, we shall make use of a relation between $\partial\Omega_{21}^a(k)/\partial k_b$ and the matrix elements $\Omega_{2i}^a(k)$ and $\Omega_{1i}^a(k)$. We shall obtain this relation by combining the commutation relations (2.9) for the coordinate and momentum with the relations (2.7):

$$\partial\Omega_{21}^a/\partial k_b = (1/\omega_{21}) \sum_i (\omega_{2i}\Omega_{2i}^a\Omega_{1i}^b + \omega_{1i}\Omega_{2i}^b\Omega_{1i}^a). \quad (5.5)$$

Assuming for definiteness that the principal contribution to the sum over the intermediate states in the expressions (5.4) and (5.5) is given by one and the same band j , putting $\omega_a = \omega_b = \omega$ we obtain for the relative magnitude η of the terms in the first and second brackets of (5.4)

$$\eta = \omega^2/(\omega_{j1}^2 - \omega^2). \quad (5.6)$$

It can be seen from (5.6) that, if the bands (1) and (2) are relatively close, i.e., if

$$\omega_{21}(k) = 2\omega < 2\omega_{j1}(k), \quad (5.7)$$

then the terms in the second bracket of (5.4) will be the crucial ones, i.e., the two-band model will be a good approximation for a quantitative description. Since, according to (5.6), $\eta < 1$ ¹¹⁾, we may expect that the two-band model will always be suitable for estimates. It should be noted, that (5.6) may not hold if it is necessary to take several different states j into account. Thus, the two-band model is unsuitable for estimates in the tight-

binding approximation, since, in the limiting case of a crystal of non-interacting atoms, all the quantities are independent of \mathbf{k} and the two-photon transition probability is determined entirely by the terms in the first bracket inside the modulus sign in (5.4). In practice, the two-band model can be used for estimates so long as the band width does not become much smaller than the interband spacings.

If we regard $\chi''_{aabb}(\omega_a, \omega_b)$ as a function of $\omega_a + \omega_b$, we can see that it has analytic singularities at the van Hove points^[85], i.e., at the points for which

$$\nabla_{\mathbf{k}}\omega_{21}(\mathbf{k}) = 0.$$

At these points, the imaginary part χ''_{aabb} of the linear susceptibility also has singularities (cusps)^[86,87]. The behavior of $\chi''_{aabb}(\omega_a, \omega_b)$ near the singularities is determined, in particular, by the composite matrix element (2.6) and can therefore differ substantially from the behavior of χ''_{aa} . Other singularities in $\chi''_{aabb}(\omega_a, \omega_b)$ can also be associated with the composite matrix element. Thus, singularities arise, e.g., when the frequency of one of the fields approaches the frequency ω_{l1} of the transition between the ground state and one of the intermediate states. A singularity of this type will be discussed in the following Section, and here we shall discuss transitions near the center of the band ($\mathbf{k} = 0$).

2) Near $\mathbf{k} = 0$, we represent the matrix elements $\Omega_{nl}(\mathbf{k})$ in the form of a series in \mathbf{k} :

$$\Omega_{nl}(\mathbf{k}) = \frac{p_{nl}(\mathbf{k})}{m\omega_{nl}(\mathbf{k})} \quad (5.8)$$

$$= \frac{p_{nl}(0)}{m\omega_{nl}(0)} + \sum_{\alpha} k_{\alpha} \frac{\partial p_{nl}}{\partial k_{\alpha}} \Big|_{k=0} \frac{1}{m\omega_{nl}(0)} - \sum_{\alpha, \beta} \frac{p_{nl}k_{\alpha}k_{\beta}}{m\omega_{nl}^2 \omega_{nl}^{\alpha\beta}} + \frac{\partial^2 p_{nl}}{\partial k_{\alpha} \partial k_{\beta}} \Big|_{k=0} \frac{k_{\alpha}k_{\beta}}{\omega_{nl}}.$$

In (5.8), Ω_{nl} is expressed in terms of the frequency of the interband transitions and the matrix element of the momentum. This form is convenient for estimates, since p_{nl} and $\omega_{nl}(\mathbf{k})$ are fundamental characteristics of semiconductors. If we are interested in transitions between valence bands and conduction bands, then, for most A_{IV} , $A_{III}B_{V}$ and $A_{II}B_{VI}$ semiconductors, these will be transitions principally between bands of the $|p\rangle$ - and $|s\rangle$ -types, in which the values of $\langle p|p_z|s\rangle$ are practically the same for all semiconductors (cf. [88,122,123]) and depend weakly on \mathbf{k} (they vary by a factor of about two over the extent of the Brillouin zone). We can assume that, in order of magnitude,

$$p_{nl}|_{k=0} \approx 1.5 \cdot 10^{-38}, \quad \partial p/\partial k|_{k=0} \approx pa/\pi \sim p/k_B, \quad \partial^2 p_{nl}/\partial k^2 = pa^2/\pi^2, \quad (5.9)$$

where k_B denotes the size of the Brillouin zone and a is the lattice constant. The estimates given for the derivatives in (5.9) are valid if the corresponding quantity does not vanish for symmetry reasons. Thus, in semiconductors with a center of inversion, $\partial p_{sp}/\partial k|_{k=0} = 0$, which follows directly from the relation (5.5). We should also add that the estimate for the derivatives in (5.9) is valid for compounds with intermediate binding strength. It is easily seen that, in the tight-binding and weak-binding approximations, the dependence of $p_{nl}(\mathbf{k})$ on \mathbf{k} is weaker (it is determined by the corresponding small parameter), although for almost free electrons near the Brillouin-zone boundary a sharp dependence of p_{nl} on \mathbf{k} , due to Umklapp processes, is also possible^[123].

If we consider (5.4) together with (5.9), we can see that, generally speaking, the expressions inside the modulus sign in (5.4) do not vanish at $\mathbf{k} = 0$ (allowed-transitions^[83]). Neglecting the dependence on \mathbf{k} in the composite matrix element, by performing the in-

tegration in (5.4) in the approximation of a parabolic dispersion law we obtain for spherically symmetric bands¹²⁾

$$\chi_{aabb}''(\omega_a, \omega_b) = \frac{2^{1/2} e^4 m^{*3/2}}{\pi \hbar^{5/2} V} \left| \sum_{j \neq 1, 2} \frac{\Omega_{2j}^a \Omega_{j1}^b}{\omega_{j1} - \omega_b} + \frac{\Omega_{2j}^b \Omega_{j1}^a}{\omega_{j1} - \omega_a} + \frac{\partial \Omega_{21}^a}{\partial k_a} \frac{1}{\omega_a} + \frac{\partial \Omega_{21}^b}{\partial k_b} \frac{1}{\omega_b} \right|_{k=0}^2 (\omega_a + \omega_b - \omega_g)^{1/2} \quad (5.10)$$

where $\omega_g = \omega_{21}(0)$ is the width of the gap and m_{21}^* is the reduced effective mass for $k = 0$. We note that the approximations made in the derivation of (5.9) from (5.4) correspond to neglecting the quantities $\omega_a + \omega_b - \omega_g = \Delta\omega$ in comparison with ω_g . With this exactness, for commensurable ω_a and ω_b , the frequency dependence of the allowed-allowed transitions obeys the well known^[8] "half-law." However, if $\omega_a \gg \omega_b$, by virtue of which $\Delta\omega \sim \omega_b$, then the last term in (5.10) becomes the crucial one and the susceptibility for fixed ω_a behaves as $\omega_b^{-3/2}$. As regards the quantity $\chi_{aabb}''(\omega_a, \omega_b)$, for estimates of this we can make use of the two-band model. Using (5.9) and putting $a \approx 5 \text{ \AA}$, we find for semiconductors with relatively closely spaced bands, with $\omega_a = \omega_b = \omega$,

$$\chi_{aabb}'' \approx 3 \cdot 10^{20} \Delta\omega^{1/2} / \omega_g^{5/2}. \quad (5.11)$$

In going from (5.4) to (5.11), we have used the fact that the reduced mass is approximately equal to the effective mass of the electrons, it being assumed that

$$m_{21}^* \approx m^2 \omega_g \hbar / (p |p_z| s)^2, \quad (5.12)$$

as is the case for A_{IV} , $A_{III}B_{IV}$ and $A_{II}B_{VI}$ semiconductors¹³⁾.

3) It may turn out by virtue of the symmetry that, for $k = 0$, there are no states j for which $\Omega_{2j} \neq 0$ and $\Omega_{j1} \neq 0$ (e.g., states 2 and 1 of different parity in a crystal with a center of symmetry); then the composite matrix element (5.4) (cf. (5.8)) goes to zero with k . In treating two-quantum transitions in this case, we must retain the terms linear in k (the allowed-forbidden transitions^[8,3]) in the composite matrix element. If $\Omega_{21}(0) \sim a$, then for the description it is sufficient to make use of the two-band model. After integration in (5.4), we find for spherical bands¹⁴⁾

$$\chi_{aabb}'' = (2^{3/2} e^4 m^{*1/2} / 3\pi \hbar^{7/2}) [(|\Omega_{21}^a|^2 / \omega_a^2) + (|\Omega_{21}^b|^2 / \omega_b^2) + (2 / \omega_a^2 \omega_b^2) \text{Re}(\Omega_{21}^a \Omega_{21}^b \cos(\hat{e}_a, \hat{e}_b))] (\omega_a + \omega_b - \omega_g)^{3/2}. \quad (5.13)$$

Thus, the frequency dependence for the allowed-forbidden transitions obeys the "three-halves law" to within $\Delta\omega / \omega_g$. An estimate with those parameter values which were used in (5.12) gives

$$\chi_{aabb}'' \sim 1.5 \cdot 10^{23} (\omega_a + \omega_b - \omega_g)^{3/2} \omega_g^{-11/2}. \quad (5.14)$$

It should be noted that, even for relatively small values of $(\omega_a + \omega_b - \omega_g) \sim 2 \times 10^{-33} \omega_g^3$, the estimates (5.12) and (5.14) are found to be the same. One can convince oneself that, for such frequencies, χ_{aabb}'' is described by the sum of the expressions (5.11) and (5.13)¹⁵⁾.

4) In a quantizing magnetic field, two-quantum transitions have a number of characteristic features. These features are associated primarily with the change of the energy spectrum in the band. For bands with a quadratic dispersion law¹⁶⁾

$$\epsilon_{n,jkz} = (\hbar e H / m_n^* c) (j + 1/2) + (\hbar^2 k^2 / 2m_n^*). \quad (5.15)$$

j labels the Landau levels, each of which is g -fold degenerate:

$$g = 2V^3 \beta_e H / \pi \hbar c. \quad (5.16)$$

For allowed-allowed transitions, in which it is possible

to neglect the dependence of the composite matrix element on k , by substituting (2.6) into (5.2) and summing over all the final states taking (5.15) and (5.16) into account, we find¹⁷⁾

$$\chi_{aabb}'' = \frac{e^4 \omega_H m_n^{*3/2}}{2^{1/2} \pi \hbar^{5/2}} \left| \sum_l \left(\frac{\Omega_{l1}^a \Omega_{l1}^b}{\omega_{l1} - \omega_b} + \frac{\Omega_{l1}^b \Omega_{l1}^a}{\omega_{l1} - \omega_a} \right) + \frac{1}{\omega_b} \frac{\partial \Omega_{l1}^a}{\partial k_b} + \frac{1}{\omega_a} \frac{\partial \Omega_{l1}^b}{\partial k_a} \right|_{k=0}^2 \sum_j \left[\omega_a + \omega_b - \omega_g - \omega_H \left(j + \frac{1}{2} \right) \right]^{-1/2}, \quad (5.17)$$

where

$$\omega_H = eH / m_n^* c$$

is the cyclotron frequency corresponding to the reduced effective mass m_{21}^* of the bands 2 and 1.

It can be seen from (5.17) that the magnitude of the two-quantum absorption for fixed frequency $\omega_a + \omega_b$ oscillates like the one-quantum absorption with the magnetic field. An estimate, analogous to (5.10), of the susceptibility gives

$$\chi_{aabb}'' \sim 10^{20} \omega_g^{-5/2} \omega_H \sum_j [\omega_a + \omega_b - \omega_g - \omega_H (j + 1/2)]^{-1/2}. \quad (5.18)$$

5) We shall consider forbidden-allowed transitions in a magnetic field, confining ourselves to the two-band model, as in subsection (3) of this Section.

If we neglect terms of order ω_H / ω_a , ω_H / ω_b compared with unity, we can obtain the composite matrix element from (2.6) by replacing the quasi-momentum k by the operator \hat{k} :

$$\hat{k}_x = k_x - (ieH/2c\hbar) \partial / \partial k_y, \quad (5.19)$$

$$\hat{k}_y = k_y + i(eH/2c\hbar) \partial / \partial k_x, \quad \hat{k}_z = k_z. \quad (5.20)$$

In the approximations used here,

$$M_{2j1j'} = (e^2 \Omega_{21}^b / \omega_b^2) (\hbar \hat{k}_{ajj'} / m_n^*) + (e^2 \Omega_{21}^a / \omega_a^2) \hbar \hat{k}_{bjj'} / m_n^*. \quad (5.21)$$

The non-zero matrix elements $\hat{k}_{jj'}$ have the form

$$\kappa_{xj,j-1} = \kappa_{xj-1,j} = -i\kappa_{yj,j-1} = i\kappa_{yj-1,j} = (eH/j/2\hbar c)^{1/2}, \quad \kappa_{zjj'} = k_z. \quad (5.22)$$

We shall assume that the field E_a is polarized along $H(z)$ and the field E_b is perpendicular to H (along x). In this case, we can see from (5.21) and (5.22) that the first term in the composite matrix element describes transitions in which j remains the same, while the second term describes transitions with change of j by ± 1 .

For a transition with no change of j , from (5.2), (5.21), (5.22), (5.15) and (5.16) we have

$$\chi_{xxxx}^{jj} = (2^{1/2} e^4 \omega_H / \Omega_{21}^b)^2 m_n^{*1/2} / \pi \omega_b^4 \hbar^{7/2} \sum_j [\omega_a + \omega_b - \omega_g - \omega_H (j + 1/2)]^{1/2}. \quad (5.23)$$

For transitions with change of j ($-j \pm 1$),

$$\chi_{xxxx}^{j,j \pm 1} = (e^4 m_n^{*1/2} \omega_H^2 / \Omega_{21}^a)^2 / 2^{3/2} \omega_a^4 \hbar^{7/2} \times \sum_j [\omega_a + \omega_b - \omega_g - \omega_H (j + 1/2) \pm (eH/m_n^* c)]^{-1/2}. \quad (5.24)$$

Attention should be called to the different dependence of (5.23) and (5.24) on the magnetic field: (5.23), as a function of the magnetic field, has zeroes, (but does not have singularities), (5.24) oscillates, like (5.17), in a magnetic field (it has root singularities), and its monotonic part depends quadratically on the field. Estimates, analogous to (5.14), of the susceptibility give

$$\chi_{xxxx}^{jj} \sim 10^{23} \omega_g^{-11/2} \omega_H [\omega_a + \omega_b - \omega_g - \omega_H (j + 1/2)]^{1/2},$$

$$\chi_{xxxx}^{j,j \pm 1} \sim 3 \cdot 10^{23} \omega_g^{-11/2} \omega_H^2 [\omega_a + \omega_b - \omega_g - \omega_H (j + 1/2) \pm (eH/m_n^* c)]^{-1/2}. \quad (5.25)$$

b) Two-photon transitions with exciton states taken into account. 1) The Coulomb interaction of an electron and a hole in a semiconductor leads to the appearance of bound exciton states, lying below the bottom of the con-

duction band^[94]. The energy of these states is described by a hydrogen-like formula and represents the energy of the relative motion of the electron and hole:

$$E_{21} = -m_{21}^* e^4 / 2\hbar^2 e^2 n^2 = -G_{21} / n^2; \quad (5.26)$$

n is an integer. Here and below, the energy is reckoned from the bottom of the conduction band. The electron-electron interaction not only leads to a change of the spectrum but also modifies the wavefunctions of the eigenstates. The eigenfunctions of the relative motion of the electron and hole with allowance for the Coulomb interaction are characterized by the orbital number l and the principal quantum number n for the discrete spectrum or by the energy $E = \hbar^2 k^2 / 2m_{12}^*$ for the continuous spectrum. The wavefunctions of the exciton states and the matrix elements of the dipole moments are well-known^[95]. Below we shall need the matrix elements of transitions to s - and p -states:

$$\begin{aligned} \langle 0 | d | j1s \rangle &= ie\Omega_{j1} U_s^j(0), \\ \langle 0 | d | j1p \rangle &= ie \int (\partial\Omega_{j1} / \partial k_i)_{\hbar=0} (\partial U_p^j(r) / \partial r_i)_{r=0}; \end{aligned} \quad (5.27)$$

$U_s^j(r)$ and $U_p^j(r)$ are hydrogen-like functions of the s - and p -type. The form of these functions depends on the quantum numbers n or E of the exciton states considered.

2) We shall consider transitions to s -states of the discrete spectrum for allowed-allowed transitions¹⁹⁾. Using the relations (5.27), we obtain from (2.4) and (5.2)

$$\begin{aligned} \chi_{aabb}(\omega_a; \omega_b) &= \frac{2e^4}{n^2 a_e^2 \hbar^2} \left| \sum_j \left(\frac{\Omega_{2j}^a \Omega_{2j}^b}{\omega_{j1} - \omega_a} + \frac{\Omega_{2j}^b \Omega_{2j}^a}{\omega_{j1} - \omega_b} \right) \right. \\ &\quad \left. + \left(\frac{1}{\omega_b} \frac{\partial \Omega_{21}^a}{\partial k_b} + \frac{1}{\omega_a} \frac{\partial \Omega_{21}^b}{\partial k_a} \right) \right|_{\hbar=0}^2 \delta(\omega_a + \omega_b - \omega_g + \frac{G}{\hbar n^2}); \end{aligned} \quad (5.28)$$

a_e is the radius of an exciton formed by a hole in band 1 and an electron in band 2:

$$a_e = \hbar^2 \epsilon / m_{21}^* e^2. \quad (5.29)$$

In obtaining the expression (5.28) from (5.22), we have taken into account that

$$|U_{ns}(0)|^2 = v_0 / \pi a_e^2 n^3, \quad (5.30)$$

where v_0 is the volume of the unit cell, and

$$\sum_n U_n^j(0) U_n^j(r) = \delta(r), \quad (5.31)$$

which follows from the completeness and orthonormalization of the hydrogen-like functions^[97]; we have also neglected terms of order $G/\hbar\omega_a$ in comparison with unity. The terms in the second bracket in (5.28) are determined entirely by the properties of the bands 1 and 2.

It can be seen from the expression (5.28) that the spectrum of allowed-allowed transitions is a set of peaks whose relative intensity falls like n^{-3} as $\omega_a + \omega_b$ approaches ω_g . An estimate for semiconductors is conveniently performed in the two-band model (cf. subsection 2(a)). For $a \sim 5 \times 10^{-8}$ cm, $m^* = 0.1m_0$, $\omega_a \sim \omega_b \sim 10^{15}$, $\epsilon = 10$ ($a_e \sim 5 \times 10^{-7}$, $G = \hbar \times 10^{13}$ erg) and for an exciton line width of order $0.1G/\hbar$, we have for $n = 1$

$$\chi_{aabb}(\omega_a + \omega_b = \omega_g - (G/\hbar)) = 5 \cdot 10^{-10} \text{ cgs esu} \quad (5.32)$$

For large values of n , the different levels overlap and we must sum over n in (5.28). The density of states is $n^3/2G$ and, after summation over n , in place of (5.28) we obtain

$$\begin{aligned} \chi_{aabb}(\omega_a, \omega_b) &= \frac{e^4}{a_e^2 \hbar^2 G} \left| \sum_j \frac{\Omega_{2j}^a \Omega_{2j}^b}{\omega_{j1} - \omega_a} + \frac{\Omega_{2j}^b \Omega_{2j}^a}{\omega_{j1} - \omega_b} \right. \\ &\quad \left. + \frac{1}{\omega_b} \frac{\partial \Omega_{21}^a}{\partial k_b} + \frac{1}{\omega_a} \frac{\partial \Omega_{21}^b}{\partial k_a} \right|^2. \end{aligned}$$

It can be seen from (5.33) that, for $\omega_a + \omega_b \sim \omega_g$, the susceptibility does not depend on the frequency. As re-

gards the magnitude of the susceptibility, it is smaller than the susceptibility in the region of the first exciton peak by a factor of $\hbar\Delta\omega/G$ ($\Delta\omega$ is the width of the first exciton peak).

For the continuous spectrum, in place of (5.2) we have

$$\begin{aligned} \chi_{aabb}''(\omega_a, \omega_b) &= \frac{2^{1/2} m^* 3/2 e^4}{\hbar^{9/2}} \frac{\alpha \epsilon^{\pi\alpha}}{\text{sh}(\pi\alpha)} \left| \sum \frac{\Omega_{2j}^a \Omega_{2j}^b}{\omega_{j1} - \omega_a} \right. \\ &\quad \left. + \frac{\Omega_{2j}^b \Omega_{2j}^a}{\omega_{j1} - \omega_b} + \frac{1}{\omega_b} \frac{\partial \Omega_{21}^a}{\partial k_b} + \frac{1}{\omega_a} \frac{\partial \Omega_{21}^b}{\partial k_a} \right|^2 (\omega_a + \omega_b - \omega_g)^{1/2}; \end{aligned} \quad (5.34)$$

here,

$$\alpha = (\omega_a + \omega_b - \omega_g)^{-1/2} \hbar^{-1/2} G^{1/2}. \quad (5.35)$$

For $\alpha^{-2} \ll 1$, (5.34) goes over into (5.33) and does not depend on the frequency. For $\alpha^{-2} \gtrsim 30$, when the Coulomb interaction can be neglected, (5.34) coincides with the expression (5.9) obtained in the one-electron approximation. We note that the spectrum considered is very similar to the spectrum for allowed one-quantum transitions.

3) In studying allowed-forbidden transitions¹⁹⁾, as shown in subsection (b) we can make use of the two-band approximation. The composite matrix element (2.6) for such transitions has the form

$$M_{21}(np) = e^2 \sum_n U_n^s(0) \left[\frac{\langle U_n^s | r^b | U_{np} \rangle \Omega_{21}^a}{\omega_{n'snp} + \omega_b} + \frac{\langle U_n^s | r^a | U_{np} \rangle \Omega_{21}^b}{\omega_{n'snp} + \omega_a} \right]; \quad (5.36)$$

here, r is the coordinate of the relative motion of the electron and hole. It can be seen from (5.36) that allowed-forbidden transitions are possible only to p -states. By expanding the expression in the square brackets in (5.36) in a series in the parameters $\omega_{n'snp}/\omega_a$ and $\omega_{n'snp}/\omega_b$ and retaining the first two terms of the expansion, we find²⁰⁾

$$M_{21}(np) = (e^2 \hbar / m_{21}^*) \{ (\partial U_{np} / \partial r_a) (\Omega_{21}^a / \omega_a^2) + (\partial U_{np} / \partial r_b) (\Omega_{21}^b / \omega_b^2) \}_{r=0}. \quad (5.37)$$

In going from (5.36) to (5.37), we have used the relation (5.31) and

$$i\omega_{n'snp} r_{n'snp} = (1/m_{21}^*) p_{n'snp} = (i\hbar/m_{21}^*) \langle n's | \partial / \partial r | np \rangle. \quad (5.38)$$

For discrete states,

$$(\partial U_{np} / \partial r)_{r=0} = (v_0 / 3\pi a_e^5) (n^2 - 1) / n^5, \quad (5.39)$$

and for the susceptibility we obtain from (5.2), (5.37) and (5.39)

$$\begin{aligned} \chi_{aabb}''(\omega_a, \omega_b) &= \frac{e^4}{3\hbar m_{21}^*} \sum \frac{n^2 - 1}{a_e^5 n^5} \left[\frac{|\Omega_{21}^a|^2}{\omega_a^4} + \frac{|\Omega_{21}^b|^2}{\omega_b^4} \right. \\ &\quad \left. + \frac{2}{\omega_a^2 \omega_b^2} \text{Re}(\Omega_{21}^a \Omega_{21}^b) \cos(\hat{e}_a, \hat{e}_b) \right] \delta(\omega_a + \omega_b - \omega_g + (G/\hbar n^2)). \end{aligned} \quad (5.40)$$

The spectrum starts from $n = 2$, and the intensity of the peaks falls with increasing n . An estimate for transitions to the state $n = 2$ for the same parameter values as in (5.32) gives

$$\chi_{aabb}'' \approx 10^{-11} \text{ cgs esu} \quad (5.41)$$

i.e., an order of magnitude smaller than for allowed-allowed transitions to a state with $n = 2$. For large n , where the spectrum is quasi-continuous, by summing over n we obtain in place of (5.40)

$$\begin{aligned} \chi_{aabb}''(\omega_a, \omega_b) &= \frac{e^4 (n^2 - 1)}{6m^* G a_e^5 n^2} \left[\frac{|\Omega_{21}^a|^2}{\omega_a^4} + \frac{|\Omega_{21}^b|^2}{\omega_b^4} \right. \\ &\quad \left. + \frac{2}{\omega_a^2 \omega_b^2} \text{Re}(\Omega_{21}^a \Omega_{21}^b) \cos(\hat{e}_a, \hat{e}_b) \right]. \end{aligned} \quad (5.42)$$

It follows from (5.42) that χ'' increases linearly as the energy of the final state increases. An estimate for large n ($\omega_a + \omega_b \approx \omega_g$) gives a value of the order of (5.41). In the continuous spectrum

$$(\partial U_{np} / \partial r)_{r=0}^2 = [\pi\alpha (1 + \alpha^2) e^{\pi\alpha} / 3 \text{sh}(\pi\alpha)] (2m_{21}^* / \hbar) (\omega_a + \omega_b - \omega_g),$$

and for the susceptibility we have

$$\chi_{aabb}(\omega_a, \omega_b) = \frac{2^{3/2} m^{*1/2} e^4}{3\hbar^{7/2}} \frac{\alpha(1+\alpha^2) e^{\pi\alpha}}{\text{sh}(\pi\alpha)} \left[\frac{|\Omega_{21}^a|^2}{\omega_a^2} + \frac{|\Omega_{21}^b|^2}{\omega_b^2} + \frac{2}{\omega_a^2 \omega_b^2} \text{Re}(\Omega_{21}^a \Omega_{21}^b) \cos(\hat{e}_a, \hat{e}_b) \right] (\omega_a + \omega_b - \omega_g)^{3/2}. \quad (5.43)$$

For $\alpha^{-2} \ll 1$ the expression (5.43) coincides with (5.42), while for $\alpha^{-2} \gtrsim 30$ it coincides with (5.13), which was obtained in the one-electron approximation.

4) The forbidden-forbidden transitions are transitions to d-states. As in the case of allowed-forbidden transitions, we shall perform the analysis in the two-band model. If we use (5.31) and (5.38), we can convince ourselves that

$$M_{12}(nl) = \frac{\hbar e^2}{m_2^2} \sum_{\alpha} \left(\frac{1}{\omega_a^2} \frac{\partial \Omega_{21}^a}{\partial k_{\alpha}} \frac{\partial^2 U_{nl}}{\partial r_{\alpha} \partial r_b} + \frac{1}{\omega_b^2} \frac{\partial \Omega_{21}^b}{\partial k_{\alpha}} \frac{\partial^2 U_{nl}}{\partial r_{\alpha} \partial r_a} \right)_{\hbar=0}. \quad (5.44)$$

For $a \neq \alpha$ or $b \neq \alpha^{21}$, (5.44) describes transitions to d-states. It is possible to obtain expressions for χ'' in different regions of the spectrum, as was done earlier. However, because the susceptibility is so small, we shall confine ourselves to treating only the discrete spectrum, where the d-states can differ from the s- and p-states in energy. In this case, we have

$$(\partial^2 U_{nd} / \partial r_{\alpha} \partial r_b)_{\hbar=0}^2 = (1/120\pi) [(1-n^2)(1-4n^2)/n^3] v_0/a_c^2 \quad (5.45)$$

and

$$\chi_{aabb}(\omega_a, \omega_b) = \frac{\pi e^4}{\hbar m_2^2} \sum_n \left| \sum_{\alpha} \frac{1}{\omega_a^2} \frac{\partial \Omega_{21}^a}{\partial k_{\alpha}} \frac{\partial^2 U_{nd}}{\partial r_{\alpha} \partial r_b} + \frac{1}{\omega_b^2} \frac{\partial \Omega_{21}^b}{\partial k_{\alpha}} \frac{\partial^2 U_{nd}}{\partial r_{\alpha} \partial r_a} \right|_{\hbar=0}^2 \delta(\omega_a + \omega_b - \omega_g + (G/\hbar n^2)). \quad (5.46)$$

An estimate for $n = 3$, with the parameters used in the estimate (5.32), has the form

$$\chi_{aabb} \approx 10^{-16} \text{ cgs esu}$$

5) Exciton states are found to be crucial in transitions to the interior of the band if the frequency of one of the fields is close to the frequency of the exciton transition^{[99]22)}. We shall consider the allowed-forbidden transitions. Suppose, e.g., that

$$\omega_g - (G/\hbar) - \omega_a = \Delta\omega_a \ll G/\hbar.$$

It follows from the form of the composite matrix element (2.6) that it will have a singularity (a pole) when $\Delta\omega_a$ tends to zero. This singularity is associated with the intermediate exciton state $n = 1$. We shall be interested in that part of the susceptibility which is determined by this intermediate state. Using (5.2), (2.6) and (5.27), and also the expression for the matrix element of the coordinate between the ground state and a state of the continuous spectrum for hydrogen-like atoms^[100], we find

$$\chi_{aabb}(\omega_a, \omega_b) = (2^6 e^4 / 3\hbar^3) (|\Omega_{21}^a|^2 / a_0) [C^2 / (\hbar \Delta\omega_a)^2 \omega_b^2] (G/\hbar \omega_b)^{3/2}. \quad (5.45)$$

The relative magnitude of the resonance part of the susceptibility compared with the non-resonance part (5.13) is $u = 2^4 \times \pi (G/\hbar \Delta\omega_a)^2 (G/\hbar \omega_b)^2$. Putting $G/\hbar \Delta\omega_a \sim 10$, we find that the resonance part of the susceptibility will be crucial only for frequencies $\omega_b < 100G/\hbar$.

c) **Polarization characteristics of two-quantum transitions in crystals.** The polarization properties, associated with the composite matrix element M_{21}^{ab} , of two-photon allowed-allowed transitions have been studied by means of group theory in^[79b,101,102] for all 32 crystal-symmetry point groups. In^[79b] the polarization dependence was studied for the case when the state 1 is fully symmetric and the two-photon transition occurs at the center of the Brillouin zone or at one of the high-symmetry points of the zone. Spin-orbit interaction was not

taken into account in^[79b]. In^[101], the polarization properties were discussed for cubic crystals in the presence of external perturbations (under pressure and in external fields)²³⁾. The most complete data are contained in^{[102]24)}, in which a Table is given of all the symmetries allowed when the spin-orbit interaction in the transitions is taken into account.

The crystals principally used in experiments on two-quantum absorption are crystals of the cubic, hexagonal, trigonal and tetragonal classes. The polarization dependence of the allowed-allowed two-quantum transitions for such crystals is given in the Table. This Table is compiled from the data of^[102], with the assumption that the effective and macroscopic fields are the same. This assumption is apparently justified for semiconductor crystals and metals, since we can assume that the electrons in them are spread over the volume of the unit cell. It is possible to obtain the angular dependences for allowed-forbidden transitions, if we make use of the same Table. For this, for transitions to a band we must decompose the direct product of the representation of the initial state and the representation Γ_{∇} (according to which the operator p or d transforms) into irreducible

$D_2, C_{2v}, D_{2h}, D_{4h}$	Γ^0	Γ^8	Γ^7	Γ^6	Γ^5	Γ^4	Γ^3	Γ^2	Γ^1
	Γ^0_{\pm}	Γ^8_{\pm}	Γ^7_{\pm}	Γ^6_{\pm}	Γ^5_{\pm}	Γ^4_{\pm}	Γ^3_{\pm}	Γ^2_{\pm}	Γ^1_{\pm}
Γ^1	Γ^1_{\pm}	Γ^1_{\pm}		E_2	$E_1(\lambda)$	Forbidden		A_2	$A_1(\lambda)$
Γ^2	Γ^2_{\pm}	Γ^2_{\pm}		E_2	$E_1(\lambda)$	Ditto		$A_1(\lambda)$	
Γ^3	Γ^3_{\pm}	Γ^3_{\pm}		$E_1(\lambda)$	E_2	A_2			
Γ^4	Γ^4_{\pm}	Γ^4_{\pm}		$E_1(\lambda)$	E_2	$A_1(\lambda)$			
Γ^5	Γ^5_{\pm}	Γ^5_{\pm}		$E_1(\lambda)$	$A_1(\lambda) +$	$A_1(\lambda) +$			
Γ^6	Γ^6_{\pm}	Γ^6_{\pm}		$A_1(\lambda) +$	$+c_1 A_2 +$	$+c_1 A_2 +$			
Γ^7	Γ^7_{\pm}	Γ^7_{\pm}	$E_1(\lambda) +$	E_2	$A_1(\lambda) +$	$+c_2 E_2$			
Γ^8	Γ^8_{\pm}	Γ^8_{\pm}	$E_1(\lambda) +$	$A_1(\lambda) +$	$+c_1 A_2 +$	$+c_2 E_1(\lambda_2)$			
Γ^9	Γ^9_{\pm}	Γ^9_{\pm}	$A_1(\lambda) +$	$+c A_2$					

T	T_h	$(\Gamma^6 \Gamma^7)$	Γ^5	Γ^4	$(\Gamma^2 \Gamma^3)$	Γ^1
		$(\Gamma^6_{\pm} \Gamma^7_{\pm})$	Γ^5_{\pm}	Γ^4_{\pm}	$(\Gamma^2_{\pm} \Gamma^3_{\pm})$	Γ^1_{\pm}
Γ^1	Γ^1_{\pm}			$T(\lambda)$	E	A
$(\Gamma^2 \Gamma^3)$	$(\Gamma^2_{\pm} \Gamma^3_{\pm})$			$T(\lambda)$	$A + cE$	
Γ^4	Γ^4_{\pm}			$A + c_1 E +$	$+c_2 T(\lambda) +$	
Γ^6	Γ^6_{\pm}	$E + cT(\lambda)$	$A + cT$		$+c_3 T(\lambda)$	
$(\Gamma^6 \Gamma^7)$	$(\Gamma^6_{\pm} \Gamma^7_{\pm})$	$A_1 + c_1 E + c_2 T(\lambda)$				

O, T_d	O_h	Γ^8	Γ^7	Γ^6	Γ^5	Γ^4	Γ^3	Γ^2	Γ^1
		Γ^8_{\pm}	Γ^7_{\pm}	Γ^6_{\pm}	Γ^5_{\pm}	Γ^4_{\pm}	Γ^3_{\pm}	Γ^2_{\pm}	Γ^1_{\pm}
Γ^1	Γ^1_{\pm}				T_2	T_1	E	Forbidden	A_1
Γ^2	Γ^2_{\pm}				T_1	T_2	E	A_1	
Γ^3	Γ^3_{\pm}				$T_1 + cT_2$	$T_1 + cT_2$	$A_1 + cE$		
Γ^4	Γ^4_{\pm}				$E + cT_1 +$	$A_1 + c_1 E +$	$+cE$		
Γ^5	Γ^5_{\pm}				$+c_2 T_2$	$+c_2 T_1 + c_3 T_2$			
Γ^6	Γ^6_{\pm}	$E + c_1 T_1 +$	T_2	$A_1 +$	$+c_2 T_1 + c_3 T_2$				
Γ^7	Γ^7_{\pm}	$E_1 + c_1 T_1 +$	$A_1 +$	$+cT_1$					
Γ^8	Γ^8_{\pm}	$E_1 + c_1 T_1 +$	$A_1 +$	$+cT_1$					
		$+c_2 T_2$							

In the Table, Bethe's notation is used for the representations (cf., e.g., [103]); its relation to other notations is to be found in [102]. The capital Latin letters in the Table denote the following expressions:

$$A_1(\lambda) = [(l_1 l_2 + m_1 m_2) + \lambda n_1 n_2]^2, \quad A_1 = \bar{A}_1(1), \quad A_2 = (l_1 m_2 - l_2 m_1)^2; \\ E_1(\lambda) = (m_1 n_2 - m_2 n_1) + \lambda (m_1 n_2 + m_2 n_1)^2 + [(n_1 l_2 - n_2 l_1) + \lambda (n_1 l_2 + n_2 l_1)]^2, \\ E_2 = (1 - n_1^2)(1 - n_2^2), \quad E = (l_1^2 l_2^2 + m_1^2 m_2^2 + n_1^2 n_2^2) - (l_1 l_2 m_1 m_2 + m_1 m_2 n_1 n_2 + n_1 n_2 l_1 l_2); \\ T_1 = (m_1 n_2 - m_2 n_1)^2 + (l_2 n_1 - l_1 n_2)^2 + (l_1 m_2 - l_2 m_1)^2; \\ T_2 = (l_1 m_2 + l_2 m_1)^2 + (m_1 n_2 + m_2 n_1)^2 + (l_1 n_2 + l_2 n_1)^2; \\ T(\lambda) = [(m_1 n_2 - m_2 n_1) + \lambda (m_1 n_2 + m_2 n_1)]^2 + [(l_2 n_1 - l_1 n_2) + \lambda (l_1 n_2 + l_2 n_1)]^2 + \\ + [(l_2 n_1 - l_1 n_2) + \lambda (n_1 l_2 + n_2 l_1)]^2 + [(l_1 m_2 - l_2 m_1) + \lambda (l_1 m_2 + l_2 m_1)]^2.$$

l, m and n are the direction cosines of the electric vectors e_1 and e_2 with respect to the symmetry axes of the crystal, λ_1 are real numbers and c_1 are positive numbers, which cannot be determined by means of group theory.

representations. The angular dependence is found from the Table as the linear combination corresponding to the final state and to each of the irreducible representations obtained.

For allowed-allowed transitions to exciton states, we must decompose the direct product of the representations of the conduction band (band 2) and of the function of the relative motion of the electron and hole into irreducible representations.

d) Two-photon absorption in Group-IV semiconductors. The Group-IV semiconductors Ge, Si form a lattice of symmetry O_h [104]. The valence band in these is four-fold degenerate at $\mathbf{k} = 0$ (Γ_8 symmetry). The nearest conduction band at $\mathbf{k} = 0$ has Γ_7 symmetry. Near $\mathbf{k} = 0$, only allowed-forbidden transitions are possible. To describe transitions from a band of heavy or light holes, we can make use of the $(\omega_a + \omega_b - \omega_g)$ -dependent expressions (5.13) or (5.43) obtained in the two-band model. The total susceptibility is equal to the sum of the contributions of the light-hole and heavy-hole bands. Generally speaking, the angular dependence of the susceptibility is rather complicated. From symmetry considerations (cf. subsection (c)), it follows that it is a linear combination of A, E, T₁ and T₂ functions (see the Table). However, the quantity $\chi''_{aabb}(\omega_a, \omega_b)$ can be calculated sufficiently accurately for Ge in the two-band approximation. In this approximation, it follows from (5.13) that the angular dependence of the susceptibility is determined entirely by the relative orientation of the fields a and b:

$$\chi''_{aabb}(\omega_a, \omega_b) \sim \{1 + [2\omega_a^2\omega_b^2/(\omega_a^4 + \omega_b^4)] \cos^2(\hat{e}_a, \hat{e}_b)\}. \quad (5.47)$$

Up to now, the two-quantum absorption experiments have been performed in Ge [105, 106]. The absorption at frequency $\omega = 8 \times 10^{14}$ rad/sec (a laser using a CaF₂:Dy crystal) due to two-quantum transitions was measured. From the results of [106], the value of the imaginary part χ''_{aaaa} of the susceptibility is $(1.5 \pm 0.8) \times 10^{-9}$. A calculation from (5.13) with allowance for the contribution of light and heavy holes gives 1.9×10^{-9} esu, which is in good agreement with the experiment. It is possible, however, that the experimental results of [106] are somewhat too high, since the authors of [106] assumed that the spatial distribution of the laser radiation was Gaussian, whereas the laser operated in the multi-mode regime.

e) Two-photon absorption in the semiconductor compounds $A_{III}B_{IV}$. The semiconductor compounds $A_{III}B_{IV}$ crystallize in a lattice of the zinc-blend type (symmetry group T_d) or of the wurtzite type (symmetry C_{6v}). However, two-photon measurements have been performed only on crystals with a lattice of the zinc-blend type.

In crystals of T_d symmetry, the valence band Γ_8 is four-fold degenerate and the conduction band Γ_6 is doubly degenerate [107]. Near $\mathbf{k} = 0$, both allowed-allowed and allowed-forbidden transitions are possible. The angular dependence in the general case is complicated (according to the Table, we have E + c₁T₁ + c₂T₂ for allowed-allowed transitions only). We shall make use of the fact that in $A_{III}B_{IV}$ semiconductors the entire treatment can be carried through in the two-band approximation (cf. subsection (a)). It follows from (5.9)–(5.14) that the relative magnitudes of the susceptibilities for both allowed-allowed and allowed-forbidden transitions can be expressed with sufficient accuracy in terms of a single parameter—the gap width E_g . For allowed-allowed transitions, assuming for simplicity that $\omega_a = \omega_b$, from (5.10), (5.12) and (5.34) we have

$$\chi''_{aaaa}(\omega, \omega) = \frac{2^{3/2} e^4 \tilde{m}^{*3/2} p_{12}^2 a^2 (\tilde{\Delta}\omega)^{1/2}}{\pi^2 \hbar^9/2m^2 \omega_g^2} \frac{\alpha e^{\pi\alpha}}{\text{sh } \pi\alpha}, \quad (5.48)$$

where $\tilde{\Delta}\omega = (2\omega - \omega_g)/\omega_g$ and $\alpha = (G/\hbar\Delta\omega)^{1/2}$, G is the exciton binding energy. For allowed-forbidden transitions, we obtain from (5.9) and (5.43)

$$\chi''_{aaaa}(\omega, \omega) = \frac{2^{13/2} e^4 \tilde{m}^{*1/2} p_{12}^2 (\tilde{\Delta}\omega)^{3/2}}{\hbar^7/2m^2 \omega_g^4} \frac{\alpha(1+\alpha^2) e^{\pi\alpha}}{\text{sh } \pi\alpha}. \quad (5.49)$$

In the general case, the susceptibility is determined by the sum of (5.48) and (5.49). It can be seen from (5.48) and (5.49) that the two mechanisms of two-photon transitions will give the same contribution to χ'' if

$$\tilde{\Delta}\omega^* = (\tilde{m}^* a^2/4\pi\hbar) \omega_g^2 - (G/\hbar\omega_g) \approx 2 \cdot 10^{-33} \omega_g^2 - (G/\hbar\omega_g). \quad (5.50)$$

The value of $\tilde{\Delta}\omega^*$ following from (5.50) is 0.13 for GaP, 0.05 for GaAs, 0.013 for GaSb and 0.001 for InSb. For $\tilde{\Delta}\omega < \tilde{\Delta}\omega^*$ the susceptibility is determined by the allowed-allowed transitions (5.11) or (5.48)), and for $\tilde{\Delta}\omega > \tilde{\Delta}\omega^*$ the allowed-forbidden transitions ((5.13) or (5.49)) make the main contribution. In the model considered, for $\tilde{\Delta}\omega > \tilde{\Delta}\omega^*$ the angular dependence of the susceptibility is the same as that for the Group-IV semiconductors—(5.47).

We shall compare the magnitudes of the susceptibilities for different semiconductors with the experimental data.

1) Measurements of two-photon absorption in GaP have been performed at frequency $\omega = 2.7 \times 10^{15}$ rad/sec (a ruby laser) [108, 109]. For this frequency, $\tilde{\Delta}\omega = 0.5 \tilde{\Delta}\omega^*$ and the allowed-forbidden transitions must be taken into account. According to (5.48) and (5.49), the theoretical value of χ'' equals 1.2×10^{-11} esu. The experimental value of 6×10^{-12} , recalculated from the data of the papers [108, 109], is in agreement with the theoretical value, within the limits of experimental error.

2) Two-photon absorption in GaAs at frequency 1.7×10^{15} rad/sec (a neodymium laser) has been studied in [89, 110–112]. The value $\tilde{\Delta}\omega = 0.55 \gg \tilde{\Delta}\omega^*$; χ'' , calculated from (5.49), equals 5×10^{-10} esu. The values of χ'' obtained from the absorption coefficients measured in the papers [89, 113] are equal to 10^{-7} and 10^{-8} respectively. The discrepancy between the theoretical and experimental results is appreciable, and a further analysis of the experiment is evidently necessary. A theoretical estimate performed using the expressions of [89] leads to the value $\chi'' = 10^{-8}$ esu. The discrepancy between the theoretical estimates is due to an error in formula (2) of [89] (a factor 1/12 is omitted), and, in addition, the result is too high by a factor of 4 because of neglect of the contribution (2.13) of the higher bands when (2.2) is used.

3) Two-quantum absorption in InSb has been studied in more detail than in any other $A_{III}B_{IV}$ semiconductor [114–120, 177–179] 25). The measurements were mainly carried out at frequency 1.8×10^{14} rad/sec (a CO₂ laser). Since $\tilde{\Delta}\omega = 0.23 \gg \tilde{\Delta}\omega^*$, we can use (5.49) to describe the two-quantum transitions. As already remarked (cf. (5.47)), the quantity χ'' is then independent of the orientation of the field relative to the crystal. This is confirmed experimentally in [115, 118]. As regards the magnitude of χ'' , by substituting the parameters of InSb into (5.49) we find the value $\chi'' = 1.5 \times 10^{-7}$ esu. In the absence of a magnetic field, the existing experiment [115, 118, 178, 179] permits us to determine only χ'' . This estimate ($\chi'' \sim 10^{-8}$) is close to the theoretical estimate in order of magnitude.

The larger part of [114, 116, 117, 119–121] on two-quantum absorption in InSb is concerned with two-quantum transi-

tions in a quantizing magnetic field. The two-quantum transitions have been investigated mainly with a mutually perpendicular orientation of the external field H and the field of the electromagnetic wave. For simple bands, transitions (cf. (5.24)) in which the magnetic quantum number j changes by ± 1 are possible. In InSb, however, the degeneracy of the light-hole and heavy-hole bands leads to the result that transitions with changes of j by ± 1 up to ± 3 are possible. In particular, transitions with $\Delta j = \pm 1$ and $\Delta j = \pm 3$ have been detected experimentally. A typical form of the spectrum is shown in Fig. 8, which is taken from [119]. The theoretical value of χ'' at resonance, obtained using (5.24) with $\Delta j = 1$ and a line width of $5 \times 10^{12} \text{ sec}^{-1}$, is 10^{-8} , which is approximately an order of magnitude smaller than that following from the experimental data given in [119]. The discrepancy is possibly associated with the neglect of the contribution of light-hole and heavy-hole bands as intermediate states. The theoretical calculation of [119] with allowance for the explicit form of the wavefunctions in the magnetic field leads to agreement between the theoretical and experimental results when the contribution of the higher bands is neglected.

f) Two-photon absorption in $A_{II}B_{VI}$ compounds.

1) Like the $A_{III}B_{V}$ semiconductors, the compounds $A_{II}B_{VI}$ form a lattice of the zinc-blende type (T_d symmetry) or wurtzite type (C_{6v} symmetry). The energy spectra of these compounds have been much less studied than those of the $A_{III}B_{V}$ semiconductors; however, it can be assumed that the band structures of the $A_{III}B_{V}$ and $A_{II}B_{VI}$ compounds are similar. Therefore, we should expect that the two-band approximation for the description of two-quantum transitions will also turn out to be sufficiently good in the analysis of experiments for the $A_{II}B_{VI}$ compounds. It should be noted that the difference between structures of the T_d and C_{6v} groups are not very important in the calculation of the magnitude of the susceptibility, since, for C_{6v} symmetry, the potential is small in the majority of $A_{II}B_{VI}$ semiconductors and can be taken into account by perturbation theory (the quasi-cubic model) [122]. The available data [88, 122, 123] on the band structure (the relation between the effective masses and the interband spacings and spin-orbit splitting) makes it possible, as in subsection (e), to express the probability of two-quantum transitions between the bands Γ_2 (Γ_1) and Γ_{15} in terms of the gap width. If we take into account [88] that the dipole moment of the transition between the states Γ_2 (Γ_1) and Γ_{15} is the same as in the $A_{III}B_{V}$ semiconductors, it turns out that the two-quantum transitions in $A_{II}B_{VI}$ are also described by the expressions (5.48) and (5.49), but with less accuracy.

The angular dependence of the susceptibility of semiconductors with T_d symmetry was given above. For the wurtzite structure, the angular dependence for allowed-

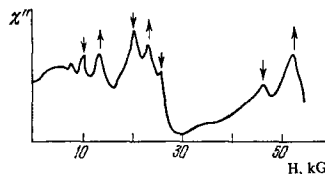


FIG. 8. Typical dependence of χ''_{aaaa} on the magnetic field ($E \perp H$) at frequency 1046.8 cm^{-1} (CO_2 -laser) for n-InSb [119]. \downarrow —transitions with $\Delta j = 1$, \uparrow —transitions with $\Delta j = -1$.

allowed transitions is described by the function (see the Table)

$$A_1(\lambda_1) + c_1 A_2 + c_2 E_1(\lambda_2) + c_3 E_2.$$

As regards the allowed-forbidden transitions, the angular dependence of the susceptibility is also expressed by the formula (5.47) for semiconductors with the wurtzite structure.

2) Two-photon absorption has been studied in more detail in cadmium sulfide [124-141, 173, 174] than in any other $A_{II}B_{VI}$ compound: the crystal symmetry is C_{6v} , the gap width is 2.45 eV at room temperature, and the reduced mass is 0.18m. Measurements have been performed in a wide frequency range, from 2.45 to 3.5 eV. Since the exciton binding energy in CdS equals 0.027 eV, the frequency spectrum should be described by the expression (5.34) or (5.43). If we make use of the estimate (5.50) for the relative contribution of the allowed-allowed transitions, we should expect a linear [26] dependence of χ'' on $\Delta\omega = \omega_a + \omega_b - \omega_g$ for $\Delta\omega > 0.2 \text{ eV}$ [27]. A theoretical calculation of χ'' using (5.43) gives, for the ruby-laser frequency, the value $5 \times 10^{-11} \text{ esu}$. The values of χ'' found from the experimental data of [113, 125, 133, 139] are equal to 6×10^{-11} , 4×10^{-11} , 1.5×10^{-11} and 15×10^{-11} respectively. The frequency dependence was investigated experimentally in [124, 126-128, 134] for different polarizations of the radiation. The authors assume that the frequency dependence follows a square-root law, except in the case [124] when the polarization vectors are mutually perpendicular and perpendicular to the c-axis. In this latter case, the authors of [124] approximate the dependence by a three-halves law. The discrepancy between experiment and theory requires a more detailed analysis, although even a linear approximation is possible in all cases, when the experimental error bars are taken into account [28]. The polarization dependence for transitions from the bands Γ_7 and Γ_9 to the band Γ_7 are described in the general case by the expression

$$\chi'' \sim c_1 A_1(\lambda_1) + c_2 A_2 + c_3 E_1(\lambda_3) + c_4 E_2.$$

In the two-band isotropic model, for the allowed-forbidden transitions the angular dependence has the form (5.47) and, consequently, does not depend on the orientation of the fields relative to the crystal axes. The dependence of the imaginary part χ'' of the susceptibility on the orientation of the fields with respect to the c-axis has been reliably established experimentally [124, 128, 134, 139]. It follows from the general relations (see the Table) that, in the case of one linearly polarized field,

$$\chi'' \sim (A_1 + A_2 \cos^2 \theta + A_3 \cos^4 \theta),$$

where θ is the angle between the polarization vector and the crystal axis. According to the data of [124, 134],

$$A_1 = 0.98, \quad A_2 = 0.3, \quad A_3 = -0.84, \quad (A_2 + A_3)/A_1 = -0.55.$$

From the measurements of [189], $(A_2 + A_3)/A_1 = -0.33$. It follows from the polarization measurements that the isotropic model for allowed-forbidden transitions is too crude an approximation in CdS. It is also possible that the contribution of the allowed-allowed transitions is greater than we should expect from the estimate expression (5.50). We must discuss the theoretical interpretation by the authors of [124] of their experimental results. From their experimental data, the authors of [124] found the parameters of the conduction band lying at a distance of 6.2 eV from the valence band. This, apparently, is the only attempt to extract information about the higher bands in semiconductors from data from two-quantum

spectroscopy. Unfortunately, the theoretical analysis of^[124] requires clearer justification²⁹⁾. For the analysis, the authors used (2.2), neglecting the contribution of the higher bands. However, with the assumptions of the authors of^[124], the sum rules (2.11) lead, in particular, to incorrect values for the effective masses of the conduction band and valence bands.

Measurements near the absorption-band edge at low temperatures have been performed in^[136,173], and transitions to exciton states^[136,173] and also transitions between Landau levels at 188 kGs^[136] have been detected.

As is well known, the band-structure parameters, and, consequently, the two-photon absorption, can depend on the pressure. For CdS, this effect was detected experimentally in^[174].

3) Two-quantum absorption in cadmium selenide has been studied at the neodymium-laser frequency $\hbar\omega = 1.17$ eV^[112,142-144]. CdSe has the wurtzite structure C_{6v} ; $m^* = 0.13m$, the gap width is 1.84 eV, and the spin-orbit splitting of the valence band is 0.43 eV. At the neodymium-laser frequency, $\Delta\tilde{\omega} > \Delta\tilde{\omega}^*$ in transitions from the upper valence bands Γ_9 and Γ_7 , and we can use (5.43). A calculation in the isotropic-band approximation gives $\chi'' = 6 \times 10^{-11}$ esu. The values recalculated from the experimental data of^[142,143] are 8×10^{-10} and 1.8×10^{-9} for light polarized parallel and perpendicular to the c-axis, respectively. The results of theory and experiment differ widely³⁰⁾ and a more detailed analysis is evidently needed. Theoretically, the angular dependence is, generally speaking, the same as in CdS. As in the case of CdS, the dependence, established in^[143,144], of χ'' on the orientation of the field with respect to the crystal axis indicates the inadequacy of the isotropic model.

4) Two-quantum absorption in zinc sulfide is the subject of the papers^[138,145-150]. The investigations were carried out using two sources, of which one was a laser ($\hbar\omega_a = 1.17$ eV^[145,148] or $\hbar\omega_a = 1.78$ eV^[147,149]). The measurements of^[145,147] were performed in a broad frequency range $\hbar(\omega_a + \omega_b) = 4-5$ eV at room temperature, and near the absorption-band edge^[146] at various temperatures. Zinc sulfide crystallizes in two modifications—hexagonal C_{6v} and cubic T_d . The properties of the two modifications are similar^[123], and we shall assume in the calculation of the magnitude of χ'' and of the frequency dependence that $\hbar\omega_g = 3.9$ eV and that the reduced effective mass is $m^* = 0.25m$. In the whole range of frequencies in which the measurements were performed, χ'' is described in the isotropic model by the expression (5.43). The theoretical value of χ'' for $\hbar\omega_a = 1.8$ eV and $\hbar\omega_b = 2.2$ eV is 2×10^{-11} . From the data of the experiments of^[147,150], this quantity equals 8×10^{-12} , 1.6×10^{-11} respectively. For $\hbar\omega_a = 1.17$ eV and $\hbar\omega_b = 2.8$ eV, the theoretical and experimental^[145] values of χ'' are 9×10^{-12} and 4×10^{-11} . There is agreement throughout, within the limits of experimental error. The experimental data were always taken at room temperature. The frequency dependence of χ'' (Fig. 9) is described by the change of the contribution (5.43) with change of $\omega_a + \omega_b - \omega_g$. Investigations at different temperatures^[146] have shown that, near $\hbar(\omega_a + \omega_b) \approx 3.7$ eV, χ'' falls with decreasing temperature; clearly, this is associated with a temperature shift of the band edge. Exciton peaks were not detected on cooling down to 10°K^[146]. In the opinion of the authors of^[146], this is explained by the imperfection of the crystals. The anisotropy of the two-quantum

absorption in cubic (T_d) ZnS was studied in the papers^[147,149]. The crystal studied consisted of cubic micro-twins, rotated through 180° relative to each other about one of the third-order axes. The directions of the electric vectors of the laser radiation and of the light from the second source were arranged to be parallel or perpendicular to each other; the light beams propagated in a direction parallel or perpendicular to the optical axis. The dependence of the absorption on the angle of rotation of the crystal with respect to the direction of propagation of the light was measured. The dependences obtained correspond to the two-photon transition $\Gamma_1 \rightarrow \Gamma_5$ (Γ_{15}) (see the function T_2 in the Table) when the complicated crystal structure is taken into account.

5) Two-quantum absorption at the frequency of a ruby laser has been measured in ZnSe^[113,144]. This crystal has T_d symmetry, $\hbar\omega_g = 2.8$ eV and $m^* = 0.12m$. The theoretical value of χ'' calculated from (5.34) and (5.43) is 4×10^{-10} and is close to the values resulting from the experiment ($(1.5 - 2) \times 10^{-10}$ ^[113,144]).

6) Two-quantum absorption in a series of mixed crystals CdS_xSe_{1-x} , $Zn_xCd_{1-x}Se$ and $Zn_xCd_{1-x}S$ has also been investigated at the ruby-laser frequency^[139,144,151,152]. The dependence of χ'' on the composition is shown in Fig. 10³¹⁾. In the region 2.3 eV $< \hbar\omega_g < 3.5$ eV, the results are well described by the expressions (5.34) and (5.43). The sharp increase in the region $\hbar\omega_g < 2.1$ eV is possibly due to transitions via intermediate exciton states (cf. (5.45)), although this region requires a detailed analysis (e.g., it is necessary to take into account the high-frequency Stark shift).

7) Detailed studies of transitions to exciton states have been performed on the crystal ZnO ^[25,153,154]. This crystal has symmetry C_{6v} , $\hbar\omega_g = 3.44$ eV and reduced effective mass 0.2m; the exciton spectrum of ZnO at liquid-helium temperatures has been well studied.

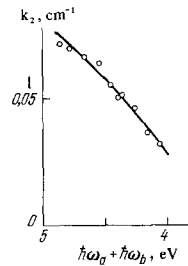


FIG. 9

FIG. 9. Two-photon absorption spectrum of ZnS^[147]. The ruby-laser radiation flux was 3.5×10^{25} cm⁻² sec⁻¹.

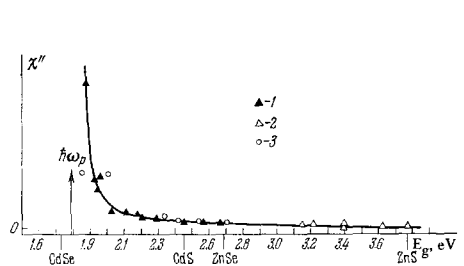


FIG. 10

FIG. 10. Dependence of χ'' on the gap width E_g for mixed crystals at ruby-laser frequency, for CdS_xSe_{1-x} (1), $Zn_xCd_{1-x}S$ (2) and $Zn_xCd_{1-x}S$ (3)^[139, 144, 151, 152].

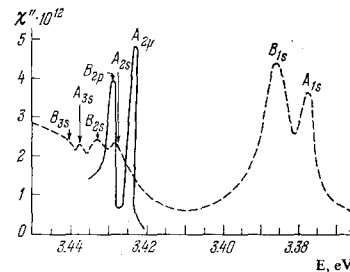


FIG. 11. Two-photon spectrum (solid curve) of ZnO at 1.6°K and the one-photon spectrum^[153] (dashed curve).

In^[158], transitions to 2p exciton states A and B have been observed (Fig. 11). The fact that the exciton states are of the p-type is confirmed by the splitting of these states in a magnetic field. In addition, in^[154] a transition to an exciton 2p-state C has been observed and the polarization dependence of the two-quantum absorption investigated. The polarization dependence corresponds to the crystal symmetry. It follows from the experiments of^[25,153,154] that χ'' is determined by the allowed-forbidden transitions (5.43). A calculation using (5.43) gives the value 9×10^{-12} for χ'' in a transition to a 2p-state. The value obtained from the experimental data of^[25,153,154] equals 5×10^{-12} , i.e., is close to the theoretical estimate. The absence of two-photon absorption for transitions to 1s- and 2s-states, which are also allowed by the symmetry, remains to be understood. For these transitions, the values of χ'' are respectively 7×10^{-10} and 9×10^{-12} . It is possible that the symmetry of the crystals studied in^[25,153,154] was higher.

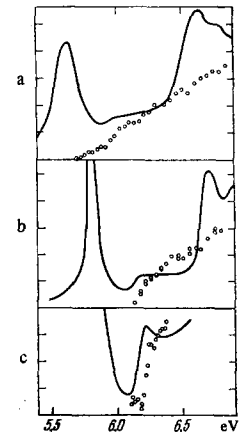
g) Two-photon absorption in ionic crystals. 1) In two-photon spectroscopy of ionic crystals, attention has been paid mainly to alkali-halide crystals. These crystals form cubic lattices. In spite of the considerable successes in understanding the fundamental absorption spectra of the alkali-halide crystals (cf., e.g.,^[155,156]), there is still no complete explanation of all the details of their structure. However, it is well established that the two longest-wave fundamental-absorption bands in bromides and chlorides with the NaCl structure are associated with the spin-orbit doublet of an s-exciton. (In the iodides, the spin-orbit splitting is large and its second component is superimposed on other bands.) The lower conduction band of the alkali-halide crystals has a minimum at the Γ -point and symmetry Γ_1 (Γ_6^+ in the double groups). It is formed by the electron s-functions of the metal. The upper valence band has a maximum, also at the Γ -point, and symmetry Γ_{15} (Γ_8^- and Γ_6^- in the double groups). The valence band is formed by the p-functions of the halogen. Therefore, both the s-exciton transition and the interband transition $\Gamma_8^- \rightarrow \Gamma_6^+$ at the Γ -point are forbidden by parity in the two-photon spectrum.

Consequently, the two-photon absorption should be determined by the allowed-forbidden transitions. Thus, in these crystals, transitions to exciton p-states only are possible. The alkali-halide crystals have a large gap width (5–7 eV). The Bohr radius of a Wannier-Mott exciton in these crystals is small (comparable with the dimensions of the cell). However, the hydrogen-like model turns out to be a fairly good approximation, at least for $n > 2$ (n is the principal quantum number in the hydrogen-like model).

It has been reliably established^[24,157] that the first (1s) exciton maxima are absent in the two-photon absorption spectra of KI and CsI. Figure 12 shows the two-photon absorption spectra of KI, from^[182]. The linear increase of absorption with frequency is in agreement with the predictions of the theory (cf. (5.42) and (5.43)).

Improvement in experimental technique has made it possible to find fine details in the two-photon spectrum of KI in the region 6.2–6.4 eV. In^[158], structure associated with 2p-, 3p- and 4p-excitons was detected, along with a maximum (at 6.285 eV) which was identified with a transition in which the absorption of two photons leads to the appearance of an exciton and a longitudinal optical phonon (Fig. 13). A calculation based on third-

FIG. 12. Two-photon absorption spectrum (circles) and one-photon absorption spectrum (in relative units) of a KI crystal at room temperature (a)^[182], liquid-nitrogen temperature (b), and liquid-helium temperature (c).



order perturbation theory shows that this transition must be separated from the 2p-exciton by an interval of 26 MeV, which is in good agreement with the experimental value of 22 MeV.

In^[159], measurements of the two-photon spectrum of KI were extended into the ultra-violet, to a region in which the sum of the two photon energies was 7.5 eV. In this case, the wavelength of the second source (a ruby laser was used as the first source) now falls in the ultra-violet region (about 220 nm), where the intensity is low and it is difficult to select suitable light-filters. Nevertheless, a two-photon absorption spectrum was obtained with two well defined maxima at 7.21 and 7.375 eV. The polarization dependence in the region of the first maximum was also measured. The maximum at 7.21 eV in the two-photon spectrum is very close to a maximum in the one-photon spectrum (7.24 eV). This made it possible to conclude that the maxima in both spectra have a common origin and cannot be ascribed to a transition at the centro-symmetric points of the Brillouin zone. Taking the angular dependence into account, the authors assume that this maximum most probably corresponds to a $\Delta_6 - \Delta_6$ transition.

The band structure of crystals with a lattice of the CsCl type differs somewhat from that of crystals with a face-centered lattice of the NaCl type. As is shown by a calculation^[160,161] of the band structure for CsI (with a lattice of the CsCl type), the conduction band Γ_{12} (Γ_8^-) in this case has a minimum at the Γ -point and is very close in energy to the lower conduction band Γ_1 (Γ_6^+). This is associated with the different splitting of the d-states (Γ_{12} and Γ_{25}') in these two types of lattice; in lattices of the CsCl type, this splitting is much larger. These features of the band structure of CsI are reflected in the complicated structure of the fundamental-absorption edge^[155].

As is shown in^[162,163], these features of the band structure also affect the two-photon spectrum. Taking the two-band model, for the intermediate states in the two-photon transition we must take into account not only the exciton states split off from the band Γ_1 but also the exciton states split off from the d-band Γ_{12} ^[32]. This leads, in particular, to the result that the angular dependence ceases to be determined only by the angle between the electric vectors \mathbf{e}_a and \mathbf{e}_b , and depends also on the angles with the crystal axes.

In^[162], the spectra of CsI and CsBr were measured by means of an automatic two-photon spectrometer. Especially interesting is the polarization dependence obtained for CsI. In a large part of the spectrum, the ratio of the two-photon absorption coefficients for $\mathbf{e}_a \parallel \mathbf{e}_b$ and

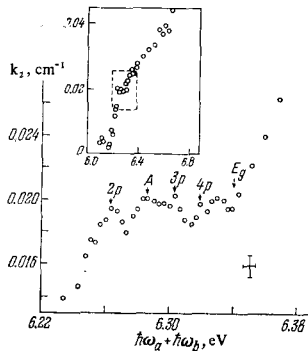


FIG. 13

FIG. 13. Fine structure of the two-photon spectrum of KI [158]. 2p-4p are the exciton maxima and A is the photon-doubling peak. Inset is the spectrum obtained in a previous paper [159].

FIG. 14. Two-photon absorption spectrum (a) and polarization ratio (b) for CsI [162] at 20°K.

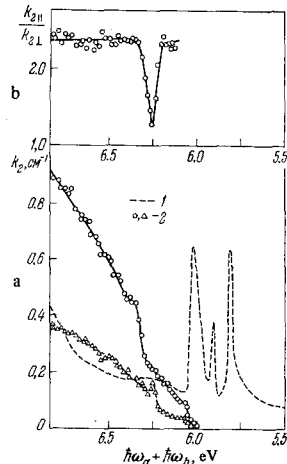


FIG. 14

$\mathbf{e}_a \perp \mathbf{e}_b$ is constant and equal to 2.4. This region is interpreted as an interband transition at the Γ -point, the rise at 6.05 eV being associated with the transition $\Gamma_6^- - \Gamma_6^+$. Near 6.25 eV, there is a peak in the spectrum and a dip in the curve of the polarization ratio (Fig. 14). It is assumed that this peak in the spectrum is due to an exciton at the X-point.

2) Two-photon absorption in PbI has been studied in [114,115,117]. The band width in PbI is 0.2 eV and $m^* = 0.018m$. The two-quantum absorption in PbI, as in InSb, was measured at the frequencies of the radiation of a CO₂-laser. The measurements were made at low temperatures, in the presence of a strong magnetic field. Transitions with $\Delta j = \pm 1, 0$ were detected (where Δj is the change in the magnetic quantum number).

3) Two-quantum absorption in CuCl was studied in the papers [164,165]. The CuCl crystal has T_d symmetry, and its gap width is 3.4 eV. Two-quantum transitions to discrete s-type exciton states belonging to two series, which are formed by the conduction band Γ_6 and the pair of valence bands Γ_7 and Γ_8 , were observed in [164]. Transitions in the region of frequencies corresponding to excitons with $n > 1$ have a complicated polarization dependence, which is possibly explained by the admixture of allowed-forbidden transitions into the exciton p-states. The investigation [165] of one of the transitions to a 1s-state at 1.5°K has made it possible to distinguish the transverse and longitudinal excitons³³, and has also demonstrated the possibility of studying the dispersion of polaritons.

4) Two-quantum absorption in TlCl was studied in the papers [166,167,180,181]. This crystal has symmetry O_h and gap width $\hbar\omega_g = 3.56$ eV. The spectral dependence of χ'' is linear ($\hbar\omega_a = 1.17$ and 2.2 eV $< \hbar\omega_b < 3.4$ eV), in agreement with the expression (5.43). The polarization dependence [167] agrees in general with the two-band model ($\chi'' \sim \cos^2 \theta$, where θ is the angle between the polarizations of the two fields), although in [167] small deviations, apparently associated with the contribution of the allowed-allowed transitions, were observed.

Thus, near the absorption-band edge, the polarization dependence obtained in [180] corresponds to a superposition of allowed-allowed transitions to the states Γ_1^+ and Γ_3^+ . Measurements of the two-photon absorption near the

band edge [181] at low temperatures (77–300°K) have made it possible to observe the multi-phonon structure of the band edge for the first time, and also to measure the dependence of the gap width on the temperature.

5) Two-quantum absorption in TiO₂ (rutile) was studied in [168]. By means of a two-source technique, measurements were made in the interval from 3.3 to 4.1 eV. In accordance with the symmetry, allowed-allowed transitions occur when the electric vectors of both sources are parallel to one of the crystal axes. According to [168], in the frequency dependence there is an exciton peak at about 3.6 eV (a transition to a 1s-state), and according to (5.43) there is a linear increase for $\omega_a + \omega_b > 3.8$ eV. When the electric vectors are directed along mutually perpendicular axes, transitions to p-states are possible and the frequency dependence corresponds to (5.43) in its general features. The value 3.75 ± 0.08 eV for the gap width at the Γ -point follows from the form of the frequency dependence; this agrees with the value obtained by another method.

6) There is a fairly large number of papers on two-quantum absorption at impurity centers [169]. The description of two-photon transitions in these cases, with allowance for the local vibrations, is analogous, to a considerable extent, to the description of transitions in molecular crystals. Lack of space prevents us from considering this question in detail here.

The authors are grateful to A. P. Aleksandrov for useful discussions.

¹Here, we should keep in mind that, in the strong radiation fields of lasers, the kinetics of luminescence can depend on the intensity of the exciting light [170] in particular, as a result of induced transitions to the absorption-band edge [170,171].

²Stimulated Raman scattering (SRS) has also been used as a tunable source [22,23]. It should be noted that the space-time structure of the radiation in SRS is very complicated, and this makes quantitative measurements difficult.

³Another explanation [27], associated with the assumption of random degeneracy of electronic terms of different parity, was rejected after the discovery of two-quantum transitions between levels of different parity in many molecules. Multipole transitions may be of interest for monatomic vapors and gases.

⁴There have been attempts to calculate the sum over m inside the modulus sign in (4.8) for a number of specific compounds: benzantracene, benzopyrene [67] and benzene [64]. It should be noted that, in these calculations, wavefunctions optimized for the determination of the energy eigenvalues were used. The accuracy of calculations of dipole moments with such functions requires further analysis.

⁵In one-quantum transitions between electronic states of the same parity, the vibrational structure is determined by asymmetric vibrations.

⁶We note that, in [57], an odd angular dependence was observed for an anthracene crystal observed perpendicular to the a, c-plane. In connection with the birefringence, such a dependence ought not to be observed, and its origin is incomprehensible.

⁷The probability of transitions under the action of one field differs from (5.1) by the factor 1/4.

⁸One sometimes speaks of an absorption exponent for a field of frequency ω_a in the presence of a field of frequency ω_b : $k(\omega_a) = 8\pi^2 \omega_a \omega_b \text{Im} \chi_{aabb}(\omega_a, \omega_b) F_b c^{-2} [\epsilon_{aa}(\omega_a) \epsilon_{bb}(\omega_b)]^{-1/2}$.

⁹This approximation is applicable if the kinetic energy of the electron and hole formed in the transitions is large compared with the energy of the electron-electron and electron-phonon interactions.

¹⁰There is a treatment of this type, but with the use of the composite matrix element of formula (2.2), in, e.g., the papers [83,84]. Two-photon absorption in a magnetic field has been treated theoretically in the paper [175], which is devoted to the theory of multi-photon transitions in a magnetic field.

¹¹An exception is the resonance situation, in which $\omega_{lj}^2 - \omega^2 \ll \omega^2$ and $\eta \ll 1$. The principal contribution to χ_{aabb} in this case is associated with a resonance intermediate state j .

- ¹²⁾The expressions obtained in the papers [^{89,124}] in this approximation differ by the factor $(\omega_a + \omega_b)^2/\omega_a\omega_b$. As was shown in Sec. 2, this divergence is due to an incorrect estimate of the contribution of the higher bands in the papers [^{83,124}].
- ¹³⁾For crystals of the type A_1B_{VII} , the relation (5.12) no longer holds and the dependence of χ_{aabb} on ω_g can be weaker.
- ¹⁴⁾See footnote 12.
- ¹⁵⁾This can be seen from (5.4), if we take into account that the matrix elements r_{nl} ($k = 0$) are real and, consequently, the Ω_{nl} are imaginary. Therefore, the interference terms associated with the product of the two parts of the composite matrix element are absent.
- ¹⁶⁾The expression (5.15) is correct to within aeH/hc , where a is the lattice constant.
- ¹⁷⁾For a composite matrix element of the form (2.2), a treatment of this type is contained in [⁹⁰⁻⁹³].
- ¹⁸⁾A study of this case is carried through in [^{82,96}], using the interaction with the field in the form $\mathbf{p} \cdot \mathbf{A}$.
- ¹⁹⁾Such transitions have been considered [^{97,98}], using an interaction energy of the form $\mathbf{p} \cdot \mathbf{A}$. The correct frequency dependence was obtained; as regards the magnitude of the susceptibility, the results must be multiplied by $\omega_a\omega_b/(\omega_a + \omega_b)^2$.
- ²⁰⁾When one of the field frequencies is close to G/h , the following treatment is inapplicable and one must use the expressions of [⁹⁸].
- ²¹⁾For $\alpha = a$ or $\alpha = b$, the composite matrix element (2.2) is non-zero only for s -states, and its magnitude relative to (5.28) is $(G/h\omega)^2 \ll 1$; we shall therefore not consider it further. We note that precisely this term for the s -states is considered in the paper [⁹⁸].
- ²²⁾The frequency dependence near the absorption edge obtained in [⁹⁹] is incorrect.
- ²³⁾The theory of two-quantum transitions in a strong electric field is the subject of [¹⁷⁶]. The analysis is performed in a three-band model, using an interaction energy in the form $\mathbf{p} \cdot \mathbf{A}$.
- ²⁴⁾Another paper in which the symmetry properties of two-photon transitions are analyzed has recently appeared [¹⁷²]. This contains more accurate tables for the angular dependences of allowed-allowed transitions for all 32 crystal classes. In addition, the symmetry properties arising from the difference between the properties of the transverse and longitudinal excitons are investigated in [¹⁷²].
- ²⁵⁾A theoretical study of the two-photon absorption spectrum for InSb and the lead chalcogenides (PbTe, PbSe and PbS), with the real band structure taken into account (in the Kane model) is carried through in the paper [¹⁷⁷]. The calculation is performed with the interaction energy in the form $\mathbf{p} \cdot \mathbf{A}$. In this paper (cf. also [¹⁷⁸]), the optical orientation of the carriers excited in the two-photon transitions is discussed. Attempts to detect this effect [¹⁷⁸] have had no success as yet.
- ²⁶⁾In reality, because of the factors ω_a^{-4} and ω_b^{-4} in (5.43), the dependence of χ'' on $\omega_a + \omega_b$ is weaker.
- ²⁷⁾In the region $\Delta\omega < 0.2$ eV, it is necessary in the analysis to take into account the spin-orbit splitting of the valence bands.
- ²⁸⁾It is possible that an important role in determining the frequency dependence in this region is played by ionized impurities, if their concentration is greater than or of the order of a_e^{-3} (a_e is the exciton radius).
- ²⁹⁾This is also noted in [¹⁷³].
- ³⁰⁾The theoretical estimate in [¹⁴³] gives 2×10^{-9} esu for χ'' ; the discrepancy between the theoretical estimates is due to an error (a factor 1/12 is omitted) in formula (1) of [¹⁴³], and, in addition, the result is too high by a factor of 4 because of the neglect of the contribution (5.13) of the higher bands.
- ³¹⁾The figure was kindly provided by the authors of these papers.
- ³²⁾Two-quantum transitions to p -states may turn out to be relatively strong when a third band is taken into account, since in alkali-halide crystals the size of the exciton is of the order of the dimensions of the cell.
- ³³⁾The polarization properties of such transitions are discussed in [¹⁷²].
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