Electron absorption in nonpolar liquids

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Electron absorption of light is considered in a system of polar particles that interact via dispersion forces. The generalized oscillator strengths are calculated for the combination-frequency absorption that arises in the coupled molecule pairs. A sum rule is obtained connecting the probabilities of the one-photon and two-photon processes in the interacting systems. Estimates of the exctinction coefficient $\Sigma_{2\omega}$ of single-photon absorption at double the frequency, carried out for liquefied inert gases, show that this coefficient is comparable with the absorption Σ_ω at single frequencies.

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1. INTRODUCTION

Intermolecular interactions (IMI) in dense media give rise to a number of effects that influence the spectral and integral characteristics of the electron emission and absorption bands. In particular, dispersion forces shift the maxima of the band, alter their shapes, and change the oscillator strengths of the electronic transitions.

The most peculiar manifestation of the IMI is the appearance of new transition frequencies for the system of interacting particles. For example, paired interactions of molecules should lead to the appearance of combination frequencies equal to the sum or to the difference of the absorption frequencies of the individual particles. This effect is known in magnetic resonance,[1] where absorption at the frequency $\Omega = 2\omega_0$ takes place in a system of two interacting magnetic dipoles each of which can absorb at the frequency ω_0. Absorption at the doubled frequency Ω is the result of simultaneous transitions between two nondegenerate collectivized terms of a system consisting of a pair of identical particles, but in the case of magnetic interaction this absorption is negligibly small. At the same time, in electric dipole–dipole (DD) interaction of atoms and molecules, the dispersion forces cause the probabilities of the simultaneous transitions between the collectivized energy levels to become, generally speaking, comparable with the probabilities of the transitions between the terms in the isolated particles. For this reason, it is of interest to analyze quantitatively the onset of combined electron-absorption bands in interacting molecular and atomic systems.

It is obvious that a complete dynamic theory for a condensed medium such as a liquid must take into account the molecule-motion kinetics. However, as shown by Linder and Abdulnar,[2] by using Kubo's linear-response formalism it is possible to describe the electron absorption in a liquid on the basis of a double perturbation theory: nonstationary in the interaction of the molecules with the external field $\mathbf{E}(t)$ of the light wave, and stationary in the Hamiltonian of the DD interaction between the molecules. Since the electron motion inside the molecules is incomparably faster than the thermal motion of the molecules, it follows, as shown in[2], that the quantum-mechanical mean value of the induced dipole moment $\mathbf{M}$ in the molecule system becomes independent of the kinetics of the molecule motion. In other words, when describing the integral characteristics of the electron absorption in liquids we can assume, with good accuracy, that the centers of the interacting molecules are immobile, since the times of emission and absorption of the light quanta are shorter by several orders of magnitude than the translational and rotational relaxation times of the nuclei of the molecules.

In this paper, quantum perturbation-theory methods are used to calculate the oscillator strengths of the electron absorption at the combined frequencies in nonpolar liquids. The numerical estimates obtained in a reasonable approximation for liquefied inert gases show that the integral absorption coefficient at the doubled frequencies is large enough to be observed in experiment. The effect considered here is therefore of interest both for linear spectroscopy of condensed media and for the consideration of the feasibility, in principle, of developing lasers operating at combined, particularly doubled, frequencies. The theory presented below is valid for interactions in binary solutions and in pure liquids.

2. GENERALIZED OSCILLATOR STRENGTHS

We consider a pair of nonpolar particles that are coupled by dispersion forces; the Hamiltonian of the interaction between them is

$$\hat{H}_{int}^{(12)} = (\hat{d}_1)_\alpha T_{\alpha\beta}^{(12)} (\hat{d}_2)_\beta, \qquad \alpha, \beta = x, y, z, \tag{1}$$

where $\hat{\mathbf{d}}$ is the operator of the electric dipole moment of the particle, and

$$T_{\alpha\beta}^{(12)} = \frac{1}{R_{12}{}^3}\left[\delta_{\alpha\beta} - \frac{3(R_{12})_\alpha (R_{12})_\beta}{R_{12}{}^2}\right] \tag{2}$$

is the tensor of the DD interaction of the particles; summation of the vector indices is implied in (1). We introduce the dipole-moment operator of the coupled particle pair

$$\hat{\mathbf{M}} = \hat{\mathbf{d}}_1 + \hat{\mathbf{d}}_2 \tag{3}$$

and consider the dipole absorption of light by such a "dimerized" pair. Let each of the molecules be respectively in the energy states $E_{m_1}^{(0)}$ and $E_{m_2}^{(0)}$ in the absence of

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the perturbation (1). The total energy of the particle pair is then

$$E_m^{(0)} = E_{m_1}^{(0)} + E_{m_2}^{(0)}. \tag{4}$$

It follows from this relation that combined transition frequencies appear in the bound system ($\hbar = 1$)

$$\Omega_{nm}^{(0)} = E_n^{(0)} - E_m^{(0)} = \omega_{n_1 m_1} + \omega_{n_2 m_2}, \tag{5}$$

where $\omega_{n_1 m_1}$ is the transition frequency in the first isolated molecule. This circumstance follows directly also from an analysis of the polarization diagrams for pair interactions of the DD type, which were considered earlier.[3]

In the nonzero orders of perturbation theory in $\hat{H}_{\text{int}}^{(12)}$, the system energy, naturally, ceases to be additive relative to the energies of the stationary states of the particles, and in second order there appears the known[4] "red" dispersion shift $\Omega_{nm}^{(2)}$ of the electron absorption in liquids. The integrated absorption coefficient in the bound system should be expressed in terms of the mean value of the tensor generalized oscillator strength, which was introduced in[2]

$$\hat{F}_{mn} = \frac{2m_e}{e^2} \Omega_{nm} \hat{\mathbf{M}}_{mn} \hat{\mathbf{M}}_{nm}, \tag{6}$$

where the matrix elements of the operator $\hat{\mathbf{M}}$ are calculated with the aid of the wave functions Ψ_m of the interacting system. In second order perturbation theory in $\hat{H}_{\text{int}}^{(12)}$, expression (6) takes the form

$$\hat{F}_{mn}^{(2)}(\Omega_{nm}) = \frac{2m_e}{e^2} \{\Omega_{nm}^{(0)} [|\hat{\mathbf{M}}^{(1)}|_{mn}{}^2 + \hat{\mathbf{M}}_{mn}^{(0)} \hat{\mathbf{M}}_{nm}^{(2)} + \hat{\mathbf{M}}_{mn}^{(2)} \hat{\mathbf{M}}_{nm}^{(0)}] + \Omega_{nm}^{(2)} |\hat{\mathbf{M}}^{(0)}|_{mn}{}^2\}. \tag{7}$$

We note that the first-order correction $\Omega_{nm}^{(1)}$ to the transition frequencies is equal to zero for nonpolar molecules, since the diagonal matrix elements of the operator $H_{\text{int}}^{(12)}$ in (1) are equal to zero from parity considerations.

Neglecting the shift $\Omega_{mn}^{(2)}$ of the combined absorption frequencies in Ω_{nm}^{0}(7), we shall calculate subsequently the generalized oscillator strength $F_{nm}^{(2)}(\Omega_{nm}^{0})$ for a transition at an exact combination frequency. The wave function Ψ_m of the interacting system can be represented in the absence of exchange effects in the form of a non-antisymmetrized product of the wave functions ψ_{m_i} ($i = 1, 2$) of the molecules. The expressions for the off-diagonal matrix elements of the operator $\hat{\mathbf{M}}$, which enter in (7), will then contain matrix elements of the interaction Hamiltonian (1) of the particle pair

$$(H_{int})_{m_1 m_2, n_1 n_2} = \int \psi_{m_1}^{*} \psi_{m_2}^{*} \hat{H}_{int}^{(12)} \psi_{n_1} \psi_{n_2} d\tau. \tag{8}$$

Taking into account the multiplicative character of the operator $\hat{H}_{\text{int}}^{(12)}$ in (1), we note on the basis of (8) that the radiative transition $m \to n$ between the collective levels in the coupled pair of molecules corresponds to simultaneous transitions $m_1 \to n_1$ and $m_2 \to n_2$ in each of the particles. Single-photon absorption of light takes place then at the combined frequency $\Omega_{nm}^{(0)}$ defined in (5).

The diagram rules previously proposed[3] for the stationary perturbation theory make it possible to write down automatically expressions for the matrix elements contained in (7). These expressions are too cumbersome to be presented here. The measured quantity is the average generalized oscillator strength $\overline{F_{mn}^{(2)}}(\Omega_{nm}^{(0)})$, which is obtained from the expression for $\hat{F}_{mn}^{(2)}(\Omega_{nm}^{(0)})$ by averaging over the directions of all the vectors that enter in the matrix elements of the operators $\hat{\mathbf{M}}$ in $\hat{H}_{\text{int}}^{(12)}$, and by summation over all pairs of interaction particles. In binary solutions, the interacting pair consists of a molecule of the dissolved matter and a molecule of the solvent. In pure liquids, the interacting molecules are of the same sort (and therefore an additional factor 1/2 must be introduced in the summation over the pairs of interacting particles in the case of liquids).

The expression obtained for the average generalized oscillator strength turns out to be very cumbersome, since it contains perturbation-theory sums over all the intermediate stationary states of the interacting molecules, as well as the matrix elements $(d_1)_{k_1 l_1}$ and $(d_2)_{k_2 l_2}$ of the operators of the moduli of the dipole moments of the particles. The customary procedure for calculating these sums by calculating several terms with the aid of the empirical values of the oscillator strengths of the non-interacting molecules is not very reliable. It is more reasonable to use in this case the approximation of equal energy denominators,[5] which gives good account of itself in the case of the inert-liquid atoms considered below. In this approximations, the frequencies $\omega_{k_i m_i}$ of all the transitions from the virtual states k into the observable stationary state m of the i-th particle (assuming that $m < k$) are replaced by the ionization potential U_{m_i} of the molecule in this state:

$$\omega_{k_i m_i} \approx U_{m_i}. \tag{9}$$

In the approximation (9), the sums over the virtual transitions in the molecules are expressed in terms of observable quantities, namely the static electronic polarizability $\alpha(m)$ of the molecules in the given stationary state m

$$\frac{1}{U_m} \sum_{k \neq m} |d|_{km}^2 = \frac{3}{2} \alpha(m) \tag{10}$$

and the static limit of the scalar part of the tensor of the electronic Raman scattering of the light $C_{mn}^{0}(0)$[6]

$$\frac{U_m + U_n}{3 U_m U_n} \sum_k{}' d_{mk} d_{kn} = C_{mn}^{(0)}(0). \tag{11}$$

Here $d^2 = d_\alpha d_\alpha$ and we have introduced the notation

$$C_{mn}^{(0)}(0) = \lim_{\omega \to 0} C_{mn}^{0}(\omega). \tag{12}$$

The sums containing products of three matrix elements of dipole moments, of the form

$$\sum_{k,l}{}' d_{nk}{}^{\alpha} d_{kl}{}^{\beta} d_{lm}{}^{\gamma},$$

are analogously connected with the value of the static limit of the tensor of the hyper-Raman scattering of light[7] $(\beta_{mn})_{\alpha\beta\gamma}$. We shall, however, neglect these terms, since they are small corrections to the tensor $C^0_{mn}(0)$.

Taking the foregoing into account as well as relation (5), the expression for the average generalized oscillator strength takes the form

$$\overline{F^{(2)}_{mn}}(\Omega^{(0)}_{nm})=4\frac{m_e}{e^2}(\omega_{n_1m_1}+\omega_{n_2m_2})\sum_{i,j\neq i}\langle R_{ij}^{-6}\rangle$$
$$\times\left\{\frac{U_{m_2}{}^2U_{n_2}{}^2|C^0(0)|^2_{m_2n_2}|d_1|^2_{m_1n_1}}{(\omega_{n_1m_1}+U_{m_2})^2(\omega_{n_1m_1}-U_{n_2})^2}+\frac{U_{m_1}{}^2U_{n_1}{}^2|C^{(0)}(0)|^2_{m_1n_1}|d_2|^2_{m_2n_2}}{(\omega_{n_2m_2}+U_{m_1})^2(\omega_{n_2m_2}-U_{n_1})^2}\right.$$
$$\left.-\frac{1}{4}\left[|d_1|^2_{m_1n_1}+|d_2|^2_{m_2n_2}\right]\left[\frac{\alpha(m_1)\alpha(n_2)U_{m_1}U_{n_2}}{(U_{m_1}+U_{n_2})^2}+\frac{\alpha(m_2)\alpha(n_1)U_{m_2}U_{n_1}}{(U_{m_2}+U_{n_1})^2}\right]\right\}. \tag{13}$$

The factor

$$\sum_{i,j}{}'\langle R_{ij}^{-6}\rangle,$$

which is proportional to the product of the concentrations of the interacting particles in the case of a solution and to the square of the density of the medium in the case of pure liquids, can be calculated from the data on the radial distribution function $g(R)$ of the molecules, which is usually measured in x-ray structure analysis of liquids. We have (for a unit volume of the solution)

$$\sum_{i,j\neq i}\langle R_{ij}^{-6}\rangle=N_1N_2\int_0^\infty R_{ij}^{-6}g(R_{ij})4\pi R_{ij}^2\,dR_{ij}, \tag{14}$$

where N_1 and N_2 are the concentrations of the components of the binary solution.

The quantities that enter in (13), of the form $|C^0(0)|^2_{mn}$, determine the probability of the electronic Raman scattering in a static field and can in principle be obtained from the scattering cross sections $\sigma(\omega)$ by extrapolating the latter to zero frequency ω of the incident field. Then, by definition,[6]

$$|C^0(0)|_{mn}{}^2\sim\frac{1}{\omega_{nm}{}^3}\lim_{\omega\to0}\left[\frac{\sigma(\omega)}{\omega}\right]. \tag{15}$$

To obtain numerical estimates of the generalized oscillator strength, we use additional simplifying assumptions in (13). Neglecting the difference between the polarizabilities and ionization potentials of the particles in the different stationary states, and also neglecting the frequencies of the radiative transitions from the initial to the final state compared with the ionization potentials, we put

$$\alpha(m_i)=\alpha(n_i)=\alpha_i, \tag{16}$$
$$U_{m_i}=U_{n_i}=U_i, \tag{17}$$
$$\omega_{n_im_i}\ll U_i. \tag{18}$$

In these approximations, expression (13) takes the form

$$\overline{F^{(2)}_{mn}}(\Omega^{(0)}_{mn})=4\frac{m_e}{e^2}(\omega_{n_1m_1}+\omega_{n_2m_2})\sum_{i,j}{}'\langle R_{ij}^{-6}\rangle$$
$$\times\left\{|d_1|^2_{m_1n_1}\left[|C^0(0)|^2_{m_2n_2}-\frac{1}{2}\alpha_1\alpha_2\frac{U_1U_2}{(U_1+U_2)^2}\right]\right.$$
$$\left.+|d_2|^2_{m_2n_2}\left[|C^0(0)|^2_{m_1n_1}-\frac{1}{2}\alpha_1\alpha_2\frac{U_1U_2}{(U_1+U_2)^2}\right]\right\}. \tag{19}$$

The last relation becomes additionally simplified in the case of a pure liquid, where like molecules interact, so that $\alpha_1=\alpha_2=\alpha$ and $U_1=U_2=U$. If, however, the two molecules undergo unequal transitions but of close frequency, then a photon of double the frequency $\Omega^{(0)}_{nm}\approx2\omega_{n_1m_1}$ is absorbed. The generalized oscillator strength of the bound system, which describes the integral probability of absorption at double the frequency, then takes the form (with allowance for the factor 1/2 for pure liquids)

$$\overline{F^{(2)}_{mn}}(2\omega_{n_1m_1})=\frac{3}{2}f_{m_1n_1}\sum_{i,j}{}'\langle R_{ij}^{-6}\rangle[8|C^0(0)|^2_{m_1n_1}-\alpha^2], \tag{20}$$

where $f_{m_1n_1}$ is the oscillator strength of absorption in a single particle at a frequency $\omega_{n_1m_1}$ and is equal by definition to

$$f_{m_1n_1}=\frac{2}{3}\frac{m_e\omega_{n_1m_1}}{e^2}|d_1|^2_{m_1n_1}. \tag{21}$$

We note that the obtained relation (20) establishes a sum rule between the probabilities of the single-photon and two-photon processes, a rule due exclusively to the intermolecular interactions in the condensed medium and vanishes in the case of non-interacting particles. Indeed, expression (2) relates the probabilities $\overline{F^{(2)}_{mn}}$ and $f_{m_1n_1}$ of single-photon absorption at the doubled and single frequencies, respectively, with the probabilities $|C^0(0)|^2_{m_1n_1}$ and α^2 of two-photon processes, which describe the static limits of the electronic Raman and Rayleigh scattering of light. The latter processes are due to virtual transitions between the stationary states of the interacting particles, which are accompanied by absorption and re-radiation of photons of vanishingly low frequency $\omega\to0$. It is characteristic that a similar sum rule arises also in the case of vibrational spectra of interacting molecules: as shown in[8], the probability of infrared absorption in a liquid A_{liq} is connected with the probability A_g of absorption in a gas and with the intensity I_g of the vibrational Raman scattering in a gas. Thus, the intermolecular interaction give rise to connections between radiative processes of different nature, and this distinguishes qualitatively between the behavior of interacting and isolated particles in the field of a light wave.

3. ABSORPTION COEFFICIENTS

We introduce the integral absorption coefficient $\varkappa$ and extinction coefficient $\mathscr{E}$ for a given band in accord with Lambert–Beer law:

$$I=I_0e^{-\varkappa l}=I_0\exp(-\mathscr{E}N_0l), \tag{22}$$

where N_0 is the concentration of the absorpting particles at the lower level. The extinction coefficient, as is well known,[9] is connected in trivial fashion with the oscillator strength f of the corresponding band:

$$\mathscr{E}=\pi e^2f/m_ec. \tag{23}$$

Relation (23), however, is valid only for absorption by a system of non-interacting particles. In a condensed medium it is necessary to take into account the difference between the average (Maxwellian) field E and a certain effective field $\mathbf{E}_{\text{eff}}$ acting directly on the molecule. Since the coefficients $\varkappa$ and $\mathscr{E}$ are determined experimentally from measurements of light fluxes connected with the average field $\mathbf{E}$, and the probability W_{mn} of the radiative transitions must be calculated relative to the field $\mathbf{E}_{\text{eff}}$ in which the molecule itself is located, a correction must be introduced for the difference between these fields. This can be done by starting from the relations for the probability

$$W_{mn} \sim |\mathbf{d}\mathbf{E}_{\text{eff}}|_{mn}^2 = |\mathbf{d}_{\text{eff}}\mathbf{E}|_{mn}^2, \tag{24}$$

where $\hat{\mathbf{d}}_{\text{eff}}$ is the operator of the effective dipole moment of the molecule and plays the role of the response of the molecule to the average field $\mathbf{E}$ in the condensed system. Thus, the observed absorption (or extinction) coefficient must contain an effective-field factor, which is equal according to (24) to

$$L = |d_{\text{eff}}|^2/|d|^2 = (E_{\text{eff}}/E)^2. \tag{25}$$

We emphasize that if the difference between the oscillator strengths $f_{m_1n_1}$ and $\overline{F}_{mn}$ is due to the inclusion of the dispersion forces that act between the particles also in the absence of an external field $\mathbf{E}$, the factor L reflects the difference between $\mathbf{E}$ and the true field $\mathbf{E}_{\text{eff}}$ acting on the molecule, and must be taken into account if one is to obtain correct information from spectroscopic observations. This factor can be easily calculated and, e.g., in the Onsager[10] for the internal field in the case of nonpolar liquids consisting of isotropic particles, its value is

$$L = \left(\frac{G}{1-\alpha R}\right)^2; \tag{26}$$

$$G = \frac{3n^2}{2n^2+1}, \quad R = \frac{2(n^2-1)}{(2n^2+1)a^3}, \tag{27}$$

where n is the refractive index of the liquid, and a is the radius of the Onsager cavity, the calculation of which was discussed earlier.[11,8] Equation (26) should contain the polarizability α of the interacting liquid molecules, but we shall neglect from now on the difference between this polarizability and the polarizability α_0 of the isolated particle.

Taking the foregoing into account, and also taking into consideration the change of the speed of light in the liquid, we write down the extinction coefficient for absorption at the single frequency $\omega = \omega_{n_1m_1}$, in the form

$$\mathscr{E}_\omega = \frac{\pi e^2}{m_e c} f_{m_1n_1} n(\omega) L(\omega). \tag{28}$$

The integral absorption for the band at the doubled frequency 2ω will accordingly be determined by an extinction coefficient

$$\mathscr{E}_{2\omega} = \frac{\pi e^2}{m_e c N_0} \overline{F_{mn}^{(2)}}(2\omega_{n_1m_1}) n(2\omega) L(2\omega). \tag{29}$$

Using the last relation and expression (20) obtained above for $\overline{F_{mn}^{(2)}}$, we get the ratio of the extinction coefficients at the doubled and single frequencies:

Table I

Parameters	Liquid				
	He	Ne	Ar	Kr	Xe
α, Å^3 [12]	0.205	0.39	1.63	2.46	4.0
$\sum_{j\neq i} \langle R_{ij}^{-6}\rangle \cdot 10^{-45}$, cm^{-6} [3]	5.897	11.87	3.905	2.43	2.01 [13]
$\mathscr{E}_{2\omega}/\mathscr{E}_\omega$, %	0.26	1.89	10.89	15.44	33.76

$$\frac{\mathscr{E}_{2\omega}}{\mathscr{E}_\omega} = \frac{3n(2\omega)L(2\omega)}{2n(\omega)L(\omega)} [8|C^0(0)|_{m_1n_1}^2 - \alpha^2] \sum_{j\neq i} \langle R_{ij}^{-6}\rangle. \tag{30}$$

To obtain numerical estimates of this ratio, we shall neglect the dispersion of the refractive indices $n(\omega)$ and put approximately

$$|C^0(0)|_{m_1n_1}^2 \approx \alpha^2. \tag{31}$$

In this case $(L(2\omega)/L(\omega) \to 1)$ we obtain

$$\frac{\mathscr{E}_{2\omega}}{\mathscr{E}_\omega} \approx \frac{21}{2} \alpha^2 \sum_{j\neq i} \langle R_{ij}^{-6}\rangle. \tag{32}$$

The results of the calculations of this ratio in accord with the approximate formula (32) for liquefied inert gases are listed in the table.

We note in conclusion that the presented estimated values of $\mathscr{E}_{2\omega}/\mathscr{E}_\omega$ can differ, as a result of all the assumptions made, from the real values. Therefore an additional check on the proposed theory may be the observation of the dependence of this ratio on the density ρ of the liquid, inasmuch as according to (14) the factor

$$\sum_{j\neq i} \langle R_{ij}^{-6}\rangle,$$

which enters in (32), depends on the concentration of the absorbing molecules.

Simultaneous transitions in the induced infrared spectra were investigated many times experimentally and theoretically (see, e.g., [14] where a bibliography can be found). It seems on the other hand that no electronic combined absorption bands have heretofore been observed. An experimental investigation of the phenomena discussed here would be of undoubted interest both for linear electron spectroscopy and for applications in laser physics.

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Ionization broadening of atomic spectra

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The spontaneous emission by an atom and the stimulated absorption of a weak test wave are considered with account taken of the process of resonant ionization induced by an intense pumping wave. The spontaneous and stimulated emission (and absorption) spectra are found for atomic transitions in a system of levels coupled by a resonant field, as well as for transitions to some third level. Spectral curves describing two-photon transitions with emission or absorption of a photon having a frequency close to the pumping frequency are obtained.

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1. INTRODUCTION

Earlier investigations of the influence of the intense resonant emission on atoms and molecules dealt with the absorption of a resonant wave by a two-level system with allowance for the saturation effect,[1,2] and with transitions of such a system to a third level with absorption or emission of photons of a different frequency.[3] The spontaneous emission by a two-level system in a resonant field and the stimulated absorption of a weak test wave with a frequency near the resonant frequency by this field have been studied by many authors.[4–7] The resonant interaction between groups of closely spaced levels was the subject of[8,9], while the resonant interaction in a three-level system was examined in[10]. In addition to the resonant interaction between two discrete levels, the possibility of ionization was also taken into account.[11–13]

In studying the emission and absorption spectra of a two-level system,[1–7] the broadening mechanisms that are frequently studied are collisions between atoms, radiative decay of the levels, and Doppler broadening. It is to be noted that in the interaction between atoms and an intense optical radiation, single-photon and multiphoton ionizations of the atoms can also play a significant role in the formation of the spectra.[14]

The present study is devoted to an investigation of spontaneous emission, as well as to stimulated transitions in the field of a weak electromagnetic test wave, when an intense resonant pumping wave acts upon the atom, and when account is taken of resonant ionization of the atom.

An interesting methodological feature of the problem of ionization broadening of atomic spectra is that the corresponding results can be obtained directly from the Schrödinger equation for a single atom, without the use of the concept of the density matrix and without introducing any phenomenological constants into the equations. This is due to the fact that in the case of ionization the irreversibility of the processes is due to the continuity of the spectrum of the ionized atom rather than to its multiparticle character. In this respect ionization broadening resembles greatly the spectral broadening due to radiative decay of levels.[15]

Resonant ionization of an atom in the field of a strong electromagnetic wave $\mathbf{F}^{(0)}=\mathbf{F}_0\cos\omega t$ has been studied both in particular cases[16,17] and in a more general formulation of the problem.[11–13] The possibility of solving such a problem for a single atom is actually due to a single principal requirement[12] $F_0 \ll F_{\mathrm{at}}$, where $F_{\mathrm{at}} = 5\times10^9$ V/cm is the field strength inside the atom. A system of quasi-energy wave functions of the atom in the field of a resonant wave (we assume $h=1$) was determined:

$$\Psi_E=e^{-iEt}\psi_E, \tag{1.1}$$

$$\psi_E=a_E{}^0e^{i(n+m)\omega t}\varphi_0+a_E{}^1e^{im\omega t}\varphi_1+\int b_{EE'}\varphi_{E'}\,dE'$$

with the known functions $a_E^{0,1}$, and $b_{E,E'}$ that are independent of time.[12] Here E is the quasi-energy, $0\leqslant E<\infty$, $\varphi_{0,1}$ are the wave functions of the ground and resonant states (with energies $E_{0,1}$), φ_E are the wave functions of the continuous spectrum with energy E, while n and m are the multiplicity of the resonance and the minimum number of quanta required for the transition $\varphi_1\to\varphi_E$.

The state of an atom in the field of an intense reso-