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Vibrational spectra of molecular systems exposed to microwave radiation

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Abstract. Vibrational spectra of molecular systems exposed to low-intensity microwave radiation are analysed within an approach that makes the quantum formalism physically integral with the classical one. It is shown that the collective nature of excited vibrational states of molecular aggregates can be the reason for a perceptible transformation of the spectra under microwave radiation even at high temperature.

1. Introduction

Recent experiments [1, 2] have manifested the transformation of the infrared spectrum of monocrystalline β -alanine (a representative of amino acids forming part of a number of cellular structures) under low-intensity microwave radiation. The authors draw attention, in particular, to the formation of 'new' lines split off the corresponding bands of the reflection spectrum at certain frequencies of microwave (extremely high-frequency, EHF) exposure. The effect is of interest in terms of a general question concerning the possibility of perceptible transformation of high-frequency spectra of a molecular system by weak low-frequency irradiation at temperatures much higher than the energy of molecular interaction with the radiation, and, in particular, in connection with the problem of so-called EHF bioeffect—a biological effect of microwave radiation of non-thermal power. Conventional approaches to theoretical study of the optical spectra of molecular systems are based, as a rule, on various modifications of the linear response concept, such as the density matrix method, quantum Green function formalism, etc (see e.g. [3, 4]). At the same time, the peculiarities of microwave vibrations—their classical (non-quantum) character in the presence of a high-temperature thermostat—require an elaboration of a special modification of the above methods. Also, a special theoretical technique has to be developed for the purpose of direct analysis of the effects caused by EHF exposure.

In the following sections the methods of theoretical analysis of the vibrational absorption spectrum of molecular systems characterized by the interaction of high-frequency (in particular, infrared) and low-frequency (microwave) vibrations are developed and exemplified first by pairs of bounded oscillators. The impossibility of a perceptible transformation of the infrared absorption spectrum of an individual separate pair under low-intensity microwave radiation at high temperature of the environment is shown. Then models of molecular aggregates formed by the above-mentioned pairs of oscillators are considered, taking account of the resonant interaction of the high-frequency vibrations. It is demonstrated that the influence of a coherent low-frequency exposure increases owing to the collective nature of the system excited states. A clear illustration of the effect is given first in the simplest case of a molecular dimer. The calculation of the absorption spectrum of an

infinite molecular chain is then carried out by applying perturbation methods. The results obtained show that the spectrum gets perceptibly transformed under the influence of a low-intensity microwave field. In particular, a distinct splitting of spectral bands corresponding to the collective excitations of the chain is predicted. The effects obtained are resonant with respect to the frequency of the microwave radiation.

2. Franck–Condon absorption spectrum of two-mode molecular gas

As an object of study in this section let us consider an oriented gas of non-interacting molecules each characterized by a pair of coupled vibrational modes: high-frequency quantum mode q and low-frequency classical vibration Q . Within the Born–Oppenheimer approximation, stationary wavefunctions of the molecules $\psi_f(q, Q)$ depend on the corresponding variables q and the parameters Q ; the quantum numbers f label the (high-frequency) vibrational terms. The energy eigenvalue of the state described by the function ψ_f is given by the sum

$$\mathcal{E}_f(Q, P) = T(P) + \mathcal{E}_f^0 + U_f(Q - Q_f) \quad (2.1)$$

where $T \equiv P^2/2M$ is the kinetic energy of the low-frequency vibration (M is the mass, P is the momentum conjugate with respect to the coordinate Q), \mathcal{E}_f^0 is the energy of high-frequency vibration at the minimum $Q = Q_f$ of the potential energy of the term. In the harmonic approximation

$$U_f = M\Omega_f^2(Q - Q_f)^2/2 \quad (2.2)$$

where Ω_f is the frequency of the Q vibration in the state f .

Taking into account the ground ($f = 0$) and the first excited ($f = 1$) states, let us use the Fermi operators of annihilation V and creation V^+ of the Franck–Condon molecular excitation† [5, 6], defined by the identity $V\psi_1(q, Q) \equiv \psi_0(q, Q)$. The Hamiltonian of a free molecule could then be given by the expression

$$H_0(Q, P) = \mathcal{E}_0(Q, P) + \Delta\mathcal{E}(Q)V^+V \quad (2.3)$$

where V^+V is the operator of the excitation number,

$$\Delta\mathcal{E}(Q) \equiv \mathcal{E}_1^0 - \mathcal{E}_0^0 + U_1(Q - Q_1) - U_0(Q - Q_0) \equiv \Delta\mathcal{E}^0 + \Delta U(Q) \quad (2.4)$$

is the excitation energy. Within the harmonic approximation (2.2) the expression $\Delta U(Q)$ can be represented in terms of the differences $\Delta Q \equiv Q_1 - Q_0$, $\Delta\Omega^2 \equiv \Omega_0^2 - \Omega_1^2$ (the values $\Delta\mathcal{E}^0$, ΔQ , $\Delta\Omega^2$ are supposed to be positive). In the particular cases of the absence of (a) the ‘frequency defect’ and (b) the shift in the equilibrium position, one obtains

$$\Delta U(Q) = -M\Omega_0^2\Delta Q[Q - (Q_0 + Q_1)/2] \quad (\Delta\Omega^2 = 0) \quad (2.5a)$$

$$\Delta U(Q) = -M\Delta\Omega^2(Q - Q_0)^2/2 \quad (\Delta Q = 0). \quad (2.5b)$$

(The general case is considered in [7].) Thus, in the case (a) the expressions (2.4), (2.5) depend linearly on the coordinate Q , besides $\Delta\mathcal{E}(Q_0) = \Delta\mathcal{E}^0 + M\Omega_0^2(\Delta Q)^2/2$; in the case

† There is no point in taking account of higher excited levels (Bose statistics) of the q mode when considering the absorption processes in the frequency range of one-quantum transition at low (as against the transition energy) temperature.

(b) they are represented by symmetrical parabolae relative to Q_0 , and there is a maximum value $\Delta\mathcal{E}(Q_0) = \Delta\mathcal{E}^0$ in the equilibrium position $Q = Q_0$.

The operator of the molecule interaction with an electromagnetic wave in the frequency range ω of the vibrational transfer $0 \rightarrow 1$ can be written in the dipole approximation as

$$H_{\text{int}} = -dE \equiv -(d_0 E)(V + V^+) \quad (2.6)$$

where $E \equiv E_0(e^{i\omega t} + e^{-i\omega t})$ is the electric component of the wave, $d_0 \equiv \int dq \psi_1(q, Q_0) d \psi_0(q, Q_0)$ is the matrix element of the operator d of the molecule dipole moment (we use the Condon approximation, putting here $Q = Q_0$). The true absorption curve $S(\omega) = 4\pi v^{-1} \text{Im} \beta_{xx}$ of the molecular gas (v is the molecular volume) could then be calculated using an explicit form of the molecule polarizability tensor $\hat{\beta}$ related with the average of the dipole moment d by the formula $\langle d(t) \rangle = \hat{\beta} E_0 e^{-i\omega t} + \hat{\beta}^* E_0 e^{i\omega t}$.

Thus, within the formalism of the retarded Green functions (see [5, 6]), allowing generalization to the case of an ensemble of interacting molecules, the final expression is represented as†

$$S(\omega) = 4\pi^2 v^{-1} |d_0|^2 s_0(\omega) = -4\pi v^{-1} |d_0|^2 \text{Im}\{G(\omega)\}_0 \quad (2.7)$$

where

$$G(\omega) \equiv \langle\langle V; V^+ \rangle\rangle_\omega \equiv \int_{-\infty}^{\infty} \langle\langle V; V^+ \rangle\rangle_t e^{i\omega t - \eta t} dt \quad (\eta \rightarrow +0) \quad (2.8)$$

is the Fourier transform of the Green function

$$\langle\langle V; V^+ \rangle\rangle_t \equiv -i\theta(t) \langle V(t) V^+ \rangle_0 \quad (2.9)$$

$V(t) \equiv e^{iH_0 t} V e^{-iH_0 t}$ is the annihilation operator in the interaction representation; the symbol $\langle \dots \rangle_0$ denotes the diagonal matrix element of the corresponding operator in the ground state $f = 0$; and $\{ \dots \}_0$ designates the thermal average (at a given temperature T), over the classical oscillations corresponding to the 0-term:

$$\{A\}_0 \equiv \left(\iint_{-\infty}^{\infty} dP dQ e^{-\mathcal{E}_0(P, Q)/T} \right)^{-1} \iint_{-\infty}^{\infty} dP dQ A e^{-\mathcal{E}_0(Q, P)/T}. \quad (2.10)$$

In the interaction representation the Fourier transforms (2.8) of the Green functions of arbitrary operators K, L satisfy the chain of equations (see e.g. [3])

$$\omega \langle\langle K; L^+ \rangle\rangle_\omega = \langle [K, L^+] \rangle_0 + \langle\langle [K, H_0]; L^+ \rangle\rangle_\omega \quad (2.11)$$

with the subsequent substitution $\omega \rightarrow \omega + i\eta$. Taking into account the explicit form (2.3) of the Hamiltonian H_0 and Fermi commutation relations of the operators V and V^+ , the equation (2.11) could be represented with reference to the function (2.8) as

$$\omega \langle\langle V; V^+ \rangle\rangle_\omega = 1 + \Delta\mathcal{E}(Q) \langle\langle V; V^+ \rangle\rangle_\omega. \quad (2.12)$$

In accordance with the definitions (2.1) and (2.10) (eliminating the integration over the momentum P in the numerator and the denominator) one thus obtains

$$\{G(\omega)\}_0 = \{[\omega - \Delta\mathcal{E}(Q)]^{-1}\}_0 = \int_{-\infty}^{\infty} \frac{f_0(Q) dQ}{\omega - \Delta\mathcal{E}(Q)} \quad (2.13)$$

$$f_0(Q) \equiv (\alpha/\pi)^{1/2} \exp[-\alpha(Q - Q_0)^2] \quad \alpha \equiv M\Omega_0^2/2T. \quad (2.14)$$

† In what follows we use a system of units in which Planck and Boltzmann constants are equal to unity: $\hbar = 1$, $k_B = 1$.

In the case of a pure shift of the oscillation equilibrium position, after substituting (2.4) and (2.5a) into (2.13) and replacing ω by $\omega + i\eta$, with regard to the identity

$$\lim_{\eta \rightarrow 0} [\eta / (\eta^2 + a^2)] \equiv \pi \delta(a)$$

one obtains the explicit expression of the function

$$s_0(\omega) = [\Omega_0 \Delta Q (2\pi MT)^{1/2}]^{-1} \exp\left(-\frac{(\omega - \omega_m)^2}{2M\Omega_0^2(\Delta Q)^2 T}\right) \quad (2.15)$$

$$\omega_m \equiv \Delta \mathcal{E}(Q_0) = \Delta \mathcal{E}^0 + M\Omega_0^2(\Delta Q)^2/2 \quad (2.16)$$

which, in accordance with (2.7), defines the absorption spectrum of the molecular gas. Thus, in the case concerned, the absorption is characterized by a Gaussian peak symmetrical with respect to the frequency (2.16), with the maximum value decreasing with temperature rise in inverse proportion to $T^{1/2}$ and the half-width (more precisely, the 'distance' at which the intensity gets decreased by a factor of e)

$$h/2 = (2MT)^{1/2} \Omega_0 \Delta Q \quad (2.17)$$

increasing in direct proportion to $T^{1/2}$, so that the integral intensity remains invariable: $\int d\omega s_0(\omega) \equiv 1$. In low-temperature ($T \rightarrow 0$) and no-interaction ($\Delta Q \rightarrow 0$) limits, equation (2.15) turns into Dirac delta functions (correspondingly $\delta(\omega - \omega_m)$ or $\delta(\omega - \Delta \mathcal{E}^0)$).

In the case of a change in the oscillation frequency the substitution of (2.4) and (2.5b) into (2.13) gives, after some transformations, the formula

$$s_0(\omega) = \frac{\Omega_0 \theta (\Delta \mathcal{E}^0 - \omega)}{[\pi T \Delta \Omega^2 (\Delta \mathcal{E}^0 - \omega)]^{1/2}} \exp\left(-\frac{\Omega_0^2 (\Delta \mathcal{E}^0 - \omega)}{T \Delta \Omega^2}\right). \quad (2.18)$$

When $\omega \rightarrow \Delta \mathcal{E}^0$ this function diverges as $(\Delta \mathcal{E}^0 - \omega)^{-1/2}$. The integral intensity of the band depends neither on the parameter of interaction $\Delta \Omega^2$ nor on the temperature and is equal to unity. Equation (2.18) coincides with the well known Urbach empirical rule determining the form of the long-wavelength edge of the local centre absorption curve. The theoretical substitution of such a character of the spectrum has been proposed by Toyozawa [8] (see also [4]), who considered the interaction of the centre with local crystal vibrations. Equation (2.18) corresponds then to the two-quantum approximation of the theory [8]. In the context of our paper it is interesting to take note of the fact that a quantitative agreement of the Toyozawa theory with the experimental data could be reached when the vibration frequency is about a few inverse centimetres.

3. Molecular spectra under low-frequency radiation

In the Condon approximation the influence of low-frequency (microwave) irradiation on the high-frequency molecular absorption manifests itself in the corresponding variation of the ground vibrational state of the molecule. To take the effect into account in terms of microscopic (Langevin) equations of motion, describing the 0-term oscillations, one should add to their right-hand sides the driving forces responsible for the action of the microwave field, thus obtaining

$$M \frac{d^2 Q}{dt^2} + \frac{dU_0(Q - Q_0)}{dQ} + \gamma \frac{dQ}{dt} = \mathcal{F}(t) + F(t) \quad (3.1)$$

where γ is the friction coefficient, $\mathcal{F}(t)$ is the Langevin source (a random force describing the dynamical action of the thermostat), $F(t) \equiv \tilde{e}E_m(t)$ is the driving force (\tilde{e} is the effective charge, $E_m(t)$ is the intensity of the coherent microwave field). In the harmonic approximation (2.2) equation (3.1) is linear and, therefore, its solution can be represented as $Q = X + \tilde{Q}$, where a determinate function $X \equiv X(t)$ describes the constrained oscillations under the force $F(t)$ (with friction taken into account), and the random function $\tilde{Q}(t)$ represents the solution of (3.1) when the force $F(t)$ is absent. The equilibrium distribution of Q vibrations transforms correspondingly. Within the formalism used, the transformation of the molecular absorption spectrum comes to the substitution of the function $\mathcal{E}_0(Q, P)$ in the RHS of (2.10) for $\mathcal{E}(Q - \bar{X}(t), P)$, where $\bar{X}(t)$ is the asymptotic expression of the function $X(t)$, describing steady-state oscillations. Besides, the procedure (2.10) has to be supplemented by time averaging (during the period τ of the constrained vibration $\bar{X}(t)$) in accordance with the substitution

$$A(\bar{X}(t)) \rightarrow \int_0^\tau d(t/\tau) A(X(t)) = \int dX \frac{A(X)}{dX/d(t/\tau)}. \quad (3.2)$$

Thus, at given frequency Ω and amplitude E_m^0 of the microwave electric field (more precisely, its Q component) the stationary distribution function (2.14) with allowance for the irradiation effect is converted into

$$f_a(Q) \equiv \frac{1}{\pi} \int_{-1}^1 dx \frac{f_0(Q - ax)}{(1 - x^2)^{1/2}} \quad (3.3)$$

where

$$a \equiv \frac{\tilde{e}E_m^0}{M[(\Omega^2 - \Omega_0^2)^2 + \gamma^2\Omega^2]^{1/2}} \quad (3.4)$$

is the amplitude of the constrained 0-term vibrations. Owing to singularity characterizing the factor $(1 - x^2)^{-1/2}$ in the vicinity of the turning points ($x = \pm 1$), equation (3.3) can be represented approximately by the half-sum

$$f_a(Q) \simeq \frac{1}{2}[f_0(Q + a) + f_0(Q - a)]. \quad (3.5)$$

The corresponding transformation of the functions (2.15) and (2.18) describing the molecular gas absorption gives the spectral band doublet

$$s_a(\omega) \simeq \frac{1}{2}[s_0^+(\omega) + s_0^-(\omega)] \quad (3.6)$$

with the components $s_0^\pm(\omega)$, which in the case (a) could be derived from the unperturbed function (2.18) by the substitution

$$\omega_m \rightarrow \omega_m^\pm \equiv \omega_m \pm aM\Omega_0^2\Delta Q \quad (3.7)$$

and so represent the Gaussian peaks shifted from the 'initial' band centre ω_m in the long- and in the short-wave directions. The resolvability of the spectral doublet is determined by the ratio of the shift and the peak width (2.17):

$$k \equiv (\omega_m^+ - \omega_m^-)/h = (\omega_m - \omega_m^-)/h \equiv (M\Omega_0^2a^2/T)^{1/2}. \quad (3.8)$$

The expression bracketed on the right-hand side coincides with the ratio of the constrained vibration energy and the thermal energy per degree of freedom. Thus, at 'non-thermal' power of the irradiation the value (3.8) is small in accordance with the definition.

In the case (b) the summands of the RHS of (3.6) are defined by the expression

$$s_0^\pm(\omega) = \frac{\Omega_0 \theta (\Delta \mathcal{E}^0 - \omega)}{[\pi T \Delta \Omega^2 (\Delta \mathcal{E}^0 - \omega)]^{1/2}} \exp \left\{ - \left[\left(\frac{\Omega_0^2 (\Delta \mathcal{E}^0 - \omega)}{T \Delta \Omega^2} \right)^{1/2} - \left(\frac{M \Omega_0^2 a^2}{2T} \right)^{1/2} \right]^2 \right\}. \quad (3.9)$$

At low intensity of the microwave field ($k \ll 1$), the second term in the square brackets is small.

Thus, in both the cases under consideration the shape of the absorption spectrum does not vary perceptibly under low-intensity irradiation: $s_1(\omega) \simeq s_0^+(\omega) \simeq s_0^-(\omega) \simeq s_0(\omega)$.

It may not be out of place to note here that a quantitative analysis of the microwave irradiation effect has, in general, to take into account the vibration (libration) anharmonicity manifesting itself critically at energies of the order of $k_B T$ corresponding to room temperature. For low-intensity irradiation, however, the above approach is, on the whole, valid as well in reference to the case of anharmonic molecular vibrations. Developing the term dU_0/dQ of the LHS of (3.1) as a series in powers of the coherent component X of the coordinate Q , in linear approximation one comes to the distribution function of the form (3.3) with the constrained oscillation amplitude (3.4) calculated proceeding from the effective (temperature-dependent) frequency value $\Omega_0 \equiv \{d^2 U_0/dQ^2\}_0$ of the anharmonic oscillator.

4. Absorption spectrum of molecular dimers

The collective nature of the excited states of a system of interacting molecules causes the effect of narrowing of the high-frequency absorption bands as compared to the case of an ideal molecular gas. For this reason, the spectrum transformation under a coherent microwave field can be perceptible even at low-intensity irradiation.

The essence of the effect can be traced in the simplest case of a molecular dimer (more precisely, an oriented dimer gas). Generalization of (2.3) with account of the resonant exchange by excitations between the molecules leads to the dimer Hamiltonian of the form

$$H_0^d = \sum_{n=\pm 1} [\mathcal{E}_0(Q^{(n)}, P^{(n)}) + \Delta \mathcal{E}(Q^{(n)}) V_n^+ V_n] - L(V_1^+ V_{-1} + V_{-1}^+ V_1) \quad (4.1)$$

where the index $n = \pm 1$ numbers the identical molecules; the Pauli excitation operators V_n and V_n^+ could be treated as Bose ones when considering only one-quantum excited states of the dimer; L is the matrix element of the resonant interaction (independent of the coordinates $Q^{(n)}$ within the Condon approximation). For the sake of definiteness, the L value is assumed to be positive, which corresponds to reduction of the system energy due to excitation exchange.

Assuming the interaction of the molecules (of the same spatial orientation) with the electromagnetic wave to be determined by (2.6), one can represent the dimer absorption band in the form

$$S^d(\omega) = 4\pi^2 v^{-1} |d_0|^2 S_0^d = -2\pi v^{-1} |d_0|^2 \sum_{n,m=\pm 1} \text{Im}\{G_{n,m}(\omega)\}_0 \quad (4.2)$$

where $G_{n,m}(\omega) = \langle\langle V_n; V_m^+ \rangle\rangle_\omega$ is the Fourier transform of the Green function of the excitation operators; the symbol $\{\cdot\cdot\}_0$ means the thermal average (2.10) over the ground terms of both molecules.

The chain of the equations (2.11) with the Hamiltonian given by (4.1), using the dimensionless notation

$$g_{n,m} \equiv LG_{n,m} \quad \xi \equiv \omega/L \quad \zeta \equiv \Delta\mathcal{E}(Q^{(n)})/L \quad (4.3)$$

can be written as

$$\xi g_{n,m} = \delta_{n,m} + \zeta_n g_{n,m} - g_{-n,m}. \quad (4.4)$$

In the case of non-interacting molecules the last term on the RHS is absent (compare with (2.12)).

Solving (4.4), one obtains

$$g \equiv \frac{1}{2} \sum_{n,m=\pm 1} g_{n,m} = \frac{1}{2(\xi_+ - \xi_-)} \left(\frac{\xi_1 + \zeta_{-1} + 2(1 - \xi_-)}{\xi - \xi_-} - \frac{\xi_1 + \zeta_{-1} + 2(1 - \xi_+)}{\xi - \xi_+} \right) \quad (4.5)$$

where $\xi_{\pm} \equiv \frac{1}{2}\{\zeta_1 + \zeta_{-1} \pm [4 + (\zeta_1 - \zeta_{-1})^2]^{1/2}\}$. At a strong resonant interaction as compared to the scatter of the values $\Delta\mathcal{E}(Q)$, i.e. $\{(\zeta_1 - \zeta_{-1})^2\}_0 \ll 1$, the intensity of the absorption peak determined by the second term on the RHS of (4.5) is small, and one can approximately write down

$$g \simeq [\xi + 1 - (\zeta_1 + \zeta_{-1})/2]^{-1}. \quad (4.6)$$

The thermal fluctuations of the (dimensionless) half-width $(\zeta_1 + \zeta_{-1})/2$ are smaller than those of the separate components (ζ_1 or ζ_{-1}). Owing to that, the absorption peak of the dimer becomes narrower as compared with that of a free molecule. The effect manifests itself most clearly in the case (a) of a pure shift of the molecular terms. In accordance with (2.5a) and (2.10) the corresponding absorption curve obtained from (4.6) can be represented as

$$s_0^d(\omega) = [\Omega_0 \Delta Q (\pi MT)^{1/2}]^{-1} \exp \left[-\frac{(\omega - \omega_m + L)^2}{TM\Omega_0^2(\Delta Q)^2} \right]. \quad (4.7)$$

Thus, in the case of a strong resonant interaction the frequency dependence of dimer gas absorption, just like absorption of a free-molecule gas, is characterized (at $\Delta\Omega^2 = 0$) by a Gaussian peak. Equation (4.7) can then be obtained from (2.15) by the substitutions $\omega_m \rightarrow \omega_m^d \equiv \omega_m - L$, $T \rightarrow T_{\text{eff}} \equiv T/2$, which correspond to $\sqrt{2}$ -fold reduction of the half-width (2.17).

Under the effect of microwave radiation the absorption band (4.7) transforms into a doublet of the form (3.6) with the distance between the bands determined by (3.7). Thus, the ratio (3.8) characterizing the doublet resolvability is multiplied by the factor $\sqrt{2}$ as compared with the case of a free-molecule gas.

In the case of the 'frequency defect' the effect is less pronounced.

5. Absorption spectrum of molecular chain

One can expect a more radical manifestation of the effect of spectral line narrowing due to the action of coherent microwave radiation when studying molecular aggregates including a considerable number of subunits. Let us consider the absorption spectrum of an infinite one-dimensional molecular crystal—a chain of identical molecules of the same orientation coupled by the resonant interaction.

Generalizing (4.1), one can represent the chain Hamiltonian in the one-quantum approximation by the infinite sum

$$H_0^c = \sum_n [\mathcal{E}(Q^{(n)}) + \Delta\mathcal{E}(Q^{(n)})V_n^+V_n - LV_n^+(V_{n+1} + V_{n-1})] \quad (5.1)$$

where V_n, V_n^+ are the Bose operators of molecular excitations, L is the matrix element of the resonant interaction of the neighbouring molecules. For molecule interaction with the high-frequency radiation determined by (2.6), the chain absorption coefficient with respect to electromagnetic wave spreading in the direction perpendicular to the chain is represented by the imaginary part of the transverse tensor of dielectric permeability and, similar to equations (2.7) and (4.2), can be expressed through the Green function of the excitation operators:

$$\varepsilon'' \equiv \text{Im } \varepsilon^\perp \equiv \frac{\pi |d_0|^2}{2\nu} s_0^c(\omega) = -\frac{|d_0|^2}{2\nu N} \sum_{n,m} \text{Im}\{G_{n,m}(\omega)\}_0. \quad (5.2)$$

The notations here are the same as in the previous sections: the summation is carried out over N values of the indexes n, m with the following passage to the limit $N \rightarrow \infty$.

In what follows the dimensionless notations

$$\begin{aligned} g_{n,m} &\equiv 2LG_{n,m} & \sigma_0^c &\equiv 2Ls_0^c & \xi &\equiv (2L)^{-1}[\omega - \{\Delta\mathcal{E}(Q)\}_0] \\ \zeta_n &\equiv \varepsilon z_n & & & & \equiv (2L)^{-1}[\Delta\mathcal{E}(Q^{(n)}) - \{\Delta\mathcal{E}(Q)\}_0] \end{aligned} \quad (5.3)$$

are used (the notation $\varepsilon \ll 1$) indicates a small value of the parameters ζ_n with a strong resonant interaction L); the average frequencies of the $0 \rightarrow 1$ transfer

$$\{\Delta\mathcal{E}(Q)\}_0 = \Delta\mathcal{E}^0 - M\Omega_0^2(\Delta Q)^2/2 \equiv \omega_m \quad (5.4a)$$

$$\{\Delta\mathcal{E}(Q)\}_0 = \Delta\mathcal{E}^0 - \Delta\Omega^2 T/2\Omega_0^2 \quad (5.4b)$$

corresponding to the above cases (a) and (b) are calculated according to (2.4), (2.5), (2.10). The expression (5.4a) then coincides with a centre frequency (2.16) of the free-molecule absorption band (2.15) and does not depend on temperature; the frequency (5.4b) shifts in the long-wave direction with temperature rise.

The Green functions to be found satisfy equations of the type (2.11) with the Hamiltonian (5.1). Taking into account the notation (5.3), these equations can be written as

$$\xi g_{n,m} = \delta_{n,m} + \varepsilon z_n g_{n,m} - \frac{1}{2}(g_{n+1,m} + g_{n-1,m}). \quad (5.5a)$$

The sums $g_n \equiv \sum_m g_{n,m}$ taken over the second index then satisfy the equations

$$\xi g_n = 1 + \varepsilon z_n g_n - \frac{1}{2}(g_{n+1} + g_{n-1}). \quad (5.5b)$$

Expressing the functions g_n as power series in the parameter ε :

$$g_n \equiv \sum_l \varepsilon^l g_n^{(l)} \quad (5.6)$$

one can proceed from (5.5b) to the iteration scheme

$$\xi g_n^{(l+1)} + \frac{1}{2}(g_{n+1}^{(l+1)} + g_{n-1}^{(l+1)}) = z_n g_n^{(l)} \quad (5.7)$$

with $g_n^{(0)} = (\xi + 1)^{-1}$. In terms of Fourier transforms

$$g(k) \equiv N^{-1} \sum_n e^{-ikn} g_n \quad z(k) \equiv N^{-1} \sum_n e^{-ikn} z_n. \quad (5.8)$$

Equation (5.7) corresponds to the recurrence formula

$$g^{(l+1)}(k) = (\xi + \cos k)^{-1} \sum_{k'} z(k - k') g^{(l)}(k') \quad g^{(0)}(k) = (\xi + 1)^{-1} \delta_{k,0}. \quad (5.9)$$

Proceeding then to the calculation of the averages $\{\dots\}_0$ one has to take into account the equalities $\{z(k)\}_0 = \{z_n\}_0 = 0$, $\{z_n z_m\}_0 \equiv \{z^2\}_0 \delta_{n,m}$ stemming from the definition (5.3). Thus, in accordance with (5.9) one obtains

$$\{g^{(1)}(k)\}_0 = \frac{\{z(k)\}_0}{(\xi + 1)(\xi + \cos k)} \equiv 0 \quad (5.10a)$$

$$\{g^{(2)}(k)\}_0 = \frac{\mathcal{F}(\xi) \{z^2\}_0}{\xi + 1} g^{(0)}(k) \equiv \varphi g^{(0)}(k) \quad (5.10b)$$

where

$$\mathcal{F}(\xi) \equiv N^{-1} \sum_{k'} (\xi + \cos k')^{-1}. \quad (5.11)$$

From (5.6), (5.8), (5.10a, b) the function

$$\{g(0)\}_0 \equiv N^{-1} \sum_n \{g_n\}_0 \equiv N^{-1} \sum_{n,m} \{g_{n,m}\}_0$$

can then be represented approximately by the sum of the infinite geometric progression

$$\{g(0)\}_0 \simeq \sum_l (\varepsilon^2 \varphi)^l g^{(0)}(0) = \frac{g^{(0)}(0)}{1 - \varepsilon^2 \varphi} = [\xi + 1 - \{z^2\}_0 \mathcal{F}(\xi)]^{-1}. \quad (5.12)$$

The approximation corresponds to the decoupling (see [7])

$$\{z(k - k'') z(k'' - k') g^{(l)}(k')\}_0 \simeq \{z(k - k'') z(k'' - k')\}_0 \{g^{(l)}(k')\}_0. \quad (5.13)$$

In accordance with the definition (5.3) the average $\{z^2\}_0$ (for the cases (a) and (b)) can be represented by the ratios

$$\{z^2\}_0 = M \Omega_0^2 (\Delta Q)^2 T / 4L^2 \quad (5.14a)$$

$$\{z^2\}_0 = (\Delta \Omega^2)^2 T^2 / 8 \Omega_0^4 L^2 \quad (5.14b)$$

(small in the case of strong resonant interaction).

With the use of the substitutions $N^{-1} \sum_{k'} \rightarrow (2\pi)^{-1} \int_{-\pi}^{\pi} dk'$, $\omega \rightarrow \omega + i\eta$, the function (5.11) can be reduced to the form

$$\mathcal{F}(\xi) = \begin{cases} -(\xi^2 - 1)^{-1/2} & -1 > \xi \\ -i(1 - \xi^2)^{-1/2} & -1 < \xi < 1 \\ (\xi^2 - 1)^{-1/2} & \xi > 1. \end{cases} \quad (5.15)$$

Thus, in accordance with (5.12) and (5.15) the dimensionless function determining the absorption spectrum (5.2) of the molecular chain with strong resonant interaction is given approximately as

$$\sigma_0^c(\xi) = \begin{cases} \frac{2}{3}\delta[\xi + 1 + (\{\zeta^2\}_0/\sqrt{2})^{2/3}] & -1 > \xi \\ \frac{\{\zeta^2\}_0(1 - \xi^2)^{1/2}/\pi}{(1 - \xi^2)(1 + \xi)^2 + \{\zeta^2\}_0^2} & -1 < \xi < 1 \\ (\{\zeta^2\}_0^2/8)\delta[\xi - 1 - \{\zeta^2\}_0^2/8] & \xi > 1. \end{cases} \quad (5.16)$$

The spectrum (see figure 1) is characterized by a continuous band (the second line on the RHS of (5.16) of width $4L$ (2 in dimensionless units), with the middle point ($\xi = 0$) determined by (5.4). The function (5.16) goes to zero at the ends of the interval (in the singular points $\xi = \pm 1$), where the derivatives tend to infinity:

$$(d\sigma_0^c/d\xi) \xrightarrow[\xi \rightarrow \pm 1]{} \mp \infty.$$

The band shows a narrow peak in the vicinity of the long-wave (left) end ($\xi_{\max} \simeq -1 + (\{\zeta^2\}_0^2/10)^{1/3}$) with the maximum value $\max \sigma_0^c \approx 5^{5/6}/[3(2\{\zeta^2\}_0)^{2/3}] (\gg 1)$. The function decreases rapidly when moving away from the point ξ_{\max} , becoming small in the middle of the interval: $\sigma_0^c(0) \simeq \{\zeta^2\}_0/\pi (\ll 1)$. In a zero-order approximation with respect to the parameter $\{\zeta^2\}_0$ the integral absorption of the band is equal to $\int_{-1}^1 d\xi \sigma_0^c(\xi) \simeq 1/3$. Outside the interval $-1 < \xi < 1$ the function (5.16) is characterized by δ -type peaks. The long-wave peak (the first line on the RHS of (5.16)) is situated near the left end of the continuous band (in the point $\xi_l \equiv -1 - (\{\zeta^2\}_0^2/2)^{1/3}$), and its 'share' in the integral intensity is equal to $2/3$. The short-wave peak (the third line in (5.16)) is situated near the right end of the band ($\xi_r \equiv 1 + \{\zeta^2\}_0^2/8$) and its intensity $\{\zeta^2\}_0^2/8 (\ll 1)$ is small. Under the opposite sign of the resonant interaction ($L < 0$) the frequency dependence of the chain absorption coefficient can be obtained from (5.16) by the substitution $\xi \rightarrow -\xi$ (the insertion through the middle point (5.4)).

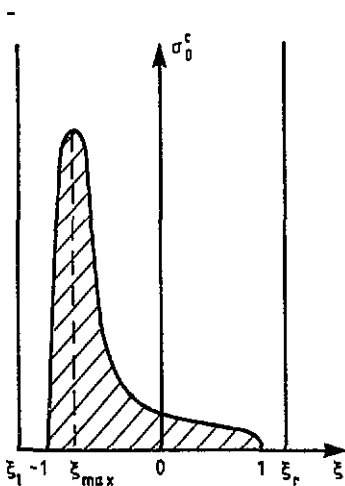


Figure 1. Schematic plot of the function $\sigma_0^c(\xi)$.

The general structure of the absorption curve of figure 1 is, on the whole, typical for systems of electro(photo)active particles with strong interaction. Narrow (δ -type, in the

framework of the approximations in use) peaks of the system spectrum correspond to the formation of collective one-particle excitations characterized by frequencies and wavevectors equal to those of the absorbed photons. Such peaks are characteristic, for example, of the excitonic absorption spectra of crystals with strong exciton-phonon binding (see [3,4]). A series of one-particle peaks in the frequency range corresponding to simultaneous formation of electronic excitation and one or few intramolecular vibrational quanta is also the most striking feature of the vibronic absorption spectra of molecular crystals (see [6]). The continuous spectral band ($-1 < \xi < 1$) in figure 1 corresponds (in terms of the quantum theory) to dissociated states of the quasiparticles (elementary excitations of the system) formed under light absorption. With the formation of a dissociated state, part of the photon energy transfers to the degrees of freedom corresponding to relative motion of the quasiparticles. The spectral band expansion is then caused by an absence of energy (frequency) selection. One can find an examination of the main properties of one-particle and dissociated vibronic states of molecular crystals in [6,9].

Under the influence of microwave radiation, the chain absorption, in accordance with the results of section 3, could be described by the half-sum of the functions $\sigma_{\pm}^{\circ}(\xi)$ obtained from (5.16) by the substitution of (5.4) and (5.14) for the corresponding averages over the distributions $f_0(Q \pm a)$ (see (3.5)):

$$\{\Delta\mathcal{E}\}_{\pm} = \{\Delta\mathcal{E}\}_0 \pm aM\Omega_0^2\Delta Q \quad (5.17a)$$

$$\{\Delta\mathcal{E}\}_{\pm} = \{\Delta\mathcal{E}\}_0 \quad (5.17b)$$

$$\{\zeta^2\}_{\pm} = \{\zeta^2\}_0 \quad (5.18a)$$

$$\{\zeta^2\}_{\pm} = (1 + k^2)\{\zeta^2\}_0 \quad (5.18b)$$

where the parameter k is determined by the identity (3.8). According to the formulae, in the case (a) every component of the spectrum (5.16) transforms into the corresponding doublet of bands of the same shape, shifted relative to the initial one at the 'distance'

$$aM\Omega_0^2\Delta Q \equiv 2L(k^2\{\zeta^2\}_0)^{1/2} \quad (5.19)$$

in the long- and short-wave direction. Owing to the small factors on the RHS of (5.19), the splitting is small in comparison with the matrix element L of the resonant interaction. The value (5.19) is also small as compared to $k_B T$ (since 'realistic' values L do not exceed thermal energy at room temperature). At the same time, the existence of narrow peaks of the absorption makes it, in principle, possible to detect the splitting of the spectrum (5.16). In particular, at $k \simeq (\{\zeta^2\}_0/8)^{1/3}$ the distance between the doublet components reaches the order of magnitude of the frequency difference between the intensive peaks of the spectrum (the peak of the continuous band and the nearest δ -peak).

In the case (b), as follows from (5.17) and (5.18), the effect of microwave radiation does not lead to band splitting but only causes the spectrum deformation characterized by the factor $1 + k^2$, which is near to unity at non-thermal power of the radiation.

6. Summary and conclusions

Thus, the above analysis of simple models has shown the possibility in principle of a perceptible transformation of high-frequency (vibrational) spectra of high-molecular aggregates under coherent microwave radiation of low intensity. The effect is caused by

the collective character of the system excitations generated with the absorption of high-frequency EM quanta. Under strong (compared to thermal energy) subunit coupling, such excitations are able to interact effectively only with a definite combination of low-frequency modes, and therefore the corresponding spectral lines are but faintly widened by thermal (incoherent) vibrations of individual subunits. At the same time, the coherent component of low-frequency vibrations, induced by microwave radiation, causes a corresponding shift of the spectral lines under consideration. The effect manifests itself most clearly in the spectral line splitting under stationary coherent microwave radiation. The frequencies of the originated doublet components then correspond to the turning points of constrained microwave oscillations. The splitting value thus depends on the intensity and frequency of the microwave field. Moreover, the latter dependence exhibits resonance. An absence of temperature widening of the doublet components makes it, in principle, possible to observe the effect even at temperatures much higher than the energy of the molecular subunit interaction with the microwave radiation.

From our point of view, the most useful investigation would be that of non-thermal effect of microwave radiation upon the spectral properties of aggregates (chains, crystals) including molecules characterized by high values of the dipole moments of infrared quantum transitions together with conformational flexibility (manifested in the microwave frequency range). In particular, some macrobiomolecular formations may be of utmost interest, as well as aggregates including NH_3^- or CO_2^+ groups (characterized by deformational vibrations of the EHF range).

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