# Aperiodic motion of nuclei and randomization in the electron-vibrational spectra of complex molecules

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(Submitted 23 July 1990)
Zh. Eksp. Teor. Fiz. **99**, 447–455 (February 1991)

The electron-vibrational excitation correlator in a two-level molecule is obtained as a functional of the vibrational variables in a closed time contour. For deformational, optically active vibrations with frequency $\omega$ and a large Stokes shift $\omega\Delta$ the values of the parameters model a number of molecules studied previously, possessing diffuse absorption and luminescence spectra. It is shown that the low-frequency vibrations near the separatrix of the phase plane of the deformation degree of freedom of the molecule resulting from their resonant nonlinear interaction $\mu$ with oscillations of the heat reservoir may be responsible for the smearing out of the spectral bands. The condition for the appearance of these almost aperiodic nuclear motions on the optical transitions is that the detuning $\Omega$ of the resonant vibrational exchange be small compared to the product $\mu\Delta$.

In complex molecules the nonlinearity of the vibrational motion, manifested in its anharmonicity, has a profound effect on the nature of the electron-vibrational spectra. The anharmonicity of the vibrations not only leads to a broadening of the energy levels and spectral lines, but also (as the amplitude and energy of the vibrations increase) influences the instability of the vibrational motion.

The role of the interaction of the vibrations in the dynamics of the conversion of the energy of a light quantum and the formation of the spectra during electron-vibrational transitions in complex molecules was considered in Refs. 1 and 2. These papers uncovered the existence of a critical value of the rate of redistribution of the vibrational energy of the molecule and established that this rate grows as a function of the energy or of the complexity of the structure of the molecule. For a number of aromatic compounds with complicated structure this effect expresses itself in the disappearance of the structure of the electron-vibrational absorption and luminescence spectra and in the formation of wide continuous bands. In Ref. 3 continuous spectra of a new type were discovered, whose origin was ascribed[4] to the extreme instability of the Franck-Condon states, leading to strong homogeneous broadening, which distinguishes these systems from systems with inhomogeneously broadened spectra.[1,2] This difference in the nature of the broadening for a number of molecules was experimentally confirmed in Ref. 5.

The interaction between highly excited vibrations in the electronic ground state of complex molecules has been studied in connection with laser chemistry problems.[6,7] In recent years new experimental and theoretical results were obtained in this area.[8–10] These include a description of the randomization of the vibrational motion due to successive absorption of quanta in the infrared region of the spectrum.

In the case of electron-vibrational spectra a similar complication of the motion of the nuclei takes place as a result of the direct excitation by a light quantum of a high vibrational state in the electronic system. Here the interaction of the electrons with the anharmonic vibrational subsystem of the molecule plays a major role. This case of randomization of the molecular spectra is distinct from that in Refs. 6–10, and the distinction has to do with the participation in the electron-vibrational transition of a deformational vibration which determines the dynamics of the vibrational excitation.[4]

The redistribution of the excess energy of the light quantum above the energy of the electronic transition between the vibrational degrees of freedom of the molecule was studied theoretically in Ref. 11. In this paper the vibrational motion characteristic of the molecules investigated in Refs. 3 and 4 was explained by the resonant interaction of the optically active, deformational vibration with the high-frequency vibrations. It was shown that in the case of a large shift of the minimum of the potential energy of the deformational vibration the intermode vibrational anharmonicity results in an aperiodic motion of the nuclei, manifesting itself in the smearing out of the absorption spectrum. The points of the spectrum were treated in the spirit of $S$-matrix theory as resonances of the dipole-transition matrix elements of the molecule.

In the present paper we propose to investigate the peculiarities of the electron-vibrational transitions associated with the zero-dimensional "soliton" and "kink" analogs of the aperiodic excitations of the vibrational subsystem of the molecule for the model of Ref. 11 through nonlinear semiclassical mechanics by the method of integrating over a closed time contour. The character of the spectrum of the temperature-time correlation function of the electron-vibrational excitations is also delineated.

## 1. CORRELATION FUNCTION OF THE ELECTRON-VIBRATIONAL EXCITATION

We take the Hamiltonian of the molecule with electron excitation energy $E$ to be in the form

$$H=\begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}h_\Delta+\begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix}(h-E).$$

The vibrational subsystem with energy operator in the electronic ground state

$$h=\omega c^+c+\sum_{g=1}^{N}(a^+b^+)_g\begin{pmatrix}\omega_a & \mu c\\ \mu c^+ & \omega_b\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix}_g$$

0038-5646/91/020249-05$03.00

is modeled by $2N+1$ Bose oscillators. The optically active, deformational vibration with frequency $\omega$ interacts resonantly with the $N$ vibration pairs of the band of Franck-Condon states with frequencies $\omega_a \approx \omega_b + \omega$; $\mu$ is the intervibrational coupling constant. The minimum of the energy of the oscillator with frequency $\omega$ in the excited electronic state is shifted relative to the energy minimum in the ground state by $\Delta$, so that $h_\Delta = h|_{c\to c+\Delta, c' \to c' + \Delta}$.

The excitation of the molecule by a weak light field in the Condon approximation is described by the correlation function

$$K(t)=(\mathrm{Sp}\,\rho)^{-1}I(t),\quad I(t)=\mathrm{Sp}\,(\rho e^{-iHt}\sigma^- e^{iHt}\sigma^+),$$

$$\sigma^+=\begin{pmatrix}0&1\\0&0\end{pmatrix},\quad \sigma^-=\begin{pmatrix}0&0\\1&0\end{pmatrix},\quad \rho=\exp(-\beta H).$$

Evaluating the trace in terms of the electronic variables, we obtain

$$I(t)=e^{-iEt}\,\mathrm{Sp}\,(e^{-h(\beta+it)}e^{ih\Delta t}). \tag{1}$$

With the goal of an approximate description of the vibrational subsystem, we avail ourselves of the functional representation (1) in the limit $N\to\infty$. Toward this end, we write Eq. (1) in the basis of coherent states of the Bose oscillators, the set of whose indices we denote by the symbol $z$:

$$I=\int d^2z\,d^2z'\,d^2z''\langle z|e^{it(h_\Delta-E)}|z'\rangle\langle z'|e^{-\beta h}|z''\rangle\langle z''|e^{-iht}|z\rangle,$$

$$d^2z=d^2z_c\prod_{g=1}^{N}(d^2z_a\,d^2z_b)_g,\qquad d^2z_\varkappa=\exp(-|\varkappa|^2)\,\frac{d\varkappa^*\,d\varkappa}{i\pi},$$

$$\varkappa=a,b,c. \tag{2}$$

Each of the matrix elements in Eq. (2) can be represented in the form of an integral over trajectories:

$$\begin{gathered}I=\int d^2z\,d^2z'\,d^2z''\int D^2\psi_-\,D^2\psi\,D^2\psi_+\exp(\Phi-iEt)\\ \Phi=iS^+(t,0)+S(\beta,0)-iS_\Delta^-(t,0),\\ D^2\psi_\pm=D^2c_\pm\prod_{g=1}^{N}(D^2a_\pm\,D^2b_\pm)_g,\\ D^2\psi=D^2c\prod_{g=1}^{N}(D^2a\,D^2b)_g.\end{gathered} \tag{3}$$

The actions $S$, $S^+$, and $S_\Delta^-$ are functionals of the usual sort, which depend on the trajectories of all the oscillators on the corresponding segments of the integrations. The boundary conditions on the trajectories of each oscillator with frequency $\omega_a$ have the form

$$a_-^*(t)=z_a'^*,\quad a^*(\beta)=z_a'^*,\quad a_+^*(t)=z_a''^*,$$

$$a_-(0)=z_a,\quad a(0)=z_a'',\quad a_+(0)=z_a,$$

and analogously for the trajectories $b$, $b_\pm$, $c$, and $c_\pm$.

Formula (3) allows one to represent the evolution of the vibrational subsystem from the state of thermodynamic equilibrium at the time 0 to the time $t$ as a motion "forward" with Hamiltonian $h$, and from the time $t$ to the time 0 as motion "backward" with Hamiltonian $h_\Delta$. This mode of description, well known by the name "integration over a closed time contour," was developed in the quantum statistical physics of irreversible processes.[12,13] Such an approach is convenient for electron-vibrational transitions in molecules since the motions forward and backward take place from different electronic states and the difference between them can be understood as a difference between the vibrational dynamics during absorption and during luminescence.

## 2. VARIATIONAL PRINCIPLE FOR VIBRATIONAL SUBSYSTEMS

Let us calculate in Eq. (3) the Gaussian integrals over the trajectories $c$ and $c_\pm$ and over the coherent states $z_c$, $z_c'$, and $z_c''$:

$$I=ne^{\omega\beta-iEt}\int d^2z_{a,b}\,d^2z'_{a,b}\,d^2z''_{a,b}\int D^2\psi^-_{a,b}\,D^2\psi_{a,b}\,D^2\psi^+_{a,b}\exp S_{\text{eff}},$$

$$n=(e^{\omega\beta}-1)^{-1},\qquad S_{\text{eff}}=-i\int_0^t\mathscr{L}_-\,d\tau+\int_0^\beta\mathscr{L}\,d\tau+i\int_0^t\mathscr{L}_+\,d\tau+F,$$

$$\mathscr{L}_\pm=\sum_{g=1}^{N}\Big[a_\pm^*\Big(i\frac{d}{d\tau}-\omega_a\Big)a_\pm+b_\pm^*\Big(i\frac{d}{d\tau}-\omega_b\Big)b_\pm\Big]_g,$$

$$\mathscr{L}=\sum_{g=1}^{N}\Big[a^*\Big(-\frac{d}{d\tau}-\omega_a\Big)a+b^*\Big(-\frac{d}{d\tau}-\omega_b\Big)b\Big]_g, \tag{4}$$

$$\begin{aligned}F=&\int_0^\beta d\tau\,d\tau'\,P^*(\tau)P(\tau')[n+\vartheta(\tau-\tau')]\\ &+nie^{i\omega t}\int_0^\beta P\,d\tau\int_t^0(P_-^*-P_+^*)\,d\tau'\\ &-nie^{-i\omega t}\int_0^\beta P^*\,d\tau\int_t^0(P_+-P_-)\,d\tau'\\ &+\int_t^0 d\tau\,d\tau'[n(P_-^*-P_+^*)|_\tau(P_+-P_-)|_{\tau'}\\ &+P_-(\tau')(P_+^*-P_-^*)|_\tau\vartheta(\tau-\tau')+P_+^*(\tau)(P_--P_+)'|_{\tau'}\vartheta(\tau'-\tau)]\\ &-\mu\Delta\int_0^\beta(K+K^*)\,d\tau-i\mu\Delta\int_0^t(K_-+K_-^*-2\omega\Delta)\,d\tau.\end{aligned}$$

The rows of the formula for $F$ which are bilinear in $P$ and $P_\pm$ coincide with the phase of the transformation function of the oscillator with equilibrium boundary conditions in the field of prescribed $P_\pm$ forces calculated by Schwinger.[12] In the present case these forces arise thanks to the intervibrational interaction and the electronic transition, and they describe the motion forward (superscript "plus") and backward (superscript "minus") and are equal to

$$P_\pm=e^{i\omega\tau}K_\pm,\quad P=e^{\omega\tau}K,\quad P^*=e^{-\omega\tau}K^*,$$

$$K_+=\sum_{g=1}^{N}k_g^+,\qquad K_-=\omega\Delta+\sum_{g=1}^{N}k_g^-,\qquad K=\sum_{g=1}^{N}k_g,$$

$$k^\pm=\mu a_\pm b_\pm^*,\quad k=\mu ab^*.$$

From Eq. (4) one can obtain an expression for $I(t)$ by using the stationary phase method at large $N$. In this case the equations obtained by varying $S_{\text{eff}}$ over the trajectories $b$, $b_{\pm}$, $a$, $a_{\pm}$, and their conjugates form a closed system of Euler-Lagrange equations for the extremals which in the limit $N \to \infty$ describe the semiclassical motion of the nuclei. For example, for each of the oscillators with frequencies $\omega_a$ and $\omega_b$ the equations for $a^*_-$, $a_-$, $b^*_-$, and $b_-$ are integro-differential equations of the form

$$\left(i\frac{d}{d\tau}-\omega_a\right)a_-+ib_-\mu e^{-i\omega\tau}u_-=0,$$

$$\left(-i\frac{d}{d\tau}-\omega_b\right)b_-^*+ia_-^*\mu e^{-i\omega\tau}u_-=0,$$

$$\left(-i\frac{d}{d\tau}-\omega_a\right)a_-^*+ib_-^*\mu e^{i\omega\tau}v_-=0,$$

$$\left(i\frac{d}{d\tau}-\omega_b\right)b_-+ia_-\mu e^{i\omega t}v_-=0, \tag{5}$$

$$u_-=\int_0^\tau P_-\,d\tau'-n\int_0^t(P_+-P_-)\,d\tau+ine^{i\omega t}\int_0^\beta P\,d\tau-n\tilde{\Delta}+i\Delta,$$

$$v_-=-\int_0^\tau P_-^*\,d\tau'+(n+1)\int_0^t(P_-^*-P_+^*)\,d\tau$$

$$+ine^{-i\omega t}\int_0^\beta P^*\,d\tau+e^{-i\omega t}(i\Delta+n\tilde{\Delta}).$$

For the trajectories with the index "plus" the equations have the same form, but the functions $u_+$ and $v_+$ are equal to

$$u_+=-\int_0^\tau P_+\,d\tau'+(n+1)\int_0^t(P_+-P_-)\,d\tau'$$

$$-ine^{i\omega t}\int_0^\beta P\,d\tau'+\tilde{\Delta}(n+1)',$$

$$v_+=\int_0^\tau P_+^*\,d\tau'+n\int_0^t(P_+^*-P_-^*)\,d\tau'-ine^{-i\omega t}\int_0^\beta P^*\,d\tau'+\tilde{\Delta}^*n,$$

$$\tilde{\Delta}=i\Delta(e^{i\omega t}-1).$$

Equations analogous to Eqs. (5) can also be written for the trajectories $a$, $a^*$, $b$, and $b^*$; however, the entire system of coupled equations as a whole is too complicated, and in order to study it we will make some simplifying assumptions below.

We remark that the variables $a$ and $a^*$, $b$ and $b^*$ in the latter formulas are not canonically conjugate, since the equations that can be obtained from the conjugate of Eqs. (5) differ from them and define a different set of variables (which do not follow from the variational principle). This circumstance is due to the non-Hamiltonian character for $\Delta \neq 0$ of the vibrational subsystem described by the function (1) after averaging in the correlator $K(t)$ over the electronic degrees of freedom. The noncoincidence of the levels of motion for the $\ll + \gg$ and $\ll - \gg$-trajectories means that the evolution of the vibrational subsystem of the molecule before and after the electronic transition proceeds differently. This difference increases with the growth of the shift $\Delta$ of the minimum of the potential energy of the vibrations of the nuclei with frequency $\omega$ in the excited state, but, as will be shown below, disappears at temperatures near the thermodissociation temperature.

### 3. APERIODIC MOTION OF THE NUCLEI

In the case of a large shift $\Delta$ and not too high temperatures we can write the inequality

$$\Delta^2 > n = (e^{\omega\beta}-1)^{-1}, \tag{6}$$

according to which the density of the low-frequency phonons formed during the electron transition exceeds their equilibrium occupation number. Inequality (6) allows one to neglect the vibrational interaction on the temperature segment of the integration contour. In this case the calculation of the integral (2) reduces to the calculation of the trace with the initial distribution $\rho \to \rho|_{\mu=0}$, and the equations for the bilinear combinations of the $\ll + \gg$- and $\ll - \gg$-trajectories simplify:

$$\frac{d^2u_\pm}{d\tau^2}+\mu^2u_\pm(L_\pm-2u_\pm v_\pm+2u_\pm^0v_\pm^0)=0,$$

$$L_\pm=m_\pm+\left(\frac{\Omega}{2\mu}\right)^2, \quad m_\pm=\mp(n_b-n_a), \quad u_+^0=u_+(t), \tag{7}$$

$$u_-^0=u_-(0), \quad \Omega=\omega-\omega_a+\omega_b.$$

Here $m_\pm$ is the initial difference between the numbers of excitations of the oscillators $n_b$ and $n_a$ with frequencies $\omega_a$ and $\omega_b$, and the boundary values are connected by the relations

$$u_-(0)=-u_+(0)e^{-\omega\beta}+i\Delta, \quad u_-(t)=-u_+(t)+i\Delta.$$

Analogous inequalities hold for $v_\pm$.

If condition (6) is satisfied, the function $I(t)$ can be conveniently represented in the form

$$I(t)=\exp(\Phi_0-iE_0t), \quad E_0=E+\omega\Delta^2,$$

$$\Phi_0=iS_0^+(t,0)-iS_0^-(t,0)-i\int_0^t r\,d\tau,$$

$$r=\omega\Delta(c_-+c_-^*)+\Delta(K_-+K_-^*), \tag{8}$$

where the difference of the terms $S_0^+$ and $S_0^-$ is nonzero only because the $\ll + \gg$- and $\ll - \gg$-trajectories do not coincide, and the uncanceled contribution to the phase due to the shift $\Delta$ comes only from the single term with the kernel $r(\tau)$. This kernel is found from the formula

$$r=i\Delta\frac{d}{d\tau}(c_--c_-^*),$$

which follows from the equations of motion for the trajectories of the deformational vibration

$$i\frac{dc_-}{d\tau}=\omega c_-+K_-, \qquad -i\frac{dc_-^*}{d\tau}=\omega c_-^*+K_-^*,$$

the solution of which is equivalent to the calculation of the functional Gaussian integral in transforming from Eq. (3) to Eq. (4).

The implication of the above equalities is that to calculate $I(t)$ from formula (8) it is necessary to find the solution of Eq. (7) and the analogous equation for $v_\pm$ coupled with it. The analysis of the problem simplifies if the conjugation relations for the functions $u_\pm$ and $v_\pm$ are found. With this aim, let us turn to the particular case $L_\pm = 0$, in which the solutions of Eq. (7) are constants (independent of $\tau$). This case corresponds to short interaction times $\omega t < 1$. Then at low temperatures ($n \ll 1$) the equalities $u_+ \approx v_+ \approx 0$ and $u_- = -v_-^*$ follow from the formulas for $u_\pm$ and $v_\pm$, and at high temperatures ($n \gg 1$), the equalities $u_+ \approx v_+^*$ and $u_- = v_-^*$.

Conjugation relations at low temperatures for the $\ll - \gg$-trajectories, as can be seen from system of equations (5), corresponds to the usual canonical conjugation of variables $(a^*)^* = a$ and $(b^*)^* = b$ in Hamiltonian dynamics. The conjugation relations at high temperatures correspond to non-Hamiltonian motion of the vibrational subsystem due to pre-averaging over the electronic variables in Eq. (1). Both types of motion were described previously[14] in the mechanics of three coupled oscillators for $\Delta = 0$ and arbitrary values of the parameters $\mu$, $\omega$, and $t$. In the case under consideration the classification of types of the motion is expressed by the formula

$$u_\pm = x v_\pm^*, \qquad x = \begin{cases} -1, & n<1, \quad (9.1) \\ 1, & n>1. \quad (9.2) \end{cases}$$

Equation (7) here has real coefficients and takes the closed form

$$\frac{d^2u_\pm}{d\tau^2} - x\mu^2 u_\pm (2|u_\pm|^2 + \varepsilon_{1,2}^\pm) = 0, \qquad \varepsilon_1{}^+ = L_+,$$
$$\varepsilon_1{}^- = L_- - \Delta^2, \ \varepsilon_2{}^\pm = L_\pm - n^2|\tilde{\Delta}|^2. \tag{10}$$

Equation (10) determines the trajectories of the vibrational subsystem of the molecule, and its form for each value of $x$ depends on the sign of the coefficient $\varepsilon_{1,2}^\pm$ and the magnitude of the integral of the energy $\mathscr{E}$ of the nonlinear equation (10). The self-similar solutions of Eq. (10) for $x = -1$ and $x = 1$ were investigated in detail in Ref. 15. We will make use of the results of this work, and in order to compensate for the shift term in the boundary conditions on Eq. (7) we will transform to the variable $u + xv$. The potential energy of the oscillator (10) as a function of the coordinate $c_-$, also investigated in Ref. 15, in the problem under consideration is a result of averaging (1) of the vibrational energy of the molecule over both electronic states, taking into account the transitions between them.

First let us remark that cases (9.1) and (9.2) describe nonlinear vibrational regimes of fundamentally different character. In case (9.1) if the sign of the coefficient $\varepsilon_1^\pm$ is negative the potential energy of the oscillator is represented by a double well, which ensures bounded motion of the nuclei for all values of the parameters. The particular solution $|\varepsilon_1^\pm|^{1/2}\cosh(\tau\mu|\varepsilon_1^\pm|^{1/2})$ obtains for zero value of the energy $\mathscr{E} = \mathscr{E}_0 = 0$. This aperiodic solution is the separatrix of the phase plane of the vibrations of the nuclei with three turning points. It describes resonant energy exchange $\omega \rightleftarrows \omega_a - \omega_b$ of soliton type in the vibrational subsystem and separates regions of periodic motion with different parameters.

In case (9.2) if the sign of the coefficient $\varepsilon_2^\pm$ is negative and the energy $\mathscr{E} = \mathscr{E}_{\max} > 0$, the potential energy of the oscillator (10) is represented by a curve with two maxima which are the turning points in the motion along the separatrix $|\varepsilon_2^\pm|^{1/2}\tanh(\tau\mu|\varepsilon_2^\pm|^{1/2})$. This aperiodic solution describes the kinklike resonant decays $\omega_a - \omega_b \to \omega$ and $\omega_a - \omega_b \leftarrow \omega$ and separates the region of stable motion $\mathscr{E} < \mathscr{E}_{\max}$ from the region $\mathscr{E} > \mathscr{E}_{\max}$ of unbounded motion. If $x = -1$ holds and the sign of $\varepsilon_1^\pm$ is positive, the motion is always stable and periodic; if $x = 1$ holds and the sign of $\varepsilon_2^\pm$ is positive, it is always unstable.

The influence of the relation between the anharmonicity $\mu$, the detuning of the Fermi resonance $\Omega$, and the shift $\Delta$ on the appearance of the aperiodic regimes of motion of the nuclei that cause the greatest distortion of the electron-vibrational spectrum of the molecule is of interest.

In the molecules modeled in the present work the deformational vibration with frequency $\omega \sim 200$ cm$^{-1}$ interacts with the valence vibrations with frequency $\omega_{a,b} \sim 1000$ cm$^{-1}$, so that $m < n$. For typical parameters in the molecules under consideration[3,4] we have $\mu \sim 10$ cm$^{-1}$, $\Omega \sim 5$ cm$^{-1}$, and the shift $\Delta$ is estimated from the magnitude of the Stokes shift $\omega\Delta^2 \sim 1500$ cm$^{-1}$ to be equal to 2–3. At temperatures defined by the inequalities $n < 1$ and $\omega\beta_0 > 1$ (for the frequency $\omega$ chosen here, $\beta_0^{-1} \sim 300$ K), the necessary condition for the appearance of the aperiodic regime $\varepsilon_1^\pm < 0$ is satisfied as a result of the presence of the shift term $(-\Delta^2)$ in $\varepsilon_1^-$ faster for luminescence than for absorption, and in both cases this condition is independent of the occupation number $n$. At temperatures at or above room temperature, but not so high that inequality (6) is violated, $n \gtrsim 1$ and $\varepsilon_2^\pm < 0$ give the condition $n\mu\Delta > \Omega$ of aperiodicity of the motion of the nuclei during absorption and luminescence previously established in Ref. 11 for room temperatures $n \sim 1$. At high temperatures ($n > \Delta^2$, $\omega\beta < \Delta^{-2}$) the equation for the collective vibrations differs from (10) and does not have stable solutions, which corresponds to dissociation of the molecule.

## 4. SPECTRUM OF ELECTRON-VIBRATIONAL EXCITATIONS

Let us elucidate the nature of the excitational spectrum of the molecule for the cases of periodic and aperiodic motion of the nuclei. The spectrum is characterized by singularities in the spectral density $I_p$, which is defined as the Laplace transform of the correlation function (8):

$$I_p = \int_0^\infty \exp(-pt - iE_0t + \Phi_0)\,dt, \qquad \Phi_0 = \Delta[e^{i\omega t}u_-(t) - u_-(0)]. \tag{11}$$

In the absence of the vibrational interaction ($\mu = 0$) the following relation holds

$$\Phi_0 = -\Delta^2(e^{i\omega t} - 1)(ne^{-i\omega t} + 1 - n)$$

and the excitation spectrum corresponds to a well-known result in the theory of multiphonon transitions.[16] In the presence of the nonlinear vibrational interaction ($\mu \neq 0$) for the case of motion of the vibrational subsystem along the separatrix corresponding to the case (9.1), the spectrum is determined by its asymptotic behavior at late times

$$u_-{}^0 \sim i\Delta^2 \mathrm{ch}^{-1}(\mu t\Delta) \sim i\Delta^2 e^{-\mu\Delta t}, \quad \mu\Delta t > 1$$

and has the character of a pole:

$$I_p = \sum_{k=0}^{\infty} \frac{\Delta^{2k}}{k!} \frac{1}{p - i[E_0 + (\omega - i\mu\Delta)k]}.$$

The trajectories near $u^0_-$ correspond to vibrations with long period $\nu^{-1}$. In the general case they are described by the elliptic functions cn, which satisfy Eq. (10), and the points of the spectrum are determined by combinations of the frequencies $\omega$ and $\nu$. In this case broadening due to the anharmonicity of the interaction between the vibrations $\Delta\mu$, according to the condition for motion in the vicinity of the separatrix $\mu\Delta > \Omega$, significantly exceeds the frequency $\nu$, i.e., the minimal distance between the points of the spectrum. This fact can serve as an explanation for the smearing out of the spectra of complex molecules[3,4] in the limit $\nu \to 0$.

At high temperatures, in the vicinity $\mathscr{E} > \mathscr{E}_{\max}$ of the separatrix corresponding to the case (9.2), the instability of the motion is manifested in rapid relaxations leading the phase point of the vibrational subsystem out of the region $[0, \Delta]$ of the coordinate $c_-$. This corresponds to the initial stage of the decay of the state of the molecule, which in the real situation is complicated by the fact that the lower branches of the curve (9.2) have inflection points. A description of such a process goes beyond the model of effective one-dimensional motion considered here.

## 5. CONCLUSION

Thus, the nonlinear interaction of the vibrational degrees of freedom (intermode anharmonicity $\mu$) can be a reason for the appearance of diffuse bands in the electron-vibrational spectra. The appearance of such an effect requires only moderate values of the anharmonicity $\mu$ and the temperature in the presence of a significant shift $\Delta$ of the minimum of the energy of the optically active vibration with frequency $\omega$ and a sufficient density of levels in the Franck-Condon electron-vibrational states. The frequencies $\omega$ can correspond to librational motion of large parts of molecules possessing complicated structural asymmetry. The large magnitude of $\Delta$ is connected with the smallness of the frequency of deformational vibration $\omega$ compared to that part of the quantum of light energy transferred to the vibrational subsystem.

Since the constant $\mu$ is small in comparison with the frequency $\omega$, the approximation of weak anharmonicity[8-10] in the vibrational transitions in the absence of electronic excitation is justified. For an electron-vibrational transition with a large shift $\Delta$ the vibrational subsystem can fall in the region of the separatrix of its phase space, which requires that the nonlinear dynamics of the nuclei be treated here outside the framework of the theory of perturbations in $\mu/\omega$. The motion of the nuclei is described by Eq. (10), and the condition for the appearance of the aperiodic regime at room temperature is expressed by the inequality $\mu\Delta > \Omega$. Note that in the second of the two temperature regions [(9.1) and (9.2)] the conditions for the appearance of aperiodic motion depend on the occupation number $n$. The presence of a boundary temperature region corresponding in the given model to room temperatures $n \sim 1$ can serve as an analog for the electron-vibrational transitions in the previously developed notions of "thermal explosions"[7] or "phase transitions"[8,9] in the light-excited vibrational subsystem of the molecule.

The Landau-Singer theory for a diatomic ($N = 1$) molecule follows from Eq. (1) if the commutator $[h, h_\Delta]$ is small. The latter is the case for $\Delta \ll 1$, and the corresponding result for the model considered here is described by the first terms of series (12). This approximation implies that the electron-vibrational interaction is small, and is valid for the valence vibrations, and, in particular, it is always valid for diatomic molecules. For the deformational and librational vibrations considered here for the case of complex molecules, $\Delta > 1$ holds and the electron-vibrational interaction is not small. Just this circumstance leads to the participation of a large number of degrees of freedom ($N \gg 1$) of the vibrational heat sink in the interaction and because of its anharmonicity [i.e., of the vibrational motion] leads to the spectroscopic manifestation of the randomization of the vibrations during an electron-vibrational transition in a weak field.

The large value of $\Delta$ implies a substantial change in the "landscape" for the point of the vibrational phase space during the electronic transition. This change is assumed to take place instantaneously since the condition of the semiclassical character of the motion is assumed to be fulfilled, but the nuclear shift is negligibly small. Note that a strong electron-vibrational interaction makes it necessary to depart from the Born-Oppenheimer approximation, used in the present work. In connection with this, one might expect a complication of the vibrational dynamics described here, first of all for the trajectories of the highly excited vibrations (9.2). As to the spectrum, it is doubtful that an account of the departures from this approximation would cause a narrowing of the spectrum and the disappearance of its diffuse character, but should rather open up new possibilities for introducing new interaction parameters and describing other features of the spectrum.

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Translated by P. F. Schippnick