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ABSTRACT

Numerous computations of the spectra of molecules are performed by mainstream methods based on the fundamental work by Lax [J. Chem. Phys. **20**, 1752 (1952)] for smoothing a series of individual transitions represented by delta functions. There is an assumption that the linewidth of an individual rovibronic transition spectrum is many orders of magnitude smaller than the rovibronic bandwidth. However, the presence of rotational–vibrational structure in the molecular spectrum masks the broadening of each individual rovibronic transition. In this work, in the framework of harmonic approximation of potential energy surfaces, a new kind of contribution to homogenous broadening is considered to describe the optical spectrum of any single rovibronic transition. Its origin is in zero-point oscillations and thermal fluctuations around equilibrium positions of nuclei. Franck–Condon diagrams with slanting equidistant vibrational levels are proposed. Expressions of the spectral intensity of a single vibronic transition are derived from the first principles. This theory was used to estimate the broadening magnitude of the vibronic transition due to quantum uncertainty of nuclear coordinates of linear polymethine dyes with an extended π-electron system. It was shown that the calculated magnitude of the broadening is approximately two times smaller than the bandwidth observed in the experiment but it has the same order of magnitude. The value of such broadening depends on the environment that restricts the vibrational and rotational degrees of freedom of the molecule. It was demonstrated that an organic chromophore with an extended π-electron system can be considered to be a molecular optical parametric oscillator.

I. INTRODUCTION

In large molecules, the number of possible normal vibrations is very large. Each of them has a rotational structure. Usually, spectral measurements are performed for large ensembles of molecules of this type, which are statistically distributed over energy levels in accordance with the temperature of the medium and interactions with the solvent molecules. Some excitation energies of molecules are more probable and intense than others. Experiments show that electronic–vibrational–rotational (rovibronic) terms overlap each other so extensively that the molecular spectrum looks to be their common envelope. Rovibronic transitions merge into absorption and emission bands corresponding to the energy spectrum of a molecule of this type (Ref. 1).

Thus, rotational–vibrational structure masks the broadening of an individual rovibronic transition in the molecular spectrum. Measuring the spectral width of an individual electron transition is a difficult experimental problem. However, it is generally accepted that the spectral width of an individual electronic transition is many orders of magnitude smaller than the observed width of the spectral band containing many closely spaced rovibronic transitions.

In this work, it is shown that the spectral width of an individual transition in a molecule can be commensurate with the total bandwidth. There is a mechanism of broadening of experimentally observed terms, which is usually not taken into account in quantum chemical calculations.

Here, we will consider vibronic (electronic–vibrational) terms of molecules, but the same conclusions can be made in the general

case of rovibronic (electronic–vibrational–rotational) transitions. We will also restrict ourselves to considering the absorption spectra, but the broadening of the emission spectra can be obtained in a similar way.

In the framework of adiabatic (Born–Oppenheimer) approximation (Refs. 1–3), the system of adiabatic equations is

$$[T_e + U(r,q)]\psi(r,q) = V(q)\psi(r,q), \tag{1}$$

$$[T_N + V(q)]\xi(q) = E\varphi(q), \tag{2}$$

where T_e and T_N are the kinetic energy operators of the electrons and nuclei, respectively, and $U(r,q)$ is the total potential energy of the molecule. The electronic energy $V(q)$ serves as the potential energy surface (PES) for the nucleus equation.[2] The total wave function of an isolated molecule is represented by

$$\Psi(r,q) = \psi(r,q)\varphi(q), \tag{3}$$

where $\psi(r,q)$ and $\varphi(q)$ are the electronic and nuclear wavefunctions, respectively, and r and q are the electronic and nuclear (vibrational) coordinates, respectively. The external electromagnetic wave can produce a transition between the electronic–vibrational levels of different electronic states in a molecule.

To calculate the PES of the ground state, $V_g(q)$, it is necessary to solve the electronic equation[1] for any admissible combinations of nuclear coordinates q considered as slowly changing parameters. The vicinity of the minimum of $V_g(q)$ corresponds to the ground electron state from which the vibration and rotational levels are counted. To calculate the PES of the excited state, $V_u(q)$, it is necessary to perform a similar procedure.

The probability of a transition between stationary states is $\Psi_g \leftrightarrow \Psi_u$, where g denotes the ground electronic state and u, the excited (upper) state, is proportional to the square of the matrix element of the electric dipole-moment operator $\hat{\mu}$. In addition,

$$M^2 = \left|\langle n|\mu(q)|n'\rangle\right|^2, \tag{4}$$

where $|n\rangle \equiv \varphi_g(q)$ and $|n'\rangle \equiv \varphi_u(q)$. The frequency, $\omega_{un'gn}$, is determined by the energy of a transition from an initial vibrational level n of the ground electronic state to a vibrational level n' of an excited electronic state,

$$\omega_{un'gn} = \hbar^{-1}(E_{un'} - E_{gn}), \tag{5}$$

where E_{gn} and $E_{un'}$ are the vibronic energies of ground and excited states, respectively.

In the framework of the Herzberg–Teller approximation,

$$\mu = \mu(q) = \langle\psi_u(r,q)|\hat{\mu}|\psi_g(r,q)\rangle, \tag{6}$$

where coordinates of nuclei q are slowly varying adiabatic parameters in the vibronic transition problem. In the framework of Franck–Condon (FC) approximation, transition dipole does not depend on nuclear coordinates,

$$\mu(q) \approx \mu(q_0) = \langle\psi_u(r,q_0)|\hat{\mu}|\psi_g(r,q_0)\rangle. \tag{7}$$

The oscillator strength of the transition is given by

$$f_{un'gn} = n_e\frac{2m_e\omega_{un'gn}}{3e^2\hbar}M^2, \tag{8}$$

where m_e and e are the mass and electric charge of an electron, respectively, and n_e is the number of electrons that contribute to transition. The spectral density of oscillator strength (spectral intensity) in the absence of line broadening is determined by

$$I_{un'gn}(\omega) = f_{un'gn}\delta(\omega_{un'gn} - \omega), \tag{9}$$

where δ is the Dirac delta function. Equation (9) can be rewritten as

$$I_{un'gn}(\omega) = n_e\frac{2m_e\omega_{un'gn}}{3e^2\hbar}M^2\delta(\omega_{un'gn} - \omega), \tag{10}$$

where

$$\hbar\omega_{un'gn} = \hbar\omega_{ug} + (n' - n)\hbar\Omega_n = E_{un'} - E_{gn} \tag{11}$$

is the energy of a "vertical" FC vibronic transition with fixed nuclear positions during a very quick electron excitation process; $\hbar\omega_{ug}$ is the energy of the pure electronic (0-0) transition.

The adsorption band of a complex molecule broadens into a quasi-continuum, which is an ordered collection of a great number of closely spaced electronic–vibrational terms, $\Psi_{gn} \to \Psi_{un'}$,

$$I(\omega) = \sum_{n,n'=0}^{\infty} P_n I_{un'gn}(\omega), \tag{12}$$

where P_n is the statistical probability factor averaged over the initial states (Ref. 1).

Each term under the sum in Eq. (12) is a very narrow separate vibronic band described by Eq. (10) with given numbers n and n'. One can deduce that the envelope of this quasi-continuum is a smooth spectral curve with a mean value of frequency and variance.

From a practical point of view, a direct calculation of a great number of individual lines $I_{un'gn}(\omega)$ and their summation in Eq. (12) is an unreasonably task. The idea of obtaining an effective broadening of the vibronic spectrum given by Eq. (12) by smoothing of such a set of vibronic lines can be illustrated by Lax's approach, Refs. 4 and 5. This is a simple way to obtain a mean value and variance of smoothing, which corresponds to Eq. (12).

Let us consider the vibronic problem with the Hamiltonians of Eq. (2) taken for ground and excited states in the vicinity of the minimum of their own PESs in harmonic approximation,

$$V_g(\mathbf{q}) = V_{g0} + \frac{1}{2}\sum_{k=1}^{j} M_k\Omega_{gk}^2(q_k - q_{g0,k})^2, \tag{13}$$

$$V_u(\mathbf{q}) = V_{u0} + \frac{1}{2}\sum_{k=1}^{j} M_k\Omega_{uk}^2(q_k - q_{u0,k})^2, \tag{14}$$

where j is the number of degrees of freedom in the molecule, summation over k denotes the summation over all the normal oscillations, $\mathbf{q} = (q_1, \ldots, q_j)$ is the vector of normal coordinates, and $\widetilde{M}_k$ and Ω_k are the reduced masses and nuclear vibrational eigenfrequencies, respectively.

Let us choose a certain initial nuclear configuration of the system $\mathbf{Q} = (\mathbf{Q}_1, \ldots, \mathbf{Q}_j)$ in the vicinity of minima of PESs and expand $V_g(\mathbf{q})$ and $V_u(\mathbf{q})$ around $\mathbf{Q}$ (Ref. 5),

$$V_g(\mathbf{q}) = V_g(\mathbf{Q}) + \sum_{k=1}^{j} F_{g,k}(q_k - Q_k) + \frac{1}{2}\sum_{k=1}^{j} M_k\Omega_{gk}^2(q_k - Q_k)^2, \quad (15)$$

$$V_u(\mathbf{q}) = V_u(\mathbf{Q}) + \sum_{k=1}^{j} F_{u,k}(q_k - Q_k) + \frac{1}{2}\sum_{k=1}^{j} M_k\Omega_{uk}^2(q_k - Q_k)^2, \quad (16)$$

where

$$\begin{aligned} F_{g,k} &= \left.\frac{\partial V_g(\mathbf{q})}{\partial q_k}\right|_{q_k=Q_k} = M_k\Omega_{gk}^2(Q_k - q_{g0,k}), \\ F_{u,k} &= \left.\frac{\partial V_u(\mathbf{q})}{\partial q_k}\right|_{q_k=Q_k} = M_k\Omega_{uk}^2(Q_k - q_{u0,k}). \end{aligned} \quad (17)$$

In the framework of Lax's model,

$$\Omega_{gk} = \Omega_{uk} = \Omega_k. \quad (18)$$

It follows, therefore, that Eqs. (15)–(17) give

$$\frac{\partial V_u(\mathbf{q})}{\partial q_k} - \frac{\partial V_g(\mathbf{q})}{\partial q_k} = F_u - F_g = \text{const}. \quad (19)$$

The equilibrium positions of the ground and excited electronic states can be written as

$$q_{g0,k} = Q_k - \frac{F_{g,k}}{M_k\Omega_k^2} \quad \text{and} \quad q_{u0,k} = Q_k - \frac{F_{u,k}}{M_k\Omega_k^2}. \quad (20)$$

Therefore, the distance between equilibrium positions of two states can be presented as

$$\Delta q_{0,k} = q_{u0,k} - q_{g0,k} = -\frac{F_{u,k} - F_{g,k}}{M_k\Omega_k^2}. \quad (21)$$

The dimensionless Huang–Rhys (HR) factor is determined by

$$S_k = \frac{M_k\Omega_k}{2\hbar}\Delta q_{0k}^2 = \frac{(F_{u,k} - F_{g,k})^2}{2\hbar\widetilde{M}_k{\Omega_k}^2}. \quad (22)$$

The reorganization energy R (Fig. 1) can be expressed through HR factors, taking into account Eqs. (14), (18), and (22),

$$R = V_u(\mathbf{q}_{g0}) - V_u(\mathbf{q}_{u0}) = \frac{1}{2}\sum_{k=1}^{j} M_k\Omega_k^2(\Delta q_{0,k})^2 = \sum_{k=1}^{j} S_k\hbar\Omega_k. \quad (23)$$

Thus, the HR factor for mode k can be determined as the number of vibrational quanta that are created on this mode upon vertical vibronic transition. It is important to emphasize – in the case of 00-transition, $R = 0$ – that vibrational quanta do not exist. It follows, therefore, that the HR factor is zero.

A series of closely spaced vibronic transitions like the *FC* line shown in Fig. 1 forms a spectral quasi-continuum, described by the sequence of delta functions under summation in Eq. (12). Lax's approach converts the quasi-continuum into a continuous spectrum (Fig. 1) by calculation of the envelope of this quasi-continuum, which is a smooth spectral curve, with a mean value of frequency

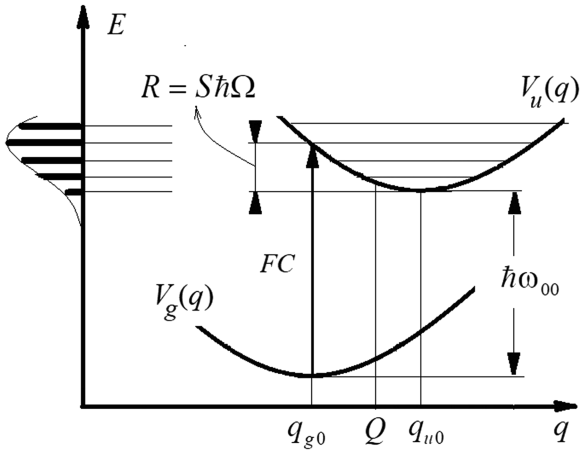

FIG. 1. Franck–Condon diagrams of vertical *FC* electronic transitions between the PES of the ground state $V_g(q)$ and the PES of the excited (upper) state $V_u(q)$. The quasi-continuous spectrum of a series of vibronic transitions located in the vicinity of the *FC* transition and their envelope, which forms a common absorption band, are shown on the left.

$$\omega_m = \omega_{ug} + \sum_{k=1}^{j} S_k\Omega_k \quad (24)$$

and variance

$$(\delta\omega)^2 = \sum_{k=1}^{j} S_k{\Omega_k}^2 \coth\frac{\hbar\Omega_k}{2k_BT}, \quad (25)$$

where k_B is the Boltzmann constant and T is the temperature.

To obtain a smooth envelope using the parameters of Eqs. (24) and (25), Lax (Ref. 4) used an integral representation of the delta functions given by Eq. (10), which are substituted under summation in Eq. (12),

$$\delta(\omega_{un'gn} - \omega) = \int_{-\infty}^{\infty} \exp\left[i(\omega_{un'gn} - \omega)t\right]dt \quad (26)$$

and, taking into account Eq. (11), transformed the sum over partial vibrational delta functions into an integral formula $\int_{-\infty}^{\infty} \exp[i(\omega_{ug} - \omega)t + g(t)]dt$, where $g(t)$ is the so-called generating function that contains information about nuclear vibrations,

$$g(t) = \sum_{k=1}^{j} S_k\left\{\coth\frac{\hbar\Omega_k}{2k_BT}(1 - \cos\Omega_k t) - i\sin\Omega_k t\right\}; \quad (27)$$

$\exp[g(t)]$ is a quantity whose Fourier transform generates the absorption band shape.

The main simplifying assumptions of Lax's smoothing procedure are harmonic approximation of PESs in ground and excited states in the vicinity of their minima [Eqs. (13) and (14)]. Another assumption is that the normal modes and harmonic vibrational frequencies in both the considered vibronic states are identical [Eq. (18)]. The generating function Equation (27) converts the

quasi-continuous set of vibronic transitions Equation (10) into a joint continuous band. This function arises from the distributions of the adiabatic minima energy separations, Δq_{0k}, Eq. (21).

Such an approach, called time-dependent treatment, was originally derived for electrons trapped in impurity centers in a crystal lattice, Ref. 4. This approach is used in a wide range of applications in modern research, particularly for modeling the optical band shape of organic dyes (Refs. 6–8). A more general expression for the generating function within the model of harmonic surfaces and its further generalization to the case of non-Condon transitions have been obtained by Kubo and Toyazawa (Refs. 5 and 9). All these approaches associate with more accurate calculations of matrix elements Equation (4) or going beyond adiabatic assumptions. In Refs. 10–16, authors have shown that by using Herzberg–Teller approximation (dependence of the transition dipole on the nuclear coordinates) and Duschinsky rotations (normal mode mixing between states), one can obtain more exact values of vibronic energies rather than in the framework of the FC transition.

All these methods have one thing in common. If there are many individual vibronic transitions overlapping each other so extensively that the entire spectrum looks to be their common envelope, then the direct calculation of individual transitions and their summation to obtain molecular vibronic spectrum becomes a very resource intensive task. Such methods smooth out the quasi-continuum of closely spaced vibronic transitions, approximately calculating the common envelope of all vibronic transitions, and thus form the continuous spectral band.

Consider an extreme case. If there is only one transition in the spectrum due to the rovibronic structure of the line being absent or very suppressed, then any smoothing is impossible. In this case, Lax's smoothing procedure results in a single delta function Equation (9) that is responsible for the transition. Indeed, in this case, the reorganization energy Equation (23) is zero, and the HR coefficients given by Eq. (22) are zero as well. Therefore, the generating function Equation (27) must be zero,

$$R = 0, \;\; S_k = 0, \;\; g(t) = 0. \tag{28}$$

An example of the case that satisfied the conditions given by Eq. (28) is zero-phonon (0-0) transition. Taking into account Eq. (10), one can obtain the spectrum of this transition,

$$I_{00}(\omega) = n_e \frac{2m_e\omega_{00}}{3e^2\hbar} M^2 \delta(\omega_{00} - \omega), \tag{29}$$

where ω_{00} is a frequency of (0-0) transition. Lax's time-dependent treatment and other similar methods (by Kubo, Toyazawa, and others) do not apply for smoothing the pure electronic zero-phonon transitions. Describing the single transition broadening is beyond the frameworks of all similar methods.

On the other hand, the individual optical line broadening is considered to be homogeneous or inhomogeneous (Ref. 1). Homogenous broadening is due to processes that broaden the optical lines in the spectrum of a single molecule (e.g., the finite lifetime of excited states in a transition, the Doppler effect). Inhomogeneous broadening arises from the effects of surroundings, for example, fluctuations in solvatochromic shift (Refs. 17–19) due to heat motion. It is generally accepted that all such broadenings are sufficiently small (10^{-6} cm^{-1}–10^{-1} cm^{-1}), many orders of magnitude smaller than the observed width of the optical absorption band of the molecule (10 cm^{-1}–10^3 cm^{-1}) (Ref. 20).

However, there is an example that the observed width of a solitary optical transition in the molecule given by Eq. (29) can be commensurable with the width of an ordinary rovibronic quasi-continuous band, represented by Eq. (12). The J-aggregation of polymethine dye monomers is manifested by a dramatic change in the spectrum. The J-band is strongly shifted to lower energies with very small Stokes shift, showing no vibrational structure (Refs. 21 and 22). Small Stokes shift indicates that rovibronic structure is considerably suppressed with the exception of (0-0) transition. Hypothetically, forming a joint coherent π-electron system in a compact J-aggregate from the separate π-systems of monomers leads to an effective elongation of the chromophore [red shift of the (0-0) transition]. The width of the J-band is rather narrower than the width of the corresponding band of the monomer. On the other hand, although the vibrational structure in the J-aggregate is considerably suppressed, both widths have the same order of magnitude. Therefore, (0-0) transition in the J-aggregate has a broadening that exceeds the generally accepted values of homogeneous and inhomogeneous broadenings of solitary optical transition by several orders of magnitude.

Thus, the theory of molecular spectra has an unsolved problem of significant broadening of an individual optical transition in the molecules and their aggregates. The presence of a rotational–vibrational structure in the spectrum masks the broadening of each individual transition. Numerous computations of the spectra of polymethine dyes have been performed by using one of the methods for smoothing a series of delta functions that were considered above (by Lax and Kubo *et al.*) (Refs. 23–26). These methods, by definition, do not describe the broadening of a single (0-0) vibronic transition, such as the one possibly taking place in the J-aggregate. At the same time, it is reasonable to assume that a certain narrowing of the absorption spectrum of polymethine dyes upon J-aggregation is precisely due to the suppression of the rovibronic structure of individual monomers and the unique manifestation of the natural width of a single rovibronic transition.

In this work, it is suggested that the wide broadening of the single electronic transition may be associated with the parametric dependence of the energy of fast electronic transition on the instantaneous values of slow oscillating nuclear coordinates. Even in the case of solitary (0-0) transition, the nuclei of a molecule have zero-point oscillations around equilibrium positions corresponding to PES minimum. The fundamental idea is that zero-point oscillations and thermal fluctuations in a signal-conducting system (nuclei) broaden the spectrum of this signal (optical electrons).

Let us consider the classical radiotechnical analogy of this effect. It can be represented by an electric oscillating circuit with a lightweight metal spring, which works as the inductance coil [Fig. 2(a) and 2(b)]. The spring is suspended vertically with a load mass m at the free end. Such a spring pendulum is an analog of vibrational moving of nuclei with an oscillating length $H(t)$ that depends on time: $H(t) = H_0 + A\cos\Omega t$; here, $\Omega = \sqrt{\frac{k}{m}}$ is a frequency of spring oscillation and k is the spring stiffness coefficient. Due to length oscillation, the magnetic inductance of the spring depends on time: $\omega(t) = \frac{1}{\sqrt{L_e(t)C}}$; here, C is the electric capacity of circuit, the inductance of the solenoid is $L_e(t) = \frac{\mu_0 NS}{H(t)}$ (in SI units),

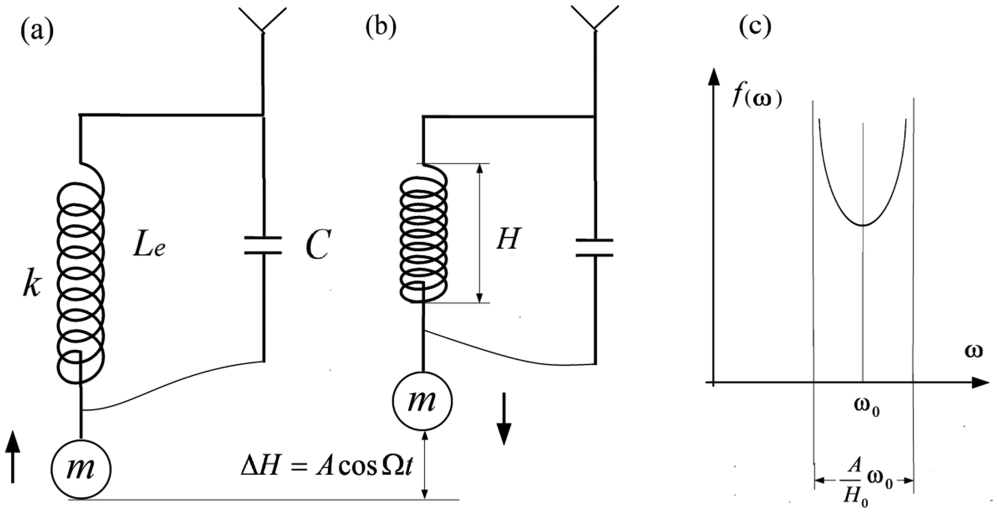

FIG. 2. [(a) and (b)] Detector radio-receiver with slow oscillating length of the inductance coil is a radiotechnical analog of a vibronic π-conjugated molecular system (two different phases of the spring oscillation). The resonant *LC*-circuit absorbs radio waves at a frequency ω modulated by small parametric oscillation with frequency Ω of the spring pendulum, which acts as an inductor ($\Omega \ll \omega$). (c) The absorption frequency spectrum of the circuit if the attenuation of the spring oscillations can be neglected.

S is a cross-sectional area of the coil (spring), N is the number of turns in the spring, and μ_0 is the vacuum magnetic permittivity; $\omega(t) \gg \Omega, H_0 \gg A$. Then, in the linear approximation, we can derive

$$\omega(t) \approx \omega_0 + \Delta\omega \cos \Omega t,$$

where

$$\omega_0 = \sqrt{\frac{H_0}{\mu_0 NSC}}$$

and

$$\Delta\omega = \frac{A\omega_0 \cos \Omega t}{2H_0}.$$

Then, characteristic relative broadening of the absorption radio band in an oscillating circuit is given by $\frac{A}{2H_0}$. The spectral probability-density distribution for a resonant frequency is shown in Fig. 2(c). Turn points of the classical pendulum (at the edges of the oscillating interval) provide the most probable values of frequency.

This example taken from classical physics shows that a slowly changing adiabatic parameter (length of spring) affects the resonant frequency. In this case, the probability-density distribution function of this parameter profiles the frequency spectrum of the resonant *LC*-circuit. The main difference between a quantum oscillator and its classical analog is that even in the absence of vibrational quanta in the oscillator, there are zero-point oscillations that produce stochastization of the spring length that leads to Gaussian-like broadening of the frequency spectrum, with maximal probability-density approximately at the central frequency value. It is clear that classical molecular dynamics does not describe zero oscillations; therefore, it cannot properly describe the oscillations that are provided to vibronic transition frequency broadening. Hence, the idea to apply classical molecular dynamics to such a kind of vibronic line broadening does not hold validity.

On the other hand, similar phenomena can be observed experimentally in many other cases, for example, in Ref. 27.

To check the suggested assumption, the magnitude of parametric broadening of electronic (0-0) transition in polymethine dye is estimated. Polymethine dye is a system with an extended π-electron system for which the energy of the electronic transition can be simply associated with the collective zero-point vibrations of nuclei in the polymethine chain. Theoretical treatment of the optical band shapes for chromophores with an extended π-electron system is still a considerable problem in chemical physics.

II. MODEL

Let us consider the vibronic energies that correspond to Hamiltonians of Eq. (2) in harmonic approximation given by Eqs. (13) and (14) taken for ground and excited states in a small vicinity of the minimum of their own PESs,

$$E_g(\Delta\mathbf{q}) = T_N + V_{g0} + \frac{1}{2}\sum_{k=1}^{j} M_k \Omega_{gk}^2 (\Delta q_k)^2, \tag{30}$$

$$E_u(\Delta\mathbf{q}) = T_N + V_{u0} + \frac{1}{2}\sum_{k=1}^{j} M_k \Omega_{uk}^2 (\Delta q_k - \Delta q_{u0,k})^2, \tag{31}$$

where j is the number of degrees of freedom in the molecule and $\Delta\mathbf{q} = (\Delta q_1, \ldots, \Delta q_j)$ is the vector of normal coordinate shifts; $\widetilde{M}_k$ and Ω_k are the reduced masses and nuclear vibrational eigenfrequencies, respectively; the coordinate shifts are denoted by

$$\Delta q_k = q_k - q_{g0,k} \quad \text{and} \quad \Delta q_{0k} = q_{u0,k} - q_{g0,k} \geq 0, \tag{32}$$

where $\Delta q_{0k} = \text{const}_k$ by definition of the PES.

The nuclear coordinates oscillate in the molecule, and Δq_k is a function of time and has a stochastic distribution for the set

of FC instantaneous transitions taking the ergodic theorem into account. Therefore, the absorption energy ΔE_{ug} of the instantaneous "vertical" transition corresponding to coordinate shifts $\Delta\mathbf{q}$ can be written as

$$\begin{aligned}\Delta E_{ug}(\Delta\mathbf{q}) &= E_u(\Delta\mathbf{q}) - E_g(\Delta\mathbf{q})\\ &\approx V_{u0} - V_{g0} + \frac{1}{2}\sum_{k=1}^{j} M_k\\ &\quad\times\left[\Omega_{u,k}^2(\Delta q_k - \Delta q_{0,k})^2 - \Omega_{g,k}^2(\Delta q_k)^2\right],\end{aligned} \tag{33}$$

where the expression under summation can be transformed as

$$\begin{aligned}&\Omega_{u,k}^2(\Delta q_k - \Delta q_{0,k})^2 - \Omega_{g,k}^2(\Delta q_k)^2\\ &\quad= (\Omega_{u,k}^2 - \Omega_{g,k}^2)(\Delta q_k)^2 - 2\Omega_{u,k}^2\Delta q_{0,k}\Delta q_k + \Omega_{u,k}^2(\Delta q_{0,k})^2.\end{aligned}$$

Denoting the constant (non-fluctuation) part of the energy as

$$\Delta E_{ug,0} = V_{u0} - V_{g0} + \frac{1}{2}\sum_{k=1}^{j} M_k\Omega_{u,k}^2(\Delta q_{0,k})^2, \tag{34}$$

one can rewrite Eq. (33) as

$$\begin{aligned}\Delta E_{ug}(\Delta\mathbf{q}) &= \hbar\omega_{ug}(\Delta\mathbf{q})\\ &= \Delta E_{ug,0} - \frac{1}{2}\sum_{k=1}^{j} M_k\\ &\quad\times\left[2\Omega_{uk}^2\Delta q_{0,k}\Delta q_k + (\Omega_{gk}^2 - \Omega_{uk}^2)(\Delta q_k)^2\right],\end{aligned} \tag{35}$$

where the term with summation describes the fluctuation part of the transition energy due to Δq_k being the quantum fluctuations of nuclear positions in the molecule.

In the stationary case, the averaged magnitude of Eq. (35) can be determined by the expression

$$\Delta E_{ug}(\mathbf{n},\mathbf{n}') = \Delta E_{ug,0} + \hbar\sum_{k=1}^{j}\left[\left(n'_k + \frac{1}{2}\right)\Omega_{uk} - \left(n_k + \frac{1}{2}\right)\Omega_{gk}\right], \tag{36}$$

where $\mathbf{n} = (n_1,\ldots,n_j)$ and $\mathbf{n}' = (n'_1,\ldots,n'_j)$ are the sets of the vibrational quantum numbers of the ground and the excited states, respectively. Transition given by Eq. (36) corresponds to frequency

$$\omega_{ug}(\mathbf{n},\mathbf{n}') = \omega_{ug,0} + \sum_{k=1}^{j}\left[\left(n'_k + \frac{1}{2}\right)\Omega_{uk} - \left(n_k + \frac{1}{2}\right)\Omega_{gk}\right], \tag{37}$$

where $\omega_0 = \hbar^{-1}\Delta E_0$.

The probability-density distribution of nuclei in the initial (ground) state $f_{gn}(\Delta\mathbf{q})$ on all possible sets of shifts $\Delta\mathbf{q}$ can be determined by taking into account Eq. (3),

$$f_{gn}(\Delta\mathbf{q}) = \varphi_{gn}*(\mathbf{q}_{g0} + \Delta\mathbf{q})\cdot\varphi_{gn}(\mathbf{q}_{g0} + \Delta\mathbf{q}). \tag{38}$$

Equation (38) is the probability of the transition with frequency $\omega_{ug}(\Delta\mathbf{q})$ given by Eq. (35). Thus, we can implicitly determine the distribution density $F(\omega_{ug})$ and then calculate the spectral intensity distribution Equation. (10),

$$I_{un'gn}(\omega) = n_e\frac{2m_e\omega}{3e^2\hbar}M_{un'gn}^2F(\omega), \qquad \int_{\omega} F(\omega)d\omega = 1, \tag{39}$$

where $M_{un'gn}^2$ is determined by Eq. (4),

$$M_{un'gn}{}^2 = \left|\left\langle\mathbf{n}\middle|\mu_{ug}(\mathbf{q})\middle|\mathbf{n}'\right\rangle\right|^2, \tag{40}$$

where

$$\mu_{ug}(\mathbf{q}) = \langle\psi_u(r,\mathbf{q})|\hat{\mu}|\psi_g(r,\mathbf{q})\rangle. \tag{41}$$

$\mu_{ug}(\mathbf{q})$ can be obtained in different approximations, for example, by the simplest Franck–Condon approximation Equation. (7),

$$\mu_{ug,0} = \left\langle\psi_u(r,\mathbf{q}_{u0})\middle|\hat{\mu}\middle|\psi_g(r,\mathbf{q}_{g0})\right\rangle, \tag{42}$$

or in the framework of the Herzberg–Teller approximation, if required.

If the spectrum consists of several vibronic transitions, they have to be summed by Eq. (12), taking into account the individual probability of each transition that is determined by temperature dependent statistical factors P_n.

In the one-dimensional case ($j = 1$), Eq. (35) can be rewritten for given n and n' as

$$\begin{aligned}\omega_{un'gn}(\Delta q) &= \omega_{un'gn,0} - \frac{1}{2\hbar}M\left[2\Omega_u^2\Delta q_0\Delta q + (\Omega_g^2 - \Omega_u^2)(\Delta q)^2\right]\\ &= \alpha - \beta\cdot\Delta q + \gamma\cdot(\Delta q)^2,\end{aligned} \tag{43}$$

where A, B, and C are the constants,

$$\alpha = \omega_{un'gn,0}, \quad \beta = M\Omega_u^2\Delta q_0 \geq 0, \quad \gamma = \frac{1}{2}M(\Omega_u^2 - \Omega_g^2).$$

The average frequency Equation. (37) is

$$\omega_{un'gn} = \omega_{ug,0} + \left[\left(n' + \frac{1}{2}\right)\Omega_u - \left(n + \frac{1}{2}\right)\Omega_g\right]. \tag{44}$$

In particular, for the (0-0) transition, Eq. (44) gives the expression

$$\omega_{u0g0} = \omega_{ug,0} + \frac{1}{2}(\Omega_u - \Omega_g). \tag{45}$$

Quantum uncertainty of the initial state described by $f_g(\Delta q)$, Eq. (38), leads to broadening of the transition vibronic band. In harmonic approximation, one can obtain

$$f_{gn}(\Delta q) = \varphi_{gn}*(q_{g0} + \Delta q)\cdot\varphi_{gn}(q_{g0} + \Delta q) = \xi_n{}^2(\Delta q), \tag{46}$$

where $\xi_n(\Delta q)$ is the harmonic oscillator eigenfunction. Using this relation, one-dimensional probability density distribution of $\omega_{un'gn}$ can be presented as

$$F(\omega) = \xi_n{}^2(\Delta q(\omega))\left|\frac{\partial\Delta q}{\partial\omega_{un'gn}}\right|, \tag{47}$$

where, taking into account Eq. (43),

$$\Delta q(\omega) = \frac{\beta \pm \sqrt{\beta^2 - 4(\alpha-\omega)\gamma}}{2\gamma} \quad \text{with} \quad \omega = \omega_{un'gn}, \tag{48}$$

$$\frac{\partial \Delta q}{\partial \omega} = \frac{\pm 1}{\sqrt{B^2 - 4(A-\omega)C}}. \tag{49}$$

Hence,

$$F(\omega) = \left[\xi_n\left(\frac{\beta \pm \sqrt{\beta^2 - 4(\alpha-\omega)\gamma}}{2\gamma}\right)\right]^2 \frac{1}{\sqrt{\beta^2 - 4(\alpha-\omega)\gamma}}. \tag{50}$$

Taking into account Eq. (39), the spectral intensity of the transition can be rewritten as

$$I_{un'gn}(\omega) = n_e \frac{2m_e\omega}{3e^2\hbar}\left[\xi_n\left(\frac{\beta \pm \sqrt{\beta^2 - 4(\alpha-\omega)\gamma}}{2\gamma}\right)\right]^2 \times \frac{M^2_{un'gn}}{\sqrt{\beta^2 - 4(\alpha-\omega)\gamma}}. \tag{51}$$

The squared normalized wave function of the linear harmonic oscillator (Ref. 28) is

$$\xi_n{}^2(\Delta q) = \frac{\exp\left(-\Delta q^2 r_0{}^{-2}\right) H_n^2\left(\Delta q \cdot r_0{}^{-1}\right)}{2^n r_0 n! \sqrt{\pi}}, \tag{52}$$

where $H_n\left(\Delta q \cdot r_0{}^{-1}\right)$ is the Hermite polynomial of degree n, the radius of the oscillator is

$$r_0 = \left(\frac{\hbar}{M\Omega_g}\right)^{1/2}, \tag{53}$$

and the normalizing condition is

$$\int_{-\infty}^{\infty} \xi_n{}^2(\Delta q) d\Delta q = 1, \tag{54}$$

$$\xi_0^2(\Delta q) = \frac{\exp(-\Delta q^2 r_0{}^{-2})}{r_0\sqrt{\pi}}. \tag{55}$$

In particular, for the (0-0) transition, Eqs. (51) and (55) give the expression that describes the spectral broadening of this transition due to zero-point oscillations of nuclei,

$$I_{u0g0}(\omega) = \frac{2n_e m_e \omega}{3\sqrt{\pi}e^2\hbar r_0} \exp\left[-\left(\frac{\beta \pm \sqrt{\beta^2 - 4(\alpha-\omega)\gamma}}{2\gamma r_0}\right)^2\right] \times \frac{M^2_{u0g0}}{\sqrt{\beta^2 - 4(\alpha-\omega)\gamma}}. \tag{56}$$

If conditions given by Eq. (18) take place, then expression Eq. (43) becomes linear,

$$\omega_{un'gn}(\Delta q) = \alpha - \beta \cdot \Delta q, \tag{57}$$

and Eq. (44) transforms to Eq. (11). In linear approximation,

$$\Delta q(\omega) = \frac{\alpha - \omega}{\beta}, \tag{58}$$

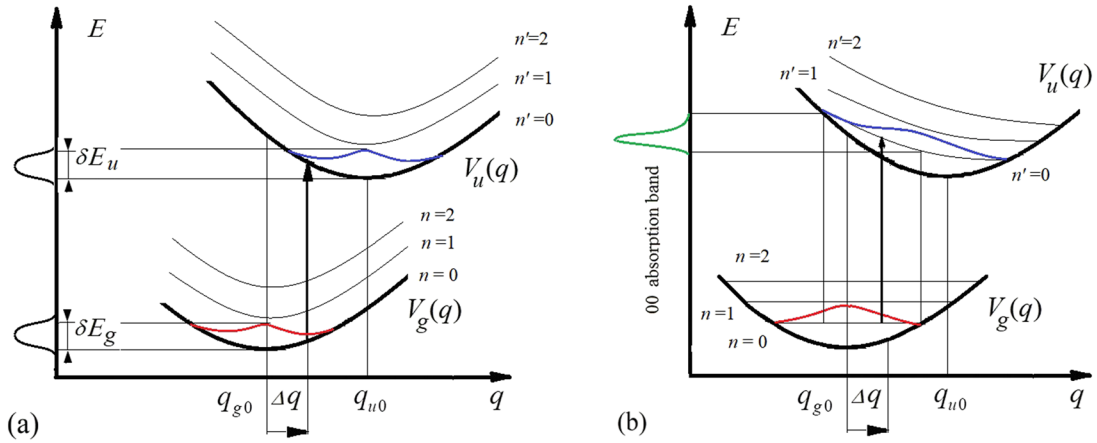

FIG. 3. Formation of a broadened spectrum of (0-0) vibronic transition in the presence of parametric dependence of the transition energy $\Delta E_{ug} = V_u - V_g$ on nuclear coordinate shift Δq relative to the position of the ground PES minimum q_{g0} [see Eq. (43)] due to zero-point oscillation of the nuclei. (a) Bending of equidistant (with distances $\hbar\Omega_g$ over the ground electronic state and $\hbar\Omega_u$ over the excited one) vibration levels of ground and excited states due to slow parametric dependence of the transition energies $E_g(\Delta q)$ and $E_u(\Delta q)$ on Δq [Eqs. (30) and (31)], respectively, δE_g and δE_u are the broadening of energy levels of the ground and the excited states, respectively. Red (blue) curve shows the probability-density of the electron distribution at the ground (excited) level as a function of shiftΔq. (b) Another diagrammatic representation of the same case, where the ground vibrational levels are drawn horizontally and the excited ones are plotted taking into account the local vertical distance to the ground level according to the second-degree polynomial given by Eq. (43). The exited vibration levels are bent on the diagram according to $\Delta E_{ug}(\Delta q) = A + B \cdot \Delta q + C \cdot (\Delta q)^2$. The vertical arrows indicate examples of vertical vibronic (0-0) transitions at randomly chosen parameters Δq. The resulting (0-0) absorption band given by the green curve is obtained by integrating all similar (0-0) transitions with respect to the parameter Δq, taking into account their statistical weight given by the red curve.

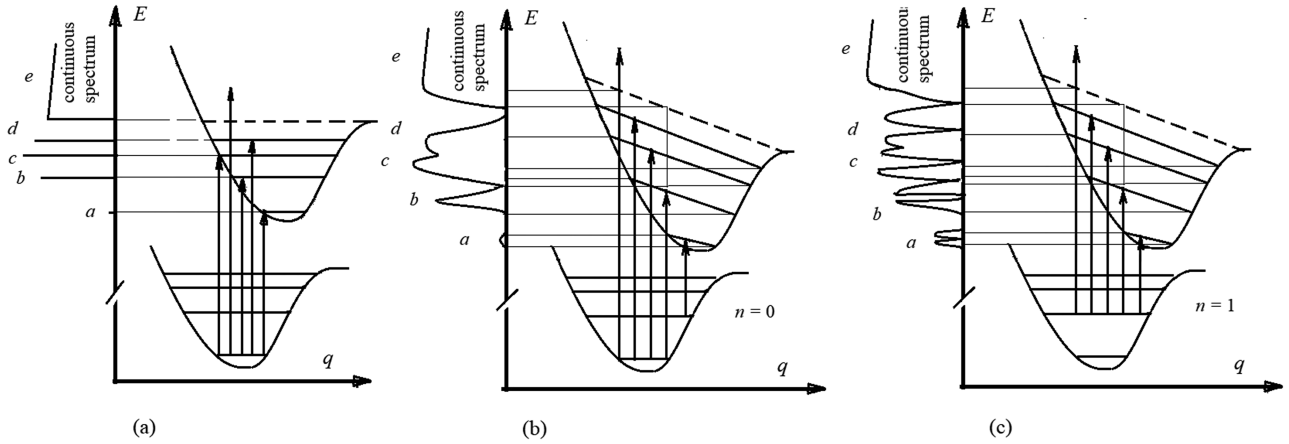

FIG. 4. (a) Generally accepted diagram of Franck–Condon vertical vibronic transitions with horizontal energy levels. [(b) and (c)] The modified Franck–Condon diagram where electron–vibrational levels are pictured by slanting lines due to their energy dependence on Δq by Eq. (57). The vertical transition of a discrete spectrum forms non-broadened bands in a conventional diagram (a); the broadened lines of a discrete spectrum arise in (b) and (c). Therefore, the squared nuclear wave function $\xi(\Delta q)$ [with a quantum index $n = 0$ in the case of (b) and $n = 1$ in the case of (c)] of the vibrational level of the initial vibronic state adiabatically *profiles* the spectral shape of the broadened vibronic line.

$$F(\omega) = \left[\xi_n\left(\frac{\alpha-\omega}{\beta}\right)\right]^2 \frac{1}{\beta}, \tag{59}$$

$$I_{un'gn}(\omega) = n_e \frac{2m_e\omega}{3e^2\hbar\beta} M^2_{un'gn}\left[\xi_n\left(\frac{\alpha-\omega}{\beta}\right)\right]^2. \tag{60}$$

The spectral intensity of the transition in linear approximation Equation. (57) can be rewritten as

$$I_{un'gn}(\omega) = \frac{n_e m_e \omega M^2_{un'gn}}{3\cdot 2^{n-1} n!\sqrt{\pi} e^2\hbar\beta r_0} \exp\left[-\left(\frac{\alpha-\omega}{\beta r_0}\right)^2\right] \times H_n^2\left(\frac{\alpha-\omega}{\beta r_0}\right). \tag{61}$$

For the (0-0) transition, Eq. (51) gives

$$I_{u0g0}(\omega) = \frac{2n_e m_e \omega M^2_{u0g0}}{3\sqrt{\pi} e^2\hbar\beta r_0} \exp\left[-\left(\frac{\alpha-\omega}{\beta r_0}\right)^2\right]. \tag{62}$$

Zero-point oscillations of nuclei in the ground vibrational state described by the Gaussian-like eigenfunction determine the Gaussian-like profile (corresponding to the squared eigenfunction of the initial vibrational state) of the electronic energy of (0-0) transition. In general, the shape of the vibronic band is formed by "reflection" of the squared vibrational wavefunction of the initial state in the profile of probability-density distribution of transition energy.

Parametrical dependence of vibronic transition energy on nuclear coordinate shift Δq leads to slanting vibrational levels in the FC diagram (Fig. 3).

The FC diagrams with slanting levels in linear approximation Equation. (57) are shown in Fig. 4.

III. CALCULATIONS

Let us estimate the characteristic magnitude of broadening of the vibronic transition due to quantum uncertainty of the values of nuclear coordinates by considering the simplified case: linear polymethine dye with an extended π-electron system. Experimental optical spectra of a series of symmetrical polymethine dyes [Fig. 5(a)] derived from benzothiazole are presented in Ref. 29.

The specificity of an extended π-electron system lies in the fact that the energy and electric dipole-moment of any electronic transition strongly depend on the instantaneous characteristic length of the π-electron transition L [Fig. 5(a)]. This length is strongly determined by instantaneous values of oscillating coordinates q of the nuclei [Fig. 5(b)]. These nuclear vibrations have very slow velocity in contrast to very fast optical electronic transition so that L can be considered a time dependent parameter of the vibronic frequency $\omega_{ug} = \omega_{ug}(L(t))$. Therefore, this vibronic system can be considered in the framework of the theory of adiabatic invariants with parameter L (Ref. 30).

Consider a simple model of free electrons derived by Kuhn for polymethine dyes (Refs. 31 and 32), Fig. 5(a). The vibrational structure of the electronic spectra of these molecules is very weakly resolved at room temperature due to considerable broadening. A characteristic feature of the vibrational structure is the main contribution of only one normal vibration to the electronic–vibrational spectrum (Ref. 1).

In Kuhn's model, the length of π-electron transition L is the length of the chain between nitrogen atoms plus one bond distance on each side, i.e., $L \propto 2(j+3)a$, where a is the bond length between atoms along the chain and j is the number of inserted links [Fig. 5(a)]. Due to the easily polarizable benzene nuclei at both ends of the polymethine chain, the potential energy of the π-electrons increases less rapidly at the ends of the chain than when the nuclei are absent. We take this into account by increasing the length L by a

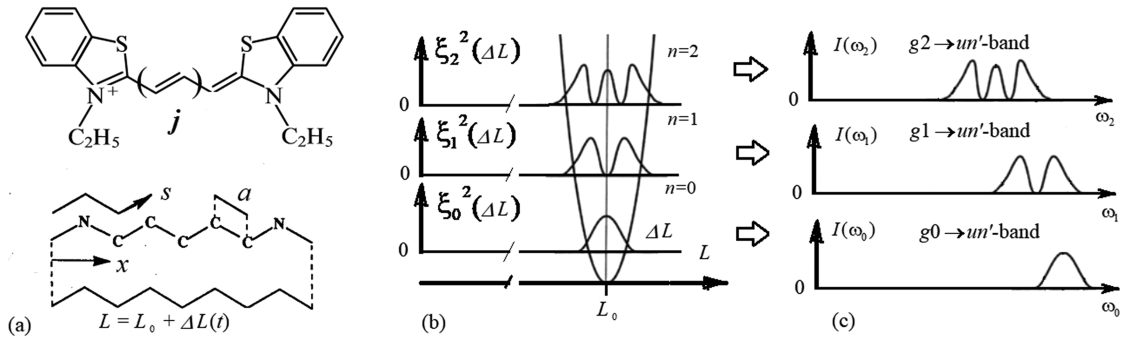

FIG. 5. (a) Structure of a series of symmetrical polymethine dyes (top); the scheme of the π-electron chain of the polymethine chromophore in the free-electron model (bottom). (b) Probability-density distribution $\xi_n^2(\Delta L)$ of characteristic length L of the linear quantum harmonic oscillator around its middle position L_0 with deviations $|\Delta L| \ll L_0$ for different numbers of vibration quanta n, where $\xi_n(\Delta L)$ is the oscillator eigenfunction and q is the nuclear coordinate. (c) Intensities of vibronic adsorption lines $I(\omega_n)$ modulated by adiabatic variations of oscillator length L, with a probability-density distribution $\xi_i^2(\Delta L)$; $gn \to un'$ (where $n = 0, 1, 2, \ldots$) denote the electronic-vibrational transitions from the ground level $|n\rangle \equiv \xi_g(\Delta L)$ to an excited level $|n'\rangle \equiv \xi_u(\Delta L)$.

constant amount $\frac{2}{3}a$ (Ref. 31), i.e.,

$$L = 2\left(j + 3 + \frac{1}{3}\right)a. \tag{63}$$

Each carbon atom in the chain contributes one π-electron, and the two nitrogen atoms together contribute three. Thus, the number of π-electrons on the length L is $N = 2(j + 3)$.

The wave functions of an electron in the ground state (the highest occupied molecular orbital, HOMO) are given by

$$\psi_g = \sqrt{\frac{2}{L}}\sin\left(\pi\frac{j+3}{L}s\right), \tag{64}$$

and the lowest unoccupied molecular orbital (LUMO) or wave function of the excited state is

$$\psi_u = \sqrt{\frac{2}{L}}\sin\left(\pi\frac{j+4}{L}s\right), \tag{65}$$

where s is the coordinate along the internuclear bonds in the chromophore [Fig. 5(a)].

The excitation energy, frequency, and wavelength of absorption, respectively, are

$$\Delta E(L) = \frac{\pi^2\hbar^2(2j+7)}{2L^2m_e}, \tag{66}$$

$$\omega(L) = \frac{\pi^2\hbar(2j+7)}{2L^2m_e}, \tag{67}$$

$$\lambda(L) = \frac{2\pi c}{\omega} = \frac{4m_ecL^2}{\pi\hbar(2j+7)}, \tag{68}$$

$$M(L) \approx \mu(L)\left|\langle n|n'\rangle\right|, \tag{69}$$

$$\mu(L) = L^2\int_0^1 \psi_g ex\cdot\cos(30^\circ)\psi_u dx, \tag{69}$$

where c is the speed of light, $x = sL^{-1}$, and $x \cdot \cos(30^\circ)$ is the direction of the long axis of the molecule [Fig. 5(a)]. The oscillator strength is

$$f = 2\frac{2m_e\Delta E(L)}{3e^2\hbar^2}M^2(L). \tag{70}$$

Using Kuhn's model, $n_e = 2$ [in Eq. (70)] because two electrons contribute to the transition. Hence,

$$f = \pi^2(2j+7)\left|\langle n|n'\rangle\right|^2\left[\int_0^1 \sin(\pi(j+3)x)\sin(\pi(j+4)x)xdx\right]^2. \tag{71}$$

The vibrational frequency of the sesquialteral C–C bond is approximately $\frac{\Omega}{2\pi c} \propto 1000\ \mathrm{cm}^{-1}$ because, in normal conditions, i.e., $\hbar\Omega \gg k_BT$, practically, only zero-point oscillation ($n = 0$) is realized; this is because the contributions of $n = 1$ and the higher non-zero vibrational modes have very small amplitudes because of the Planck distribution.

The vibronic transition from the vibrational level $n = 0$ of the ground state to $n' = 0$ of an excited level most probably generates an absorption band in such a system because the Franck–Condon factor in Eq. (71) has a maximum value, i.e., $|\langle 0|0\rangle|^2 = 1$ [Fig. 6(a)].

Note that in the case of high temperature, the 1–0 transition with the double-hunted form of band broadening, corresponding to the first excited state of the harmonic oscillator wave function, can also appear [Fig. 6(b)].

Let us estimate the broadening of the (0-0) transition spectrum in the simplest linear approximation by Eq. (62).

The bond length between atoms along the chain can be written in the form

$$a = a_0 + \Delta a, \tag{72}$$

where a_0 is the average value of the sesquialteral bond length in the polymethine chain (C–C or C–N bonds), where $a_0 \approx 1.40\mathring{A}$ is the mean length of the sesquialteral C–C bond. The radius of the oscillator of one link of the polymethine chain, r_0, can be estimated by averaging the oscillation amplitude of the C–C bond in benzene: $r_0 \approx 0.046\mathring{A}$ (Ref. 33). To derive the effective oscillator radius of all

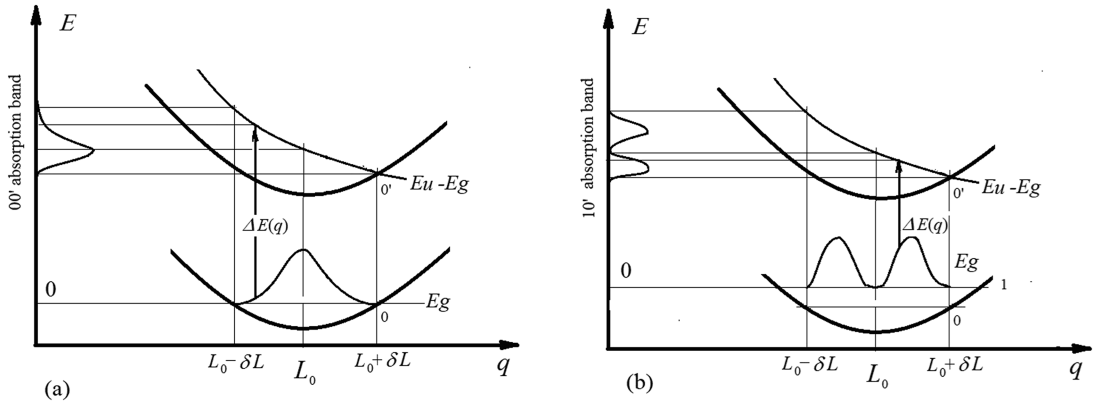

FIG. 6. Nature of the band broadening of electronic–vibrational transitions in an extended π-electron system due to the dependence of vertical-transition energy ΔE on the instantaneous length, L, of a nuclei chain; there is a restricted continuum band linked to the energy interval $E(L_0 + \delta L)$ to $E(L_0 - \delta L)$. The length L has a continuous interval of values between the turning points of the oscillator in the ground (*Eg*) state. (a) The graph describes the 0-0' transition; (b) The graph describes the 1–0' transition. The vibronic lines are adiabatically broadened, taking the shape of their initial (ground) vibrational levels.

chains, one can use the rough approximation of independent oscillators [analogous to the Einstein independent oscillator approach for solids, (Ref. 34)]. We use the representation $\Delta q = \Delta a$ in Eq. (55).

In the framework of approximation of independent oscillators, the probability that all $N = 2(j + 3)$ bonds of the chain have a given oscillator phase Δa is proportional to $\left[\exp\left(-r_0^{-2}\Delta a^2\right)\right]^{2(j+3)} = \exp\left(-2(j + 3)r_0^{-2}\Delta a^2\right)$.

Therefore, the effective oscillator radius of the chain is

$$R_0 = \frac{r_0}{\sqrt{2(j + 3)}}. \tag{73}$$

On the basis of dependence of ω on $\Delta q = \Delta a$, one can derive from Eq. (67) taking into account Eqs. (63) and (72) that

$$\omega = \frac{\pi^2\hbar(2j + 7)}{8(j + 3 + 13)^2 a^2 m_e} \approx \frac{\pi^2\hbar(2j + 7)}{8(j + 3 + 13)^2 a_0{}^2 m_e}\left(1 - 2\frac{\Delta a}{a_0}\right). \tag{74}$$

Under the assumption that the spectrum is narrow and close to the delta function [Eq. (9)], the intensity differs significantly from zero only in the region of the maximum frequency. Therefore, to determine the maximum frequency and broadening, it suffices to consider the properties of the exponential factor in intensity distribution Equation (62), $\exp\left[-\left(\frac{\alpha-\omega}{\beta R_0}\right)^2\right]$, where coefficients α and β can be obtained taking into account Eq. (74),

$$\alpha = \frac{\pi^2\hbar(2j + 7)}{8(j + 3 + 13)^2 a_0{}^2 m_e}, \quad \beta = \frac{2\alpha}{a_0}. \tag{75}$$

The frequency and wavelength at the maximum of spectral intensity are given by $\omega_m = \alpha$,

$$\omega_m = \frac{\pi^2\hbar(2j + 7)}{8(j + 3 + 13)^2 a_0^2 m_e}, \tag{76}$$

$$\lambda_m = \frac{16(j + 3 + \frac{1}{3})^2 c a_0^2 m_e}{\pi\hbar(2j + 7)}. \tag{77}$$

The half-width at half-maximum of $I(\omega)$ is

$$\delta\omega_{1/2} = \beta R_0\sqrt{\ln 2} = \frac{r_0\sqrt{2\ln 2}}{a_0\sqrt{j + 3}}\omega_m, \tag{78}$$

$$\delta\lambda_{1/2} = \beta R_0\sqrt{\ln 2} = \frac{r_0\sqrt{2\ln 2}}{a_0\sqrt{j + 3}}\lambda_m. \tag{79}$$

Table I shows the theoretical estimations and experimental magnitudes of broadening $\delta\lambda_{1/2}$ of (0-0) transition due to zero-point oscillations in a polymethine chain of a series of symmetrical polymethine dyes [see Fig. 5(a)], with $j = 0, 1, 2, 3$.

The calculated magnitude of the broadening is approximately two times smaller than the bandwidth observed in the experiment, but it has the same order of magnitude. This indicates the essential role of the parametric broadening of vibronic transitions due to zero-point oscillations and thermal fluctuations in the formation of the observed bandwidth of the vibronic spectrum in molecules. It was demonstrated that an organic chromophore with an extended π-electron system can be considered to be a molecular optical parametric oscillator.

TABLE I. Wavelengths λ_m calculated from Eq. (77) and broadening $\delta\lambda_{1/2}$ from Eq. (79), with corresponding experimental values λ_m[exp.] and $\delta\lambda$[exp.] obtained by Brooker *et al.* (Ref. 18) for a series of symmetrical polymethine dyes [see Fig. 5(a)], with j = 0,1,2,3, dissolved in liquid methanol; f is the oscillator strength of (0-0) transition derived from Eq. (71).

j	λ_m, (Å)	λ_m[exp], (Å)	$\delta\lambda_{1/2}$, (Å)	$\delta\lambda$[exp], (Å)	f
0	4100	4230	91	200	0.68
1	5389	5575	104	200	0.89
2	6680	6500	116	210	1.10
3	7970	7580	126	250	1.30

IV. CONCLUSIONS

The shape of rovibronic absorption and the emission bands are determined not only by the statistical distribution of the ensemble of molecules in the solution over their energy levels (inhomogeneous broadening) but also by the fact that each individual rovibronic transition of each molecule has its own wide spectrum due to zero-point oscillations and thermal fluctuations. In this work, for the first time, it was shown theoretically that although the magnitude of the broadening of the individual rovibronic transition energy spectrum in the molecule is smaller than a rovibronic bandwidth, it has the same order of magnitude.

Notwithstanding, until now, it was conventionally assumed that the homogeneous broadening is several orders of magnitude less than the inhomogeneous one. Numerous computations of the spectra of the molecules are performed by special methods (by Lax and Kubo *et al.*) for smoothing a series of individual transitions represented by delta functions. All these methods have one thing in common. Such methods smooth out the quasi-continuum of closely spaced vibronic transitions, approximately calculating the common envelope of all vibronic transitions, and thus form a continuous spectral band. They do not work with the broadening of single rovibronic transition.

In the framework of harmonic approximation of the potential energy surfaces, the new theory is proposed here describes the optical spectrum broadening of any single rovibronic transition due to zero-point oscillations and thermal fluctuations around equilibrium positions. Franck–Condon diagrams with slanting equidistant vibrational levels are proposed to consider this effect. Expressions of the spectral intensity of a single vibronic transition are derived from first principles. The magnitude of the broadening effect of this type is estimated using the example of linear polymethine dyes. The calculation showed that the quantum uncertainty of nuclear positions leads to a broadening of the vibronic spectrum with a magnitude that is comparable to the experimentally observed linewidth. This effect cannot be neglected in the optical spectra of any types of molecules, not only in the chromophores with an extended π-electron system, because it has fundamental origin associated with quantum uncertainty of nuclear coordinates.

For the first time, we show that an organic chromophore with an extended π-electron system can be considered as a molecular optical parametric oscillator in the framework of adiabatic invariant theory. This effect can be used in molecular electronics and optical chemosensorics to determine the properties of surrounding media by analyzing the shape of the vibronic spectral lines of fluorescent molecular probes with an extended π-electron system.

Further development of the proposed general method can be associated with the use of quantum-chemical approaches to calculate the vibrational and rotational frequencies and the multidimensional PES corresponding to all significant degrees of freedom. On the other hand, solid-state physics methods can also be used to determine the phonon spectrum in a large molecule. The separation of collective phonon vibrational modes in large molecules and determination of the occupation number of phonons corresponding to the vibrational and torsion degrees of freedom in the molecule are associated with the methods of secondary quantization of an elastic solid system.

In this paper, it was also shown that an organic chromophore with an extended π-electron system can be considered to be a molecular optical parametric oscillator in the framework of adiabatic invariant theory.

Special techniques associated with fixing the internal vibrational and rotational degrees of freedom of the molecules by embedding them into a transparent solid matrix or by laser excitation of their chromophores in a very short optical waveband allow the narrowing of these spectral lines (Refs. 35 and 36). It is clear that these experimental results can be described in the framework of the proposed approach. There is reduction of vibrational oscillating motion amplitudes of the atoms in the chromophore by their interaction with the environment, so the characteristic transition length L and, consequently, the linewidth reduce too.

These effects can be used in molecular electronics and optical chemosensorics to determine the properties of surrounding media by analyzing the shape of the vibronic spectral lines of fluorescent molecular probes with an extended π-electron system.

ACKNOWLEDGMENTS

This work is dedicated to the respectful memory of Professor Samuil Akivovich Rybak (1931–2013) who drew my attention to the importance of adiabatic invariant theory in various fields of theoretical physics. The work was supported by the Ministry of Science and Higher Education within the State assignment FSRC ≪Crystallography and Photonics≫ RAS, the "Improving of the competitiveness" program of the National Research Nuclear University MEPhI, and the Russian Foundation for Basic Research, Grant No. 19-02-00937.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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