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FEATURES OF THE ELECTRONIC STRUCTURE OF EXCITED QUADRUPOLAR MOLECULES IN NON-POLAR SOLVENTS [1]

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Abstract. Interactions of the electronic subsystem of the quadrupolar fluorophore with intramolecular high-frequency antisymmetric vibrations and solvent polarization are responsible for charge transfer symmetry breaking (SB), which is observed after optical excitation of such molecules in polar solvents. It is known that although these two interactions are mathematically described in similar ways, only the interaction of the fluorophore with solvent orientational polarization can create a state with broken symmetry if this interaction is strong enough. Nevertheless, the interaction of a quadrupolar fluorophore with intramolecular high-frequency antisymmetric vibrations in non-polar solvents leads to a considerable reconstruction of the electronic subsystem. The analysis of the excited state of quadrupolar molecules in non-polar solvents performed in this study reveals that such molecules can behave like quantum two-state systems, that is, as a quasi-spin $s = 1/2$, having an electric dipole moment instead of a magnetic one. This feature of excited quadrupolar molecules may be of interest to emerging technologies of molecular electronics.

Key words: dissymmetry parameter, electronic-vibrational interaction, symmetric donor-acceptor triad, electron transfer, molecules.

Introduction

Excited quadrupolar molecules with structures of the ADA or DAD type with identical electron donor (D) and acceptor (A) fragments can undergo nonequivalent charge transfer from the central fragment to the equivalent peripheral fragments, which results in symmetry breaking (SB) [4–6; 8; 16–19; 32; 35; 43; 48; 59; 61; 65]. Such molecular structures have a large two-photon absorption cross section, which attracts the attention of many researchers [1; 7; 15; 21; 41; 42; 45; 47; 60]. The absence of a dipole moment in the ground state and its appearance in an excited state due to SB is confirmed by observations that the solvent polarity weakly affects the electronic absorption spectra and strongly affects the fluorescence spectra [2; 13–15; 28; 30; 33; 36; 42; 44; 45; 50–55; 61–64]. The use of time-resolved femtosecond infrared spectroscopy has provided direct observation of SB in excited quadrupolar molecules [9–12; 46], This technique allows monitoring the spectra of localized stretching vibrations such as $-C{\equiv}N$ or $-C{\equiv}C-$ groups symmetrically located on both sides of quadrupolar molecules. According to the selection rules, only the absorption band of antisymmetric vibrations can be observed in the IR spectra of a quadrupolar molecules, while SB creates a new absorption band stemming from the mixing symmetric and antisymmetric vibrations.

The first theoretical model of SB was developed for molecular dyads such as the 9,9′-bianthryl [27; 57; 58] previously studied by the Mataga group.[37] These works assumed existence of the states with broken symmetry as an experimental fact and did not disclose the mechanism of SB, which was proposed and verified later in Ref 53. SB was explained in terms of the model of essential states, which includes the ground and two excited states of the quadrupolar molecule. In this model, the interaction of antisymmetric vibrations and solvent polarization with the electronic subsystem of the molecule induces SB. The model describes not only the SB phenomenon, but also one- and two-photon optic spectra of chromophores [20; 49; 50; 53–55]. Later, the essential state model was reduced to the two-level model [23] and its scope was determined [25]. The two-level model has a simple analytical solution for stationary electronic states, which quantitatively determines the degree of SB with one dimensionless parameter. Within the framework of this model, the effect of SB on vibrational spectra was studied and the possibility of the model to quantitatively describe the experimental data was shown [22; 24; 25; 38; 40; 56].

Experiments show that the dielectric properties of the solvent, in particular polarity, play a primary role in SB [9–11; 46]. It is usual practice to divide the total polarization of the solvent into fast electronic and slower rotational ones. Since the time scales of electronic motions in solute and solvent molecules are close to each other, these motions should be considered self-consistently [26; 29]. The self-consistency leads to nonlinear theory [29]. Note that in standard electron transfer theory, orientational polarization is responsible for the formation of the activation barrier and thus controls the kinetics of the reaction [34].

In this work, we explore the effect of the interaction of intramolecular high-frequency antisymmetric vibrations with the electronic subsystem of an excited quadrupolar molecule immersed in a non-polar solvent on the charge distribution. In this case, the interaction of the molecule with the low-frequency solvent fluctuations is minor and in the first approximation can be ignored. As a result, charge transfer symmetry breaking is impossible in non-polar solvents [3]. Although symmetry breaking in an excited quadrupole molecule does not occur in non-polar solvents and its average dipole moment is zero, the electronic-vibrational interaction with antisymmetric high-frequency vibrations has a strong effect on the state of the electronic subsystem. It is shown that the excited state of a molecule is a quantum superposition of two states with opposite dipole moments. In this case, the uncertainty of each dipole moment can be very small, and the behavior of the excited molecule is similar to the quasi spin $s = 1/2$ with an electric dipole moment.

1. Theoretical Methods

In this section we briefly describe the two-state model of charge transfer SB in excited quadrupolar molecules.[23; 39] The model operates only with two lowest excited electronic states. In what follows, only the molecules of the ADA structure are discussed, although the model is applicable to the DAD structures as well. The scheme of the electronic terms of a quadrupolar molecule are pictured in Figure 1.

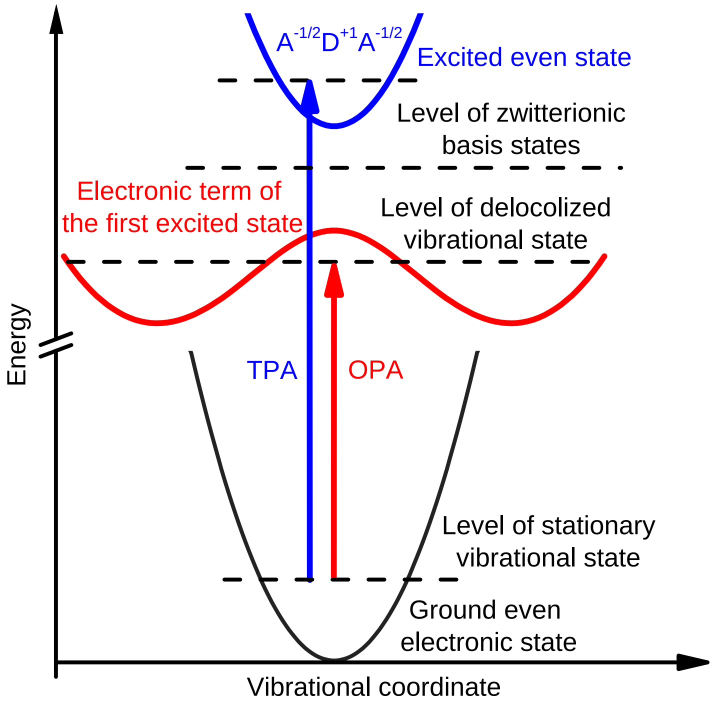

Fig. 1. Energy-level scheme of quadrupolar A-π-D-π-A or D-π-A-π-D molecules. TPA and OPA are the abbreviations of the terms two- and one-photon absorption, respectively

The two-state model is limited to considering only the states $|\varphi_{L,R}\rangle$, with the localization of the positive charge on the donor and the localization of the total negative charge on the left or right acceptor. The model is applicable if the energy gap between the first and ground states is much larger than between the second and first excited states.[25] Within the framework of this approach, the state vector of an arbitrary excited state of a quadrupolar molecule is a linear combination of these two states:

$$|\Psi\rangle = a_{\mathrm{L}}|\varphi_{\mathrm{L}}\rangle + a_{\mathrm{R}}|\varphi_{\mathrm{R}}\rangle, \tag{1}$$

where the normalized amplitudes $a_{\mathrm{L,R}}$ ($a_{\mathrm{L}}^2 + a_{\mathrm{R}}^2 = 1$) specify the acceptor charges $\delta_{\mathrm{L,R}} = a_{\mathrm{L,R}}^2 e$, e is the electron charge. The dissymmetry parameter, D, is a quantitative measure of SB

$$D = a_{\mathrm{L}}^2 - a_{\mathrm{R}}^2. \tag{2}$$

The Hamiltonian of the two-state model, which includes intramolecular electronic-vibrational interaction and the interaction of the solute with the solvent, has the form[22; 39]

$$H = H_{\mathrm{M}} + H_{\mathrm{s}}, \tag{3}$$

where

$$H_{\mathrm{M}} = H_{\mathrm{M0}} + U_{\mathrm{c}} + H_{\mathrm{v0}} + U_{\mathrm{int}} \tag{4}$$

is the Hamiltonian of the solute in vacuum and H_{s} is the Hamiltonian of the solvent and its interaction with the solute. H_{M0} is given by Eq. (5)

$$H_{\mathrm{M0}} = \begin{pmatrix} 0 & V \\ V & 0 \end{pmatrix}. \tag{5}$$

Here, the electronic coupling V is equal to half the splitting between the two- and one-photon absorption bands (see Fig. 1). The functional corresponding to this Hamiltonian with an arbitrary state vector $|\Psi\rangle$ is

$$\langle\Psi|H_{\mathrm{M0}}|\Psi\rangle = 2Va_{\mathrm{L}}a_{\mathrm{R}} = \pm V\sqrt{1-D^2}. \tag{6}$$

The operator of the Coulomb interactions between the charges on the acceptors U_{c} creates the Coulomb interaction functional [22]

$$\langle\Psi|U_{\mathrm{c}}|\Psi\rangle = -\gamma_{\mathrm{C}}D^2/2,\ \gamma_{\mathrm{C}} = \frac{e^2}{2\varepsilon_{\mathrm{im}}R_{\mathrm{LR}}}, \tag{7}$$

where R_{LR} is the distance between the centres of the charges on the acceptors, and $\varepsilon_{\mathrm{im}}$ is the "intramolecular" dielectric constant. H_{v0} and U_{int} are the Hamiltonian of intramolecular vibrations and the operator of electron-vibration interactions, respectively. They are given by Eqs. (8)–(10) [22; 39]

$$\langle\Psi|H_{\mathrm{v0}}|\Psi\rangle = \frac{1}{2}\sum_i\left[\frac{p_{\mathrm{s}i}^2}{m_{\mathrm{s}i}} + m_{\mathrm{s}i}\omega_{\mathrm{s}i}^2x_{\mathrm{s}i}^2\right] + \frac{1}{2}\sum_j\left[\frac{p_{\mathrm{a}j}^2}{m_{\mathrm{a}i}} + m_{\mathrm{a}i}\omega_{\mathrm{a}j}^2x_{\mathrm{a}j}^2\right], \tag{8}$$

$$\langle\Psi|U_{\mathrm{int}}|\Psi\rangle = U_{\mathrm{int}}^{(1)} + U_{\mathrm{int}}^{(2)}, \tag{9}$$

$$\langle\Psi|U_{\mathrm{int}}^{(1)}|\Psi\rangle = D\sum_j\zeta_jx_{\mathrm{a}j}, \tag{10}$$

where $x_{\mathrm{s}i}$, $x_{\mathrm{a}j}$, $p_{\mathrm{s}i}$, $p_{\mathrm{a}j}$, $\omega_{\mathrm{s}i}$, $\omega_{\mathrm{a}j}$, $m_{\mathrm{s}i}$, $m_{\mathrm{a}i}$ are the coordinates, the momenta, the frequencies, and effective masses of the symmetric and antisymmetric vibrational modes, respectively.

Here $U_{\text{int}}^{(1)}$ is the operator of linear electronic-vibrational interaction, the magnitude of which is specified by the parameter ζ_j, $U_{\text{int}}^{(2)}$ is also the operator of the electronic-vibrational interaction, but quadratic in vibrational coordinates. It describes the change in vibration frequencies and the Duschinsky effect in the SB process. Since the available experimental data on time-resolved IR spectroscopy show that the variations in the vibration frequencies of real molecules in the SB process are rather small,[9–11; 46] we neglect the influence of the quadratic interactions $U_{\text{int}}^{(2)}$ on the SB extent and omit this term in the total Hamiltonian Eq. (3). It is useful to introduce the reorganization energy of intramolecular vibrational modes $E_{\text{rv}}^{(D)}$, which is the difference between the potential energies of molecular vibrations in the electronic states with the dissymmetry parameter $D = 0$ and D

$$E_{\text{rv}}^{(D)} = \lambda_{\text{v}} D^2/2,\ \lambda_{\text{v}} = \sum_j \frac{\zeta_j^2}{m_{\text{a}i}\omega_{\text{a}j}^2}. \tag{11}$$

This quantity is similar to that which is well known in molecular spectroscopy and the standard theory of electron transfer, where it is one of the key parameters.

The free energy functional of the solvent and its interaction with the solute, $\langle\Psi|H_{\text{s}}|\Psi\rangle$, can be written as follows[39]

$$\langle\Psi|H_{\text{s}}|\Psi\rangle = -\lambda_{\text{el}} D^2/2 - \lambda_{\text{or}} D D_{\text{m}} + \frac{\lambda_{\text{or}} D_{\text{m}}^2}{2}, \tag{12}$$

where D_{m} is the dimensionless solvent reaction coordinate, $\lambda_{\text{el}} = \mu_0^2 f_{\text{el}}/r_{\text{d}}^3$, $f_{\text{el}} = 2(n^2 - 1)/(2n^2+1)$ with n being the refractive index of the solvent, $\lambda_{\text{or}} = \mu_0^2 \Delta f/r_{\text{d}}^3$, $\Delta f = f_{\text{s}} - f_{\text{el}}$, $f_{\text{s}} = 2(\varepsilon_{\text{s}}-1)/(2\varepsilon_{\text{s}}+1)$, with ε_{s} being the static dielectric constant, r_{d} is the cavity radius, μ_0 is the dipole moment of the solute in a state with complete electron transfer from the donor to one of the acceptors ($D = 1$). The parameters λ_{el} and λ_{or} characterize the intensity of the interaction of the solute with the electronic and orientational polarization of the solvent, respectively.

In polar solvents, the interaction of the dipole moment of the solute with the orientational polarization of the solvent is strong, so that the relaxation of the orientational polarization of the solvent controls the SB dynamics [9; 11; 40]. In this case, the electronic and vibrational subsystems of the solute adiabatically follow slow variation of the solvent state, which is determined by a single quantity D_{m} [39]. In non-polar and weakly polar solvents, the interaction of the solute with orientational polarization is weak due to the small value of the parameter Δf. As a result, the slow polarization of the solvent cannot control the dynamics of the electronic subsystem of the solute. In this case the solute and solvent electronic degrees of freedom adiabatically follow variation of the intramolecular vibrations. Neglecting the interaction of the solute with the orientational polarization, the total energy functional is rewritten as follows

$$\langle\Psi|H|\Psi\rangle = -V\sqrt{1-D^2} - \frac{1}{2}\lambda_{\text{il}} D^2 + \frac{1}{2}\sum_j \left[\frac{p_{\text{a}j}^2}{m_{\text{a}j}} + m_{\text{a}j}\omega_{\text{a}j}^2 x_{\text{a}j}^2\right] + D\sum_j \zeta_j x_{\text{a}j}, \tag{13}$$

where $\lambda_{\text{il}} = \gamma_{\text{C}} + \lambda_{\text{el}}$. The operator of symmetric vibrations is omitted here, since they do not interact with the electronic subsystem and, therefore, do not affect SB. It should be emphasized that the interaction of the molecular dipole moment with the solvent polarization plays an important role even in non-polar solvents. This is manifested through the λ_{el} parameter in Eq. (13), which is typically not small.

In the further analysis, we restrict ourselves to the case of a single vibrational mode. Omitting the coordinate and momentum indices and introducing new operators Q and P

$$x = \sqrt{\frac{\hbar}{m\omega}}Q, \quad p = \sqrt{m\hbar\omega}P, \tag{14}$$

we obtain from Eq. (13)

$$\langle\Psi|H|\Psi\rangle = \frac{\hbar\omega}{2}P^2 + \overline{W}(D,Q), \tag{15}$$

where

$$\overline{W}(D,Q) = -V\sqrt{1-D^2} - \frac{1}{2}\lambda_{\mathrm{il}}D^2 + \frac{\hbar\omega}{2}Q^2 + \sqrt{\lambda_{\mathrm{v}}\hbar\omega}DQ. \tag{16}$$

The commutator of the operators P and Q is $[P,Q] = -i$. In the adiabatic approximation, the electronic subsystem is in a stationary state for any value of the vibrational coordinate, which means that the potential of the vibrational mode $W(Q)$ can be found by minimizing $\overline{W}(D,Q)$ with respect to the variable D for each value of Q, that is

$$W(Q) = \min_{D}\{\overline{W}(D,Q)\}. \tag{17}$$

The minimization procedure Eq. (17) establishes a one-to-one mapping of Q values to D values. That is, the mapping creates a function $D(Q)$ and an inverse function $Q(D)$.

The potential $W(Q)$ has a single minimum at $Q = 0$ if the electronic coupling is quite strong $V > \lambda_{\mathrm{il}} + \lambda_{\mathrm{v}}$. In the opposite case of a weak coupling $V < \lambda_{\mathrm{il}} + \lambda_{\mathrm{v}}$, the potential has two minima at the points

$$Q_{\min} = \pm\sqrt{\frac{\lambda_{\mathrm{v}}}{\hbar\omega}\left[1 - \frac{V^2}{(\lambda_{\mathrm{il}}+\lambda_{\mathrm{v}})^2}\right]}. \tag{18}$$

The value of the potential at the minimum points is

$$W(Q_{\min}) = -\frac{1}{2}\left[\lambda_{\mathrm{il}} + \lambda_{\mathrm{v}} + \frac{V^2}{(\lambda_{\mathrm{il}}+\lambda_{\mathrm{v}})}\right]. \tag{19}$$

Vibrational stationary states are solutions of the stationary Schrödinger equation

$$\left[\frac{\hbar\omega}{2}P^2 + W(Q)\right]\Phi_n(Q) = E_n\Phi_n(Q), \tag{20}$$

where the momentum operator is $P = -id/dQ$, n is the vibrational quantum number, and $\Phi_n(Q)$ and E_n are the stationary vibrational wave function and energy, correspondingly. The functions $\Phi_n(Q)$ are even or odd, because the potential energy $W(Q)$ is an even function of Q, which leads to the parity of the Hamiltonian.

2. Results and Discussion

First of all, we note that in a typical experiment, a molecule is excited by an optical pulse with a duration of about $\tau_e \simeq 40$ fs [9]. The homogeneous spectral width of such pulses, $\hbar/\tau_e$, is considerably less than the distance between stationary states of intramolecular vibrational modes. As a result, such pulses populate intramolecular stationary vibrational states. That is why we consider solutions of the equation Eq. (20) for a number of parameters covering a region that is interesting from an experimental point of view.

The model adopted here includes four independent parameters: the electronic coupling V, the vibrational frequency ω, the sum of the intramolecular Coulomb interaction and the interaction energy of the solute with the electronic solvent polarization λ_{il}, and the parameter of the electronic-vibrational interaction λ_v. The electronic coupling V determines the splitting of the lower excited even and odd states of the quadrupolar molecule. Thus, it can be reliably estimated from the distance between the maxima of the two- and one-photon absorption spectra. Such estimates give $V \simeq 0.2$ eV.[23; 40] We use this estimate in calculations as an invariable value of V. To select the range of variable parameters λ_{il} and λ_v, note that the potential $W(Q)$ has a single minimum if the inequality $V > \lambda_{il} + \lambda_v$ is met. In this case, SB is not possible. Thus, one should consider only parameters that satisfy the condition $\lambda_{il} + \lambda_v \geq V$. The results of calculations for $\hbar\omega = 0.2$ eV and $\hbar\omega = 0.05$ eV are pictured in Figs. 2 and 3, respectively, for a few combinations of the parameters λ_{il} and λ_v.

Fig. 2 shows several trends. The energy difference between the first excited and ground states, $E_1 - E_0$, is noticeably less $\hbar\omega$ and decreases with increasing the parameter $\lambda_{il} + \lambda_v$ (see Table 1). For example, for the parameters used in the construction of graphs in Frame D, the difference is halved, $E_1 - E_0 \simeq \hbar\omega/2$. The decrease is a direct consequence of the broadening of the potential well, $W(Q)$, caused by electronic-vibrational interaction. Although in the region $\lambda_{il} + \lambda_v \geq V$ the potential $W(Q)$ has two separated minima, the height and width of the barrier between the minima are quite small, which leads to the wave function of the ground state $\Phi_0(Q)$ with a single maximum located at the point $Q = 0$. It is also seen that the stationary level of the ground state E_0 is above the barrier for all selected sets of parameters. It should be emphasized that the magnitude of the parameter $\lambda_{il} + \lambda_v$ in real molecules can hardly exceed 0.4 eV, which is adopted here as its maximum value (see Frame D).

Table 1

Energy gap between the first and zero energy levels. $V = 0.2$ **eV**

		$\hbar\omega = 0.05$ eV	$\hbar\omega = 0.2$ eV
λ_{il}	λ_v	$(E_1 - E_0)/\hbar\omega$	$(E_1 - E_0)/\hbar\omega$
0.1	0.1	0.589	0.727
0.2	0.1	0.404	0.670
0.1	0.2	0.260	0.554
0.2	0.2	0.128	0.500

A decrease in the vibration frequency $\hbar\omega$ from 0.2 eV to 0.05 eV leads to significant changes in the potential $W(Q)$ shape (compare Figs. 2 and 3). The barrier between the two minima becomes much higher and wider. The ground state energy is now lower than

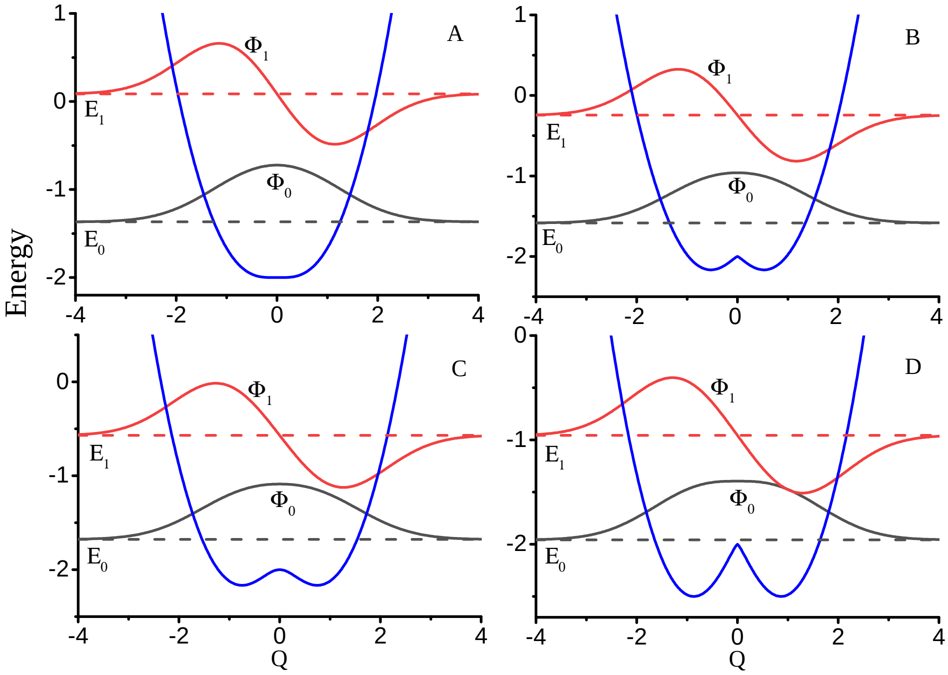

Fig. 2. The potential energies ($W(Q)$, blue lines) and stationary wave functions ($\Phi_0(Q)$ and $\Phi_1(Q)$, black and red lines, respectively) of a vibrational mode interacting with electronic subsystem. The energy levels of vibrational stationary states are pictured with dashed lines. Energy is indicated in units of $\hbar\omega/2$. The invariable parameters are: $V = 0.2$ eV, $\hbar\omega = 0.2$ eV. The variable parameters are: (A) $\lambda_{\text{il}} = 0.1$ eV, $\lambda_{\text{v}} = 0.1$ eV; (B) $\lambda_{\text{il}} = 0.2$ eV, $\lambda_{\text{v}} = 0.1$ eV; (C) $\lambda_{\text{il}} = 0.1$ eV, $\lambda_{\text{v}} = 0.2$ eV; (D) $\lambda_{\text{il}} = 0.2$ eV, $\lambda_{\text{v}} = 0.2$ eV

the barrier in Frames B, C, and D. This leads to a greater decrease in the excitation energy $E_1 - E_0$ in comparison with its value $\hbar\omega$ in the absence of electronic-vibrational interaction. Nevertheless, the changes in the shape of the vibrational wave functions of the ground and first excited states have mainly quantitative character. Only for the largest value of $\lambda_{\text{il}} + \lambda_{\text{v}} = 0.4$ eV (see Frame D in Fig. 2), the ground state wave function has a noticeable dip in the central region. Even so, the vibrations are far from being localized in one of the wells. To destroy the quantum coherence of vibrations and localize the vibrations in one well, an interaction of the vibrational mode with a bath having many degrees of freedom is required.[31] Moreover, the spectrum of the bath fluctuations should include low frequency modes extending to zero, and the density of these modes should not decrease very rapidly as the frequency approaches zero,[31] which means the presence of classical modes interacting with the molecule.

Now we can calculate the distribution over the dissymmetry parameter. Since there is a functional relationship between the quantities Q and D given by the minimization procedure Eq. (17), a normalized distribution of the systems with respect to the dissymmetry parameter in the stationary state $\Phi_n(Q)$ can be found as follows

$$P_n(D) = |\Phi_n(Q(D))|^2 \left[\frac{dQ(D)}{dD}\right]. \tag{21}$$

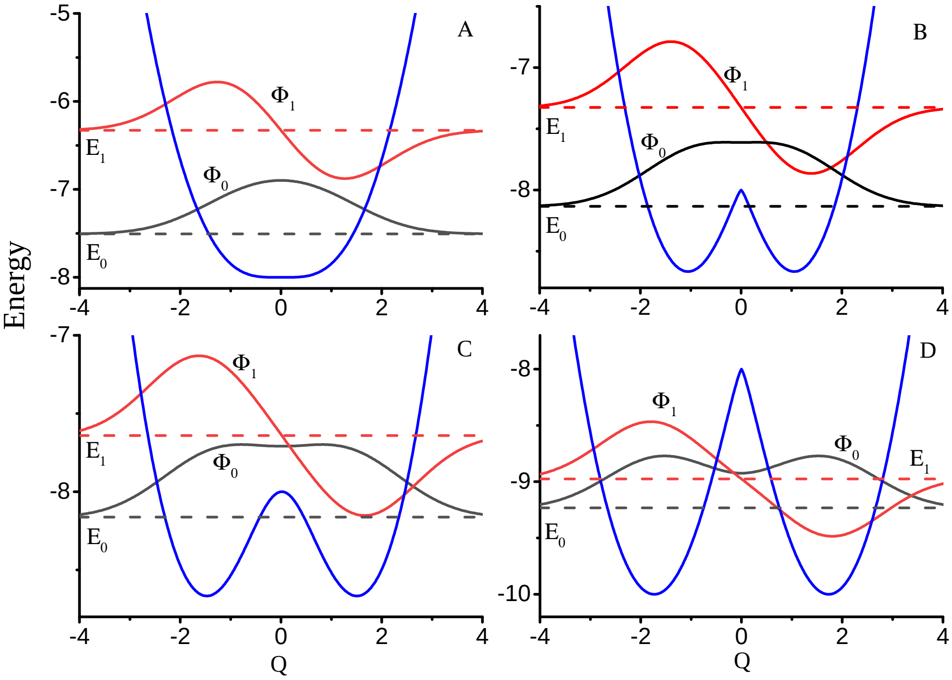

Fig. 3. The same as in Fig. 2, but $\hbar\omega = 0.05$ eV

This distribution is pictured in Fig. 4 for a few combinations of the parameters. In the range of strong electronic coupling $V > \lambda_{\rm il}$, the derivative $dQ(D)/dD$ has a minimum at the point $D = 0$. As a result, the distribution function in terms of D has a noticeable dip at $D = 0$ (see Frames A and B). For the electronic coupling $V = \lambda_{\rm il}$, the derivative $dQ(D)/dD = 0$ at the point $D = 0$ and is small enough around it, so that the distribution function turns to zero, $P(D = 0) = 0$ and the dip becomes wide (see Frames C and D). In the range of weak electronic coupling $V < \lambda_{\rm il}$, the function $Q(D)$ is equal to zero in the entire interval $-D_0 < D < D_0$, where

$$D_0 = \sqrt{1 - \frac{V^2}{\lambda_{\rm il}^2}}. \tag{22}$$

Thus, in this interval the function $P_0(D) = 0$ together with $dQ(D)/dD = 0$ (see Frames E and F). In Frame E, we see two branches of the function $P_0(D)$ in the regions $D < -D_0$ and $D > D_0$. So, in the range $V \le \lambda_{\rm il}$, the difference in distribution functions over Q and D becomes huge.

For a wide range of parameters, narrow distributions $P_0(D)$ have been obtained, localized in the vicinity of points $D = \pm\bar{D}$, where $\bar{D}$ is the position of the maximum of the right branch of $P_0(D)$ (see Frames C and E in Fig. 4). The distributions around $\bar{D}$ (the full width at half maximum) narrow further with increasing $\lambda_{\rm il}$ and decreasing electronic coupling V (see Fig. 5, which shows the distribution $P_0(D)$ for smaller V and a small set of the parameters $\lambda_{\rm il}$ and $\lambda_{\rm v}$). The electronic coupling V can be varied by adding or removing spacers between the donor and acceptor groups. The effect of variation of $\lambda_{\rm v}$ on the width is similar to that of $\lambda_{\rm il}$, but considerably weaker. With the invariable parameters $\lambda_{\rm il} > V$, $\lambda_{\rm v}$, and V the distributions are broader, the higher the vibrational frequency ω, although this

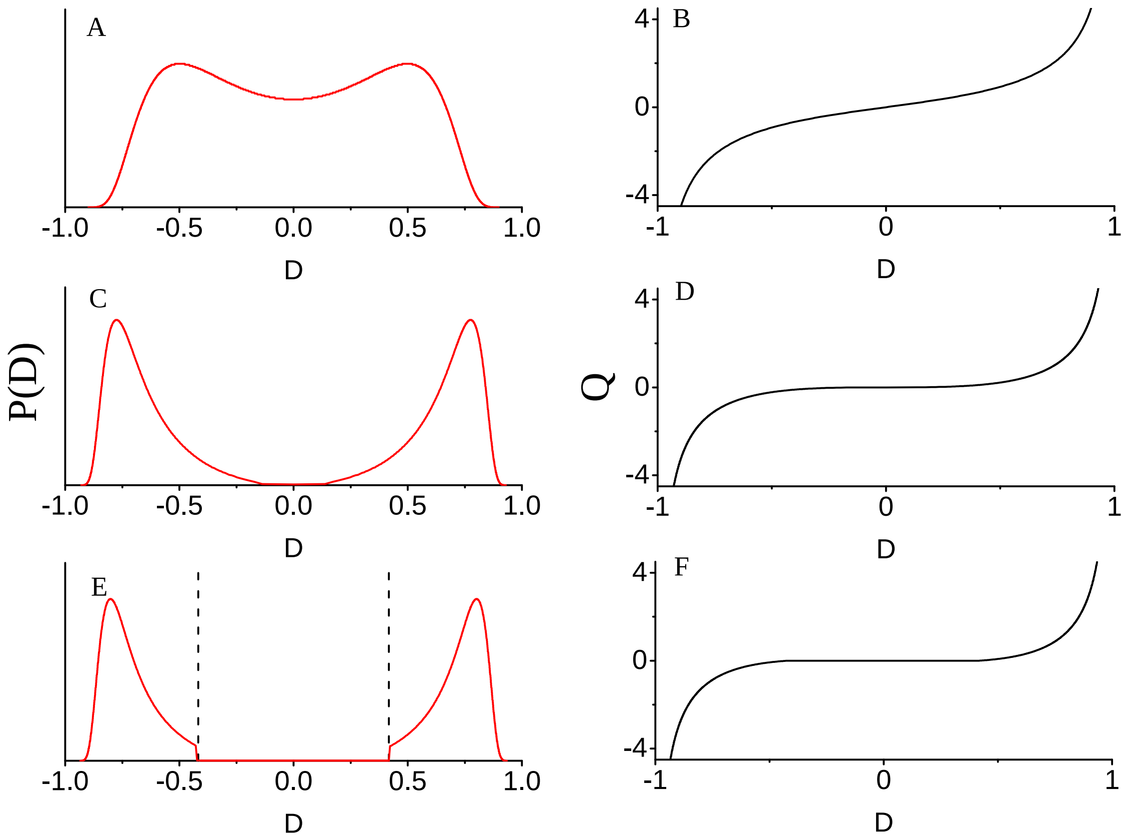

Fig. 4. Distribution functions with respect to the dissymmetry parameter $P_0(D)$ (left frames) and the dependence of the dissymmetry parameter D on the vibrational coordinate Q (right frames). The vertical dashed lines in Frame E represent asymptotes located at $D = \pm D_0$. The invariable parameters are $V = 0.2$ eV, $\hbar\omega = 0.05$ eV, and $\lambda_{\rm v} = 0.1$ eV. The variable parameters are: (Frames A and B) $\lambda_{\rm il} = 0.1$ eV; (C and D) $\lambda_{\rm il} = 0.2$ eV; (E and F) $\lambda_{\rm il} = 0.22$ eV

effect is quite small.

According to quantum mechanics, measurements of the dipole moment of molecules in the stationary state $\Phi_0(Q)$ should give values of $\mu = \pm\mu_0\bar{D}$ with rather low dispersion. What is especially important is the presence of the forbidden zone $-D_0 < D < D_0$ and the corresponding forbidden band gap of the dipole moment $-\mu_0 D_0 < \mu < \mu_0 D_0$. This means that an excited quadrupolar molecule can be treated as a quantum two-state system that behaves like a spin $s = 1/2$, having an electric dipole moment $\mu = \mu_0\bar{D}$ instead of a magnetic one. This may be of interest to emerging technologies of molecular electronics.

The dependence of the free energy on the solvent polarization coordinate in polar solvents $G(D_{\rm m})$ (see Ref. 39) and the dependence of the potential energy $W(Q)$ in non-polar solvents are very similar because they are obtained by minimizing the functions Eq. (16) and Eq. 45 in Ref. 39, which differ only in notations and, hence, are mathematically equivalent. Nevertheless, there is a fundamental distinction between them. The distinction is created by a huge difference in the characteristic frequency of fluctuations of the solvent orientational polarization and the frequency of intramolecular vibration. The characteristic frequency of the solvent fluctuations is $\omega_{\rm m} = 1/\tau_{\rm r}$, where $\tau_{\rm r}$ is the effective solvent relaxation time, which is about 1 ps. Thus, at room temperature, the inequality $\hbar\omega_{\rm m} \ll k_{\rm B}T$ holds, where

T is the temperature and k_{B} is the Boltzmann constant. The frequency of intramolecular vibrations satisfy the reverse inequality $\hbar\omega_{\mathrm{m}} \gg k_{\mathrm{B}}T$. These inequalities imply that the behavior of orientational polarization fluctuations is classical, and intramolecular vibrations is quantum. The distribution functions of particles over the vibrational coordinate Q and the solvent reaction coordinate D_{m}, and hence over the dissymmetry parameter D in non-polar ($P(D)$) and polar ($\rho_1(D,t)$ solvents, see Ref. 39) are also similar, but the meaning of these distributions is completely different. In polar solvents, the distribution of particles over the dissymmetry parameter is classical, that is, each particle has a certain value of the D parameter with a known probability. Although the average value of the dissymmetry parameter is zero,

$$\int_{-1}^{1} D\rho_1(D,t)dD = 0 \tag{23}$$

since $\rho_1(D,t)$ is an even function due to the initial inverse symmetry of the molecules, this only means that the dipole moment of the ensemble is zero, but each molecule has a nonzero dipole moment, hence is in a state with broken symmetry. In non-polar solvents, the distributions over the vibrational coordinate and the dissymmetry parameter are quantum. The probability density to find a molecule in state $\Phi_n(Q)$ with the vibrational coordinate Q and the dissymmetry parameter $D(Q)$ is equal to the probability density to find a molecule in the same state with the vibrational coordinate $-Q$ and $D(-Q) = -D(Q)$ due to the parity of the distribution $P_n(-D) = P_n(D)$. However, in this case, one and the same molecule has the values of the dissymmetry parameter D and $-D$ with the same probability density, so its average dipole moment is zero. This means that there is no SB.

Thus, it has been shown that the interaction of a quadrupole molecule with a polar solvent can lead to SB, but not with non-polar ones. Then the question arises, how strong the interaction with polar solvent must be in order to break the symmetry. The answer was obtained in the experiments, which demonstrated that SB can be observed in weakly polar and even quadrupolar solvents.[11] From theoretical point of view, the interaction should be so strong that the electronic subsystem of the molecule and, along with it, intramolecular vibrations adiabatically follow the solvent polarization fluctuations.

Conclusions

In this paper, it is shown that although the interactions of intramolecular high-frequency antisymmetric vibrations and solvent polarization with the electronic subsystem of a quadrupolar fluorophore are similarly described in current theories, their abilities to induce SB are different. The main difference lies in the disability of interaction with only intramolecular high-frequency vibrational modes for the induction of SB, whereas interaction only with the orientational solvent polarization can result in SB. This conclusion was drawn from general physical considerations[3] and is confirmed by experimental data, which do not show symmetry breaking in non-polar solvents regardless of their refractive index, although SB is observed in quadrupolar and dipolar solvents.[11]

Although the average dipole moment of a quadrupolar molecule in non-polar solvents is zero, its excited state is a quantum superposition of two states with large opposite dipole moments created by the electronic-vibrational interaction. Of course, these "hidden variables" can manifest themselves in interaction with an external electric field. When the uncertainty of each dipole moment is small, the excited molecule should behave like a quasi-particle with spin $s = 1/2$, which has a large electric dipole moment.

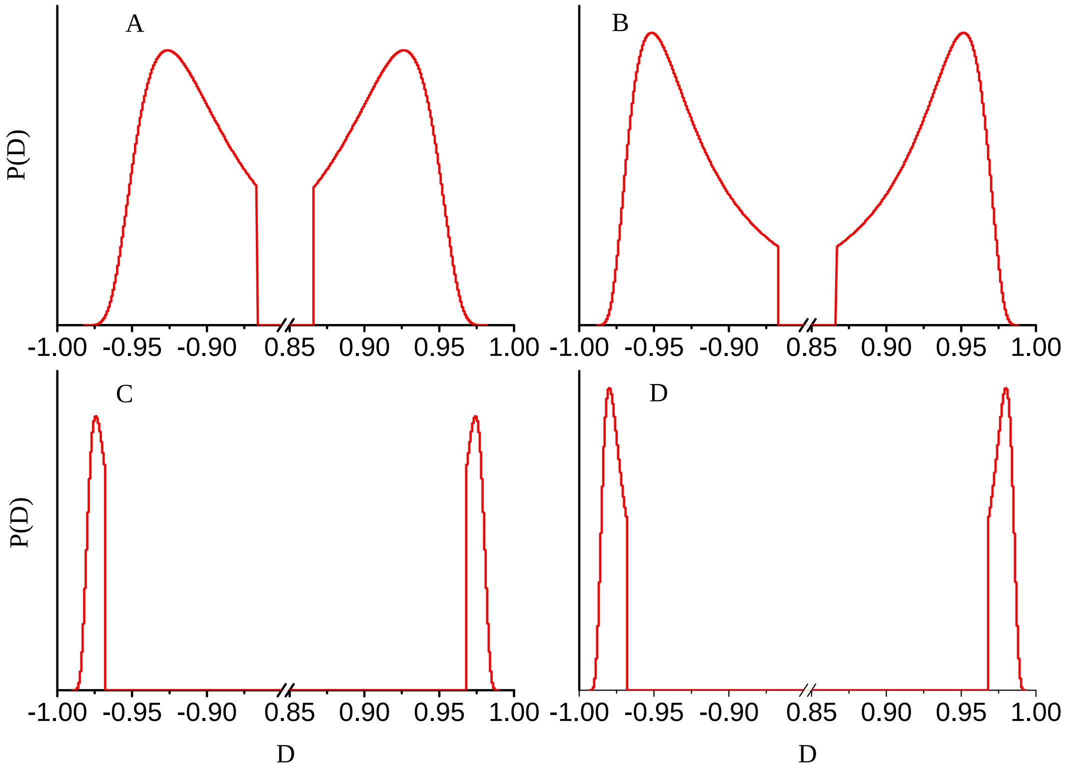

Fig. 5. Distribution functions with respect to the dissymmetry parameter $P_0(D)$. To show the shape of the maxima, there are large breaks on the abscissa ax. The invariable parameters are $V = 0.05$ eV, $\hbar\omega = 0.05$ eV. The variable parameters are: (Frame A) $\lambda_{\mathrm{il}} = 0.1$ eV, $\lambda_{\mathrm{v}} = 0.025$ eV; (B) $\lambda_{\mathrm{il}} = 0.1$ eV, $\lambda_{\mathrm{v}} = 0.05$ eV; (C) $\lambda_{\mathrm{il}} = 0.2$ eV, $\lambda_{\mathrm{v}} = 0.025$ eV; (D) $\lambda_{\mathrm{il}} = 0.2$ eV, $\lambda_{\mathrm{v}} = 0.05$ eV

Here the simplest model of electronic-vibrational interaction with a single vibrational mode is explored. The potential of vibrational modes is strongly anharmonic and, in addition, includes their indirect interaction through the electronic-vibrational interaction. In the case of many vibrational modes, a set of constants λ_{vj} appears instead of a single constant λ_{v}. From the additivity of the electronic-vibrational interaction Eq. (10), it follows that the total effect of the interaction of all modes on the SB extent is determined by the sum $\lambda_{\mathrm{v}} = \sum_j \lambda_{\mathrm{vj}}$. Dividing the total coupling constant λ_{v} into several components leads to a decrease in the constant for each vibrational modes. As a result, the barrier between two minima of the potential along each vibrational coordinates in the systems with several interacting modes is smaller than in the system with single mode. This means that for the formation of a state with a superposition of two well-defined dipole moments in systems with several interacting vibrational modes, larger total electronic-vibrational interaction constant is required than in the system with one mode considered here.

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ОСОБЕННОСТИ ЭЛЕКТРОННОГО СТРОЕНИЯ ВОЗБУЖДЕННЫХ КВАДРУПОЛЬНЫХ МОЛЕКУЛ В НЕПОЛЯРНЫХ РАСТВОРИТЕЛЯХ

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Аннотация. Взаимодействия электронной подсистемы квадрупольного красителя с внутримолекулярными высокочастотными антисимметричными колебаниями и поляризацией растворителя могут приводить к нарушению инверсионной симметрии возбужденной молекулы переносом заряда, наблюдающемуся после оптического возбуждения таких молекул в полярных растворителях. Несмотря на то, что оба взаимодействия математически описываются одинаково, только взаимодействие красителя с ориентационной поляризацией растворителя может привести к нарушению симметрии, если это взаимодействие будет достаточно сильным. Несмотря на это, взаимодействие квадрупольного красителя с внутримолекулярными высокочастотными антисимметричными колебаниями приводит к заметному изменению электронной подсистемы. Содержащийся в этой работе анализ возбужденного состояния квадрупольной молекулы в неполярных растворителях показал, что такие молекулы могут вести себя как квантовые системы с двумя состояниями, например, как квази-спин $s = 1/2$, имея при этом электрический дипольный момент вместо магнитного. Эта особенность возбужденных квадрупольных молекул может быть интересной для развивающихся технологий молекулярной электроники.

Ключевые слова: параметр нарушения симметрии, электронно-колебательное взаимодействие, симметричная донорно-акцепторная триада, перенос электрона, молекулы.