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# A simple model of solvent-induced symmetry-breaking charge transfer in excited quadrupolar molecules

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A simple model has been developed to describe the symmetry-breaking of the electronic distribution of  $A_L$ -D- $A_R$  type molecules in the excited state, where D is an electron donor and  $A_L$  and  $A_R$  are identical acceptors. The origin of this process is usually associated with the interaction between the molecule and the solvent polarization that stabilizes an asymmetric and dipolar state, with a larger charge transfer on one side than on the other. An additional symmetry-breaking mechanism involving the direct Coulomb interaction of the charges on the acceptors is proposed. At the same time, the electronic coupling between the two degenerate states, which correspond to the transferred charge being localised either on  $A_L$  or  $A_R$ , favours a quadrupolar excited state with equal amount of charge-transfer on both sides. Because of these counteracting effects, symmetry breaking is only feasible when the electronic coupling remains below a threshold value, which depends on the solvation energy and the Coulomb repulsion energy between the charges located on  $A_L$  and  $A_R$ . This model allows reproducing the solvent polarity dependence of the symmetry-breaking reported recently using time-resolved infrared spectroscopy. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4982067>]

## I. INTRODUCTION

Symmetry breaking charge-transfer processes are encountered in molecular systems characterised by two or more energy-equivalent charge-transfer pathways.<sup>1</sup> For example, photoinduced symmetry-breaking charge separation has been observed in various multichromophoric systems containing several identical molecular units.<sup>2–12</sup> In those cases, charge separation takes place between one chromophore in the electronic excited state and another identical chromophore in the ground state. In the case of a biperylene derivative, the direction of the charge separation, i.e., electron or hole transfer, was shown to be entirely determined by the fluctuations of the surrounding solvent.<sup>11</sup> Excited-state symmetry breaking has also been observed in multibranching molecules with  $DA_n$  or  $AD_n$  structures ( $n = 2$  or  $3$ ), where A and D are electron-acceptor and electron-donor groups, respectively. The electronic absorption spectra of these molecules do not exhibit a significant solvent dependence, contrary to the fluorescence spectra that characterised a strong solvatochromism. This suggests that the existence of a considerable dipole moment in the excited state in contrast to the ground state has only a quadrupolar or octupolar moment.<sup>13–24</sup> Moreover, the relative intensity of the  $S_1 \leftarrow S_0$  and  $S_2 \leftarrow S_0$  bands in the one- and two-photon absorption spectra of these molecules points to symmetric ground and Franck-Condon excited states.<sup>20,25–27</sup> These two apparently contradictory observations have been reconciled by invoking a break-up of the symmetry in the excited state

assisted by fluctuations of the structure of the molecule itself or of the surrounding solvent.<sup>28–31</sup> Although time-resolved electronic spectroscopy confirmed the dipolar nature of the excited state, it did not provide information on the dynamics of the symmetry breaking and on its magnitude.<sup>21,23,32–35</sup> Real-time visualization of the symmetry-breaking upon photoexcitation of quadrupolar D- $\pi$ -A- $\pi$ -D and A- $\pi$ -D- $\pi$ -A molecules was recently reported using femtosecond time-resolved infrared spectroscopy.<sup>36,37</sup> The symmetry breaking dynamics is directly reflected in the IR spectral dynamics associated with vibrational modes localised in the two arms of the molecules, namely,  $-\text{C}\equiv\text{C}-$  or  $-\text{C}\equiv\text{N}$  stretching vibrations. It was shown that, when the electronic structure of the excited molecules is symmetric, the frequencies of these vibrations are the same in both branches and, therefore, a single  $-\text{C}\equiv\text{C}-$  or  $-\text{C}\equiv\text{N}$  excited band is observed. However, an asymmetric distribution of the charges leads to two different vibrational bands. In the case of the A- $\pi$ -D- $\pi$ -A molecule, the frequency splitting of the two  $-\text{C}\equiv\text{N}$  bands increases with the polarity of the solvent.<sup>37</sup> The time scale associated with the transitions from quadrupolar to dipolar excited state was found to coincide with those of solvation, revealing that, in those two cases at least, symmetry breaking is governed by solvent fluctuations.<sup>36,37</sup>

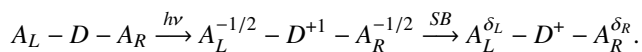
Symmetry breaking in quadrupolar molecules was successfully described in terms of an essential-state model.<sup>28</sup> This model considers three states, i.e., a neutral state and two degenerate states, corresponding to the two zwitterionic structures. The coupling between electrons and intramolecular vibrational and polar solvation modes were also taken into account. Such a description includes the ground and

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excited states and provides all information required to simulate the electronic spectra.<sup>28</sup> Here, we consider a linear A- $\pi$ -D- $\pi$ -A molecule (ADA), which is quadrupolar in the ground state and can be dipolar in the excited state due to symmetry breaking. Our aims are as follows: (i) to develop a simple model of excited-state symmetry breaking, (ii) to determine the parameters controlling the extent of asymmetry, (iii) to predict the dependence of the degree of asymmetry on the solvent polarity, and (iv) to relate this dependence with the experimental frequency splitting of the  $-\text{C}\equiv\text{N}$  stretching bands of an ADA molecule reported in Ref. 37. The dynamic aspects of the symmetry breaking will not be considered here. A similar approach was used to describe the electronic structure of exciplexes in polar solvents and in particular to investigate the influence of the solvent polarity on the magnitude of the partial charges on the donor and acceptor subunits.<sup>38</sup>

## II. THEORY AND COMPUTATIONAL DETAILS

We consider a linear and symmetric  $A_L\text{--}D\text{--}A_R$  molecule with identical electron-accepting groups,  $A_L$  and  $A_R$ . Although we explicitly refer to a  $A_L\text{--}D\text{--}A_R$  structure, the model developed here is also valid for  $D_L\text{--}A\text{--}D_R$  systems. Excitation of the molecule leads to the population of a quadrupolar Franck-Condon excited state with equal amount of charge transfer on both sides, i.e.,  $\delta_L = \delta_R = e/2$ . The transferred charge  $e$  can be less than the charge of an electron. Afterward, symmetry breaking (SB) takes place and  $\delta_L \neq \delta_R$ , while  $\delta_L + \delta_R = e$ ,



We first consider an ADA molecule in vacuum. The two lowest excited states are degenerate with the electron localized either on the left or the right acceptor,  $\varphi_L$  and  $\varphi_R$ , respectively. Taking these functions as a basis set, the Hamiltonian of ADA is

$$H_0 = \begin{pmatrix} E_L & V \\ V & E_R \end{pmatrix}. \quad (1)$$

Due to the symmetry of the molecule,  $E_L = E_R$  and we can set  $E_L = E_R = 0$ . This approach is in full agreement with the excitonic model which is normally used to discuss the absorption spectra of quadrupolar molecules with charge transfer excitons.<sup>20,39</sup> Here  $V$  is equal to the dipole-dipole interaction energy. Although the exciton model is a very crude approximation for conjugated molecules, it was used successfully to rationalize the spectral properties of quadrupolar and related molecules.<sup>39</sup> For the linear two-branched molecules considered here, the model predicts the existence of two excitonic states of opposite symmetry with an energy difference of  $2V$ , the so-called Davydov splitting. The antisymmetric and symmetric excited states can be populated by one-photon and two-photon absorption, respectively. Consequently, the quantity  $V$  can be determined by comparing the one- and two-photon absorption spectra.

For an arbitrary state

$$\Psi = a_L \varphi_L + a_R \varphi_R, \quad (2)$$

the amplitudes  $a_L$  and  $a_R$  determine the charges on the acceptors:  $\delta_L = e|a_L|^2$  and  $\delta_R = e|a_R|^2$ . The direct electrostatic interaction energy between the acceptors charges is

$$K = a_L^2 a_R^2 \frac{e^2}{\epsilon_{im} R_{LR}}. \quad (3)$$

The operator of this interaction in the mean-field approximation can be presented in an explicit symmetrical form,

$$H_C = \gamma [\langle \Psi | \hat{P}_L | \Psi \rangle \hat{P}_R + \langle \Psi | \hat{P}_R | \Psi \rangle \hat{P}_L], \quad (4)$$

where  $\hat{P}_L$  and  $\hat{P}_R$  are the projection operators for the states  $\varphi_L$  and  $\varphi_R$ , respectively,  $R_{LR}$  is the centre-to-centre distance between  $A_L$  and  $A_R$ , and

$$\gamma = \frac{e^2}{2\epsilon_{im} R_{LR}}. \quad (5)$$

This model is relatively simplistic because it describes the variation of the energy of a many-body system in terms of the variation of the Coulomb interaction between two point charges. At a phenomenological level, this drawback can be partially accounted for by considering the “intramolecular” dielectric constant,  $\epsilon_{im}$ , to be a model parameter. As we assume that symmetry breaking conserves the total charge on the acceptors,  $\delta_L + \delta_R = e$ , the total interaction energy between the charges on the acceptors and that on the donor remains constant is, thus, not considered. It should be stressed that the model does not account for possible structural distortions of the molecule due to the asymmetric charge distribution that could result in different  $A_L\text{--}D$  and  $D\text{--}A_R$  distances.

The interaction of the molecule with the surrounding medium can be considered within the framework of the linear response theory, because, as the acceptors are relatively large, the electric field around the molecule is not exceedingly strong. The free energy of this interaction varies quadratically with the charge; for example, it is  $W_L \sim \delta_L^2$  for the left acceptor. A crude estimation of this energy can be obtained with the Kirkwood model that considers a point charge in the centre of a cavity with an electric permittivity of  $\epsilon_i$ , embedded in a homogeneous, isotropic dielectric medium of electric permittivity  $\epsilon_s$ . The point charge polarizes the surrounding dielectric medium, which in turn generates a reaction field. In the case of a spherical dielectric cavity of radius  $r_d$  with a point charge  $e$  at the centre, the reaction field potential inside the cavity is expressed as<sup>40</sup>

$$\Phi_{RF} = -\frac{e}{r_d \epsilon_i} \frac{\epsilon_s - \epsilon_{im}}{\epsilon_s}. \quad (6)$$

Neglecting the mutual influence of the reaction fields created by the charges on the acceptors  $A_L$  and  $A_R$ , the solvation energy in the state  $\Psi$  is given by the equation

$$W = e \Phi_{RF} (a_L^4 + a_R^4). \quad (7)$$

Equation (6) describes the response of the medium to a point charge. It rightly reflects the response of the medium close to the acceptors. The response of the medium further from the molecule is better described by the Onsager’s reaction field. Taking into account that the total average dipole moment of an ADA molecule is connected to the dipolar parameter,  $D$ , by the equations  $\langle \Psi | \hat{\mu} | \Psi \rangle = \mu D$ , correspondingly, and

ignoring the solvation energy of the quadrupole moment, the solvation energy is

$$W = -\frac{D^2 \mu^2 \Delta f}{r_d^3}, \quad (8)$$

where the dipolar parameter,  $D$ , characterizing the degree of asymmetry of the electronic distribution in the ADA molecule is defined as

$$D = a_L^2 - a_R^2, \quad (9)$$

$\mu$  is the magnitude of the dipole moment of the ADA molecule in the state with  $D = 1$ , and  $\Delta f = f(\epsilon_s) - f(n^2)$  with  $f(x) = 2(x - 1)/(2x + 1)$ . Mathematically, this solvation energy leads to the same result as that given by Eq. (7) due to the equality  $D^2 = 2(a_L^4 + a_R^4) - 1$ . The constant  $-1$  on the right hand side of the equality can be eliminated by a proper choice of the origin of the overall energy. The only difference is the dependence of the solvation energy on the dielectric constant. One can expect that the Onsager model is better for small solutes, whereas the Kirkwood model can be better adapted for bulky solutes with two separated charges.

The Hamiltonian for the interaction of the ADA molecule with the solvent and the Coulomb repulsion of the charges can be expressed as

$$H_S = -\lambda [\langle \Psi | \hat{P}_L | \Psi \rangle \hat{P}_L + \langle \Psi | \hat{P}_R | \Psi \rangle \hat{P}_R], \quad (10)$$

where

$$\lambda = -e\Phi_{RF} > 0 \text{ and } \lambda = \frac{2\mu^2 \Delta f}{r_d^3} = \lambda_1 \Delta f \quad (11)$$

for the Kirkwood and the Onsager model, respectively. The expectation values in the square parentheses reflect a mean-field treatment of solute-solvent interaction.

Within the self-consistent field approximation, the stationary states of the zwitterionic forms of the ADA molecule are determined using the stationary Schrödinger equation,

$$H\Psi = E\Psi, \quad (12)$$

where  $H = H_0 + H_C + H_S$  is the total Hamiltonian of the molecule interacting with the surrounding medium. Inserting Eq. (2) into Eq. (12) yields the following nonlinear secular equations:

$$-\lambda a_L^3 + \gamma a_R^2 a_L + V a_R = E a_L, \quad (13)$$

$$-\lambda a_R^3 + \gamma a_L^2 a_R + V a_L = E a_R. \quad (14)$$

After adding and subtracting Eqs. (13) and (14) term by term and taking the normalization condition  $a_L^2 + a_R^2 = 1$  into account, one obtains

$$(a_L - a_R)[(\lambda + \gamma)a_R a_L + V + \lambda + E] = 0, \quad (15)$$

$$(a_L + a_R)[-(\lambda + \gamma)a_R a_L - V + \lambda + E] = 0. \quad (16)$$

Equations (15) and (16) have the following solutions: (i) symmetric with  $a_L = a_R$  and the energy  $E_+ = V - (\lambda - \gamma)/2$ ; (ii) anti-symmetric with  $a_L = -a_R$  and the energy  $E_- = -V - (\lambda - \gamma)/2$ , and (iii) asymmetric and doubly degenerate with

$$a_L^2 = \frac{1}{2} \pm \sqrt{\frac{1}{4} - \frac{V^2}{(\lambda + \gamma)^2}} \quad (17)$$

and the energy

$$E_{as} = -\lambda. \quad (18)$$

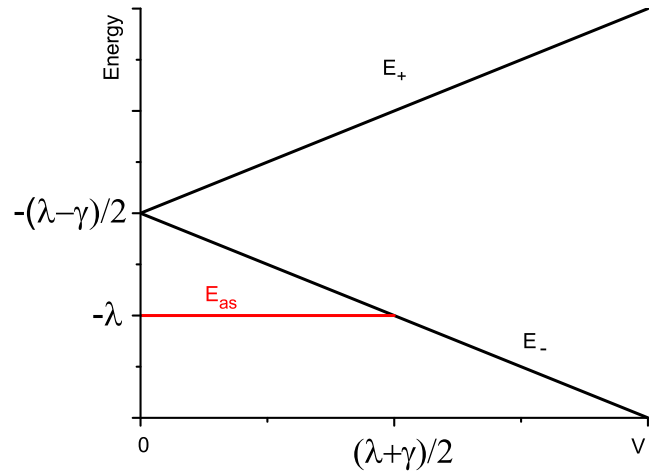


FIG. 1. Energy level scheme of a ADA molecule as a function of coupling strength,  $V$ .

The dependence of the energies  $E_+$ ,  $E_-$ , and  $E_{as}$  on the electronic coupling for a given value of the solvation energy  $\lambda$  and the Coulomb repulsion energy  $\gamma$  is illustrated in Fig. 1. The asymmetric solutions exist only as long as the inequality  $|V| \leq (\lambda + \gamma)/2$  is fulfilled. One can see from this figure that, in this region, the asymmetric states are below the symmetric and antisymmetric states. Consequently, they are the most stable states of the system. From Eq. (15), it follows that the relative phase of the amplitudes  $a_R$  and  $a_L$  in the asymmetrical state is determined by  $a_R a_L = -V/(\lambda + \gamma)$ .

From Eq. (17), one obtains a simple expression for the dipolar parameter,

$$D = 2a_L^2 - 1 = \sqrt{1 - \frac{4V^2}{(\lambda + \gamma)^2}}. \quad (19)$$

As a consequence, the degree of asymmetry is determined by a single dimensionless parameter,  $V/(\lambda + \gamma)$ .

### III. RESULTS AND DISCUSSION

To determine the dependence of the dipolar parameter on the dielectric constant of the solvent, we assume the dependence of the solvation energy on  $\epsilon_s$ ,

$$\lambda = \lambda_0 \frac{f(\epsilon_s) - f(n^2)}{1 - f(n^2)}, \quad (20)$$

for the Onsager's model, where  $\lambda_0 = 2(1 - f(n^2))\mu^2/r_d^3$  is the maximum value of the solvation energy corresponding to highly polar solvents and

$$\lambda = \lambda_0 \frac{\epsilon_s - \epsilon_{im}}{\epsilon_s}, \quad (21)$$

for the Kirkwood's reaction field. In both models,  $\lambda_0$  is considered to be a phenomenological parameter. We assume  $n^2$  and  $\epsilon_{im}$  to be constant for solvents of different polarity.

The dependence of the dipolar parameter  $D$  on the solvent dielectric constant is presented in Fig. 2 for  $\gamma = 2\lambda_0$  and different values of the ratio  $r = V/(\lambda_0 + \gamma)$ . For a given value of the ratio  $r$ , there is a threshold value of  $\epsilon_s$  below which symmetry breaking is not possible. Fig. 2 shows that the results based on the Onsager and Kirkwood models are similar although there are quantitative differences.

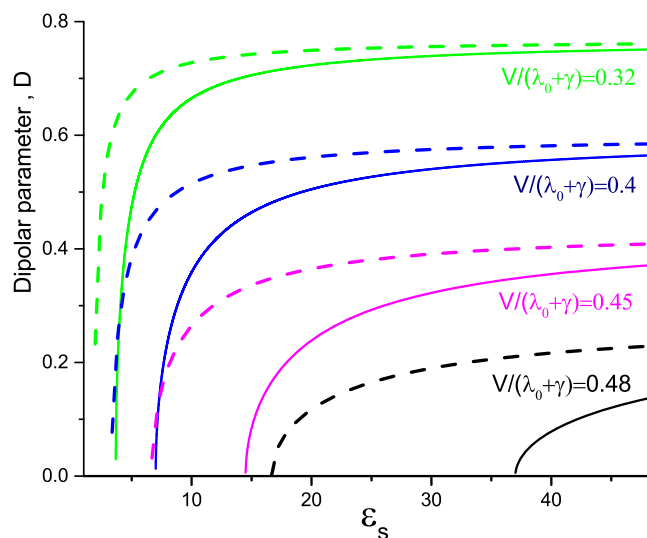


FIG. 2. Dependence of the degree of asymmetry on the solvent dielectric constant for various values of the  $V/(\lambda_0 + \gamma)$  ratio, using the Onsager (solid lines) or the Kirkwood (dashed lines) reaction field, and assuming  $n^2 = 2$ ,  $\epsilon_{im} = 2$ , and  $\gamma = 2\lambda_0$ .

It should be stressed that, in this model, the magnitude of the dipolar parameter,  $D$ , is entirely determined by the dimensionless parameter  $r$ . The most important prediction of the model is the existence of a threshold value of the solvent dielectric constant, which depends on  $r$ , below which no symmetry breaking takes place. The threshold vanishes when  $V/(\lambda + \gamma) < 0.5$  is fulfilled in the least polar solvent. In this case, symmetry is broken in the whole range of dielectric constant and the dipolar parameter is close to unity. As the ratio  $r$  increases, the threshold shifts toward a higher dielectric constant and, when  $r > 0.5$ , symmetry breaking is no longer possible at any dielectric constant. In general, the Coulomb interaction can also depend on the solvent polarity. For this threshold to be observed experimentally, the electronic coupling should lie in the  $(\lambda + \gamma)_{min} < 2V < (\lambda + \gamma)_{max}$  window, where  $(\lambda + \gamma)_{min}$  and  $(\lambda + \gamma)_{max}$  are the minimum and maximum values for the set of solvents used.

The physical meaning of these trends is fairly transparent. The energy splitting of the symmetric and antisymmetric states, which have no dipolar character, increases with the electronic coupling and the stabilization energy of the antisymmetric state is equal to  $V$ . On the other hand, the interaction between the solute and the surrounding polar medium stabilises the state with the maximum dipole moment, i.e., the asymmetric state (we neglect for the moment in the Coulomb interaction). Which of these two effect dominates depends on the relative magnitudes of the electronic coupling and solvation energy. For small  $V$ , solvation energy does not need to be large to favour symmetry breaking. On the other hand, for large  $V$ , solvation does not suffice to break symmetry. These conclusions can be discussed more quantitatively. The energy of the isolated molecule without the Coulomb interaction  $E_0 = \langle \Psi | H_0 | \Psi \rangle = 2Va_La_R$  amounts to  $-V$  for the antisymmetric state,  $a_L = -a_R$ , whereas  $E_0 = 0$  for the asymmetric state with  $a_L = 1$ ,  $a_R = 0$ . Consequently, the energy of the asymmetric state is larger than that of the antisymmetric state by  $V$ .

On the other hand, the interaction energy,  $E_S = \langle \Psi | H_S | \Psi \rangle$ , for the symmetrical states is larger than that for the asymmetrical state by  $(\lambda + \gamma)/2$  (Fig. 1). Therefore, the asymmetric state is below the antisymmetric state as long as  $V < (\lambda + \gamma)/2$ , and symmetry breaking is possible. At first sight, this result might appear surprising because, as solvation and Coulomb repulsion have an opposite effect on the total energy, one could expect a difference  $(\lambda - \gamma)$  in the denominator instead of a sum. This apparent contradiction disappears if one considers that the solvation and the Coulomb repulsion energies have an opposite dependence on the dipolar parameter,  $D$ . Indeed, at  $D = 0$ , solvation energy is the smallest, whereas the Coulomb interaction is the largest.

Real-time visualization of symmetry breaking in D- $\pi$ -A- $\pi$ -D and A- $\pi$ -D- $\pi$ -A type molecules has been achieved using ultrafast transient IR spectroscopy by probing vibrational modes localised in the two branches.<sup>36,37</sup> In the case of the ADA molecule, **1**, these modes are associated with the stretching of the cyano groups located on the acceptor ends (Fig. 3). When **1** is symmetric, the molecule is characterised by two normal  $\text{—C}\equiv\text{N}$  stretching modes, an IR inactive symmetric mode and an IR active antisymmetric mode, with the coordinates  $x_s$  and  $x_a$ , respectively. Given the large distance between the CN groups in **1**, hence their weak interaction, these modes are nearly degenerate. Upon symmetry breaking,  $x_s$  and  $x_a$  are no longer normal coordinates. Accounting for a small variation of the vibrational frequencies, the new normal coordinates can be approximately described in the form,

$$x_1 = x_a \cos \theta + x_s \sin \theta, \quad (22)$$

$$x_2 = -x_a \sin \theta + x_s \cos \theta, \quad (23)$$

where  $\theta$  is a rotation angle in the space of the molecular vibrational coordinates. Since only the antisymmetric mode is IR active, the relative intensities of the normal modes  $x_1$  and  $x_2$  are  $\cos^2 \theta$  and  $\sin^2 \theta$ , respectively. In the experiment,<sup>37</sup> the intensity ratio of the two IR bands is around 0.1 (Fig. 3), pointing to  $\sin \theta \approx 0.3$ . Considering the relations

$$x_s = (x_L + x_R)/\sqrt{2}, \quad (24)$$

$$x_a = (x_L - x_R)/\sqrt{2}, \quad (25)$$

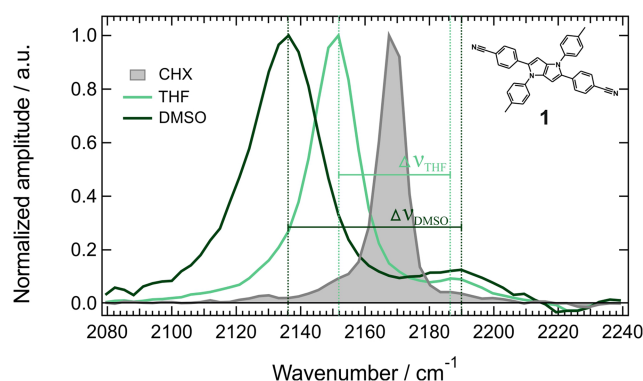


FIG. 3. Time-resolved IR spectra recorded with the ADA molecule **1** shown in the top right in the  $\text{—C}\equiv\text{N}$  stretching region in solvents of different polarity (CHX: cyclohexane, THF: tetrahydrofuran, DMSO: dimethyl sulfoxide).<sup>37</sup> Only one band is visible in CHX, whereas two bands separated by  $\Delta\nu$  are present in the polar solvents, indicative of symmetry breaking.



where  $x_L$  and  $x_R$  are the stretching coordinates in the left and right CN groups, it appears that the new normal coordinates  $x_1$  and  $x_2$  are predominantly associated with the left and right cyano groups, respectively.

The frequency splitting of the  $\text{—C}\equiv\text{N}$  stretching bands of **1** depends strongly on the dielectric constant of the solvent,  $\epsilon_s$  (Fig. 3).<sup>37</sup> As this dependence is apparently similar to that presented in Fig. 2, the fit of the model was first performed assuming that the band splitting,  $\Delta\nu$ , is proportional to the dipolar parameter, namely, that  $\Delta\nu = AD$ , where  $A$  is an arbitrary constant. A fit of the model based on the later assumption proved to not be possible, because the predicted increase of  $D$  with  $\epsilon$  in the region of moderate to large dielectric constant is much weaker than observed. However, a good fit can be obtained assuming that  $\Delta\nu$  is proportional to the square of the dipolar parameter,  $\Delta\nu = AD^2$  (Fig. 4), and that the Coulomb repulsion energy,  $\gamma$ , is independent of  $\epsilon_s$ . Such a quadratic dependence of the band splitting on  $D$  is in good agreement with the correlation between the  $[\text{—C}\equiv\text{N}]^{6-}$  stretching frequency and the fractional charge,  $\delta^-$ , recently calculated for a similar compound, 1,2-dicyanobenzene.<sup>41</sup> Similar good fits can be obtained with different  $\gamma/\lambda_0$  ratios. A variation of  $\gamma/\lambda_0$  from zero to eight has only a weak impact on the quality of the fit. This is simply due to the fact that all the experimental points are located in regions where a variation of  $\gamma/\lambda_0$  affects only weakly the  $\epsilon_s$  dependence of the dipolar parameter,  $D$ . However, an increase of  $\gamma/\lambda_0$  leads to a larger value of  $A$  and, hence, to a smaller  $D$ . For  $\gamma < \lambda_0$ ,  $D$  can be as large as 0.8, whereas for  $\gamma \gg \lambda_0$ ,  $D$  does not exceed 0.3.

The dependence of the band splitting on the dielectric constant pictured in Fig. 4 emphasizes its threshold character. A limitation of this analysis is the assumption that the refractive index  $n$  does not change with the solvent. In reality, it varies significantly and non-monotonically with changes of the dielectric constant,  $\epsilon_s$ . This problem can be corrected

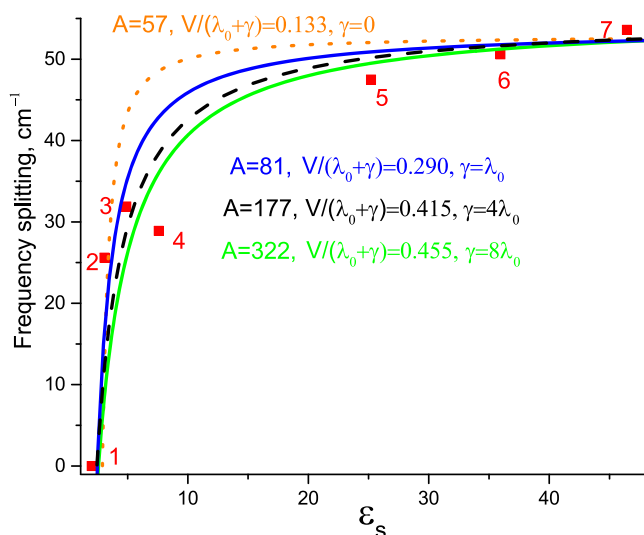


FIG. 4. Best fits of the dependence of the square of the dipolar parameter on the solvent dielectric constant to the experimental frequency splitting of the  $\text{C}\equiv\text{N}$  stretching bands of molecule **1** (red squares, from Ref. 37), using different  $\gamma/\lambda_0$  values. The dependence of the solvation energy on the dielectric constant is described using Eq. (20) ( $n^2 = 2.0$ ; 1: cyclohexane, 2: dibutylether, 3: diethylether, 4: tetrahydrofuran, 5: benzonitrile, 6: acetonitrile, 7: dimethyl sulfoxide). The resulting values of  $A$  and  $V/(\lambda_0 + \gamma)$  are also given.

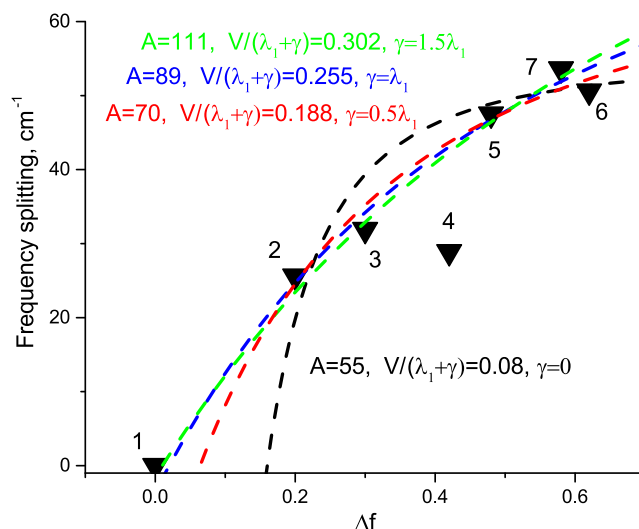


FIG. 5. Best fits of the square of the dipolar parameter vs. the Onsager polarity function to the experimental frequency splitting of the  $\text{C}\equiv\text{N}$  stretching bands of molecule **1** (black triangles, from Ref. 37) using different  $\gamma/\lambda_1$  ratios (the solvents are the same as those in Fig. 4).

by a fit of  $AD^2$  to  $\Delta\nu$  as a function of the Onsager polarity function,  $\Delta f$ , as presented in Fig. 5. Here the quantity  $\lambda_1$  is defined by  $\lambda = \lambda_1 \Delta f$ . The best-fit curves with  $\Delta\nu = 0$  at a  $\Delta f$  value located between those of the first and second experimental points should be considered as of similar quality. This arises from the threshold character of the symmetry breaking. The band splitting is nil for point 1 (cyclohexane, CHX), as symmetry-breaking is not operative in non-polar solvents, whereas it takes place in dibutylether (DBE, point 2). Therefore, the threshold is located at  $0 < \Delta f < 0.2$ . According to the present model, the absence of symmetry breaking in **1** in non-polar solvents indicates that  $V > \gamma/2$ . For a molecule with  $V < \gamma/2$ , symmetry breaking should take place even in non-polar solvents. Whereas both  $V$  and  $\gamma$  decrease with increasing conjugation between the donor and acceptor units, both quantities vary oppositely with increasing conjugation of the  $\pi$  bridges between the D and A units. Indeed, better conjugation favours  $V$  as well as the screening of the charges on the acceptors via the “intramolecular” dielectric constant,  $\epsilon_{im}$ , and, thus,  $\gamma$  should decrease.<sup>42–44</sup> As a consequence, symmetry breaking in non-polar solvents might be difficult to achieve with  $\pi$  bridges, but could be realised in  $\text{AD}_n$  or  $\text{DA}_n$  molecules with saturated bridging units. In such systems, however, the electronic coupling between the D and A units might be too small for the electronic transition from the ground to the quadrupolar excited state to have a significant oscillator strength.

The experimental data allow a relatively precise determination of the threshold polarity above which symmetry breaking takes place. According to the model, the polar solvation energy at the threshold is such that  $V = (\lambda + \gamma)/2$ . In the case of molecule **1**, the experimental results point to a threshold between CHX and DBE. The magnitude of the electronic coupling can be estimated from the splitting of the one photon and two photon absorption band maxima that is equal to  $2V$  according to the model considered. Estimation of this quantity from experimental spectra results in  $V = 1800 \text{ cm}^{-1}$ .<sup>37</sup> An additional information on the magnitudes of other model parameters can be derived from the  $\Delta E = 1600 \text{ cm}^{-1}$  shift of

the fluorescence spectrum of **1** observed by going from the apolar CHX to acetonitrile (ACN,  $\Delta f = 0.62$ ).<sup>37</sup> The average energy of the molecule expressed in terms of the dipolar parameter  $D$  is

$$E = \langle \Psi | H | \Psi \rangle = -V\sqrt{1 - D^2} - \frac{\lambda + \gamma}{2} D^2 + \text{constant}, \quad (26)$$

where the constant is independent of  $D$ . The shift of the fluorescence band reflects the change of the total average energy of the molecule upon variation of the solvent dielectric constant and can be estimated as

$$\Delta E = E(D = 0) - E(D) = V(\sqrt{1 - D^2} - 1) + \frac{\lambda + \gamma}{2} D^2. \quad (27)$$

By using Eq. (19), this equation can be rewritten as

$$\lambda + \gamma = 2(\Delta E + V). \quad (28)$$

Only the sum of  $\lambda$  and  $\gamma$  can be obtained from Eq. (28). Using the above experimental values of  $V$  and  $\Delta E$ , this sum amounts to  $\lambda + \gamma = 6800 \text{ cm}^{-1}$ . Using then Eq. (27) allows the dipolar parameter  $D^2 = 0.72$  to be calculated. From the relation  $\Delta\nu = AD^2$  with  $\Delta\nu = 51 \text{ cm}^{-1}$  at  $\Delta f = 0.62$ , we find  $A = 71$ . From the best-fits depicted in Figure 5, it appears that this value of  $A$  is very close to that obtained assuming  $\gamma = 0.5\lambda_1$ . Using the latter relationship, we now obtain  $\lambda_1 = 6070 \text{ cm}^{-1}$  ( $\lambda = 3760 \text{ cm}^{-1}$  in ACN) and  $\gamma = 3035 \text{ cm}^{-1}$ .

These extracted  $\gamma$  and  $\lambda_1$  values are physically reasonable. Indeed, according to Eq. (5), this Coulomb repulsion energy is equivalent to that between two electrons at  $10 \text{ \AA}$  in a medium with a dielectric constant of  $\epsilon_{im} = 2$ . This distance is equal to that between the centers of the two benzonitrile rings of **1**. Furthermore, according to the Onsager model, the value of  $\lambda$  corresponds to the solvation energy of a dipole of about 10 D. Finally, the polar solvation energy required for symmetry breaking to take place amounts to  $490 \text{ cm}^{-1}$ , corresponding to  $\Delta f = 0.08$ , i.e., somewhere between CHX and DBE, as observed experimentally. Of course only qualitative agreement with the experiment can be expected from this model, whose main aim is to determine which solute and solvent parameters play the most vital role in the symmetry breaking.

#### IV. CONCLUSIONS

We presented here a simple model of the symmetry-breaking charge transfer in the excited state of symmetric  $D-\pi-A-\pi-D$  or  $A-\pi-D-\pi-A$  molecules. The extent of symmetry breaking is quantified by the dipolar parameter,  $D$ , that is determined by a single dimensionless quantity  $V/(\lambda + \gamma)$ . The model predicts that symmetry breaking is only possible when  $V/(\lambda + \gamma) < 0.5$ . Since the magnitude of  $\lambda + \gamma$  depends on the solvent polarity, increasing the latter can result in a transition of  $V/(\lambda + \gamma)$  through this critical 0.5 value. In this case, the dipolar parameter, equal to zero when  $V/(\lambda + \gamma) > 0.5$ , rises quickly after passing through the critical point. The same behaviour was observed experimentally with a ADA molecule when going from apolar to polar solvents.<sup>37</sup>

Here a new contribution to the break-up of the symmetry of quadrupolar molecules, which had not been considered before, is evidenced. It involves the direct Coulomb interaction of the charges located on the acceptors. It appears that this

Coulomb interaction can be as important as the interaction of the charges with the polar solvent for the symmetry breaking. In some cases, this contribution can be large enough to enable symmetry breaking even in non-polar solvents.

It should be noted that this model could in principle be applied to any spectroscopic quantity that reflects the extent of asymmetry of the electronic distribution of a molecule and is not limited to a vibrational frequency splitting. However, unambiguous spectroscopic signatures of symmetry breaking are still scarce.

This two-level model aims mostly at a qualitative description of the solvent dependence of symmetry breaking. Its main limitation is the assumption that the charge on the central D subunit, which is equal to the sum of the absolute values of the charges on the two A moieties, is a phenomenological parameter. This quantity is considered to be a constant when the solvent polarity is varied. Partial charge transfer with  $e$  substantially smaller than the charge of an electron can be expected in most quadrupolar molecules. This problem could be alleviated with a more elaborate description of the  $A_L-D-A_R$  system including at least three states: a locally excited  $A_L-D^*-A_R$  state and two degenerate states with charge transfer to the left and right branches of the molecule,  $A_L^-D-A_R$  and  $A_L-D-A_R^-$ . The two-level model is only applicable if  $|V_{DA}| \ll |\Delta G_{CS}|$ , where  $V_{DA}$  is the electronic coupling between the donor and acceptor and  $-\Delta G_{CS}$  is the free energy of charge separation. If this condition is not fulfilled, a variation of the parameters  $V$ ,  $\lambda$ , and  $\gamma$  results in a change of the charge on the donor and, hence, of the total charge on the acceptors.

The effect of the intramolecular vibrational degrees of freedom on the symmetry breaking is not included in this model. The interaction of electronic degrees of freedom with antisymmetric intramolecular vibrations can also result in symmetry breaking.<sup>28</sup> However, the experimental data suggest that in the systems for which symmetry-breaking dynamics was directly monitored, such as the ADA molecule discussed here, the process is mainly driven by solute-solvent interactions, as its time scale coincides with that of solvent relaxation and as it is not operative in apolar solvents.<sup>36,37</sup>

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