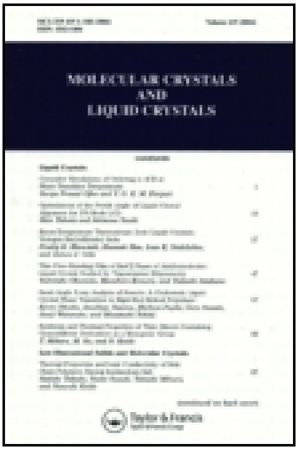

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Multivariate Diffusion Models of Dielectric Friction and Tict Transitions

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MULTIVARIATE DIFFUSION MODELS OF DIELECTRIC FRICTION AND TICT TRANSITIONS

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A multidimensional diffusional approach is proposed to describe rotational diffusion or conformational transition in molecular systems in the presence of coupling with polar solvent coordinates. The model is applied to interpret dielectric friction effects and Twisted Intramolecular Charge Transfer (TICT) kinetics. Full numerical solutions are compared with those obtained by approximate procedures.

1. INTRODUCTION

The role of polar solvents molecules in determining the dynamics of the reaction pathways in chemical kinetics has been widely discussed [1–3]. The primary importance of such effects has been demonstrated by experiments of dynamic Stokes shift [4–6] and photoisomerization of molecules in solution [7]. Calef and Wolynes [8] were the first to derive a diffusion equation for a coordinate representing the polarization component coupled to a molecular degree of freedom. Related diffusion equations were proposed on a phenomenological basis by Mazurenko [9] to describe time dependent emission and by Zusman [10] for the electron transfer problems. The same method has been used by Sumi and Marcus [11] to interpret the effects of nonequilibrium solvation in electron transfer processes. Van der Zwan and Hynes [12] have pointed out the close connection between the intimate mechanism of the time dependent fluorescence, responsible for the Stokes shifts, and the dielectric friction invoked to

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interpret the orientational relaxation of dipolar molecules measured by dielectric dispersion experiments.

In the following, we shall use a multivariate diffusion equation to describe the coupling of the solvent with some molecular coordinates of a system undergoing dynamical processes of interest. The methods described here provide the generalization of a treatment recently proposed to interpret activated twisted intramolecular charged transfer (TICT) processes [13]. The solvent coordinate can be interpreted as a fluctuating electric field generated by the polar solvent molecules surrounding the probe molecule. The results will be discussed in the context of experimental investigations aimed to gain information on orientational relaxation and photochemical conversion to charge transfer states.

2. DIFFUSION EQUATION FOR SYSTEM AND SOLVENT VARIABLES

We shall denote by $\mathbf{q}$ the stochastic variables describing the molecular state and by $\mathbf{X}$ the solvent coordinates necessary to completely specify the system. Within the Onsager picture [12], $\mathbf{X}$ should be identified with the cavity reaction field. The time evolution of the probability density $P(\mathbf{q}, \mathbf{X}, t)$ is assumed to be governed by the diffusion operator

$$\hat{\Gamma} = -D_q \left(\frac{\partial}{\partial \mathbf{q}}\right) P_{\mathrm{eq}} \left(\frac{\partial}{\partial \mathbf{q}}\right) P_{\mathrm{eq}}^{-1} - D_x \left(\frac{\partial}{\partial \mathbf{X}}\right) P_{\mathrm{eq}} \left(\frac{\partial}{\partial \mathbf{X}}\right) P_{\mathrm{eq}}^{-1} \tag{2.1}$$

where $(\partial/\partial\mathbf{q})$ and $(\partial/\partial\mathbf{X})$ are the gradient operators respectively in the internal and solvent coordinates; $P_{\mathrm{eq}}(\mathbf{q}, \mathbf{X})$ is the equilibrium distribution function determined by a potential $V(\mathbf{q}, \mathbf{X})$ of general form:

$$V(\mathbf{q}, \mathbf{X}) = V_0(\mathbf{q}) - \boldsymbol{\mu}(\mathbf{q}) \,.\, \mathbf{X} + \tfrac{1}{2}\Xi^2 \mathbf{X} \,.\, \mathbf{X} \tag{2.2}$$

In this expression, $V_0(\mathbf{q})$ is an internal potential to be specified in the absence of coupling with the polar environment, $\boldsymbol{\mu}(\mathbf{q})$ is the molecular dipole and Ξ^2 is a parameter depending on the amplitude of the cavity field fluctuations.

The diffusion tensor for the system is assumed to be constant and diagonal; and while D_q is generally well defined (e.g. by hydrodynamic considerations) when the internal coordinates $\mathbf{q}$ are specified, D_X can be evaluated from the correlation function for $\mathbf{X}$ when the coupling with the probe dipole is zero:

$$\overline{\mathbf{X}(0) \,.\, \mathbf{X}(t)} = \frac{3k_{\mathbf{B}}T}{\Xi^2} \exp\left(-\frac{D_X \Xi^2}{k_{\mathbf{B}}T} t\right). \tag{2.3}$$

By comparison with the time correlation function for a fluctuating reaction field [12,14,15]

$$\overline{\mathbf{X}(0)\,.\,\mathbf{X}(t)} = \frac{3k_{\mathrm{B}}T}{a^3}\left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + \frac{1}{2}} - \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + \frac{1}{2}}\right)\exp\left(-\frac{t}{\tau_{\mathrm{S}}}\right) \tag{2.4}$$

The following definitions for Ξ^2 and D_X are recovered

$$\frac{1}{\Xi^2} = \frac{1}{a^3}\left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + \frac{1}{2}} - \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + \frac{1}{2}}\right) \tag{2.5}$$

$$D_X\Xi^2 = \frac{k_{\mathrm{B}}T}{\tau_{\mathrm{S}}}. \tag{2.6}$$

Here a is the Onsager cavity radius, ε_0 and ε_∞ are the static and optical dielectric constants, and τ_{S} is related to the dielectric relaxation time τ_{D} [12]:

$$\tau_{\mathrm{S}} = \frac{2\varepsilon_\infty + 1}{2\varepsilon_0 + 1}\tau_{\mathrm{D}} \tag{2.7}$$

Direct estimates of τ_{S} in a number of solvents are provided by experimental determination of time-dependent Stokes shifts [4–6]. We note that the above relations, and in particular the monoexponential model for the decay to equilibrium of the solvent polarization, are the results of approximate procedures, and they should be viewed with care when evaluating the magnitude of the parameters in the theory.

We are now able, although in a simplified picture, to describe the effects exerted by a polar environment on the time evolution of different observables of the molecular system. In the following we shall consider firstly the rotational diffusion of a polar molecule in an isotropic medium, and the relation of the solvent coupling with the so called ‘dielectric friction’ phenomenon [14–16.]. We will then investigate the torsional dynamics of a molecular system undergoing conformational transitions involving electron transfer, by looking at the dependence of the rate constants upon the strength of the solvent couplings with the CT states.

3. ORIENTATIONAL RELAXATION AND DIELECTRIC FRICTION

If we wish to describe the rotational diffusion of a molecular dipole in isotropic media, the molecular coordinates $\mathbf{q}$ have to be chosen as the Euler angles $\boldsymbol{\Omega}$ specifying the dipole orientation in a laboratory frame, with a constant internal potential $V_0(\boldsymbol{\Omega})$ (in anisotropic environments a mean field potential on $\boldsymbol{\Omega}$ should be introduced [17], but such a complication need not be considered here). The dipolar vector $\boldsymbol{\mu}(\boldsymbol{\Omega})$ is expressed in terms of the unit vector $\mathbf{u}(\boldsymbol{\Omega})$

$$\boldsymbol{\mu}(\Omega) = \mu\mathbf{u}(\Omega) \tag{3.1}$$

where μ is the modulus of the molecular dipole. The operator gradient $(\partial/\partial\mathbf{q})$ is the generator of infinitesimal rotations $\hat{\mathbf{M}}$ and the diffusion coefficient is identified simply with the istropic rotational diffusion coefficients D_{R} for the molecule.

By introducing the deviation $\delta\mathbf{X} = \mathbf{X} - \mathbf{X}_{\mathrm{eq}}$ of the cavity field with respect to its equilibrium value $\mathbf{X}_{\mathrm{eq}} = \mu\mathbf{u}/\Xi^2$ for a given orientation $\mathbf{u}$ of the molecule, the potential function can be rearranged as:

$$V = \tfrac{1}{2}\Xi^2\delta\mathbf{X}\,.\,\delta\mathbf{X} - \Delta E_{\mathrm{S}}, \tag{3.2}$$

where $\Delta E_{\mathrm{S}} = \mu^2/2\Xi^2$ is identified with the energy stabilization due to the solvent, and the first term on the right-hand side represents the contribution of polarization fluctuations. In this way the model is fully specified in terms of three parameters: $\Delta E_{\mathrm{S}}/k_{\mathrm{B}}T$ (the strength of coupling with the solvent polarization), τ_{S} (the correlation time of solvent polarization fluctuations), and $\tau_{\mathrm{R}} = 1/D_{\mathrm{R}}$ (the rotational correlation time in the presence only of a viscous coupling with the solvent).

The observables of interest are expressed by the correlation functions for the reorientation of the unit vector $\mathbf{u}$ [17–19]

$$G_j(t) = \overline{P_j[\mathbf{u}(0)\,.\,\mathbf{u}(t)]} = \frac{4\pi}{2j+1}\sum_{m=-j}^{4\pi}\overline{Y_{jm}[\Omega(0)]Y_{jm}[\Omega(t)]^*} \tag{3.3}$$

which are characterized by a decay rate $j(j+1)D_{\mathrm{R}}$ in absence of coupling with the solvent ($\Delta E_{\mathrm{S}} = 0$). When the probe dipole is coupled with the solvent ($\Delta E_{\mathrm{S}} \neq 0$) the decay rate will depend also on the diffusion coefficient D_X for the reaction field. The effective relaxations times τ_j of the jth rank observables are obtained from the time integral of the correlation functions

$$\tau_j = \int_0^\infty dt G_j(t), \tag{3.4}$$

The full diffusion Eq. (2.1) for $P(\boldsymbol{\Omega}, \mathbf{X}, t)$ can be solved by expansion on a complete orthonormal set of basis functions taken as the direct product of Wigner rotation matrices $D^j_{pq}(\boldsymbol{\Omega})$ and Hermite polynomials $\mathrm{He}_n(X)$

$$|j,p,q;n_1,n_2,n_3\rangle = \frac{D^j_{pq}(\boldsymbol{\Omega})}{(2j+1)^{1/2}}\mathrm{He}_{n1}(\partial X_1)\mathrm{He}_{n2}(\delta X_2)\mathrm{He}_{n3}(\delta X_3)P_{\mathrm{eq}}(\delta X)^{1/2}. \tag{3.5}$$

The diagonalization of the resulting matrix and the calculation of the spectral densities of the functions of interest can be performed using the standard Lanczos algorithm techniques described in previous works [20,21]. For sake of simplicity, actual calculations were confined to the rotation of a dipole in a plane, so that the number of variables were reduced from six (three Euler angles and three field components) to three (one polar angle ϕ and the two in plane field components X_1, X_2); all relevant conclusions are however unaffected by the reduced dimensionality of the problem.

Analytical results for the relaxation times can be derived in the limit $\tau_S/\tau_R \rightarrow 0$, i.e. in the presence of extremely fast fluctuations of the solvent polarization. Under this condition, one can project out the solvent degrees of freedom as shown in the Appendix, so deriving a diffusion equation for the rotational degrees of freedom only, with an effective diffusion coefficient gives in Eq. (A 12). Correspondingly the rotational relaxation times are calculated from the equation:

$$\tau_j \approx \left(\tau_R + \frac{2\Delta E_S}{k_B T}\tau_S\right) \Big/ j(j+1) \tag{3.6}$$

which is essentially the same result of Nee and Zwanzig (N.Z.) [14,15], with the dielectric contributions $\Delta\zeta$ to the effective friction of the form

$$\Delta\zeta = \frac{\mu^2}{a^3}\left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + \frac{1}{2}} - \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + \frac{1}{2}}\right)\tau_S \tag{3.7}$$

in our model. The comparison with the numerical solutions for the planar rotor in the range $\tau_R \geqslant \tau_S$ shows that Eq. (3.6) is an upper bound to the true relaxation time. Table 1 presents some results for τ_1 calculated from the time integral of $\cos\phi(0)\cos\phi(t)$, together with the N.Z. approximation. Note that for planar rotors the factor $j(j+1)$ in Eq. (3.6) should be replaced by j^2.

Within the range of parameters we have considered, the N.Z. approximation overestimates the exact relaxation rates at most by 30 per cent. In the same conditions, the correlation functions display negligible deviations from a single exponential decay.

Let us discuss in some detail the condition of validity of the N.Z. equation. Of course the limit $\tau_S/\tau_R \rightarrow 0$ is required, but if the parameter $\Delta E_S/k_B T$ is kept constant the trivial case of a vanishing dielectric friction is recovered. To preserve the physical meaning of the N.Z. relation the limit should be performed with a constant contribution of the dielectric friction, by rewriting Eq. (3.6) as

$$\lim_{\tau_S/\tau_R \rightarrow 0}\left[\frac{\tau_j}{\tau_R j(j+1)}\right]_{(\Delta E_S \tau_S / k_B \mathrm{T} \tau_R = \mathrm{const})} = 1 + 2\frac{\Delta E_S}{k_B T}\frac{\tau_S}{\tau_R}. \tag{3.8}$$

This equation has been verified with the numerical calculation for the planar rotor, as shown in the Figure 1.

TABLE 1 Numerical Results of the Ratio τ_1/τ_{R} for the Planar Rotor, for Different Values of $\tau_{\mathrm{R}}/\tau_{\mathrm{S}}$ and $\Delta E_{\mathrm{S}}/k_{\mathrm{B}}T$. The Approximation Obtained from Eqs. (3.6) is Given in Parenthesis

$\Delta E_{\mathrm{S}}/k_{\mathrm{B}}T^{\tau_{\mathrm{R}}/\tau_{\mathrm{S}}}$	1.000	2.000	3.000	4.000	5.000
0.00	1.000 (1.000)	1.000 (1.000)	1.000 (1.000)	1.000 (1.000)	1.000 (1.000)
0.50	1.620 (2.000)	1.344 (1.501)	1.243 (1.333)	1.191 (1.250)	1.158 (1.200)
2.00	3.745 (5.000)	2.475 (3.000)	2.032 (2.336)	1.798 (2.000)	1.655 (1.801)
4.50	7.936 (10.00)	4.608 (5.524)	3.484 (4.000)	2.898 (3.257)	2.544 (2.801)
8.00	14.49 (17.00)	7.874 (9.000)	5.649 (6.329)	4.524 (5.000)	3.846 (4.201)
12.50	23.30 (25.97)	12.23 (13.49)	8.547 (9.345)	6.711 (7.246)	5.586 (6.024)

4. CONFORMATIONAL TRANSITIONS TO CT STATES

Upon electronic excitation, several aromatic molecules undergo crossing between a planar excited state and a highly polar state called 'twisted intramolecular charge transfer' (TICT) state because of the internal twisting between donor and acceptor moieties [3]. In the case of N,N-dimethylaminobenzonitrile, often considered a prototype system for TICT transitions, the internal twisting is described by the torsional angle θ of the

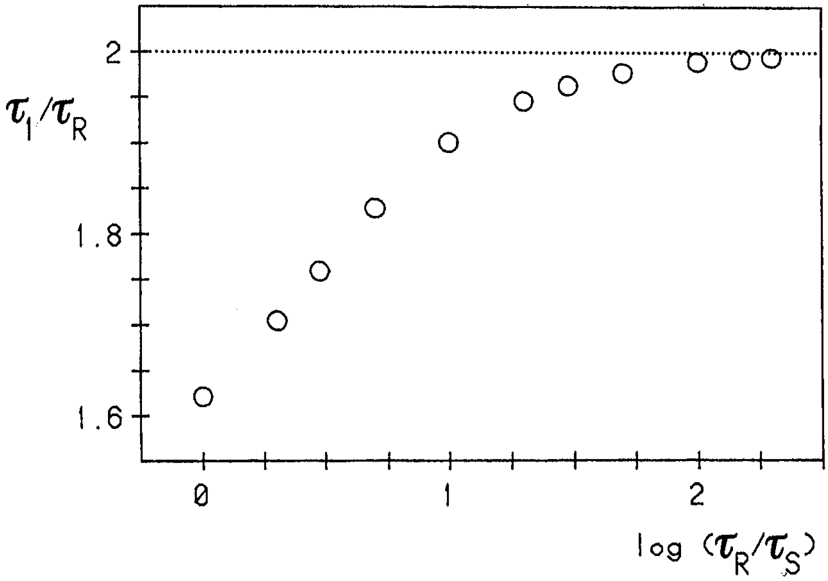

FIGURE 1 Convergence test of the limit in Eq. (3.8) for the dipole correlation time of the planar rotor calculated with $\Delta E_{\mathrm{S}}\tau_{\mathrm{S}}/k_{\mathrm{B}}T\tau_{\mathrm{R}} = 0.5$. Circles: numerical results for τ_1/τ_{R}. Dotted line: right-hand side of Eq. (3.8).

dimethylamino group with respect to the aromatic plane, the dipole moment $\boldsymbol{\mu}(\theta)$ always pointing in the direction $\mathbf{u}$ of the long molecular axis. Since our purpose is to analyse the general features of the coupling between internal motion and solvent polarization, we shall adopt in the calculations the simplest model for the dipole moment function, i.e.

$$\boldsymbol{\mu}(\theta) = \tfrac{1}{2}\mathbf{u}\mu(1 - \cos 2\theta). \tag{4.1}$$

In this way, the dipole moment is assumed to vanish in the planar state ($\theta = 0, \pi$) and the parameter μ determines its modules in the TICT states ($\theta = \pm\pi/2$). To further simplify the treatment, we shall neglect the coupling between rotational diffusion of the whole molecule and the TICT transition, by explicitly considering only the torsional variable and the component X of the solvent field along the dipole moment.

An expression for the internal potential $V_0(\theta)$ is also required. By assuming a C_{2v} symmetry for the internal rotations, $V_0(\theta)$ can be parametrized by means of the coefficients of the even cosine expansion. Quadratic and quartic terms suffice to reproduce the expected main features of the potential. Finally, the potential function is written as:

$$V(\theta, X) = \tfrac{1}{2}A_4(1 - \cos 4\theta) + \tfrac{1}{2}(A_2 - \mu X)(1 - \cos 2\theta) + \tfrac{1}{2}\Xi^2 X^2. \tag{4.2}$$

with $A_4 > 0$. In the (θ, X) plane with $0 \leqslant \theta \leqslant \pi/2$ the points $P_1 \equiv (0, 0)$, $P_2 \equiv (\pi/2, \mu/\Xi^2)$ determine the locations of the potential minima, while the saddle point is found at $P_\mathrm{S} \equiv (\theta_\mathrm{S}, X_\mathrm{S})$, with:

$$\theta_\mathrm{S} = \tfrac{1}{2}\arccos\left(\tfrac{(\mu^2/2\Xi^2) - A_2}{2A_4 + (\mu^2/2\Xi^2)}\right), \tag{4.3}$$

$$X_\mathrm{S} = \frac{\mu}{2\Xi^2}\left(\frac{2A_4 + A_2}{2A_4 + (\mu^2/2\Xi^2)}\right). \tag{4.4}$$

The stabilization energy $\Delta E_\mathrm{S} = \mu^2/2\Xi^2$ of the TICT state due to the solvent is the convenient parameter to characterize the strength of the coupling between the two degrees of freedom. When this quantity increases, the saddle point is shifted towards the planar minimum at P_1, with a corresponding decrease of the potential barrier, while the twisted minimum at P_2 becomes progressively more stabilized.

The diffusion equation with the interaction potential given in Eq. (4.2) can be solved as before by an expansion over a complete orthonormal set of basis functions. A simple choice for the θ set is provided by the rotor functions exp $(im\theta)$.

For potential barriers large enough, one expects that a discrete master equation specified by the kinetic constants k_1 and k_2 for the transition $P_1 \rightarrow P_2$ and $P_2 \rightarrow P_1$ respectively, should well approximate the long time behaviour of the system. Correspondingly, one separates in the orientational correlational functions the fast initial decay associated to small amplitude motions in the potential wells, from the slow decaying component with a relaxation time determined by the kinetic coefficients. The rates k_1 and k_2 are obtained independently by considering the slowest decay constant of the autocorrelation functions for $\cos\theta$ and $\sin\theta$, respectively.

On the other hand, analytical expressions for the kinetic constants are derived according to the Kramers theory [22] generalized to multidimensional diffusion eqs. [23–25]. Since this method is based on the local expansion of the diffusion operator in proximity of the saddle point, the results represent the asymptotic limit of the true kinetic constants with respect to the height of the potential barrier. Within this framework the rate for the transition to the TICT state can be written as:

$$k_1 = \frac{|\lambda_1|}{2\pi} \exp\left(\frac{-\Delta E_1^{\ddagger}}{k_B T}\right), \tag{4.5}$$

where $\Delta E_1^{\ddagger}$ is the free-energy barrier between the first minimum and the saddle point, and λ_1 is the unique negative eigenvalue of the matrix product $\mathbf{D}_S \mathbf{V}_S^{(2)}/k_B T$, $\mathbf{D}_S$ and $\mathbf{V}_S^{(2)}$ being the 2×2 diffusion matrix and potential curvature matrix, calculated at the saddle point [24]. Here the diffusion tensor is supposed to be again in a diagonal form, as in the previous case:

$$\mathbf{D}_S = \mathbf{D} = \begin{pmatrix} D_\theta & 0 \\ 0 & D_X \end{pmatrix} \tag{4.6}$$

and $\tau_\theta = 1/D_\theta$ is the torsional correlation time in the presence only of a viscous coupling with the solvent. The eigenvector associated to λ_1 identifies the reaction coordinate which minimizes both the energetic and the frictional effects in the barrier crossing [25].

The transition rate k_1 has been calculated according to Eq. (4.6), by choosing $A_4/k_B T = 13$ to ensure the validity of the asymptotic relations. Since the correlation time τ_θ for the torsional motion of a small molecular group is expected to be of the same order of magnitude of the solvent relaxation times (10–100 ps at 300 K and a viscosity of 1 cP), a ratio $\tau_\theta/\tau_S = 1$ has been assumed. For convenience A_2 has been put equal to zero, but this choice does not alter the main features of the calculation.

The results are illustrated in Table 2, where the stabilization energy is varied, while the remaining parameters are kept constant. One can see that a substantial decrease of the activation energy is obtained by increasing the stabilization energy, i.e. by increasing solvent polarity. Even if in principle the transition rate is controlled by both the solvent relaxation and the torsional motion through the τ_S and τ_θ dependence of λ_1, in practice the pre-exponential factor remains almost constant. If follows therefore that

TABLE 2 Asymptotic Rate of TICT State Formation, for Different Values of the Solvent Stabilization Energy, with $\tau_\theta/\tau_\mathrm{S} = 1.0$, $A_4/k_\mathrm{B}T = 13.0$ and $A_2/k_\mathrm{B}T = 0$

$\Delta E_\mathrm{S}/k_\mathrm{B}T$	$\Delta E_1^\ddagger/k_\mathrm{B}T$	$\lvert\lambda_1\rvert/D_\theta$	$10^3 k_1/D_\theta$
0.00	13.00	104.0	0.075
0.50	12.87	103.9	0.084
2.00	12.51	103.2	0.120
4.50	11.92	100.7	0.212
8.00	11.14	95.51	0.441
12.50	10.23	87.80	1.000

the increase of the kinetic constant k_1 is mainly determined by the lowering of the conformational barrier induced by the solvent interactions.

As shown in a previous paper [13], when the transition rate is calculated according to Eq. (4.5), the particular shape of the potential near the saddle point allows trajectories of barrier crossing with purely torsional displacements, but never with only solvent coordinate displacements. As a consequence, the pre-exponential factor results to be almost linearly dependent upon τ_θ, with the proportionality coefficient weakly depending upon τ_S.

It should be stressed however that these conclusions are drawn from the asymptotic calculation of the transition rates, and therefore they are valid in the limit of very high potential barriers. The numerical solution of the coupled diffusion equation opens the possibility to verify the validity of the asymptotic treatment with realistic potential barriers in the intermediate range of a few $k_\mathrm{B}T$ units. Table 3 summarizes the results for $A_4/k_\mathrm{B}T = 5.0$ and $A_2/k_\mathrm{B}T = 0$. It is clear that large deviations from the asymptotic values result in the cases of slow solvent relaxation and large stabilization energies, which lower the activation energy as seen in Table 2. In fact, the asymptotic solutions for the saddle point crossing along the reactive coordinate degrade when this is coupled to a soft coordinate characterized

TABLE 3 Exact Rate Constant for the Transition to TICT States, for Different Values of $\Delta E_\mathrm{S}/k_\mathrm{B}T$ and $\tau_\theta/\tau_\mathrm{S}$, with $A_4/k_\mathrm{B}T = 5.0$ and $A_2/k_\mathrm{B}T = 0$; in Parenthesis the Asymptotic Values Calculated by Eq. (4.5)

$\Delta E_\mathrm{S}/k_\mathrm{B}T^{\tau_\theta/\tau_\mathrm{S}}$	0.100	1.000	10.00	100.0
0.00	0.0757 (0.0857)	0.0757 (0.0857)	0.0757 (0.8757)	0.0757 (0.0857)
0.50	0.0724 (0.0958)	0.0829 (0.0958)	0.0847 (0.0963)	0.0861 (0.0975)
2.00	0.0680 (0.1301)	0.1043 (0.1304)	0.1148 (0.1328)	0.1218 (0.1394)
4.50	0.0661 (0.1972)	0.1379 (0.1984)	0.1732 (0.2073)	0.1960 (0.2306)
8.00	0.0658 (0.2973)	0.1792 (0.3014)	0.2681 (0.3296)	0.3280 (0.3953)
12.50	0.0668 (0.4075)	0.2242 (0.4200)	0.4052 (0.4961)	0.5390 (0.6491)

by longer timescales, if the energy barrier is not sufficiently high [26–29]. In this case, the rate limiting step is determined by the fluctuations of the X-coordinate which bring the reactant state near to the saddle point from the initial configuration.

In principle, the Stokes shift accompanying a TICT transition might be interpreted in terms of the correlation function for the X variable. According to Eq. (2.3) this function is described by a single exponential decay in absence of coupling with the internal variable. In the general case, however, the numerical calculations show a complex behaviour, due to the interplay of the solvent characteristic frequency and the rates of the conformational jumps.

5. CONCLUSIONS

The theoretical model proposed here is able to account for a number of physical phenomena related to the interaction of a dipolar probe with a polar solvent. In the description of rotational diffusion, probed by N.M.R. and dielectric absorption or dispersion experiments, the dielectric friction effects emerge naturally, and the theory provides a direct generalization of the results of previous treatments.

Rather different dynamical processes, such as conformational transitions to charge transfer states, can also be consistently handled within the same framework of the theory. When the conformational barriers are high, the kinetic constant is more sensitive to a static effect, the change of the activation energy due to the solvent interaction, rather than to a dynamical coupling with the solvent.

In addition, the effects on the solvent coordinate resulting from the couplings with the probe molecule can also be analyzed. In general, they are found to cause complex behaviours, determined both by the solvent and the molecule characteristic times. Significant deviations from single-exponential decays result, and they should be taken into account to interpret properly time-dependent fluorescence data.

A satisfactory understanding of the relevant effects of solvent interactions on dynamical processes has been achieved, even if a detailed comparison of the theoretical prediction with experimental data is difficult, both because of the intrinsic uncertainties of the dielectric continuum models [30] and the doubts cast on the mechanisms of the CT state formation in specific systems [31,32].

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APPENDIX

The Projection Calculation of Dielectric Friction

We start by writing the diffusion operator in terms of the new variables $(\mathbf{\Omega}, \delta\mathbf{X})$ with $\delta\mathbf{X} = \mathbf{X} - (\mu/\Xi^2)\mathbf{u}$

$$\hat{\Gamma} = -D_{\mathrm{R}}\hat{\mathbf{M}}_{\delta\mathbf{X}}P_{\mathrm{eq}}\hat{\mathbf{M}}_{\delta\mathbf{X}}P_{\mathrm{eq}}^{-1} - D_X\left(\frac{\partial}{\partial\delta\mathbf{X}}\right)P_{\mathrm{eq}}\left(\frac{\partial}{\partial\delta\mathbf{X}}\right)P_{\mathrm{eq}}^{-1}, \qquad \text{(A1)}$$

Where $\hat{\mathbf{M}}_{\delta\mathbf{X}}$ is the infinitesimal rotation operator $\hat{\mathbf{M}}$ transformed according to the new set of variables

$$\hat{\mathbf{M}}_{\delta\mathbf{X}} = \hat{\mathbf{M}} - \frac{\mu}{\Xi^2}\mathbf{u} \times \left(\frac{\partial}{\partial\delta\mathbf{X}}\right). \qquad \text{(A2)}$$

We then define the operator $\mathscr{P}$, projecting a generic function $f(\mathbf{\Omega}, \delta\mathbf{X})P_{\mathrm{eq}}$ on the reduced space of functions $g(\mathbf{\Omega})P_{\mathrm{eq}}$

$$\mathscr{P}f(\mathbf{\Omega}, \delta\mathbf{X})P_{\mathrm{eq}} = \bar{f}(\mathbf{\Omega})P_{\mathrm{eq}}, \qquad \text{(A3)}$$

$$\bar{f}(\mathbf{\Omega}) = 8\pi^2\int d(\delta\mathbf{X})f(\mathbf{\Omega}, \delta\mathbf{X})P_{\mathrm{eq}}. \qquad \text{(A4)}$$

If one considers the spectral density of a function $g(\mathbf{\Omega})$, i.e. the Fourier-Laplace transform $J(\omega)$ of the autocorrelation $\overline{g(0)g(t)^*}$, one obtains the exact expression [19]

$$J(\omega) = \langle g|\{i\omega + \mathscr{P}\hat{\Gamma}\mathscr{P} - \mathscr{P}\hat{\Gamma}(1-\mathscr{P})(\hat{\Gamma}')^{-1}(1-\mathscr{P})\hat{\Gamma}\mathscr{P}\}^{-1}|gP_{\mathrm{eq}}\rangle. \qquad \text{(A5)}$$

The brackets denote the integration on the full phase space, and $\hat{\Gamma}'$ is given by the relation

$$\hat{\Gamma}' = i\omega + (1-\mathscr{P})\hat{\Gamma}(1-\mathscr{P}). \qquad \text{(A6)}$$

When $\tau_S \ll \tau_R$, that is when the solvent polarization decays to equilibrium much faster than the orientational variables, one can neglect in the expression for $\hat{\Gamma}'$ both the rotational components and the frequency term $i\omega$

$$\hat{\Gamma}' \approx -\left(\frac{\partial}{\partial\delta\mathbf{X}}\right)\mathbf{D}'P_{\mathrm{eq}}\left(\frac{\partial}{\partial\delta\mathbf{X}}\right)P_{\mathrm{eq}}^{-1} \qquad \text{(A7)}$$

$$\mathbf{D}' = D_X\mathbf{1} - \frac{D_{\mathrm{R}}\mu^2}{\Xi^4}\mathbf{U}^2. \qquad \text{(A8)}$$

In Eq. (A8) the 3×3 matrix $\mathbf{U}$ is defined as the linear transformation of a vector $\mathbf{v}$ which generates the vector product with the dipole axis $\mathbf{u}$

$$\mathbf{U}\mathbf{v} = \mathbf{u} \times \mathbf{v}. \qquad \text{(A9)}$$

Finally the following result is recovered, after evaluating the various terms of Eq. (A5) with standard projection operator techniques [19]

$$J(\omega) = \langle g|(i\omega - \hat{\mathbf{M}}\mathbf{D}\hat{\mathbf{M}})|gP_{\mathrm{eq}}\rangle. \tag{A10}$$

This is the result that would be obtained for a purely rotational diffusion equation, but the diffusion matrix **D** is now given as

$$\mathbf{D} = D_{\mathrm{R}}\mathbf{1} + \frac{D_{\mathrm{R}}\mu^2}{\Xi^4}\mathbf{U}(\mathbf{D}')^{-1}\mathbf{U}. \tag{A11}$$

One can easily show that **D** is axially symmetric with respect to the direction of the dipole moment. The perpendicular component will be referred to as D_{eff}, and it is given as:

$$\frac{1}{D_{\mathrm{eff}}} = \frac{1}{D_{\mathrm{R}}} + \frac{\mu^2}{D_{\mathrm{X}}\Xi^4} = \tau_{\mathrm{R}} + \frac{2\Delta E_{\mathrm{S}}}{k_{\mathrm{B}}T}\tau_{\mathrm{S}}. \tag{A12}$$

Of course, D_{eff} is the effective diffusion coefficient for the rotational relaxation of the dipole vector **u**. The effective friction is therefore

$$\zeta_{\mathrm{eff}} = \frac{k_{\mathrm{B}}T}{D_{\mathrm{eff}}} = \zeta_{\mathrm{R}} + \Delta\zeta, \tag{A13}$$

and so one can separate a purely rotational term $\zeta_{\mathrm{R}} = k_{\mathrm{B}}T/D_{\mathrm{R}}$, from the dielectric friction contribution $\Delta\zeta = 2\Delta E_{\mathrm{S}}\tau_{\mathrm{S}}$. The explicit form Eq. (3.7) for the dielectric friction is obtained by substituting Eq. (2.5) in the definition of the solvent stabilization energy.

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