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INTRAMOLECULAR ELECTRON TRANSFER REACTION IN DIMETHYLAMINOBENZONITRILE

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Abstract The fluorescence emission of dimethylaminobenzonitrile in polar solvents is analysed in terms of a model which is a microscopic generalization of the Grabowski two-level kinetic scheme. The ground and the lowest excited state are described by adiabatic potential surfaces, defined in terms of an internal torsional coordinate and a solvent polarization coordinate. The potential energy functions are given by the energy of the isolated molecule plus a contribution due to the electrostatic stabilization in the polar solvent. The interconversion process between the two minima of the potential surface corresponding to the excited singlet state, i.e. a planar state with a low dipole moment and a strongly polar charge transfer state, is described by a stochastic operator. The emission features are interpreted by a minimal set of parameters, both for radiative and non-radiative channels.

INTRODUCTION

The fluorescence emission of N,N-dimethylaminobenzonitrile (DMABN) and related molecules has been the subject of extensive experimental and theoretical studies in the last few years. Several interesting phenomena are observed by changing the temperature and/or the solvent polarity. The dual fluorescence emission which is typical of the excited S_1 state of these systems has been interpreted as the result of the interconversion between a weakly polar, planar configuration (locally excited or LE state) and a perpendicular configuration with a high dipole moment (charge transfer or CT state).

It has been first shown by Grabowski and coworkers[1] that a simple kinetic scheme is able to account for most of the experimental features exhibited by the

emission signal. Lippert and Rettig[2] have confirmed this analysis, and they have further pointed out the possibility of describing the time evolution of the excited state by means of simple stochastic operators, such as Smoluchowski or Fokker-Planck operators.

In recent papers[3-6], we have attempted to describe the dynamical behavior of a prototype model in which a simple bistable potential has been assumed for the conformational motions of the excited DMABN molecule, coupled to a solvent polarization coordinate. It was shown that when solvent dielectric relaxation times are large compared to the intrinsic interconversion times, solvent effects are mainly static due to the increased stabilization of the highly polar CT state in polar solvents. In this work, we intend to go further along this interpretation line by taking a more realistic potential form for the excited state and by considering all the relevant depletion channels of the excited state, including of course the emission decay to the ground state.

The complete model assumes the form of a microscopic semiclassical analogue of the original Grabowski kinetic scheme, with a significant reduction of phenomenological data. It is essentially based on the assumption of a diffusional regime for the interconversion process in the probe molecule and the solvent polarization fluctuations, occurring in the time interval between light absorption and emission. The only parameters to be specified are the stabilization energy of the CT state, which is obviously different for each solvent and can in principle be evaluated by simple electrostatic arguments, and the intensity of the emission decay. The diffusion coefficient for the internal interconversion can be evaluated by hydrodynamical considerations, and for various solvent it will be taken, in practice, inversely proportional to the viscosity of the solvent. Finally, the solvent relaxation times are simply evaluated with the help of a straightforward Onsager-Debye model [3].

As a final output, the static and dynamic emission spectra are numerically evaluated, for several aprotic polar solvents, as functions of temperature and time. Obviously, the attempt of simulating a rather complicate phenomenon, without a detailed knowledge of some of the relevant physical parameters involved in the problem, does not allow one to obtain a perfect reproduction of all the experimental data available. We will be able, however, to interpret the main features

of the observed spectra, positions and intensities of the signal peaks, temperature dependence, solvent dependence, and time evolution of the fluorescence emission.

THE MODEL

We assume that the relevant coordinate for the ground and excited state of the system is given by θ, torsional angle which defines the orientation of the dimethylamino group relative to the aromatic plane. We adopt as potential surfaces for the two electronic states of the molecule in a gas phase the two functions calculated ab initio by Kato and Amatatsu[7], who take also into account the 'wagging' angle ϕ of the dimethylamino group with respect to the benzene ring plane. We adopt here a simplified picture by keeping this angle fixed at a zero value. The approximate potential functions for the S_0 and S_1 states are then given as

$$V_{0,1}(\theta)/k_BT = \sum_{m=0}^{2} a_{0,1}^{(m)} \cos 2m\theta \tag{1}$$

where the set of parameters $a_{0,1}^{(m)}$ are easily obtained from Kato and Amatatsu data as $a_0^{(0)} = 0$, $a_0^{(1)} = -1683/T$, $a_0^{(2)} = 204/T$ and $a_1^{(0)} = 42088/T$, $a_1^{(1)} = -2634/T$, $a_1^{(2)} = 60/T$ (the zero of energy has been chosen so that $a_0^{(0)}$ is exactly 0).

We now introduce a semiclassical coupling with the polar solvent by considering a stochastic cavity reaction field X (or rather its component along the symmetry axis of the molecule), according to a Onsager description of the solvent as a dielectric continuum, in which the solute is embedded[3,8]. The coordinate X is coupled via a simple dipole-field term to the molecule internal coordinate, and the electric dipole moments are chosen to be null in the planar configuration and to reach a maximum value at $\theta = \pi/2$. This is an approximate description since the dipole momentum of the LE configuration in the real molecule is not zero. Moreover, in the following we shall neglect altogether the dipole momentum of the ground state, compared to the high CT excited state moment. Finally we add a contribution accounting for the cavity field fluctuations, described as harmonically bound around the zero value with an amplitude Ξ^2. The total potential energies of the two states are then

$$E_{0,1}(\theta, X)/k_BT = V_{0,1}(\theta)/k_BT - \mu_{0,1} X \sin^2\theta + \Xi^2 X^2/2 \tag{2}$$

The dependence upon any other set of coordinates (e.g. the rotational and translational degrees of freedom and other internal coordinates of the solute) is neglected.

The time evolution of the probability density $P(\theta, X, t)$ for the population of the excited state S_1 is thus determined by the interplay of the diffusion motion along the adiabatic surface E_1, the spontaneous emission to the ground state and the stimulated absorption to the excited state. A reasonable description can be achieved by writing the following modified 2-variable Smoluchowski equation, containing a source and a sink term:

$$(\partial/\partial t)P(\theta, X, t) = -[\hat{\Gamma} + k(\theta)]P(\theta, X, t) + S(\theta, X) \tag{3}$$

the initial conditions being assumed simply $P(\theta, X, 0) = 0$. The first term, i.e. the two-dimensional operator $\hat{\Gamma}$, is responsible[3] for the evolution on E_1:

$$\begin{aligned}\hat{\Gamma} = &- D_R(\partial/\partial\theta)\exp(-E_1/k_BT)(\partial/\partial\theta)\exp(E_1/k_BT) \\ &- D_S(\partial/\partial X)\exp(-E_1/k_BT)(\partial/\partial X)\exp(E_1/k_BT)\end{aligned} \tag{4}$$

The diffusion coefficient for the torsional motion D_R can in principle be evaluated by a hydrodynamic model; the diffusion coefficient for the solvent coordinate D_S, together with the constant Ξ, is determined by macroscopic parameters such as the static and optical dielectric constants ϵ_0 and ϵ_∞, and the (supposedly unique in this simplified model[3,8]) solvent relaxation time τ_S.

The second contribution to be considered is the continuous depletion of the S_1 state population due to non-radiative and radiative emission. We have chosen as k, total emission rate constant, the X-independent form:

$$k(\theta) = \overline{k}(1 + \cos^2\theta). \tag{5}$$

For lack of knowledge, the radiative constant has been chosen equal to the non-radiative one, except for a very simple θ dependence, since it has been subjected to the condition that the radiative emission is zero at the CT configuration, for orbital symmetry reasons[9]. In this way a unique parameter $\overline{k}$ accounts for the emission, which in principle should be adjusted for each temperature and solvent. We have found that in order to reproduce most of the experimental spectra the solvent dependence can be safely neglected, while the temperature dependence can be given an Arrhenius form $\overline{k} \sim \overline{k}^0 \exp(-E_a/k_BT)$.

Finally, the source term $S(\theta, X)$ is defined as a peaked function around the LE configuration, in an equilibrium distribution with respect to the solvent, in the ground state

$$S(\theta, X) = \delta(\theta) \exp(-\Xi^2 X^2/2)/\sqrt{2\pi} \tag{6}$$

i.e. the stimulated absorption is taken as a Dirac delta function of θ centered in the LE configuration, with a Gaussian distribution over the solvent coordinate.

In order to evaluate the dynamic distribution on the excited state and its stationary limit $P_{st}(\theta, X)$, one can resort to eigenfunctions expansions, by representing in matrix form the operator $\hat{\Gamma}$, and then adopting linear algebra algorithms. The details of the numerical procedure have been given elsewhere[4,5]. Here it may be relevant to stress that, given a judicious choice of the computational ingredients (e.g. the basis functions form), the evaluation of the distribution at a given time is a matter of a few CPU second on a PC, while the computation of the relative fluorescence spectrum is only slightly more costly.

Once the distribution probability $P(\theta, X, t)$ is known, one is able to evaluate the emission spectrum by integrating over weighted contributions of all the microscopic states (θ, X). Following a procedure suggested by Kang et al.[10], we simply write the signal function as

$$I(\omega, t) \propto \omega^3 \int_0^{2\pi} d\theta \int_{-\infty}^{+\infty} dX F(\theta) P(\theta, X, t) g[\omega, \omega_0(\theta, X)] \tag{7}$$

where the function $F(\theta)$ is the electronic part of the total transition moment, and $g[\omega, \omega_0(\theta, X)]$ is a band shape function centered on $\omega_0(\theta, X)$, defined as the emission frequency for the (θ, X) configuration $\hbar\omega_0(\theta, X) = E_1(\theta, X) - E_0(\theta, X)$. We have taken $F(\theta)$ simply proportional to $\cos^2\theta$, i.e. to the radiative emission rate, and the shape function $g(\omega)$ equal to the normalized spectrum of DMABN in apolar solvents, such as hexane.

When the system relaxes to stationary conditions, one obtains the time independent signal $I_{st}(\omega)$, by substituting in the previous equation the stationary distribution P_{st}. This distribution, obtained as the limit at infinite time of $P(\theta, X, t)$ is quite different from the Boltzmann distribution $P_{eq}(\theta, X)$ corresponding to the potential surface E_1. In fact, the continuous pumping to the LE state maintains a LE population much higher than the equilibrium value.

RESULTS AND DISCUSSION

Because of the unavoidable approximations introduced in evaluating the functional forms of the adiabatic potential surfaces and of the decay constants, we are left with very few intrinsically free parameters. In fact, we estimate the diffusion coefficient D_R for the rotation of the dimethylamino group in a given solvent as inversely proportional to the tabulated viscosity, and we fix the ratio D_S/D_R in dependence of $\epsilon_0/\epsilon_\infty$, as it is found from continuum theories of polar solvents. For sake of simplicity, we neglect the dipole moment μ_0 in the ground state when compared to the dipole moment in the excited state. We are left with the parameters $\overline{k}^0$ and E_a which account for the temperature dependence of the emission rate, characteristic of the probe molecule, and the solvent dependent parameter ΔE_S which is equal to the stabilization energy of the CT state with respect to gas phase. In our model this simply corresponds to $\mu_1^2/2\Xi^2$.

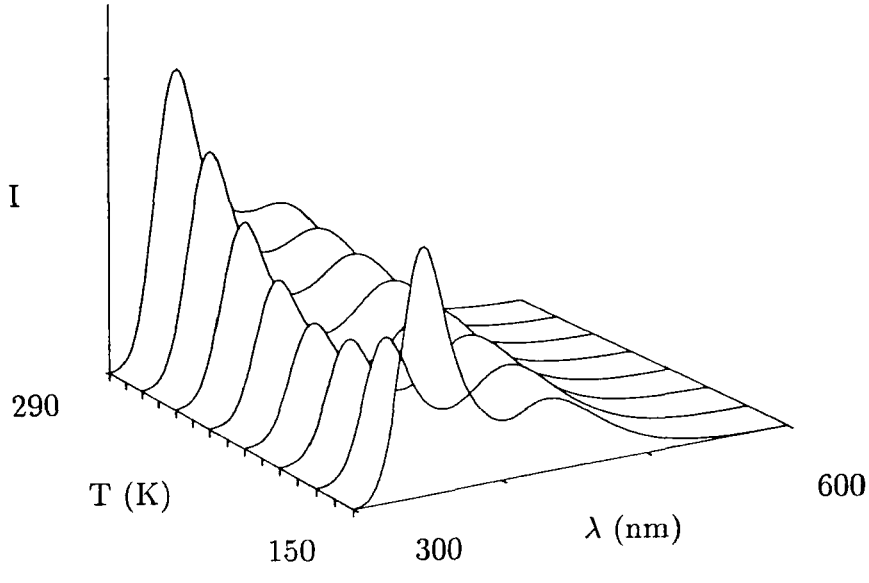

FIGURE 1. Simulated fluorescence emission of DMABN in n-butylchloride at several temperatures.

In Figure 1 we show a first set of simulated spectra, intended to reproduce the experimental data available in the literature for the static emission fluores-

cence of DMABN in n-butylchloride at several temperatures[2,11]. A satisfactory agreement has been found for $\Delta E_S \sim 55$ kJ mol^{-1}, which is not far from electrostatic evaluation[2]. The calculated spectra exhibit a minimum around 200 K for the LE band, as observed in the experiments, together with a weak red shift with decreasing temperature for the broad CT band. The unit of frequency has been chosen by taking $D_R = 1$ for $T = 290$ K and the T-dependence of the diffusion coefficients has been determined by taking an activation energy of 7 kJ mol^{-1}, corresponding to the activation energy E_η for the viscosity of n-butylchloride[2]. Lastly, values of 5×10^{-3} (in units of D_R in n-butylchloride at 290 K) and 8 kJ mol^{-1} have been assigned to $\overline{k}^0$ and E_a, respectively. Notice that an estimate of D_R based on the Stokes-Einstein relation gives a value of $10^{11} - 10^{12}$ sec^{-1} at room temperature, for the case of n-butylchloride solvent. Correspondingly, the total emission rate turns out to be of the order of 10^8 sec^{-1}.

Another set of simulations has been dedicated to study pure solvatochromic effects, at fixed temperature.

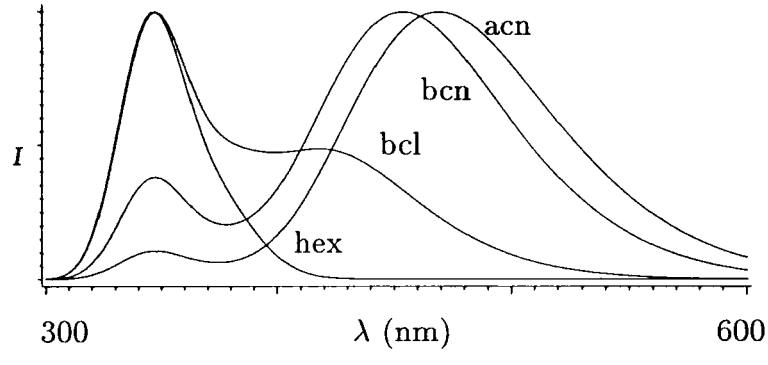

FIGURE 2. Solvatochromic effect on DMABN dual fluorescence at 290 K in different solvents.

Figure 2 shows the spectra calculated at $T = 290K$ for four different solvents:

hex = hexane, $\Delta E_S = 0$ kJ mol^{-1} and $D_R = 0.5$;

bcl = n-butylchloride, $\Delta E_S = 55$ kJ mol^{-1} and $D_R = 1$;

bcn = butyronitrile, $\Delta E_S = 66$ kJ mol^{-1} and $D_R = 0.4$;

acn = acetonitrile, $\Delta E_S = 72$ kJ mol^{-1} and $D_R = 1.4$.

For each case the probe diffusion coefficient D_R was determined by the ratio between the viscosity of n-butylchloride and the viscosity of the actual solvent. The stabilization energy ΔE_S was chosen to reproduce the CT band wavelength known from experiments, although no systematic fitting procedure was employed. The values obtained for ΔE_S are linearly proportional to other solvent dependent energy parameters, such as the difference between the CT and LE state in the excited singlet proposed and evaluated by Rettig[2].

Good agreement with actual spectra[2] is indeed reached, even if it appears that the LE band does not change significantly by changing the solvent, while real spectra exhibit a weak red shift. This is because we have neglected any solvent stabilization energy for the ground state, but this effect could be easily introduced in the model.

Dynamic emission spectra have been also computed. By the analysis of the dynamic experimental data, one can infer information about the interconversion process between the LE and CT excited metastable states[2]. It is important to remark that the theoretical analysis may provide useful suggestions for the choice of experimental conditions in which the time evolution of the spectra can be directly related to particular kinetic pathways. This in principle can be done by choosing proper initial conditions, or by following the growth or the decay of particular spectral bands.

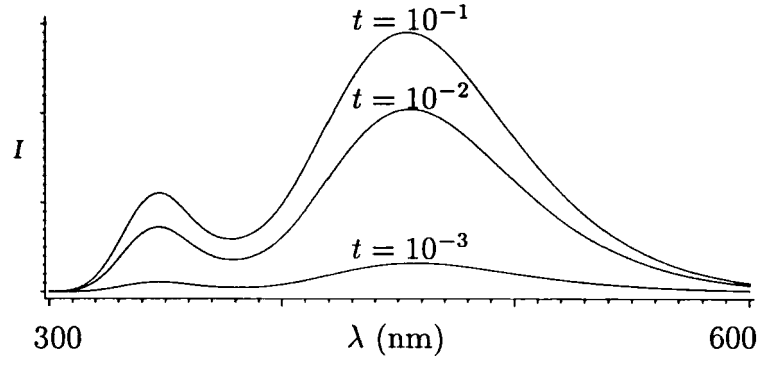

FIGURE 3. Time evolution of the fluorescence emission spectra in butyronitrile. The unit of time is defined as the inverse of D_R in n-butylchloride at 290 K.

Figure 3 shows a typical set of dynamic spectra computed for n-butyronitrile solutions at 290 K. We have calculated the increase of the fluorescence signal which is obtained by starting with a zero population in the excited state, and by turning on the continuous pumping source at $t = 0$. At any time, the emission spectrum resembles the stationary one, due to the rapid flux of the population generated by the pulse from the LE state to the highly favoured CT minimum. The rate of increase of the signal at a fixed wavelength is in general determined by the average rates of emission in the LE and CT states, and by the interconversion constants between the two minima. These constants can be obtained by the asymptotic analysis of the diffusion operator[3]. Only in particular cases the dependence of the emission on time is fitted by a single exponential. For instance, at low temperatures the dependence on time is approximately monoexponential, with a rate constant given by the interconversion constant $k_{\mathrm{LE}\to\mathrm{CT}}$.

Usually dynamic emission experiments are set up by collecting the decaying signal, after the source pulse is turned off. In our model, this situation is reproduced by putting to zero the $S(\theta, X)$ term in Eq. (3). The decay of the emission spectrum is then calculated by taking as initial condition the stationary distribution $P_{\mathrm{st}}(\theta, X)$.

In most of the physical conditions adopted in the previous simulations, the interconversion rate $k_{\mathrm{LE}\to\mathrm{CT}}$ is essentially proportional to the probe relaxation frequency D_R. Situations however may occur, when the potential barrier for the LE $\to$ CT transition practically disappears, in which the kinetic process becomes controlled by the solvent dynamics.

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