J. Phys. Chem. A **2003,** *107,* 8327−8329

Intramolecular Reorganization of the Electron Donor *N*,*N*-Dimethylaniline[†]

Philipp O. J. Scherer*

Physics Department T38, Technical University Munich, D-85748 Garching, Germany

Received: December 30, 2002; In Final Form: July 6, 2003

Intramolecular reorganization is investigated for the transition DMA → DMA^+ of the electron donor *N*,*N*-dimethylaniline. Optimized geometries and normal modes are calculated quantum chemically for DMA and DMA^+. Partial reorganization energies of the normal modes are determined. Several modes between 100 and 1700 cm^{-1} are found to couple to the transition. The Franck−Condon weighted density of states is evaluated, which enters the nonadiabatic rate expression. It is found that the intramolecular modes can be effective as energy acceptors over a wide range of excess energies.

Introduction

Photoinduced electron transfer is a very important elementary step in physical, chemical, and biological processes. According to the Marcus[1,2] theory of intermolecular electron transfer the reorganization of the solvent plays a very important role. Within the framework of linear response theory applied to a dielectric medium the electron-transfer rate can be calculated using the free energy change of the reaction ΔG, the reorganization energy λ, and the coupling matrix element **V** by

$$k = \frac{2\pi}{\hbar}\mathbf{V}^2 \frac{1}{\sqrt{4\pi\lambda kT}} \exp\left(-\frac{(\Delta G + \lambda)^2}{4\lambda kT}\right) \qquad (1)$$

This expression was derived on the assumption that the coupling matrix element **V** is small and the process is nonadiabatic. If larger molecules with extended π-electron systems are involved as electron donor or acceptor, the Marcus equation has to be corrected for the contribution of intramolecular vibration to the reorganization.[3,4] Usually, the assumption is made that low-frequency (i.e., $\hbar\omega < kT$) intramolecular vibrations only add to the reorganization energy λ. High-frequency stretching modes, which often show up in the structure of the optical spectra have to be treated quantum mechanically. This can be done by including the progression of a dominant mode at $\hbar\omega_i \approx 0.2$ eV, which leads to the often used equation

$$k = \frac{2\pi}{\hbar}\mathbf{V}^2 \frac{1}{\sqrt{4\pi\lambda kT}} \sum_m \frac{e^{-S}S^m}{m!} \exp\left(-\frac{(\Delta G + \lambda + m\hbar\omega_i)^2}{4\lambda kT}\right) \qquad (2)$$

with $S = \lambda_i/\hbar\omega_i$ where λ_i is the vibrational reorganization energy.

Recently,[5,6] electron-transfer times in the subpicosecond regime have been reported for solutions of electron accepting molecules in an electron-donating solvent such as *N*,*N*-dimethylaniline. Here dielectric relaxation is less important for the transfer process because it takes much longer than the transfer and the solvent is only weakly polar. Hence intramolecular reorganization becomes a rate-determining factor. Treating all intramolecular vibrations quantum mechanically and applying the Born−Oppenheimer and Franck−Condon approximations yields the rate as given by the Golden Rule expression

$$k = \frac{2\pi}{\hbar}\mathbf{V}^2\ \mathrm{FCD}(-\Delta E) \qquad (3)$$

with the Franck−Condon weighted density of states

$$\mathrm{FCD}(\hbar\omega) = \sum P(i,kT)|\langle\Phi_\mathrm{i}|\Phi_\mathrm{f}\rangle|^2\delta(\hbar\omega - \hbar\omega_\mathrm{i} + \hbar\omega_\mathrm{f}) \qquad (4)$$

where $\Phi_{\mathrm{i,f}}$ denote the vibrational wave function of the initial or final state and $P(i,kT)$ is the thermal occupation probability. Evaluation of eq 4 needs the detailed knowledge of the vibrational wave functions. In two recent papers we studied intramolecular reorganization after electron transfer in DMA/oxazine and DMA/cyanoanthracene solutions.[7,8] Here we present more detailed results on the vibrations of the donor DMA and its cation DMA^+. Within the harmonic approximation we calculate the normal modes of DMA and DMA^+ quantum chemically together with their IR absorption intensities. We calculate frequency changes and equilibrium shifts and evaluate the Franck−Condon weighted density of states relevant for the transition DMA → DMA^+ .

Results

All quantum chemical calculations were performed with the GAMESS[9] program package. We used the 631G(p,d) basis set and the RHF/MP2 or UHF/MP2 level of theory. For the geometry optimization and the subsequent normal-mode analysis we used internal coordinates to allow for a proper treatment of large amplitude motions, e.g., rotation of the methyl groups (Figure 1).The calculated IR spectrum of DMA agrees quite well with the experimental data[10] (see Figure 2). The calculated frequencies are somewhat too high, especially in the CH stretch region around 3000 cm^{-1}.

Several modes show considerable equilibrium shifts but only little normal mode mixing. Besides a typical stretching mode at 1689 cm^{-1}, there are four further coupling modes around 1200 cm^{-1}, another three around 400 cm^{-1}, and two strong coupling low vibrations at 130 and 184 cm^{-1}. Table 1 shows the calculated reorganization energies and frequency changes of the 10 strongest coupling modes. Obviously representation by only one high-frequency mode must lead to a poor approximation of the FCD. The total reorganization energy of 5400

[†] Part of the special issue “A. C. Albrecht Memorial Issue”.

* Corresponding author. E-mail: philipp.scherer@ph.tum.de.

10.1021/jp027855d CCC: $25.00

TABLE 1: Strongest Coupling Normal Modes of DMA (Reorganization Energies Larger Than 100 cm^{-1})

normal mode	DMA frequency (cm^{-1})	DMA$^+$ frequency (cm^{-1})	reorganization energy (cm^{-1})
ν2	130	140	1374
ν3	184	193	860
ν5	288	320	1234
ν8	424	390	444
ν12	564	568	564
ν20	981	1000	14
ν26	1183	1142	274
ν29	1247	1207	150
ν40	1393	1367	155
ν43	1689	1464	525

cm^{-1} is somewhat larger the value of 3500 cm^{-1}, which resulted of an energy minimization of the DMA$^+$ cation starting from the ground-state equilibrium structure. This is probably mainly due to the neglect of anharmonic effects. Table 2 relates the strongest coupling modes to the structure of the molecule and shows which internal coordinates are mostly involved.

Within the approximation of independent harmonic oscillators we calculated the FCD for the transition DMA → DMA$^+$. We neglected the effects of normal mode mixing. Our calculations showed that this approximation is justified at least for the strong coupling modes. From a polynomial fit to five energy values along each normal coordinate we estimated the frequency changes and reorganization energies in the cationic state. The Franck−Condon factors were calculated by standard procedures.

To avoid a complicated convolution procedure, we first calculated the product of harmonic oscillator correlation functions in the time domain[11]

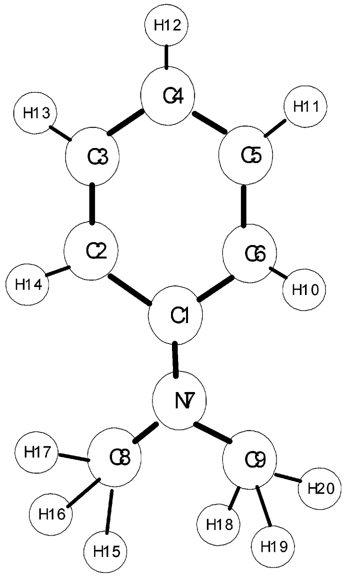

Figure 1. Atom numbers used to define the internal coordinates.

$$g_{\mathrm{p}}(t) = \sum_{m=0,n=0}^{\text{Max.}} \frac{e^{-m\hbar\omega_{\mathrm{p}}/kT}}{1 - e^{-\hbar\omega_{\mathrm{p}}/kT}} \mathrm{FC}(m,n)^2 e^{it(m\omega_{\mathrm{p}} - n\omega_{\mathrm{p}}{}^{+})} \qquad (5)$$

and performed a fast Fourier transformation. The sum was cut off at a maximum quantum number of Max. = 25, which gives

TABLE 2: Analysis of the Strongest Coupling Modes[a]

mode	bonds	bond angles	torsion angles
ν2		(+)C9−N7−C1 (+)C8−N7−C1	(−)N7−C1−C2−C3, (−)C8−N7−C1−C2, (+)C9−N7−C1−C2 (+)H15−C8−N7−C1, (+)H16−C8−N7−C1, (+)H17−C8−N7−C1 (−)H18−C9−N7−C1, (−)H19−C9−N7−C1, (−)H20−C9−N7−C1
ν3			(−)N7−C1−C2−C3, (+) C8−N7−C1−C2, (−) C9−N7−C1−C2 (+)H15−C8−N7−C1, (+)H16−C8−N7−C1, (+)H17−C8−N7−C1 (−)H18−C9−N7−C1, (−)H19−C9−N7−C1, (−)H20−C9−N7−C1
ν5		(+)C8−C1−C2 (+)C9−C1−C2	(+)N7−C1−C2−C3, (−)C8−N7−C1−C2, (+)C9−N7−C1−C2 (+)H15−C8−N7−C1, (+)H16−C8−N7−C1, (+)H17−C8−N7−C1 (−)H18−C9−N7−C1, (−)H19−C9−N7−C1, (−)H20−C9−N7−C1
ν8			(+)N7−C1−C2−C3, (−)C8−N7−C1−C2, (+)C9−N7−C1−C2 (+)H15−C8−N7−C1, (+)H16−C8−N7−C1, (+)H17−C8−N7−C1 (−)H18−C9−N7−C1, (−)H19−C9−N7−C1, (−)H20−C9−N7−C1
ν12		(+)C5−C4−C3 (+)C8−N7−C1 (+)C9−N7−C1	(+)C4−C3−C2−C1 (+)N7−C1−C2−C3, (−)C8−N7−C1−C2, (−)C9−N7−C1−C2 (+)H15−C8−N7−C1, (+)H16−C8−N7−C1, (+)H17−C8−N7−C1 (−)H18−C9−N7−C1, (−)H19−C9−N7−C1, (−)H20−C9−N7−C1
ν20	C8−N7 C9−N7		
ν26	(−) N7−C1	(−)H15−C8−N7 (+)H16−C8−N7 (−)H18−C9−N7 (+)H20−C9−N7	(+)N7−C1−C2−C3, (−)C8−N7−C1−C2, (+)C9−N7−C1−C2 (+)H15−C8−N7−C1, (+)H16−C8−N7−C1, (−)H17−C8−N7−C1 (−)H18−C9−N7−C1, (+)H19−C9−N7−C1, (−)H20−C9−N7−C1
ν29	(+)C1−C2 (−)C3−C2 (−)C6−C5 (−)N7−C1	(−)H10−C6−C5 (+)H11−C5−C4 (−)H13−C3−C2 (+)H14−C2−C1	
ν40	(−)N7−C1 (+)C8−N7 (+)C9−N7	(−)H10−C6−C5 (+)H13−C3−C2 (+)H14−C2−C1 (−)H16−C8−N7 (−)H20−C9−N7	(−)H15−C8−N7−C1, (+)H18−C9−N7−C1
ν43	(+)C1−C2 (−)C2−C3 (+)C4−C3 (+)C5−C4 (−)C6−C5 (−)C1−C6	(−)C5−C4−C3 (+)H10−C6−C5 (−)H11−C5−C4 (+)H13−C3−C2 (−)H14−C2−C1	

[a] The internal coordinates with the largest changes are shown. The signs show the relative phases for each mode.

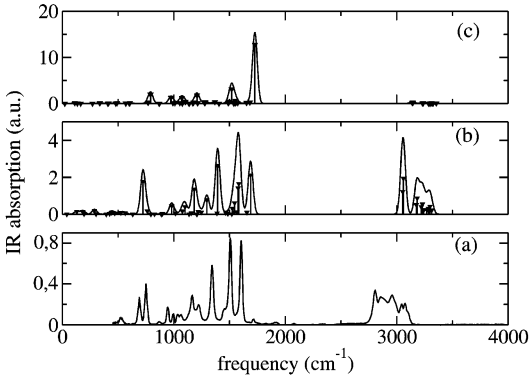

Figure 2. Experimental infrared absorption spectra of DMA (a) compared with the calculated spectrum for DMA (b) and DMA$^+$ (c).

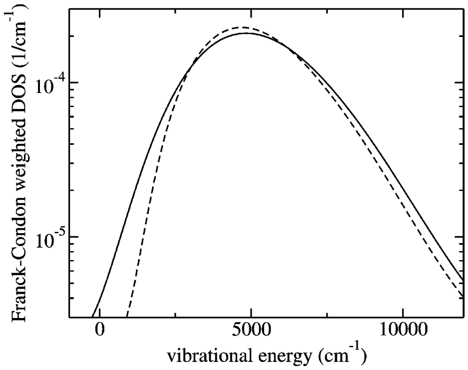

Figure 3. Calculated Franck−Condon weighted density of states as a function of the vibrational excess energy for two different temperatures: full line, 300 K; dashed line, 30 K.

a sufficiently converged result. A damping factor was included to smooth the resulting Franck−Condon weighted density of states FCD which is shown as a function of the vibrational excess energy in Figure 3. The resulting FCD shows a maximum around 5000 cm^{-1}.

Conclusions

In a weakly polar solvent intramolecular reorganization may be very important for ultrafast electron-transfer processes. For DMA we find that a larger number of modes between 100 and 1700 cm^{-1} change their equilibrium positions upon formation of the cation. The calculated FCD shows a rather broad distribution that is in accord with the experimental observation that DMA is an efficient electron donor in many cases. In contrast to low-frequency polarization modes that are the origin of reorganization in polar media, such intramolecular modes can also show significant frequency changes. In the standard model, the maximum of the rate appears when the reaction free energy equals the solvent reorganization energy. If frequency changes are important, however, the position of the maximum becomes temperature dependent. This leads to a more complicated temperature dependence of the reaction rate, which cannot be described adequately by the standard expression eq 2. The intramolecular reorganization of DMA should be observable by changes in the IR spectrum as the calculated spectra show quite significant differences.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft project SFB377

References and Notes

(1) Marcus, A. *J. Chem. Phys.* **1956**, *24*, 966.

(2) Marcus, A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(3) Miller, J. R.; Beitz, J. V.; Huddleston, K. *J. Am. Chem. Soc.* **1984** , *106*, 5064.

(4) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 193.

(5) Seel, M.; Engleitner, S.; Zinth, W. *Chem. Phys. Lett.* **1997**, *275*, 363.

(6) Iwai, S.; Murata, S.; Tachiya, M. *J. Chem. Phys.* **1998**, *109*, 5963.

(7) Scherer, P. O. J. *J. Phys. Chem. A* **2000**, *104*, 6301.

(8) Scherer, P. O. J.; Tachiya, M. *J. Chem. Phys.* **2003**, *118*, 4149.

(9) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; , S. S.,. T.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(10) Linstrom, P. J., Mallard, W., Eds. *NIST Chemistry WebBook*; NIST Standard Reference Database Number 69; National Institute of Standards and Technology, Gaithersburg MD, 20899, March 2003 (http://webbook.nist.gov).

(11) Yan, Yi Jing; Mukamel, Shaul. *J. Chem. Phys.* **1986**, *85*, 10, 5908.