THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 107, NUMBER 50, DECEMBER 18, 2003

ARTICLES

Ultrafast Vibrational and Thermal Relaxation of Dye Molecules in Solutions

Jian-Yong Liu, Wen-Hui Fan, Ke-Li Han,* Wei-Qiao Deng, Da-Li Xu, and Nan-Quan Lou

Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
Dalian 116023, The People's Republic of China

Received: March 20, 2003; In Final Form: September 17, 2003

Intra- and intermolecular relaxations of dye molecules are studied after the excitation to the high-lying excited states by a femtosecond laser pulse, using femtosecond time-resolved stimulated emission pumping fluorescence depletion spectroscopy (FS TR SEP FD). The biexponential decays indicate a rapid intramolecular vibrational redistribution (IVR) depopulation followed by a slower process, which was contributed by the energy transfer to the solvents and the solvation of the excited solutes. The time constants of IVR in both oxazine 750 and rhodamine 700 are at the 290−360 fs range, which are insensitive to the characters of solvents. The solvation of the excited solutes and the cooling of the hot solute molecules by collisional energy transfer to the surrounding takes place in the several picoseconds that strongly depend on the properties of solvents. The difference of Lewis basicity and states density of solvents is a possible reason to explain this solvent dependence. The more basic the solvent is, which means the more interaction between the solute and the neighboring solvent shell, the more rapid the intermolecular vibrational excess energy transfer from the solute to the surroundings and the solvation of the solutes are. The higher the states density of the solvent is, the more favorable the energy transfer between the solute and solvent molecules is.

Introduction

The excited-state relaxation dynamics of organic dye molecules in solution has been the subject of experimental interest ever since the development of pico- and femtosecond lasers.[1−19] An improved knowledge of relevant photophysical processes may result in additional discoveries, leading to the availability of more efficient laser dyes covering the entire spectral range.

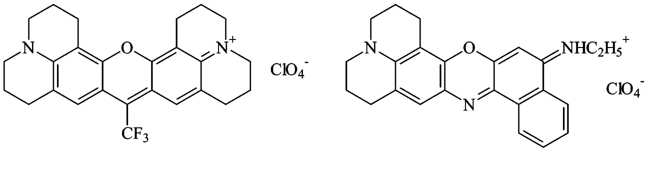
Following an optical excitation of a solute molecule in polar solvent, several ultrafast dynamic processes will take place: first, the intramolecular vibrational redistribution (IVR) occurs mostly on the subpicosecond time scale.[1−6] This rapid process results in a quasiequilibrium distribution in the vibrational manifold equivalent to an elevated temperature of the molecule. Second, the vibrational hot S_1 state is cooled by energy dissipation to the solvent molecules.[20−23] Time scales are 5−50 ps depending on the specific solvent and the amount of excess energy.[10] Another ultrafast process that contributes to the slower time constants is the solvation of the excited solute molecules, whose time scales are the same as the cooling of the hot solute molecules.[36−39] The studies have been reviewed by some authors.[24−29]

A theoretical model of the energy transfer in liquid phase is developed to simulate the kinetics of thermal relaxation by Elsaesser and co-workers.[26,30] In this analysis, two different processes contribute to the randomization of energy. Vibrational and translational excess energy is transferred from the hot solute to the neighboring solvent shell by binary collisions. The transport of energy within the solvent is described by the conduction of heat. In this model, the interaction of the solute and the first solvent shell is treated in perturbation theory, in which a Lennard-Jones potential is used. For heat conduction,

---

* Corresponding author: e-mail klhan@dicp.ac.cn.

10.1021/jp034722z CCC: $25.00



Rhodamine 700 Oxazine 750

Figure 1. Structural formulas of rhodamine 700 and oxazine 750.

the thermal diffusivity κ of the solvent represents the most important material parameter. Because κ does not vary strongly between different liquids, the authors consider that the thermal conduction is not very sensitive to the specific solvent. However, a linear relationship between the vibrational cooling time constant in $[Ru(bpy)_3]^{2+}$ and the thermal diffusivity of the solvent has been reported, too.[31]

In the previous paper, we have studied the ultrafast relaxation of the exited oxazine 750 and rhodamine 700 dye molecules as a function of the temperature using the femtosecond time-resolved stimulated emission pumping fluorescence depletion (FS TR SEP FD) method.[32] To understand the influence of the solvent in the excited-state relaxation process of dye molecules even more, FS TR SEP FD experiments are performed on oxazine 750 and rhodamine 700 in the different solvents. Some new phenomena about the fast IVR, solvation, and intermolecular energy transfer between solute and solvent are observed.

Experimental Section

The setup used in this experiment is the same as that shown in the previous paper.[32] A homemade Ti:sapphire femtosecond laser with amplifier is used. The output pulses of 60 fs (energy 0.25 mJ, wavelength 800 nm) are used for the generation of UV laser pulses (pulse wide 120 fs, wavelength 400 nm, energy 60 μJ) by frequency doubling with a BBO crystal. In the FS TR SEP FD experiments, the probe beam (800 nm) is collinear with the pump beam (400 nm). The fused quartz sample cell is placed in a spot behind the focus where the beam diameter is 2 mm to avoid the thermal effect of the sample due to the laser heating. The optical path of pump beam is controlled by a translation stage. The probe polarization is at the magic angle with respect to the pump polarization to avoid the influences of rotational relaxation and the reorientation of solvent molecules. The intensity of the fluorescence (730 nm) perpendicular to the incident beams is measured as a function of delay between the pump and probe pulses. A frequency-tripling BBO crystal is used to generate 266 nm pulse by both the pump and probe pulses, which is fixed at the same position as the sample cell. The zero time point and the time resolution are evaluated by detecting the correlation of 266 nm pulse power and the time delay between the probe pulse and the pump pulse.

Oxazine 750 and rhodamine 700 used in the present study were purchased from Exciton. Oxazine 750 was solved at a concentration of 7.23×10^{-4}M in acetone, DMF, DMSO, and formamide. Rhodamine 700 was solved at a concentration of 1.23×10^{-3}M in acetone, methanol, ethanol, and DMSO.

Result and Discussion

Both oxazine 750 and rhodamine 700 are important laser dye molecules used in the infrared region, whose structural formulas are shown in Figure 1. Both of them are ionized when they are dissolved in solution. By the pump pulse at 400 nm, oxazine 750 molecules are excited from the ground state to the S_1 state and rhodamine 700 molecules reach the mixed state of the S_1 and S_2. Following the optical excitation, both oxazine 750 and rhodamine 700 reach the high vibrational states in their excited electronical state with high excess energy (10 589 and 10 342 cm^{-1} in acetone, respectively, and similar values in other solutions used in the experiment).

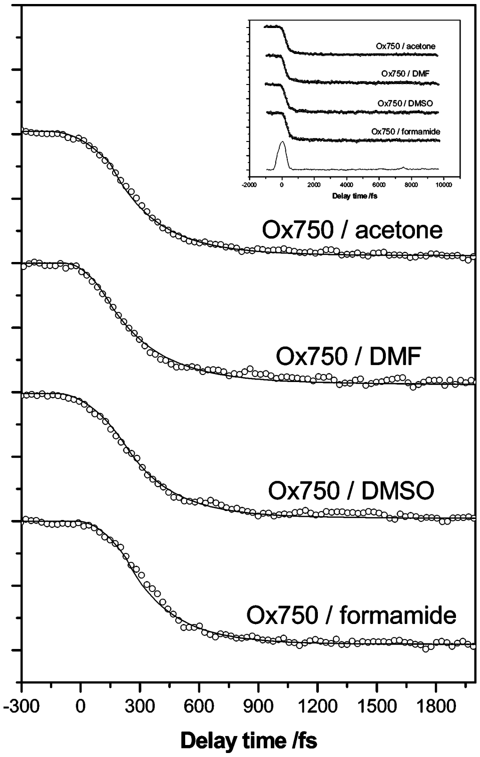


Figure 2. Time-resolved stimulated emission pumping fluorescence depletion of oxazine 750 (Ox750) in different solvents. (○) Experimental data; (—) simulated results.

In Figures 2 and 3, the fluorescence depletion signals of oxazine 750 and rhodamine 700 in different solvent are shown. As shown above, two decay processes are found: a faster decay with a few hundred femtoseconds and a slower decay with a picosecond time scale. The experimental results can be fitted by the deconvolution of eq 1:[17]

$$\Delta I(\tau) = \int_{-\infty}^{\infty} R(t-\tau)\,\mathrm{d}t - S_{e0}\int_{-\infty}^{\infty} \exp(-t/\tau_e)R(t-\tau)\,\mathrm{d}t - S_{p0}\int_{-\infty}^{\infty} \exp(-t/\tau_p)R(t-\tau)\,\mathrm{d}t \quad (1)$$

Here$R(t - \tau)$ is the correlation function. The time constants of ultrafast dynamics of electronically excited oxazine 750 and rhodamine 700 molecules in solutions are given in Tables 1 and 2. The properties of the solvents are shown in Table 3. The constants of the rapid decay process of both oxazine 750 and rhodamine 700 are ranged between 290 and 360 fs, and they seem to be independent of the solvents. For the picosecond process, the time constants change dramatically with the variation of the solvents. For oxazine 750, this process takes about 7 ps in acetone and DMF as well as DMSO solutions; however, it takes 21 ps in formamide. For rhodamine 700, the time constant of this slow relaxation is less than 2 ps in acetone, nearly 7 ps in methanol and ethanol, and about 10 ps in DMSO.

Following the excitation of the dye molecules, both the oxazine 750 and rhodamine 700 molecules reach the excited state with the high excess energy, where the number density of vibrational state is significantly high. The quasicontinuum of states gives rise to the possibility of the intramolecular redistribution, which leads to a quasiequilibrium population of the vibrational manifold, characterized by a temperature higher

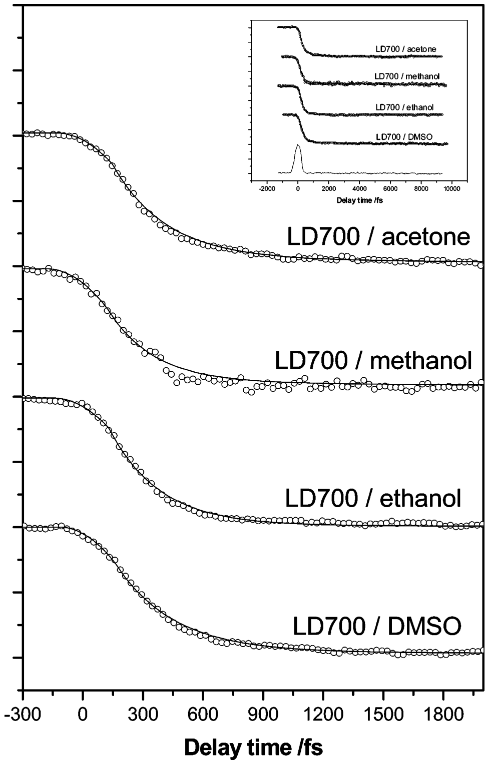


Figure 3. Time-resolved stimulated emission pumping fluorescence depletion of rhodamine 700 (LD700) in different solvents. (○) Experimental data; (—) simulated results.

TABLE 1: Time Constants of Ultrafast Relaxation for Oxazine 750 in Different Solvents

solvent	S_{p0}	τ_p (fs)	S_{e0}	τ_e (ps)
acetone	0.95	350 ± 65	0.05	7.09 ± 1.50
DMF	0.92	310 ± 78	0.08	6.89 ± 1.70
DMSO	0.97	360 ± 75	0.03	7.84 ± 1.92
formamide	0.95	359 ± 65	0.05	21.3 ± 3.9

TABLE 2: Time Constants of Ultrafast Relaxation for Rhodamine 700 in Different Solvents

solvent	S_{p0}	τ_p (fs)	S_{e0}	τ_e (ps)
acetone	0.96	333 ± 54	0.04	1.84 ± 0.58
DMSO	0.97	359 ± 75	0.03	10.2 ± 1.9
ethanol	0.99	330 ± 50	0.01	6.51 ± 0.90
methanol	0.92	290 ± 60	0.08	7.27 ± 1.20

than that of the surrounding solvent. In comparison with the situation in gas phase, the hot molecules could be cooled by the interaction with solvent molecules. The time constants of this process depended on the amount of vibrational excess energy and on the specific solvent. Since the electronic transition is rapid compared to nuclear motions of the solvent, the excited state is initially prepared with a solvation environment that is characteristic of equilibrium in S_0, not S_1. Over time the solvent reorganizes or progresses along the “solvation coordinate”, to lower the solvation energy in the excited state. The time scales of the cooling of the hot solute molecules and the solvation process are similar. As discussed above, the fast relaxation processes found in this experiment are IVR. The energy transfer between solute and solvent molecules and the solvation of the excited solutes contribute to the slow processes.

The experimental results indicate that the IVR of the excited oxazine 750 and rhodamine 700 molecules, which is insensitive to the solvent, is controlled only by the coupling of the vibrational modes of the solute molecules and seems independent with the solvent mode. It is almost a pure intramolecular process despite in the solutions.

Two steps are involved in the vibrational energy transfer of the hot solute molecules to the surrounding: first, vibrational excess energy is transferred from the hot solute to the neighboring solvent shell by collisions. The collisional rate and the amount of transferred energy per collision depend on the interaction between solute and solvent molecules. Second, the resulting temperature gradient between the inner shell and the remaining (cold) solvent leads to heat transmit by the collisions among solvent molecules, which continues until an equilibrium temperature is reached in the whole solution.

According to the theoretical model of Sukowski et al.,[30] the dissipation of energy within the solvent can approximated by the macroscopic equation of the conduction of heat.[34] The thermal diffusivity $\kappa = \{\lambda M\}/\{(C\rho)\}$ of the solvent represents the most important material parameter (λ, thermal conductivity; M, molecular weight; C, specific heat; ρ, density). The thermal diffusivities of solvents used in our experiment are presented in Table 3. Because κ does not vary strongly between different solvents, the thermal conduction is not very sensitive to the specific solvent, which is consistent with the analysis of the theoretical model.[34] This fact indicates that it is the collisional energy transfer from the hot solute to the neighboring solvent shell, not the heat transmit among solvent molecules, which controls the whole rate of the intermolecular vibrational energy transfer from the solute to the surroundings.

The Lennard-Jones potential is used in ref 30 to describe the interaction of the solute and the first solvent shell. But for the systems used in our experiment, both oxazine 750 and rhodamine 700 are ionized when they are dissolved in solution. The interaction of a cation and a neutral molecule cannot describe by a Lennard-Jones potential.

To compare the intensity of the interaction between the ionized dye molecule and solvent shell, Lewis acid−base theory provides some useful information. According to Lewis acid−base theory, any molecules and ions that can afford an electron pair are Lewis bases and that can accept electron pair are Lewis acids.[33] The ionization process in solution to produce solvated anion (or solvated cation) can be regarded as a replacement of the Lewis acid (or Lewis base) between the solute and the solvent. The interaction of the cation and the neighboring solvent shell can be considered as the interaction of a Lewis acid (the cation) and a Lewis base (the solvent), which means that the intensity of this interaction is controlled by the acidity of the solute cation and the basicity of the solvent. And the frequencies of the binary collisions between the solute and solvent molecules

TABLE 3: Material Constants of the Different Solvents

solvent	acceptor number	thermal conductivity (10^{-3} W/m·K)	molecular mass (g/mol)	density (g/cm^3)	specific heat (J/mol·K)	thermal diffusivity (10^{-3} cm^2/s)
acetone	12.5	159.4	58.08	0.791	126.8	0.923
DMF	16.0	165.7	73.09	0.945	164.9	0.78
DMSO	19.3	165.3	78.13	1.095		
ethanol	37.1	180.5	46.07	0.789	109.4	0.96
formamide	39.8	315.9	45.04	1.133	123.3	1.02
methanol	41.3	219.8	32.04	0.792	79.26	1.12

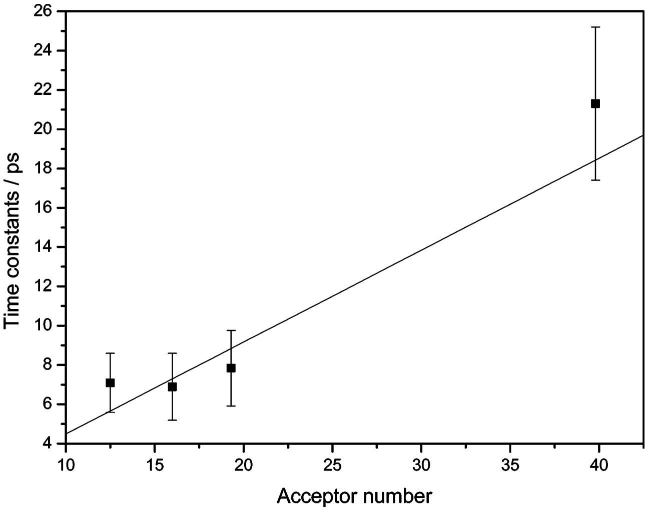


Figure 4. Plot of vibrational cooling time constant in oxazine 750 versus the acceptor number of the solvent.

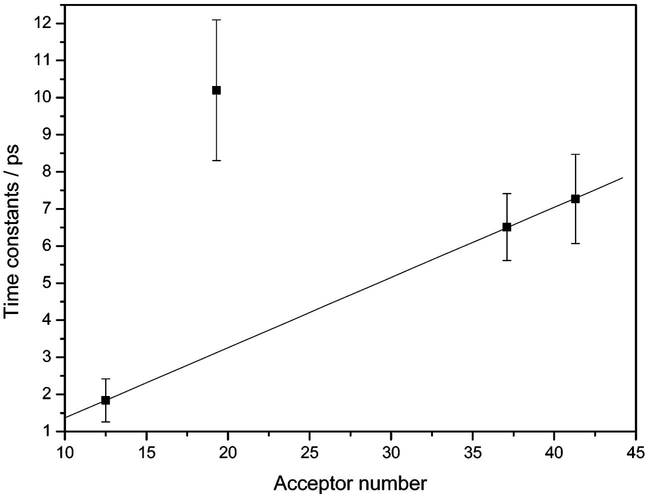


Figure 5. Plot of vibrational cooling time constant in rhodamine 700 versus the acceptor number of the solvent.

are affected by the interaction of these molecules greatly. The stronger the intermolecular interaction is, the bigger the collisional frequency is. This shows that the basicity of the solvent plays an important role in the collisional energy transfer from the hot solute to the neighboring solvent shell.

Acceptor number (AN) is used to indicate the acidity or basicity of solvents quantitatively by Mayer and Gutmann.[35−38] The larger the AN of a solvent is, the more acidic and less basic it is. The values of the AN of solvents used in this experiment are listed in Table 3. These values show that acetone, DMF, and DMSO are more basic, which means stronger interaction with the cation than ethanol, formamide, and methanol. In Figures 4 and 5, the relation between the time constants of the intermolecular vibrational energy transfer and the basicity of the solvents can be found easily: the more basic the solvent is, which mean there is stronger interaction with the solute, the faster this process is. Only one exception is there.

Another parameter that is important for the energy transfer between the solute and solvent molecules is the states density of the solvents. When one vibrational mode of the solvent molecules is excited by the collisions with the vibrational hot solute molecules, these molecules find it difficult to accept more energy from the solute if its energy cannot dissipate to other modes quickly. This shows that the rate of the IVR of solvent, which is correlated with the states density, will influence the whole energy transfer process. The higher the states density is, the fast the IVR is. So these solvents whose states density are high are favored to accept energy from solute molecules. The values of the states density of solvents at 300 K are listed in Tables 4 and 5. To calculate the states density $\rho(\epsilon)$, the following equation was used:[39,40]

TABLE 4: States Density of the Different Solvents and the Time Constants of the Picosecond Process of Oxazine 750

solvents	states density ρ (eV^{-1})	time constants (ps)
DMF	6.39×10^7	6.89 ± 1.70
DMSO	3.16×10^6	7.84 ± 1.92
acetone	2.88×10^6	7.09 ± 1.50
formamide	1.00×10^3	21.3 ± 3.9

TABLE 5: States Density of the Different Solvents and the Time Constants of the Picosecond Process of Rhodamine 700

solvents	states density ρ (eV^{-1})	time constants (ps)
DMSO	3.16×10^6	10.2 ± 1.9
acetone	2.88×10^6	1.84 ± 0.58
ethanol	7.97×10^4	6.51 ± 0.90
methanol	3.63×10^2	7.27 ± 1.20

$$\rho(\epsilon) = (\epsilon + \epsilon_{zp})^{s-1}/(s-1)!\prod_i h\nu_i \qquad (2)$$

Here ϵ is the internal energy and s is the vibrational freedom. The zero-point energy ϵ_{zp} and vibrational frequencies ν_i are from the results of density functional theory (DFT) calculation (use b3lyp/6-311++g** method). From Table 4, it can be found that the states densities of DMF, DMSO, and acetone are much higher than other solvents, which is identical with the experimental result of the picosecond process, basically, except the result of rhodamine 700 in DMSO.

The solvation of the excited solute molecules is also influenced by the interaction of the solute and the neighboring solvent shell. The more intensity of interaction is, the more rapid the solvation is. So the solvents with high Lewis basicity are also favored in the solvation process. Since the solvation process includes reorientation of the solvent molecules, the viscosity of the solvent will also affect the solvation rate constant.

A possible reason for the unexpected big time constant of the energy transfer of rhodamine 700 in DMSO is that its solvation process is very slow, due to the bigger viscosity of the DMSO (1.996 cps) than other solvents. And because of the big dipole moment of DMSO (4.3 D), the picosecond process of this solution maybe be interfered by the solvation process harder than others. More study about the contribution of the solvation process in the relaxation process of dye molecules in solution will be reported later.

Conclusion

Summarizing, we have measured the ultrafast vibrational relaxation of the dye molecules in different solvents. Following an intramolecular vibrational redistribution, the vibrational energy of the hot solute molecules would transport to the solvent. The IVR is insensitive to the specific of the solvent, and the energy dissipation of the vibrational hot solute molecules to the surrounding is closely related to the Lewis basicity and the states density of solvents effectively. The more basic the solvent is, which mean the more interaction of the solute and the neighboring solvent shell, the more rapid of the intermolecular vibrational energy transfer from the solute to the surroundings is. The higher the states density of the solvent is, the more favorable the energy transfer between the solute and solvent molecules is.

Because the vibrational cooling of the solute molecules is interfered with by the solvation process, and both of them are complicated and can be influenced by many parameters of the system, it is difficult to discuss the experimental results with single parameter. To understand the detail of the IVR process of electronically excited molecules in solution and the energy transfer between the solute and solvent molecules, more theoretical and experimental work are deserved.

Acknowledgment. This work is supported by the National Natural Science Foundation of China (Grant 29833080), the Knowledge Innovation Program of the Chinese Academy of Sciences (Grant DICP K200/E3), and NKBRSF.

References and Notes

(1) Weiner, A. M.; Ippen, E. P. *Chem. Phys. Lett.* **1985**, *114*, 456.

(2) Brito Cruz, C. H.; Fork, R. L.; Knox, W. H.; Shank, C. V. *Chem. Phys. Lett.* **1986**, *132*, 341.

(3) Taylor, A. J.; Erskine, D. J.; Tang, C. L. *Chem. Phys. Lett.* **1984**, *103*, 430.

(4) Wild, W.; Seilmeier, A.; Gottfried, N. H.; Kaiser, W. *Chem. Phys. Lett.* **1985**, *119*, 259.

(5) Laermer, F.; Israel, W.; Elsaesser, T. *J. Opt. Soc. Am. B* **1990**, *7*, 1604.

(6) Laermer, F.; Elsaesser, T.; Kaiser, W. *Chem. Phys. Lett.* **1989**, *156*, 381.

(7) Ashworth, S. H.; Hasche, T.; Woerner, M.; Riedle, E.; Elsaesser, T. *J. Chem. Phys.* **1996**, *104*, 5761.

(8) Schneider, S.; Bierl, R.; Seischab, M. *Chem. Phys. Lett.* **1994**, *230*, 343.

(9) Weiner, A. M.; De Silvestri, S.; Ippen, E. P. *J. Opt. Soc. Am. B* **1985**, *2*, 654.

(10) Mokhtari, A.; Chesnoy, J. *Chem. Phys. Lett.* **1989**, *155*, 593.

(11) Walker, G. C.; Jarzeba, W.; Kang, T. J.; Johnson, A. E.; Barbara, P. F. *J. Opt. Soc. Am. B* **1990**, *7*, 1521.

(12) Mokhtari, A.; Chebira, A.; Chesnoy, J. *J. Opt. Soc. Am. B* **1990**, *7*, 1551.

(13) Yoshihara, K.; Yartsev, A.; Nagasawa, Y.; Kandon, H.; Douhal, A.; Kemnitz, K. *Pure Appl. Chem.* **1993**, *65*, 1671.

(14) Bardeen, C. J.; Shank, C. V. *Chem. Phys. Lett.* **1993**, *203*, 535.

(15) Lenz, K.; Pfeiffer, M.; Lau, A.; Elsaesser, T. *Chem. Phys. Lett.* **1994**, *203*, 340.

(16) Laubereau, A.; Seilmeier, A.; Kaiser, W. *Chem. Phys. Lett.* **1975**, *36*, 232.

(17) Zhong, Q.; Wang, Z.; Sun, Y.; Zhu, Q.; Kong, F. *Chem. Phys. Lett.* **1996**, *248*, 277.

(18) Zhong, Q.; Wang, Z.; Liu, Y.; Zhu, Q.; Kong, F. *J. Chem. Phys.* **1996**, *105*, 5377.

(19) He, Y.; Xiong, Y.; Wang, Z.; Zhu, Q.; Kong, F. *J. Phys. Chem. A* **1998**, *102*, 4266.

(20) Yamaguchi, S.; Hamaguchi, H. *Chem. Phys. Lett.* **1994**, *227*, 255.

(21) Foggi, P.; Pettini, L.; Santa, I.; Righini, R.; Califano, S. *J. Phys. Chem.* **1995**, *99*, 7439.

(22) Terazima, M. *Chem. Phys. Lett.* **1999**, *305*, 189.

(23) Seifert, G.; Patzlaff, T.; Graener, H. *Chem. Phys. Lett.* **2001**, *333*, 248.

(24) Stratt, R. M.; Maroncelli, M. *J. Phys. Chem.* **1996**, *100*, 12981.

(25) Owrutsky, J. C.; Rattery, D.; Hochstrasser, R. M. *Annu. Rev. Phys. Chem.* **1994**, *45*, 519.

(26) Elsaesser, T.; Kaiser, W. *Annu. Rev. Phys. Chem.* **1991**, *42*, 83.

(27) Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1.

(28) Miller, D. W.; Adelman, S. A. *Int. Rev. Phys. Chem.* **1994**, *13*, 359.

(29) Ravichandran, S.; Bagchi, B. *Int. Rev. Phys. Chem.* **1995**, *14*, 271.

(30) Sukowski, U.; Seilmeier, A.; Elsaesser, T.; Fischer, S. F. *J. Chem. Phys.* **1990**, *93*, 4094.

(31) Bhasikuttan, A. C.; Suzuki, M.; Nakashima, S.; Okada, T. *J. Am. Chem. Soc.* **2002**, *124*, 8398.

(32) Liu, J. Y.; Fan, W. H.; Han, K. L.; Xu, D. L.; Lou, N. Q. *J. Phys. Chem. A* **2003**, *107*, 1914.

(33) Lewis, G. N. *Valence and the Structure of Atoms and Molecules*; The Chemical Catalog Co.: New York, 1923.

(34) Carslaw, H. S.; Jaeger, J. C. *Conduction of Heat in Solids*; Oxford University Press: London, 1959.

(35) Mayer, U.; Gutmann, V.; Gerger, W. *Monatsh. Chem.* **1975**, *106*, 1235.

(36) Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions*; Plenum Press: New York, London, 1978.

(37) Gutmann, V. *Coordination Chemistry in Nonaqueous Solutions*, Springer, Vienna, Austria, 1968.

(38) Mayer, U.; *Ions and Molecules in Solutions*, Elsevier: Amsterdam, 1983; p 219.

(39) Marcus, R. A.; Rice, O. K. *J. Phys. Colloid Chem.* **1951**, *55*, 894.

(40) Smith, Ian W. M. *Kinetics and dynamics of elementary gas reactions*; Butterworths: London, 1980; p 158.