

Molecular Dynamics Simulation of Time-Resolved Fluorescence and Nonequilibrium Solvation of Formaldehyde in Water

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The results of molecular dynamics simulations of nonequilibrium solvation and time-resolved fluorescence from the first excited singlet state of formaldehyde in water are reported. The laser excitation is simulated by instantaneously switching the solute charges and force constants from ground- to excited-state values during the course of a molecular dynamics simulation of the ground-state species in water. Eighty nonequilibrium trajectories were completed, starting from different configurations obtained from the ground-state simulation. The fluorescence shift and solvation relax nonexponentially on a very fast time scale. The major portion of the relaxation occurs within 100 fs; additional relaxation is observed up to 1 ps. Time-dependent radial and angular distribution functions for solute-solvent interactions have been calculated. The relaxation is dominated by changes in the structure of the first solvation shell. Translational motion of the solvent provides the major mechanism for the relaxation. The relationship of the present computer experiments to theories of nonequilibrium solvation is discussed.

Introduction

Time-resolved-fluorescence measurements provide a powerful way to probe the dynamics of solvation. The development of subpicosecond laser technology has spurred investigation of the very fast solvent response to the laser-induced electronic transitions within a solute molecule.¹⁻⁴ When the two molecular electronic states involved have different charge distributions, the solvent will begin to relax around the new charge distribution immediately following the vertical excitation. The subsequent fluorescence shift depends on both the solute and solvent dynamics. On the theoretical side, there has been considerable effort to develop an explicit molecular framework for analyzing the time-resolved experiments using both analytical and simulation tools.⁵⁻¹⁴ In the continuum picture, the solvation energy is characterized by a single-exponential relaxation time τ_1 , whereas explicit molecular treatments emphasize the solvation structure and especially the dynamical behavior of the first solvation shell. For polar solvents, the solvation energy relaxation is predicted by the continuum model to be very fast (on the order of 0.1-0.5 ps). This very fast relaxation is attributed, within the model, to the collective behavior of the solvent. The consideration of solvent molecularity leads to a multitude of relaxation times. In the dynamical MSA model proposed by Wolynes, for example, a second and slower relaxation time appears that is identified with the dynamical response of the first solvation shell.⁶ In the recent computer simulations of nonequilibrium solvation of ions in water by Maroncelli and Fleming, however, the response of the first solvation shell to a charge perturbation is very fast (on the order of τ_1) and accounts for a large fraction of the complete response.¹⁰ Thus, at present, the contribution of the hydration shell relative to the bulk to either the magnitude or the rate of the solvent relaxation is unclear, even qualitatively.

We have been engaged in a series of calculations on the effects of solvation on the electronic and spectral properties of model solute-solvent systems.¹⁵⁻¹⁷ In a previous paper, we used a hybrid classical-quantum approach to calculate the solvent (water) contribution to the blue shift and line width of the ultraviolet absorption spectrum of a solute formaldehyde molecule in water.¹⁶ The solute energy levels were calculated by using ab initio molecular orbital methods and the solute-solvent electrostatic interactions were incorporated in the one-electron Hamiltonian, with the solvent configurations sampled from a molecular dynamics trajectory. The spectral shift and line width were related to the solvation structure as determined by solute-solvent radial and angular distribution functions. In this paper, we report the results of classical molecular dynamics simulations of the time-dependent

fluorescence from formaldehyde following a sudden electronic excitation.

Formaldehyde serves as a prototypical molecule to study the solvation and spectroscopic properties of the carbonyl group. The $n \rightarrow \pi^*$ transition of the carbonyl group involves the promotion of an electron from an in-plane oxygen lone pair, oriented perpendicular to the C=O axis and mostly of 2p character, into the out-of-plane π^* C=O orbital that has its largest coefficient on the carbon atom.¹⁸ The transition causes a large reduction in the dipole moment, from 2.33 D (ground state) to 1.57 D (excited state).^{19,20} The classical molecular dynamics simulations of ground-state formaldehyde in water showed structured binding to the carbonyl oxygen by several water molecules.¹⁶ Additional simulations of the solvated molecule using atomic partial charges corresponding to the excited-state species were carried out. Analysis of solute-solvent radial and angular distribution functions with solvent equilibrated around the excited state indicate a nearly complete loss of the structured solvation shell.¹⁶ We also report here the results of simulations that follow the time course of the solvent relaxation. Finally, preliminary results concerning intramolecular relaxation are presented.

Method

Molecular dynamics simulations of a formaldehyde solute molecule in a cubic box of 209 water molecules were carried out

- (1) Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy*, Oxford University Press: New York, 1986.
- (2) Barbara, P.; Jarzaba, W. *Acc. Chem. Res.* **1988**, *21*, 195.
- (3) Simon, J. D. *Acc. Chem. Res.* **1988**, *21*, 128.
- (4) Maroncelli, M.; Mac Innes, J.; Fleming, G. R. *Science* **1989**, *243*, 1674.
- (5) Rao, M.; Berne, B. J. *J. Phys. Chem.* **1981**, *85*, 1498.
- (6) Wolynes, P. G. *J. Chem. Phys.* **1987**, *86*, 5133.
- (7) Loring, R.; Yan, Y.; Mukamel, S. *J. Chem. Phys.* **1987**, *87*, 5841.
- (8) Nichols, A. L.; Calef, D. J. *J. Chem. Phys.* **1988**, *89*, 3783.
- (9) Karim, O.; Haymet, A. D. J.; Banet, M. J.; Simon, J. D. *J. Phys. Chem.* **1988**, *92*, 3391.
- (10) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1988**, *89*, 5044.
- (11) Hwang, J. K.; Creighton, S.; King, G.; Warshel, A. *J. Chem. Phys.* **1988**, *89*, 859.
- (12) Van der Zwan, G.; Hynes, J. T. *J. Phys. Chem.* **1985**, *89*, 4181.
- (13) Robinson, G. W.; Thistlethwaite, P. J.; Lee, J. J. *J. Phys. Chem.* **1986**, *90*, 4224.
- (14) Friedrich, V.; Kivelson, D. *J. Chem. Phys.* **1987**, *86*, 6425.
- (15) Blair, J. T.; Westbrook, J. D.; Levy, R. M.; Krogh-Jespersen, K. *J. Phys. Chem. Lett.* **1989**, *154*, 531.
- (16) Blair, J. T.; Krogh-Jespersen, K.; Levy, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 6948.
- (17) Blair, J. T.; Levy, R. M.; Krogh-Jespersen, K. *J. Phys. Chem. Lett.* **1990**, *166*, 429.
- (18) Streitwieser, A.; Kohler, B. *J. Am. Chem. Soc.* **1988**, *110*, 3769.
- (19) Jones, V. T.; Coon, J. B. *J. Mol. Spectrosc.* **1969**, *31*, 137.
- (20) Buckingham, A. D.; Ramsey, D. A.; Tyrell, J. *Can. J. Phys.* **1970**, *48*, 1242.

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TABLE I: Formaldehyde Ground (1A_1) and Excited ($^1A''$) State Parameters Used in Molecular Dynamics Simulations

Equilibrium Geometries ^a					
coordinate	1A_1	$^1A''$	coordinate	1A_1	$^1A''$
C-O	1.184	1.355	H-C-H	115.5	118.2
C-H	1.093	1.078	φ^b	180.0	135.4
O-C-H	122.3	113.1	α^c	0.0	40.3
Force Constants ^d					
coordinate ^d	$^1A_1^e$	$^1A''$	coordinate ^d	$^1A_1^e$	$^1A''$
C-O	7.91	6.15	H-C-H	0.46	0.39
C-H	4.72	4.83	V_2^f	10.0	8.82
O-C-H	0.46	0.37	V_3^f	0.0	6.20
Partial Atomic Charges					
atom	1A_1	$^1A''$			
O	-0.576	-0.280			
C	0.331	-0.040			
H	0.123	0.160			
Lennard-Jones Parameters ^{e,f}					
atom	σ	ϵ			
O	1.425	0.20			
C	1.648	0.12			
H	1.372	0.01			

^aBond lengths in Å; angles in deg. ^b φ is the H-H-C-O dihedral angle used in the potential energy function for the barrier to inversion. ^c α is the conventional wag angle, the angle between the C-O bond and the H-C-H plane. ^dStretch constants in mdyn/Å; bend constants in mdyn Å; inversion barrier constants in kcal/mol. ^eWeiner, S. J.; Kollman, P. A.; Nguyen, D. T.; Case, D. A. *J. Comput. Chem.* **1986**, *7*, 230. ^fThe inversion barrier is modeled by $V = 0.5V_2(1 - \cos(2\varphi)) + 0.5V_3(1 - \cos(3\varphi))$. ^gSame set of Lennard-Jones parameters was used for both electronic states. σ in Å; ϵ in kcal/mol.

in the NVT ensemble using the IMPACT program.²¹ The equations of motion were integrated with the Verlet algorithm using the SHAKE and RATTLE algorithms to maintain bond length and angle constraints for water.²²⁻²⁴ Nonbonded interactions were truncated at 7.5 Å. The box edge length was 18.6 Å and periodic boundary conditions were employed. For water, the SPC model was used.²⁵ The molecular mechanics parameters for ground-state formaldehyde were the same as those used in our previous work.¹⁶ An approach to generating molecular mechanics parameters for electronically excited states has been described recently.¹⁷ In this work, we use the optimized (ROHF/6-31G+d) geometry for the $^1A''$ state as the excited-state reference geometry and the force constants are obtained from fits to computed, scaled vibrational frequencies and the barrier to inversion.¹⁷ A natural population analysis was used to extract the partial charges from the ab initio wave functions without further scaling.²⁶ The dipole moment of the ground- and excited-state species is larger in the point-charge model (3.9 and 2.5 D, respectively) as compared with the experimental gas-phase values for formaldehyde. The parameters used for formaldehyde are listed in Table I. With the exception of the Lennard-Jones parameters and the ground-state force constants, all the parameters are derived from ab initio Hartree-Fock calculations with a split valence plus polarization function basis set (6-31G+d).

The equilibrium geometry of ground-state (S_0) formaldehyde is planar (C_{2v} symmetry, 1A_1) whereas the structurally relaxed, excited singlet state (S_1) is pyramidal around the C atom (C_s

symmetry, $^1A''$). In the current series of simulations, the vertical excitation of formaldehyde is simulated by instantaneously switching the formaldehyde charges and force constants from 1A_1 ground-state values to those corresponding to the $^1A''$ excited state. Then the system is propagated forward in time by integrating the equations of motion. Eighty such trajectories corresponding to different initial conditions were calculated and averaged. In order to generate initial coordinates and velocities for these nonequilibrium trajectories, a 160-ps simulation of ground-state formaldehyde in water was first completed. Coordinates and velocities were sampled from the ground-state simulation every 2 ps, and these served as the starting points for the excited-state trajectories. Several time-dependent quantities have been analyzed including time-dependent solute-solvent radial and angular distribution functions and the solute-solvent interaction energy which, in the classical model, corresponds to the solvent-induced fluorescence shift. It was necessary to run a large number of nonequilibrium trajectories to obtain the time dependence of these distribution functions with reasonably good statistics.

Results and Discussion

Time Dependence of the Fluorescence Shift. A polar solvent induces a shift to higher energy, i.e., a blue shift, in the $S_0 \rightarrow S_1$ transition of formaldehyde and related molecules containing the carbonyl group.²⁷ The solvent shift probes the differences in the interaction energy between the ground (1A_1) and excited ($^1A''$) state of the solute with solvent. Since the ground state of formaldehyde has a larger dipole moment than the excited state, the ground-state interactions with polar solvent are more attractive than those of the excited state and provides the blue shift of the absorption maximum. In the ground state, the average interaction energy of the formaldehyde with water was calculated from the ground-state simulations to be ~ -26 kcal/mol.¹⁶ Immediately following excitation, but before any relaxation, the formaldehyde-water interaction energy is reduced by ~ 12 kcal/mol in the classical model, leading to a calculated solvent-induced blue shift for absorption of ~ 4000 cm^{-1} . An experimental absorption spectrum is not available for monomeric formaldehyde in water due to the formation of oligomers, but the blue shift of acetone ($(\text{CH}_3)_2\text{CO}$) in water is close to 1900 cm^{-1} .²⁷ In our quantum mechanical treatment of the formaldehyde solute in water, we obtained an average blue shift of 1900 cm^{-1} with a spread of more than 2000 cm^{-1} .¹⁶ We are pursuing an analysis of the reasons for the difference in the quantum and classical results. After the excitation, the solvent begins to relax around the excited-state species. The time dependence of the fluorescence shift, calculated from the nonequilibrium trajectories, is plotted in Figure 1.

$$\langle \Delta E(t) \rangle = \langle E_{A'' \text{ solvent}}(t) - E_{A_1 \text{ solvent}}(t) \rangle \quad (1)$$

In eq 1 the brackets indicate the average is taken over the 80 nonequilibrium trajectories propagated with the solute in the excited state. As seen in Figure 1, there is a very rapid nonexponential relaxation within the first 100 fs following the excitation. It is of interest to note that although the solvent is relaxing around the excited $^1A''$ state charge distribution following the excitation, $E_{A'' \text{ solvent}}(t)$ and $E_{A_1 \text{ solvent}}(t)$ are both actually decreasing with time. The solvation energy of the excited state, $E_{A'' \text{ solvent}}(t)$, immediately following the vertical excitation is ~ -11 kcal/mol, whereas at 1 ps $E_{A'' \text{ solvent}}$ has decreased to ~ -7.5 kcal/mol. Thus the excited state is more favorably solvated by the solvent structure organized around the ground state. Because the excited-state species, with the smaller dipole moment, is not able to keep the solvent as tightly bound, the solvation energy of the excited state decreases with time as the solvent relaxes. The decreasing blue shift with time shown in Figure 1 results because the rate of solvation energy loss following the excitation is greater for the ground-state distribution than for the excited state. In Figure 1a the solvation energy is calculated by including all water molecules within 7.5 Å from the formaldehyde oxygen (the results are very similar when the center

(21) Bassolino, D. A.; Hirata, F.; Kitchen, D. B.; Kominos, D.; Pardi, A.; Levy, R. M. *Int. J. Supercomput. Appl.* **1988**, *28*, 41.

(22) Verlet, L. *Phys. Rev.* **1967**, *159*, 98.

(23) Ryckaert, J. P.; Cicotti, G.; Berendsen, H. J. C. *J. Comput. Phys.* **1977**, *54*, 327.

(24) Andersen, H. C. *J. Comput. Phys.* **1983**, *52*, 24.

(25) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; Hermans, J. In *Intermolecular Forces*; Pullman, B., Ed.; Reidel: Dordrecht, 1981; p 331.

(26) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(27) Jaffe, H. H.; Orchin, M. *Theory and Applications of U. V. Spectroscopy*; Wiley: New York, 1962.

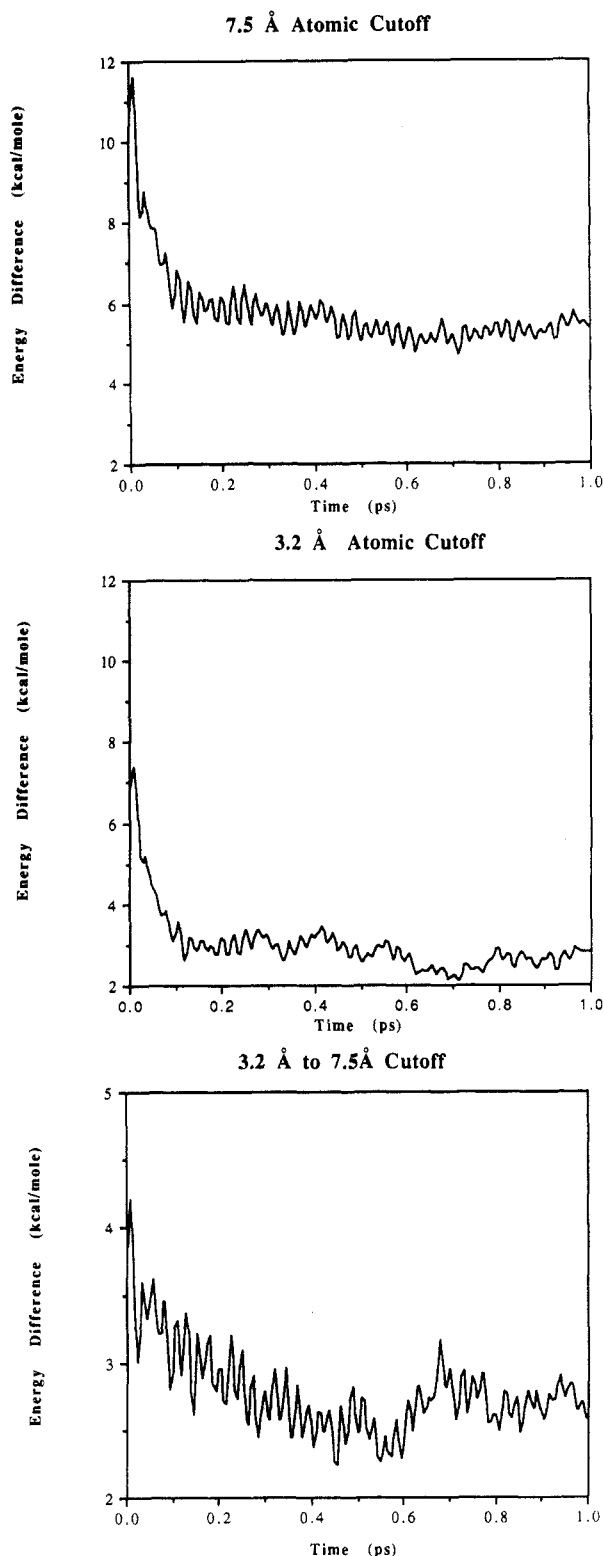


Figure 1. Difference in formaldehyde solvation energy (eq 1) versus time following excitation. (a) Solvent within a spherical shell of radius $R = 7.5$ Å from the formaldehyde oxygen was included in the evaluation of the solvation energy; (b) solvent within a spherical shell of radius $R = 3.2$ Å from the formaldehyde oxygen included; (c) solvent in the region 3.2 Å $< R < 7.5$ Å included.

of mass of the formaldehyde is used). In Figure 1b the solvation energy difference is calculated including only those water molecules within the first solvation shell $R = 3.2$ Å. As shown by the figure, in the classical model the first solvation shell accounts for about two-thirds of the total fluorescence shift. The contribution to the time-dependent fluorescence shift from waters between 3.2 and 7.5 Å, which includes the second solvation shell, is shown in Figure 1c. As can be seen in Figure 1, the relaxation of the fluorescence

shift is nonexponential with at least two distinct time scales apparent. The fastest time scale, which accounts for the major portion of the relaxation, corresponds to the solvent response of the first solvation shell, with relaxation on the order of 100 fs. The response of the second solvation shell and waters further removed from the formaldehyde to the excitation is much slower, on the order of 600 fs (Figure 10). It is of interest to note that the oscillations in the energy response in Figure 1 resemble those observed by Maroncelli and Fleming¹⁰ for small spherical solutes in water. The large number of trajectories averaged in Figure 1 and the regularity of the oscillations suggest that they reflect solvent librational motions and are not simply statistical noise. To develop a more detailed picture of the structural changes associated with the solvent relaxation, we have calculated solute-solvent radial and angular distribution functions at various times following the excitation.

Time Evolution of the Solvation Structure. In Figure 2 is shown the radial distribution function for the formaldehyde oxygen-water oxygen atom pair as it evolves in time during the first 200 fs following the excitation; also shown for comparison are distribution functions before the excitation and at very long time following the excitation. Prior to the excitation there is a large peak in this radial distribution function at 2.6 Å. Integration of the first peak to the first minimum (3.25 Å) gives ~ 2.6 waters in the first solvation shell that are hydrogen bonded to the formyl group. A well-defined second peak at ~ 4.4 Å is also observed, with approximately 19 water molecules in the second shell.¹³ The time course of the change in the radial distribution function is complicated, and the decay of the first peak is nonexponential. Up to ~ 10 fs following the excitation, the O-O (formaldehyde-water) radial distribution function appears essentially unchanged (not shown). At 20 fs, the first peak has moved out slightly and actually appears to have increased. Although the radial distribution functions are noisy because statistics are being gathered over a single solute molecule, the initial increase in the radial distribution function may well correspond to the inertial response of the water molecules in the first hydration shell of the formaldehyde oxygen. These waters will feel a strong Lennard-Jones repulsion from the formaldehyde oxygen and an electrostatic repulsion from neighboring waters as the compensating electrostatic attraction from the formaldehyde is lost following the excitation. Their movement away from the solute will be hindered by waters in the second shell that do not feel a strong Lennard-Jones repulsion from the solute. Thus initially, there is a small increase in the solvent density at the outer boundary of the first solvation shell. By 50 fs, the decrease in the magnitude of the first peak is evident. The peak position has moved out to ~ 2.8 Å with the first and second peaks still clearly separated. By 100 fs, the first peak has almost vanished and moved out to about 3.0 Å. The structure of the radial distribution function is very similar to those calculated at much longer times. The analysis of the time evolution of the O-O distribution function clearly shows that translational motion makes a major contribution to the solvent relaxation on this very fast time scale.

The time course of the angular reorientation of waters in the first solvation shell of the solute formyl group can be analyzed with the aid of angular distribution functions. In Figure 3 we show the angular distribution function (formaldehyde O-water H-water O) calculated for waters in the first solvation shell before the excitation and at various times up to 100 fs following the excitation. Note that there are two peaks in the angular distribution at $\cos(\theta) = -1.0$ and 0.6. The first peak corresponds to a linear O-H-O geometry in which waters in the first shell are pointing an OH bond directly at the formaldehyde oxygen ($\theta = \angle\text{OHO} = 180^\circ$), while the second peak corresponds to the angle formed by the other OH bond on the same molecule with the formaldehyde oxygen. Angular reorientation of the waters can be detected in the distribution functions shown in Figure 2 as early as 10 fs following the excitation. By 50 fs, the peak corresponding to the linear geometry has decreased by 50%. Thus the hydrogen bonds from the water to formaldehyde are broken within the first 50 fs by a combination of angular reorientation and translational

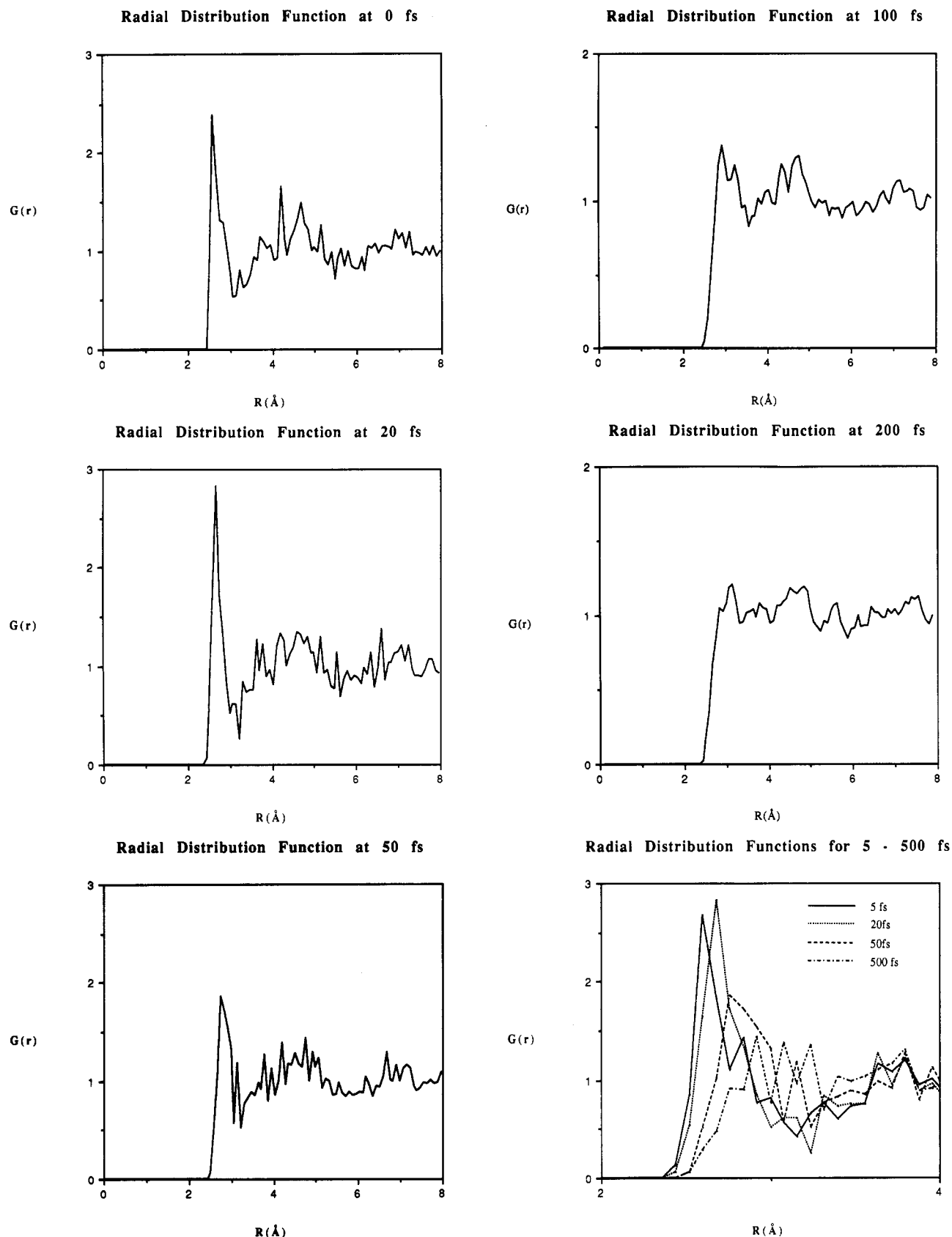


Figure 2. Time evolution of the oxygen-oxygen (formaldehyde-water) radial distribution function following excitation. (a) $t = 0$ fs (ground-state radial distribution function); (b) $t = 20$ fs; (c) $t = 50$ fs; (d) $t = 100$ fs; (e) $t = 200$ fs; (f) superposition of radial distribution functions (solid line 5 fs, dotted 20 fs, dashed 50 fs, dot-dash 500 fs). Notice that the scale has been changed in (d) and (e) in order to clearly display the remnants of the first and second peaks in the distribution function.

motion of the waters away from the solute involving at least the first and second hydration shells.

Previous simulations of time-resolved fluorescence have modeled the solute as a simple monopole or dipole. Real polyatomic solutes

have internal structure, and in the analysis of nonequilibrium solvation it is necessary to consider the excited-state surface on which the solute molecule moves. In a recent molecular dynamics study of energy dissipation following photoisomerization, Ohmine

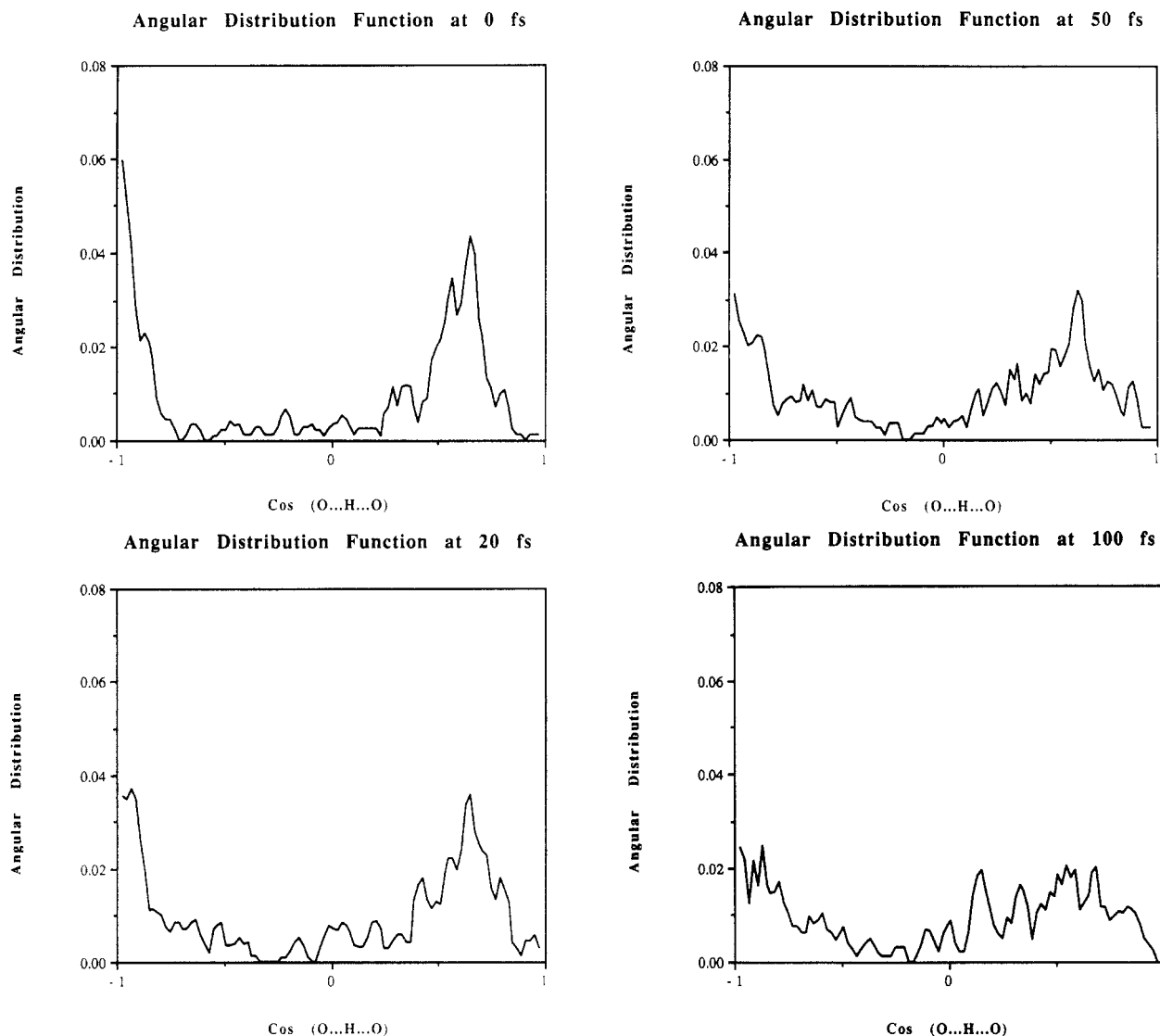


Figure 3. Time evolution of the O-H-O (formaldehyde-water-water) angular distribution function following excitation. (a) $t = 0$ fs (ground-state angular distribution function); (b) $t = 20$ fs; (c) $t = 50$ fs; (d) $t = 100$ fs.

found that solute energy transfer to water could be extremely fast, with several kilocalories per mole dissipated within 100 fs.²⁸ Although we have not yet analyzed in detail the internal relaxation of formaldehyde following the excitation to the $^1A''$ surface, we briefly discuss some aspects of this interesting problem and its relation to solvent relaxation. The formaldehyde geometry at the minimum of the excited $^1A''$ state is nonplanar, with the carbon atom approximately 0.6 Å above the plane of the other three atoms. The barrier to interconversion is ~ 1.0 kcal/mol in the gas phase. At the planar geometry corresponding to a vertical transition from the ground state, the energy of the excited state is ~ 20 kcal/mol above its minimum. Thus the solute initially contains a large amount of excess energy, which will eventually be transferred to the solvent as the solute moves toward the adiabatic minimum of the $^1A''$ state. In Figure 4, we plot the internal temperature of formaldehyde as a function of time, averaged over the 80 trajectories. Following the simulated absorption, the formaldehyde molecule is very hot. The molecule is subsequently cooled via collisions that transfer energy to the solvent. Superimposed on the large high-frequency fluctuations in temperature, which are due to the harmonic character of the solute motions, is a slower cooling over the course of the picosecond trajectory. The time scale for the solute cooling is clearly much slower than the major component of the solvation relaxation but will contribute to the time-dependent red shift of the fluorescence

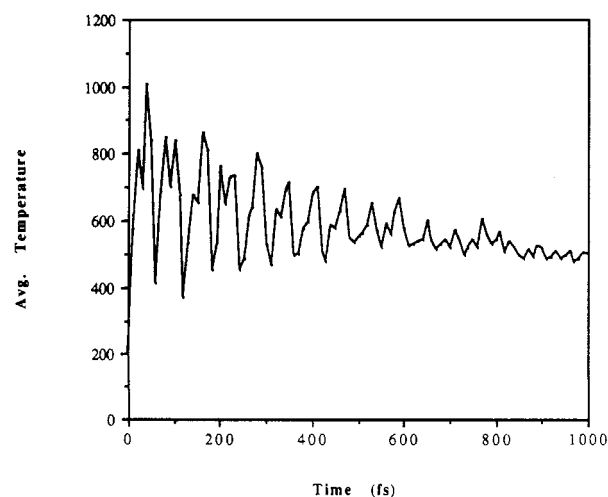


Figure 4. Internal temperature of formaldehyde during the first picosecond following excitation averaged over 80 trajectories.

relative to the absorption spectrum (the contribution of solute cooling to the fluorescence shift is excluded from Figure 1). The cooling shown in Figure 4 corresponds to a loss of about 7 kcal/mol to the solvent during the first picosecond following the excitation. In Figure 5 we show the time dependence of the out-of-plane displacement coordinate during a representative trajectory. It can

(28) Ohmine, I. *J. Chem. Phys.* **1986**, *85*, 3342.

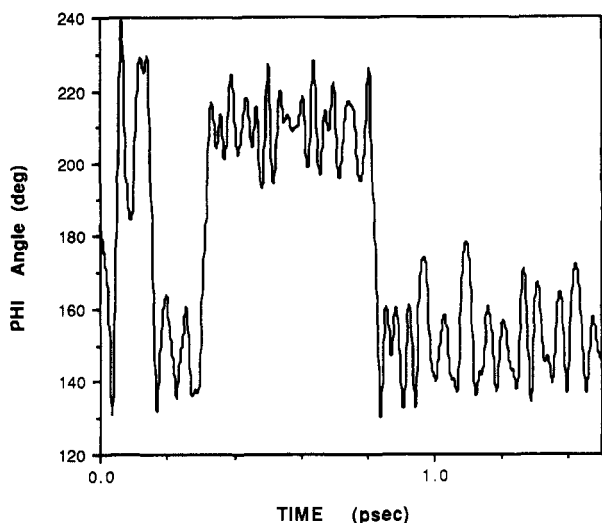


Figure 5. Time evolution of the formaldehyde out-of-plane coordinate following excitation in a single trajectory.

be seen that in this excited-state trajectory the carbon atom is flipping above and below the plane formed by the other three atoms. Thus the internal formaldehyde "umbrella" motion contributes to the breakup of the first solvation shell following the excitation, and because the formaldehyde remains hot, the re-formation of a solvation shell around the excited-state species is impeded.

Comparison with Theories of Nonequilibrium Solvation. The results of the nonequilibrium simulations demonstrate the importance of the solute-solvent interactions and the motions involving the first solvation shell in the solvation response to the excitation. How does this picture fit in with theory? In the continuum limit, the solvation response is determined by the longitudinal relaxation time $\tau_l = (\epsilon_\infty/\epsilon_0)\tau_D$, where the quantity in parentheses is the ratio of the infinite frequency to the static dielectric constant and τ_D is the Debye relaxation time. For highly polar solvents ($\epsilon_\infty/\epsilon_0$) is small and τ_l is therefore much smaller than τ_D . The longitudinal and Debye relaxation times of water, for example, are about 0.2 and 8 ps, respectively.^{12,29} The longitudinal relaxation describes the time variation of the solvent (reaction) field at the solute, which depends on the orientation of many solvent molecules; the correlations between the solvent orientations decay much faster than the Debye relaxation time, which is essentially the single-molecule rotational relaxation time.³⁰ The effect of introducing molecular corrections to continuum theories is to increase the relaxation time when the solvent dynamics is described by rotational diffusion.^{6,14} Thus in the dynamical MSA model, solvent in the first solvation shell slows down the relaxation.⁶ What is happening in the formaldehyde in water simulation is quite different. In this case, the relaxation is caused by the breakup of the first solvation shell on a very fast time scale. Translational motion of waters in the first solvation shell is the major relaxation mechanism. The effects of translational diffusion have been incorporated in dielectric relaxation theories.^{12,31-33} Hynes et al., using a continuum solvent model, point out that the size of the solute (modeled as a dipolar cavity) will affect the relative importance of translational versus rotational solvent relaxation.¹² This observation also applies to the nondiffusional translational relaxation observed in the formaldehyde-water simulation. This is due to the fact that the R^{-3} dependence of the dipole-dipole interaction weights changes in the interaction

energy due to translation heavily at small distances; for example, an increase in the center to center distance from 2.6 to 2.8 Å, which corresponds to the change in the peak position of the formaldehyde-water radial distribution function at 50 fs following the excitation, leads to a 20% decrease in the solute-solvent dipole interaction energy.

Maroncelli and Fleming have recently completed a thorough molecular dynamics study of the time dependence of ion solvation.⁴ There are striking similarities between their results for the solvation response following a jump charge change from +1 to 0 for a small ion and the present results for dipolar formaldehyde. They found relaxation following the charge jump (+1 \rightarrow 0) was much faster ($\tau < 100$ fs) than the reverse (0 \rightarrow +1) charge jump. This was attributed to the impulsive disruption of the coordination sphere following the neutralization of the ion charge. Waters that are tightly bound by the solute are suddenly repelled by both the solute and other waters in the first shell following the neutralization of the ion charge. A similar description applies to the solvation response at the carbonyl oxygen of formaldehyde to the change in dipole moment from 3.9 to 2.5 D. An impulsive response by solvating waters will be accentuated at the surface of a small negatively charged group like the carbonyl oxygen, because the hydrogen-bonding waters can approach the solute charge more closely³⁴ and thus feel a much larger repulsion when the solute charge is switched off. In this regard it is instructive to calculate the electric field strength at the positions of the water protons in the first solvation shell of the carbonyl oxygen. In the point dipole approximation, the field on the formaldehyde dipole axis at the location of the maximum in the formaldehyde oxygen-water oxygen radial distribution function (water proton 1.7 Å from the carbonyl oxygen) is $\sim 1.0 \times 10^{10}$ V/m in the ground state. The field is about twice as large if the extended charge distribution of the solute is considered. It is of interest to note that fields of this magnitude are well beyond the linear (orientational) dielectric response regime of "real" water.²⁹ As to the SPC water model used in these simulations, recent simulations of the polarization response of the SPC model to an applied field indicate that saturation effects begin to set in at $\sim 10^9$ V/m.³⁵

We emphasize that there is still uncertainty regarding the bulk dielectric properties of the water models employed under different simulation conditions. With some boundary conditions and long range cutoff schemes, the SPC and similar water models do indeed exhibit dielectric behavior close to that of "real" water,^{35,36} but questions remain regarding the dielectric response under other simulation conditions, including the boundary conditions used in the present simulations.³⁷ Although the specific boundary conditions employed in simulations of solvation will have a large effect on some properties such as the dielectric screening of charges at long range, the short-range solute-solvent structure and dynamics will be much less sensitive to boundary effects. These observations, together with the large magnitudes of the interaction energies and forces involving the solute and the first solvation shell, provide further support for a model in which, at least for small molecular solutes in water, the inertial dynamics of the first solvation shell rather than the bulk dielectric response of the water governs the relaxation.

Concluding Remarks

The intimate relationship between effects observed in time-resolved-fluorescence experiments and solvent effects on fundamental aspects of chemical reactions such as electron transfer has been discussed by several authors.¹⁻¹⁴ The dramatic improvements that have occurred in the technology of these experiments makes it possible to obtain much more detailed information about the solvent response to changing charge distributions. Computer simulations provide a natural bridge between the experiments and molecular theories of the solvation response. The simulations

(29) Davies, M. In *Dielectric Properties and Molecular Behavior*; Hill, N. E., Price, A. H., Davies, M., Eds.; van Nostrand-Reinhold: New York, 1969.

(30) Botcher, C. J. F.; Bordewijk, P. In *Theory of Electric Polarization*; Elsevier: New York, 1978; Vol. II.

(31) Calef, D. F.; Wolynes, P. G. *J. Chem. Phys.* **1983**, *78*, 4245.

(32) Hubbard, J. B.; Kayser, R. F.; Stiles, P. J. *Chem. Phys. Lett.* **1983**, *95*, 399.

(33) Chandra, A.; Bagchi, A. *J. Chem. Phys.* **1989**, *90*, 1832.

(34) Hirata, F.; Levy, R. M. *Int. J. Quantum Chem.* **1988**, *15*, 179.

(35) Alper, H.; Levy, R. M. *J. Chem. Phys.* **1989**, *91*, 1242.

(36) Neumann, M. *J. Chem. Phys.* **1986**, *85*, 1567.

(37) Alper, H.; Levy, R. M. Manuscript in preparation.

should not only be able to provide a guide as to the range of validity for the classical continuum theory of solvation relaxation but should also clarify which aspects of solvent molecularity are important in the solvation response and need to be included in microscopic theories of nonequilibrium solvation. From the present work and other simulations^{5,9-11} it is apparent that the solute shape and charge distribution will have a large effect on the particular relaxation mechanism that governs the solvent response to an electronic excitation. For a large polyatomic solute where changes in the atomic charges are small and/or shielded from the solvent by bulky solute groups, the classical cavity model should provide an adequate description of the solvent response to the excitation. When the solute is small and/or there are large surface charges generated, the solvation shell structure and dynamics will dominate the relaxation. For this situation, the forces on the solvent molecules will be large and rapidly varying and the relaxation will occur via nondiffusional translation and rotation. In this regime, the dynamics of the solvation shell speeds up rather than slows down the solvent response compared with the bulk response. Also, we expect in this regime that linear response theory will not adequately describe the relaxation because of the highly anharmonic, impulsive nature of the forces exerted on the solvation shell following the excitation. In this context we note the very surprising results of Bader and Chandler in their recent simulations of photoinduced electron transfer in the aqueous ferrous-ferrous system.³⁸ They found that linear response theory predicted the nonequilibrium response to a surprising degree of accuracy despite the fact that the reorganization energies associated with the perturbation were very large for their model system. Calculations of the corresponding equilibrium correlation functions of the solvation dynamics of formaldehyde in water are being completed by us for comparison with the nonequilibrium simulations reported in the present paper.

(38) Bader, J.; Chandler, D. *Chem. Phys. Lett.* **1989**, *157*, 501.

The present study of the time dependence of the fluorescence shift for formaldehyde in water complements our recent study of hydration effects on the absorption line shape of this molecule.¹⁶ The choice of formaldehyde was dictated in part by the methods we used to parameterize the excited-state potential surface.^{15,17} In the context of time-resolved simulations, we regard formaldehyde as representative of a class of small solute molecules that have a sufficiently large change in the dipole moment upon excitation to couple the solvent response to the fluorescence. The probes of choice for experimental time-resolved-fluorescence studies such as the coumarin dyes^{39,40} or bis(4-(dimethylamino)phenyl) sulfone (DMAPS)⁴¹ tend to have much larger dipole moment changes upon excitation than does formaldehyde, but they are also considerably larger polyatomics. Since the details of the solute shape and atomic charges control which of several possible solvent relaxation mechanisms is dominant, it is of considerable interest to carry out simulations on corresponding polyatomic dyes for which nonequilibrium solvation measurements are available. Work along these lines is in progress in our laboratory.

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Registry No. HCOH, 50-00-0.

(39) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 6221.
(40) Kahlow, M. A.; Kang, T. J.; Barbara, P. F. *J. Chem. Phys.* **1988**, *88*, 2372.

(41) Su, S. G.; Simon, J. D. *J. Phys. Chem.* **1987**, *91*, 2693.

Gas-Phase Inorganic Chemistry: Laser Spectroscopy of Calcium and Strontium Monopyrrolate Molecules

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The gas-phase calcium and strontium monopyrrolate molecules were synthesized by the direct reaction between the metal vapor and pyrrole. The electronic and vibrational structures of these molecules were probed by low-resolution laser techniques. The spectra are consistent with a ring-bonding, ionic, $M^+(C_4H_4N)^-$ structure of pseudo- C_{5v} symmetry. The assignments of the $\tilde{A}^2E_{1(1/2)}-\tilde{X}^2A_1$, $\tilde{A}^2E_{1(3/2)}-\tilde{X}^2A_1$, and $\tilde{B}^2A_1-\tilde{X}^2A_1$ electronic transitions were made by analogy to the isoelectronic metal monocyclopentadienide molecules, CaC_5H_5 and SrC_5H_5 .

Introduction

Although cyclopentadienyl compounds are very common, the isoelectronic pyrrolyl derivatives are rare.¹ Only a few molecules such as $(C_5H_5)Fe(C_4H_4N)^2$ and $(C_4H_4N)Mn(CO)_3$ ^{3,4} have been characterized. The neutral pyrrole molecule can also serve as a ligand, for example, $[C_4H_4NH]Cr(CO)_3$.⁵

Very recently, the replacement of hydrogen atoms by methyl groups was found to increase the stability of pyrrolyl-metal complexes analogous to the effect in cyclopentadienyl-metal complexes.⁶ This strategy allowed the preparation of a derivative of 1,1'-diazaferrocene,⁷ $[C_4(CH_3)_4N]_2Fe[C_4(CH_3)_4NH]_2$.

We report the gas-phase synthesis and laser spectroscopic characterization of $Ca(C_4H_4N)$ and $Sr(C_4H_4N)$. These free radicals are isoelectronic with the CaC_5H_5 and SrC_5H_5 molecules

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1977; p 1180.

(2) Joshi, K. K.; Paulson, P. L.; Qazi, A. R.; Stubbs, W. H. *J. Organometal. Chem.* **1964**, *1*, 471-475.

(3) King, R. B.; Efraty, A. *J. Organometal. Chem.* **1969**, *20*, 264-268.

(4) (a) Ji, L.-N.; Kershner, D. L.; Rerek, M. E.; Basolo, F. *J. Organometal. Chem.* **1985**, *296*, 83-94. (b) Kershner, D. L.; Rheingold, A. L.; Basolo, F. *Organometallics* **1967**, *6*, 196-198.

(5) Ófele, K.; Dotzauer, E. *J. Organometal. Chem.* **1971**, *30*, 211.

(6) Kuhn, N.; Horn, E.-M.; Zauder, E.; Bläser, D.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 579-580.

(7) Kuhn, N.; Horn, E.-M.; Boese, R.; Angart, N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1368-1369.

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