stronger interaction between the orbitals of the benzene ring and the exocyclic p orbital in the planar conformers, relative to the analogous interaction between the π (or π^*) orbitals of the double bond and the p orbital at C_3 in the allylic systems. In the case of the cation, for example, the benzene HOMO of appropriate symmetry is higher in energy than the allyl π orbital, and the magnitude of the stabilizing interaction between the filled orbital and the vacant p orbital on the cationic center is therefore larger for the aromatic species. Analogous arguments can be applied to the other systems as well. An alternative explanation is that more resonance structures are possible for the benzylic systems than for the allylic ones. The benzyl cation and radical are additionally stabilized since delocalization in the ring places the

charge (or odd electron) on *secondary* carbon atoms, which bear the charge (spin) better than the exocyclic primary carbon.

The intramolecular reactivity toward nucleophiles or double bonds on ortho substituents is found to *increase* in the same order as the rotational barrier decreases. This strongly suggests a relationship between ease of internal rotation and intramolecular reactivity.[2,46]

Solvent Effects on Optical Absorption Spectra: The $^1A_1 \rightarrow {}^1A_2$ Transition of Formaldehyde in Water

John T. Blair, Karsten Krogh-Jespersen,* and Ronald M. Levy*

Contribution from the Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903. Received March 16, 1989

Abstract: We have examined solvation of the singlet ground ($^1A_1$) and excited ($^1A_2$) states of formaldehyde by water using a combination of classical molecular dynamics and ab initio quantum mechanics techniques. Molecular dynamics simulations were carried out for a formaldehyde solute molecule in a bath of 209 water molecules. The solute was represented by Lennard–Jones plus electrostatic terms with net atomic natural charges generated from ab initio Hartree–Fock calculations using a 6-31G+d-type basis set. The SPC model was used to describe the water–water interaction potential. Radial distribution functions show structured binding by several water molecules at the oxygen end of formaldehyde in its ground state. This structure is largely, but not completely, destroyed for formaldehyde in its lowest excited singlet state. The $^1A_1 \rightarrow {}^1A_2$ vertical transition energy of formaldehyde was calculated at the ab initio Hartree–Fock level including the electrostatic interactions with the solvent molecules for 70 configurations along the trajectory. No single water molecule or first solvation shell (cluster model) adequately describes the formaldehyde–solvent interactions in both electronic states. When an ensemble of water configurations is considered, the calculated spectral blue shift and bandwidth of about 1900 and 4400 cm^{-1}, respectively, are in reasonable accord with the available experimental data.

I. Introduction

The modeling of quantum mechanical properties for molecules in liquids is an important and challenging topic. A major difficulty is the very large number of intermolecular interactions that must be considered in order for the results to correctly reflect the physics of the liquid state. A full quantum mechanical treatment of an entire solute–solvent system is far too complicated to carry out, and various approximations must be made. A variety of pure quantum or mixed-mode quantum/classical computational procedures have been proposed.[1–8] Some investigations[9–13] have been

performed using fully quantum mechanical calculations on very small systems containing, for example, a single solute clustered with one or several water molecules. Such calculations on small clusters may account for two and perhaps three body interactions, but cannot reproduce the large-scale static or dynamical effects of a full solvent bath. Other investigators[14,15] have incorporated various continuum solvent models in the solute Hamiltonian. This approach does permit certain bulk properties to be simulated by quantum mechanical calculations on the solute alone, but it cannot give any information about the microscopic details of solvation. Problems associated with developing a theoretical framework for modeling electronic transitions in the condensed phase are particularly formidable due to the high computational levels that are often required to describe the excited-state electronic structure of even the isolated solute species correctly. For studying solvent

(1) (a) Warshel, A.; Levitt, M. *J. Mol. Biol.* **1976,** *103,* 227. (b) Warshel, A. *J. Phys. Chem.* **1979,** *83,* 1640. (c) Warshel, A.; Weiss, R. M. *J. Am. Chem. Soc.* **1980,** *102,* 6218. (d) Warshel, A.; Weiss, R. M. *J. Am. Chem. Soc.* **1981,** *103,* 446. (e) Warshel, A.; Russell, S. T. *Q. Rev. Biophys.* **1984,** *17,* 283.

(2) (a) Herman, M.; Berne, B. *J. Chem. Phys.* **1983,** *78,* 4103. (b) Thirumalai, D.; Berne, B. *J. Chem. Phys. Lett.* **1985,** *116,* 471.

(3) Kuharski, R. A.; Bader, J. S.; Chandler, D.; Sprik, M.; Klein, M. L.; Impey, R. W. *J. Chem. Phys.* **1988,** *89,* 3248.

(4) Ohime, I. *J. Chem. Phys.* **1986,** *85,* 3342.

(5) (a) Singh, U. C.; Kollman, P. A. *J. Comput. Chem.* **1986,** *7,* 718. (b) Weiner, S.; Singh, U. C.; Kollman, P. A. *J. Am. Chem. Soc.* **1985,** *107,* 2219. (c) Cieplak, P.; Bash, P.; Singh, U. C.; Kollman, P. A. *J. Am. Chem. Soc.* **1987,** *109,* 6283.

(6) (a) Madura, J. D.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986,** *108,* 2517. (b) Chandrasekhar, J. Smith, S.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985,** *107,* 154.

(7) Bash, P. A.; Field, M. J.; Karplus, M. *J. Am. Chem. Soc.* **1987,** *109,* 8092.

(8) Tapia, O.; Lluch, J. M.; Cardenas, R.; Andres, J. *J. Am. Chem. Soc.* **1989,** *111,* 829.

(9) Clementi, E.; Kolos, W.; Lie, G. C.; Ranghino, G. *Int. J. Quantum Chem.* **1980,** *17,* 377.

(10) Lybrand, T. P.; Kollman, P. A. *J. Chem. Phys.* **1985,** *83,* 2923.

(11) Gao, J.; Garner, D. S.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986,** *108,* 4784.

(12) Koehler, J. E. H.; Saenger, W.; Lesyng, B. *J. Comput. Chem.* **1987,** *8,* 1090.

(13) Curtiss, L. A.; Halley, J. W.; Hautman, J.; Rahman, A. *J. Chem. Phys.* **1987,** *86,* 2319.

(14) (a) Loring, R. F.; Mukamel, S. *J. Chem. Phys.* **1987,** *87,* 1272. (b) Sparpaglione, M.; Mukamel, S. *J. Chem. Phys.* **1988,** *88,* 3263, 4300.

(15) Buckingham, A. D.; Fowler, P. W. *Can. J. Chem.* **1985,** *63,* 2018.

Solvent Effects on Optical Absorption Spectra

J. Am. Chem. Soc., Vol. 111, No. 18, 1989 6949

effects on atomic and molecular spectra, theoretical models have been developed in which the solvent is treated by continuum,[16] cluster,[17] liquid-state theory,[18,19] and computer simulation[1,2] methods. In most of these studies, highly simplified potentials were used to represent the electronic surfaces. Establishing a computationally feasible methodology for modeling of excited-state molecule–solvent interactions on realistic potential surfaces poses a very challenging problem.

In this paper we employ a microscopic model suitable for computer simulations, which is sufficiently detailed to provide insight into the structural origins of the solvent-induced line shift and broadening in the optical absorption spectrum of a solvated molecule. We couple ab initio quantum mechanical calculations of the solute electronic energy levels to classical molecular dynamics simulations of the solvent. The model is similar in spirit to simulations of solvent effects on optical absorption spectra by Herman and Berne[2] and by Warshel.[1] Herman and Berne combined Rayleigh–Schroedinger perturbation theory with Monte Carlo sampling of solvent configurations to calculate solvent-induced broadening in the electronic spectra of model diatomics. Warshel, using semiempirical quantum methods, has carried out the most extensive calculations to date of the solvent-induced shift in transition energies of chromophoric polyatomics, with emphasis on retinal[1b] and porphyrin.[1c,d] We have chosen as a paradigm for study the first optical absorption band of formaldehyde in water. The formaldehyde–water system has several desirable features. The solute is sufficiently small so that it was possible for us to study the effects of several different levels of approximation on the calculated energy gap between the ground and first excited state for the isolated solute.[20] Also, the optical absorption spectrum for formaldehyde in the gas phase has been well characterized experimentally.[21] Formaldehyde has previously served as a model compound for ground- and excited-state electronic structure calculations[22-25] and classical dynamics simulations of solute–solvent interactions.[26,6a] Furthermore, the molecule has a large dipole moment in the ground state, which is considerably reduced in the first excited state; this ensures that upon electronic excitation there will be a significant change in the solute–solvent interaction energy. The main features of the formaldehyde–water optical absorption spectrum are summarized below.

Brand reports the most intense line in the gas-phase spectrum of formaldehyde at 34 035 cm^{-1} (294 nm).[21] A polar solvent induces a shift to higher energy, i.e., a blue shift, in the $S_0 \rightarrow S_1$ transition of formaldehyde (H_2CO) and related molecules containing the carbonyl group.[27,28] The blue shift of the formaldehyde transition in water has not been determined very accurately by experimental means due to the formation of oligomers, ketals, or both. The maximum absorption of dilute formaldehyde–water solutions was reported at temperatures over the range 54–64 °C, with an average value at 34 650 cm^{-1},[29] implying a solvent shift relative to the maximum in vacuo of approximately 600 cm^{-1} if no vibrational intensity redistribution has occurred. However, the absorption bands are wide (FWHM $\simeq$ 5000 cm^{-1}) and the positions of the frequency maxima show unusually large temperature effects. In a more recent extensive investigation by Becker

et al.,[30] this entire absorption was attributed to oligomeric formaldehyde with a maximum at 290 nm (34 500 cm^{-1}) reported at room temperature. The solvent shift for monomeric acetone (($CH_3)_2CO$) in water is well determined and close to 1900 cm^{-1}.[27] The true solvent shift exhibited by monomeric formaldehyde in water is therefore likely to be in the 600–1900-cm^{-1} range.

Traditional explanations of this effect emphasize the hydrogen-bonding ability of water.[28] The lowest singlet absorption in carbonyl-containing molecules is typically labeled the $n_O \rightarrow \pi^*_{CO}$ transition. It may simplistically be described as involving 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^*_{CO} orbital that has its largest coefficient on the carbon atom.[31] Since the excitation shifts electron density from oxygen to carbon, the excited-state dipole moment (1.57 D[32]) is less than that of the ground state (2.33 D[33]). It is assumed that an optimal hydrogen bond formed in the ground state between one water and the formaldehyde molecule is broken in the excited state, and that the loss of the hydrogen bond energy becomes reflected in the observed blue shift.[28] Ab initio molecular orbital calculations with minimal basis sets were carried out on small formaldehyde–water complexes by Morokuma[34] and Del Bene,[35] primarily with the aim of studying hydrogen bonding. These early calculations tended to corroborate the traditional view. Later, Tomasi et al.[36] and Taylor[37] provided evidence from ab initio calculations with larger basis sets that substantial hydrogen bonding remained in the excited state of the optimal 1:1 formaldehyde–water complex. Taylor made the interesting alternative suggestion that "the major component of the blue shift arises from the changes induced in the component molecule geometries by hydrogen bonding".

We previously reported a small series of calculations on isolated formaldehyde and formaldehyde solvated by one or two water molecules.[20] The formaldehyde molecule was always treated quantum mechanically by using ab initio techniques, whereas the water molecules were treated by ab initio techniques as well as classically with empirical potentials. Several configurations with good hydrogen-bonding abilities were investigated, and all produced blue shifts with magnitude comparable to the inferred experimental shift. This was true in both the pure ab initio and the hybrid-type calculations. However, there were clearly many configurations of formaldehyde and a few water molecules that were energetically very close on the electronic ground-state surface. The magnitude of the blue shift was by no means determined solely by one optimal hydrogen-bonding water molecule; the second water molecule always showed a significant energetic effect as well. In addition, the solute–solvent interactions are dynamic rather than static. We concluded that more water molecules had to be included and extensive sampling of the accessible configuration space would be required to properly describe the differential solvation between the two electronic states. In this paper we provide a molecular description of the formaldehyde–water interactions in the electronic ground as well as excited state based on combined ab initio and statistical mechanics techniques, leading to a detailed analysis of the factors producing the blue shift in the position of the first absorption band.

In our approach, we successively apply two computational procedures. First we generate an ensemble of configurations representing the solvation of formaldehyde (in its ground state) by water using completely classical molecular dynamics techniques. Next, for selected configurations from the ensemble, we carry out ab initio electronic structure calculations for the formaldehyde ground and first excited singlet states, which include explicit terms

(16) Jortner, J. *J. Mol. Phys.* **1962**, *5*, 257.

(17) Sun, H.; Rice, S. A.; Jortner, J. *J. Chem. Phys.* **1964**, *41*, 3779.

(18) Schweizer, K. S.; Chandler, D. *J. Chem. Phys.* **1983**, *78*, 4118.

(19) Hall, R. W.; Wolynes, P. G. *J. Chem. Phys.* **1985**, *83*, 3214.

(20) Blair, J. T.; Westbrook, J. D.; Levy, R. M.; Krogh-Jespersen, K. *Chem. Phys. Lett.* **1989**, *154*, 531. This describes preliminary aspects of the work performed for the present paper.

(21) Brand, J. C. D. *J. Chem. Soc.* **1956**, 858.

(22) Hsieh, H. C.; Ermler, W. C. *J. Comput. Chem.* **1987**, *9*, 95.

(23) Lavenir, E.; Bouteiller, Y.; Mijoule, C.; LeClerq, J. M. *Chem. Phys. Lett.* **1985**, *117*, 427.

(24) Goddard, J. D.; Schaefer, H. F., III *J. Chem. Phys.* **1979**, *70*, 5117.

(25) Bell, S. *Mol. Phys.* **1979**, *37*, 255, and references included therein.

(26) Mehrotra, P. K.; Beveridge, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 4287.

(27) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, CA, 1960.

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

(29) Beiber, R.; Truempler, G. *Helv. Chim. Acta* **1947**, *30*, 1860.

(30) Bercovici, T.; King, J.; Becker, R. S.; *J. Chem. Phys.* **1972**, *56*, 3956.

(31) Streitwieser, A.; Kohler, B. *J. Am. Chem. Soc.* **1988**, *110*, 3769.

(32) Jones, V. T.; Coon, J. B. *J. Mol. Spectrosc.* **1969**, *31*, 137.

(33) Buckingham, A. D.; Ramsey, D. A.; Tyrell, J. *Can. J. Phys.* **1970**, *48*, 1242.

(34) Iwata, S.; Morokuma, K. *Chem. Phys. Lett.* **1973**, *19*, 94.

(35) Del Bene, J. *J. Am. Chem. Soc.* **1973**, *95*, 6517.

(36) Cimiraglia, R.; Miertus, S.; Tomasi, J. *Chem. Phys. Lett.* **1981**, *80*, 286.

(37) Taylor, P. R. *J. Am. Chem. Soc.* **1982**, *104*, 5248.

in the electronic Hamiltonian coupling the solvent water atomic positions to the formaldehyde. We are able to evaluate the contribution of successive hydration shells to the absorption spectrum by including different numbers of water molecules in the electronic structure calculations. We note that the vertical transition energies corresponding to *absorption* provide a probe of the solvent structure around *ground*-state formaldehyde. In this first series of calculations we exclude dynamical effects arising from either solute or solvent relaxation following electronic excitation. In order to obtain a qualitative understanding of the changes induced in solvent structure at "long times" (picoseconds or longer) following excitation of the formaldehyde, we have also performed a second classical molecular dynamics simulation of formaldehyde in water, but the partial charges assigned to the formaldehyde atoms were those corresponding to the $^1A_2$ excited state. The very different solvation structure of formaldehyde in its first excited state could be probed experimentally by fluorescence experiments. With small modifications, our computational procedure can be used to study the time course of solute and solvent relaxation following sudden electronic excitation, and thus, there is the possibility of simulating time-resolved fluorescence spectra in solution. Finally, we note that our procedure for calculating the optical absorption spectrum of a solvated molecule is in some respects similar to the recent simulations of the optical absorption spectrum of the hydrated electron.[38,39]

II. Computational Methods

(A) Classical Mechanics Calculations. Molecular dynamics simulations of a formaldehyde solute molecule in a box of 209 solvent water molecules were carried out using the IMPACT program.[40] The box was cubic with an edge of 18.6 Å and periodic boundary conditions were imposed; the temperature was held at 298 K. The dynamics time step was 10^{-15} s. The intermolecular potential function consisted of electrostatic and Lennard–Jones terms, with a 7.5 Å potential energy cutoff. The water molecules were simulated by the SPC model,[41] consisting of point charges ($q_H = +0.41$ and $q_O = -0.82$), Lennard–Jones constants on O, and fixed intramolecular geometry ($R_{OH} = 1.00$ Å, $\angle HOH = 109.47°$). The formaldehyde geometry and atomic charges ($q_O = -0.576$, $q_C = +0.331$, $q_H = +0.123$) were obtained from ab initio calculations; see below. Literature values were used for the formaldehyde molecular mechanics parameters (bond, angle, torsion, and Lennard–Jones constants).[42] The Lennard–Jones interaction terms between the atoms in H_2CO and the water oxygen atoms produce a small attraction at long intermolecular distances but a large repulsion at short distances.

A molecular dynamics simulation was carried out to generate solute–solvent configurations corresponding to the multitude of local environments experienced by formaldehyde solute molecules in the water solvent. The simulation was started by placing the H_2CO at the center of a previously equilibrated box containing 216 SPC water molecules. Seven water molecules, which had positive Lennard–Jones interactions with and thus overlapped the H_2CO molecule, were removed and the system was allowed to reequilibrate. The simulation was run for 24 000 time steps (corresponding to 24 ps), and the solute–solvent coordinates from every tenth step were saved for later analysis. This sampling procedure was repeated using a box of water molecules equilibrated with the $^1A_2$ excited-state charges on the H_2CO ($q_O = -0.238$, $q_C = -0.143$, $q_H = +0.191$), maintaining the equilibrium geometry and force constants appropriate for the ground state. We approximate the effects of the altered H_2CO charge distribution on the interactions with the surrounding water cage by allowing solvent relaxation only. Dynamical effects arising in conjunction with geometrical relaxation of the excited state will not be investigated here. The stored configurations were used to produce radial distribution functions and angular distribution functions for both ground- and excited-state formaldehyde–water simulations. In addition, selected

configurations formed the input to ab initio calculation of transition energies; see below.

(B) Quantum Mechanics Calculations. Ab Initio molecular orbital calculations were performed on isolated H_2CO and on H_2CO in the presence of SPC waters using a locally modified version of the GAMESS electronic structure program package.[43] For the present studies, modifications were made to conveniently allow communication with IMPACT (charges and coordinates) and various data analysis and graphics routines were implemented. The point charges affect the quantum mechanical wave function via the Coulombic operator in the one-electron Hamiltonian and via the nuclear–nuclear repulsion terms. In all the ab initio calculations we used the standard split valence 6-31G[44] basis set augmented by a set of polarization functions ($\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$),[45] hereafter referred to as 6-31G+d. Initially, the geometry of isolated ground-state H_2CO ($^1A_1$, C_{2v}) was optimized at the RHF/6-31G+d level ($R_{CO} = 1.184$ Å, $R_{CH} = 1.093$ Å, $\angle HCH = 115.5°$), a Natural Population Analysis[46] of the H_2CO ground state was performed, and the Net Natural Atomic Charges were computed ($q_O = -0.576$, $q_C = +0.331$, $q_H = +0.123$). The excited state ($^1A_2$) was generated by using the restricted open-shell Hartree-Fock (ROHF) method[47] at the ground-state equilibrium geometry, followed by a natural population analysis; the corresponding excited-state charges are $q_O = -0.238$, $q_C = -0.143$, and $q_H = +0.191$. As described above, these charges and the ground-state equilibrium geometry were used as input parameters for molecular dynamics simulations of H_2CO in water, which produced representative solute–solvent configurations. Subsequent calculations (see below) used the 6-31G+d basis set on H_2CO at the RHF or ROHF level and included the effect of the SPC charges directly.

Seventy atomic configurations were chosen from the previously selected 2400 ground-state molecular dynamics data set. For each configuration a total of six quantum mechanical calculations were performed on formaldehyde: three for the ground $^1A_1$ state and three for the excited $^1A_2$ state. The first pair of calculations took the configurational coordinates of all 210 molecules (1 H_2CO and 209 waters), providing our best model for the full effects of the water bath. Included in the second pair of calculations were the formaldehyde and those water molecules situated within the first solvation shell about the H_2CO oxygen (i.e., those waters with a $H_2CO(O)$–$SPC(O)$ distance less than the first minimum in the radial distribution function, at 3.25 Å). Only the bare H_2CO molecules were included in the third pair of calculations; that is, all the coordinates for the H_2O molecules were deleted from the configuration files. These calculations on unsolvated H_2CO indicate the energetic effects of geometric distortions occurring within the H_2CO molecules as the result of hard sphere type collisions and hydrogen bonding with H_2O molecules, and internal vibrations as modeled by the IMPACT program. Thus, ground- and excited-state energies may be compared for each of the 70 selected configurations to give three *vertical* excitation energies: all water molecules present, only first solvation shell water molecules, and no water molecules at all. Within the Condon approximation the ensemble of electronic excitation energies calculated with all water molecules included will correspond to the observed aqueous-phase formaldehyde spectrum.

Approximate times required on a Convex C210 minisupercomputer to perform the calculations described above are as follows: one step of classical dynamics (formaldehyde + 209 water molecules) takes less than 3 CPU s; an electronic structure calculation on ground-state formaldehyde with no water molecules takes ~30 CPU s; an electronic structure calculation on ground-state formaldehyde with 209 water molecules takes ~1.5 CPU min; an electronic structure calculation on excited-state formaldehyde with 209 water molecules takes slightly over 8 CPU min.

III. Results and Discussion

(A) Molecular Dynamics Simulations: Solvation of Formaldehyde in the Ground and Excited State. Parts a and b of Figure 1 show the SPC(O)–SPC(O) and SPC(O)–SPC(H) radial distribution functions obtained from the simulation of ground-state formaldehyde and 209 SPC water molecules. These are virtually identical with previously published[48] radial distribution functions

(38) Rossky, P. J.; Schnitker, J. *J. Phys. Chem.* **1988**, *92*, 4277.

(39) Wallqvist, A.; Martyna, G.; Berne, B. J. *J. Phys. Chem.* **1988**, *92*, 1721.

(40) The Integrated Modeling Program Using Applied Chemical Theory (IMPACT) program is a package developed by R. M. Levy and co-workers at Rutgers Univ.; for details see, e.g.: Bassolino, D. A.; Hirata, F.; Kitchen, D. B.; Kominos, D.; Pardi, A.; Levy, R. M. *Int. J. Supercomputer Appl.* **1988**, *2*, 41.

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

(42) Weiner, S. J.; Kollman, P. A.; Nguyen, D. T.; Case, D. A. *J. Comput. Chem.* **1986**, *7*, 230.

(43) Dupuis, M.; Spangler, D.; Wendoloski, J. *GAMESS, NRCC Software Catalogue*, Vol. 1, Program No. QC01, 1980. This original version of GAMESS has been heavily modified by M. Schmidt, M. Gordon, and S. Elbert at Iowa and North Dakota State Universities, and by J. D. Westbrook, J. T. Blair, and K. Krogh-Jespersen at Rutgers University.

(44) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(45) Dunning, T. H.; Hay, P. J. *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 1.

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

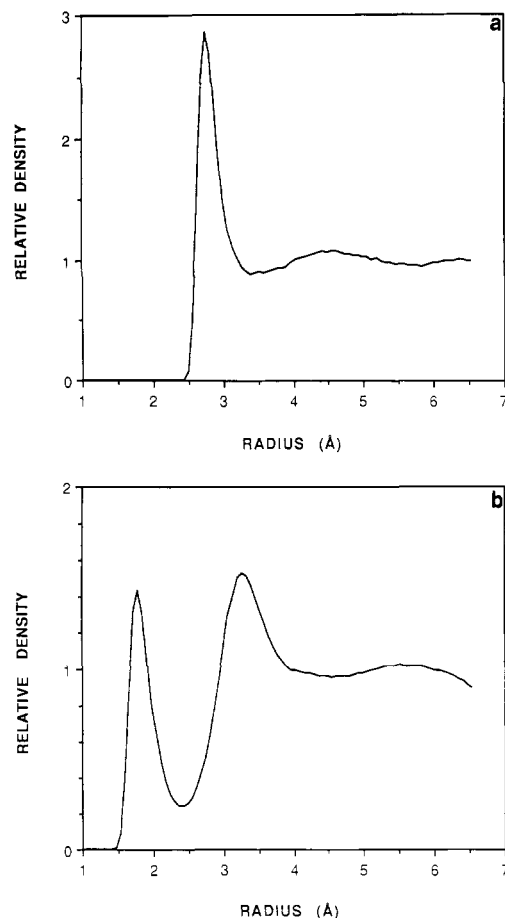(47) Davidson, E. R. *Chem. Phys. Lett.* **1973**, *21*, 565.

Figure 1. (a) SPC(O)-SPC(O) radial distribution function from the ground-state simulation. (b) SPC(O)-SPC(H) radial distribution function from the ground-state simulation.

Figure 2. (a) $H_2CO(O)$-SPC(O) radial distribution function from the ground-state simulation. (b) $H_2CO(O)$-SPC(H) radial distribution function from the ground-state simulation.

for pure water with the SPC model, which demonstrates that the bulk water structure is that of the pure solvent. Parts a and b of Figure 2 show the corresponding ground-state $H_2CO(O)$-SPC(O) and $H_2CO(O)$-SPC(H) radial distribution functions. The poorer quality of the solute–solvent radial distribution functions, particularly beyond the first peak, reflects the statistical problem associated with simulating a single solute in a solvent bath, relative to the statistical sampling of the bulk solvent. The solute–solvent radial distribution functions clearly show a well-defined local intermolecular structure developed at the oxygen end of H_2CO, which is different from the one present in bulk water (Figure 1a,b). The O–O radial distribution function for water (Figure 1a) exhibits a sharp peak at ∼2.8 Å and a barely discernible second peak at ∼4.4 Å. In contrast, the first maximum in the $H_2CO(O)$-SPC(O) radial distribution function (Figure 2a) occurs at a slightly shorter distance (∼2.7 Å) than the first bulk water maximum, and the second maximum near 4.4 Å is more clearly defined. Thus there appears to be a more fully developed second solvation shell around the carbonyl oxygen as compared with a bulk water oxygen. The $H_2CO(O)$-SPC(H) radial distribution function (Figure 2b) has a sharp peak at 1.7 Å and a second smaller peak near 3.2 Å. Since the OH bond length is 1.00 Å in a SPC water molecule, the first set of peaks in Figure 2a,b corresponds to structures where one water OH bond is pointed straight toward the H_2CO oxygen with the angle $H_2CO(O)$-SPC(H)-SPC(O) near 180°, forming a linear hydrogen bond. Integration of the first peak in Figure 2a to a distance of 3.25 Å gives 2.6 oxygen atoms in this first "solvation shell". Thus, there are effectively more than two waters attached to the H_2CO oxygen, rather than only a single water positioned for an optimal hydrogen bond. The outer peak in Figure 2a corresponds to the second water
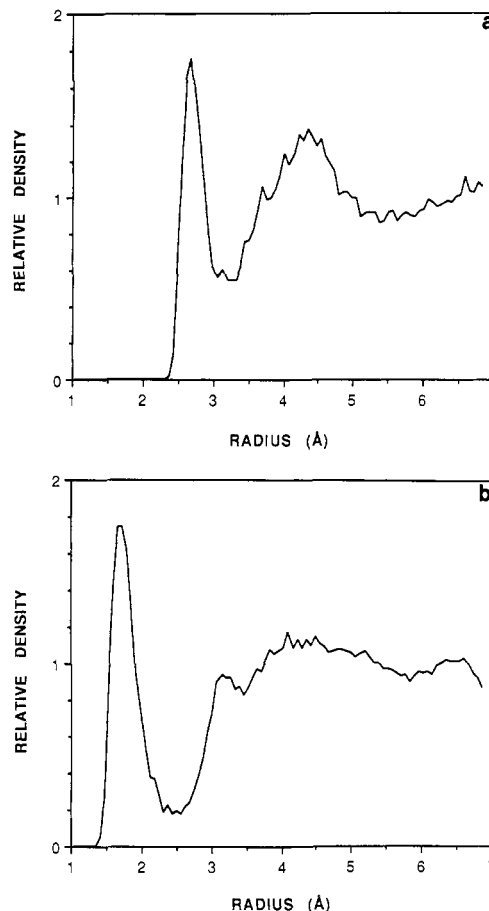
solvation shell around the formyl oxygen. Integration of the peak area gives roughly 19 water molecules in this second solvation shell. In contrast, solute–solvent radial distribution functions (not reproduced here) constructed with a formaldehyde hydrogen as the local origin indicate little or no intermolecular structure at that end of the H_2CO molecule. The $H_2CO(H)$-SPC(O) radial distribution function is zero until ∼2.5 Å, when it rises steeply to 1 and remains roughly at 1 for longer distances.

Parts a–c of Figure 3 depict angular distribution functions produced from the ground-state simulation. Figure 3a shows the distributions of the $H_2CO(O)$-SPC(H)-SPC(O) angles for water molecules in the first solvation shell around the formaldehyde oxygen (i.e., those water molecules that have their oxygen within 3.25 Å of the H_2CO oxygen). This figure clearly shows that there is a strong preference for one water hydrogen to be pointed straight toward the $H_2CO(O)$, that is cos θ = -1.0, with the other water hydrogen pointed 109° away (cos θ = 0.33), in agreement with the radial distribution functions (Figure 2a,b). Figure 3b shows the equivalent angular distribution function for water molecules in the second solvation shell (i.e., those water molecules between 3.25 and 5.5 Å from the H_2CO oxygen). In contrast to the first shell, the water molecules in the second solvation shell tend to have one hydrogen pointed 180° away from the formaldehyde oxygen, although there is a much less well defined structure. On the basis of the $H_2CO(C)$-$H_2CO(O)$-SPC(O) angles for first solvation shell water molecules (Figure 3c), we infer that there is a broad range of probable water positions (angles to the SPC oxygens between 109 and 180°), and that a water O–H bond collinear with the formaldehyde C=O bond (cos θ = -1.0) is a less favorable position than having an angle of ∼130° (cos θ = -0.64) between the two bonds. This most probable angle is close to the optimal $H_2CO(C)$-$H_2CO(O)$-SPC(O) angle of 121° obtained for a system of only a single SPC water molecule and a H_2CO. It is very interesting that ab initio supermolecule calcu-

(48) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.
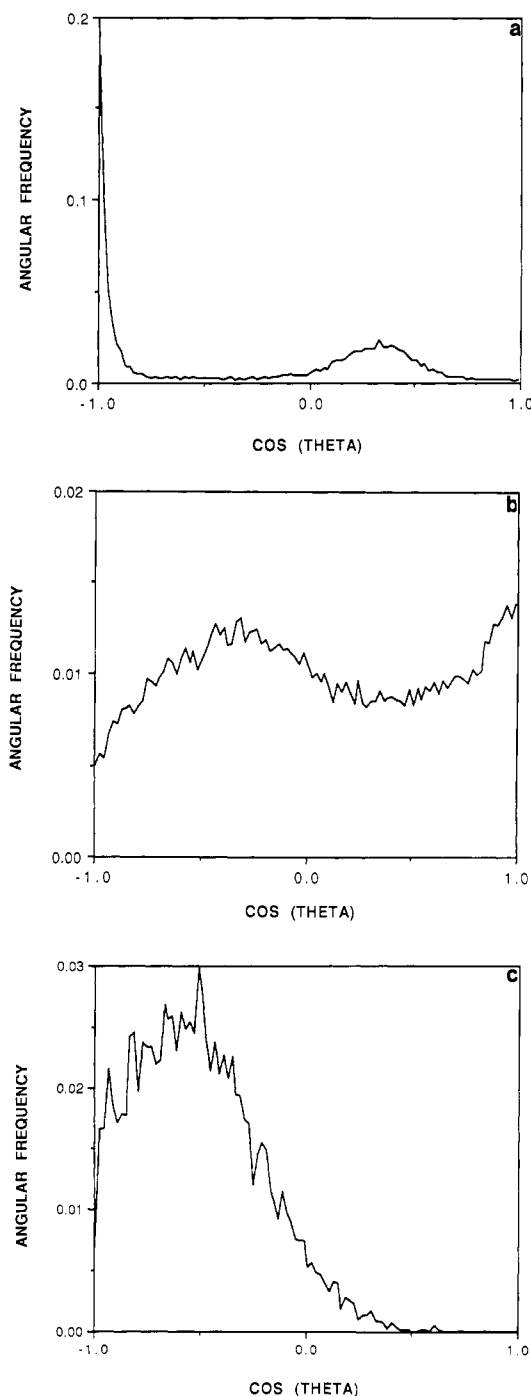
6952   *J. Am. Chem. Soc., Vol. 111, No. 18, 1989*

Blair et al.

Figure 3. (a) $H_2CO(O)-SPC(H)-SPC(O)$ angular distribution function for the first shell of SPC water molecules from the ground-state simulation. (b) $H_2CO(O)-SPC(H)-SPC(O)$ angular distribution function for the second shell of SPC water molecules from the ground-state simulation. Notice the change in vertical scale relative to (a). (c) $H_2CO(C)-H_2CO(O)-SPC(O)$ angular distribution function for the first shell of SPC water molecules from the ground-state simulation. Notice the change in vertical scale relative to (a).

lations on the H_2CO-H_2O complex inevitably find the most stable configuration to be planar with a $H_2CO(C)-H_2CO(O)-(O)H_2O$ angle near $120°$.[20,34,35,37] Thus, in this aspect, the classical potential, which only includes electrostatic and Lennard–Jones terms, reproduces the full ab initio potential, which includes effects of intermolecular orbital overlap as well as electrostatic effects. Further analysis of water molecule positions in the first solvation shell shows that on average 22% have oxygens within 1.0 Å of the plane defined by the formaldehyde. This is significantly higher than the percentage that would be approximately coplanar if the water positions were randomly distributed. Thus, there is some

tendency for water molecules of the first solvation shell to be near the minimum energy positions (coplanar with the H_2CO and bent away from the $C=O$ axis $\sim 120°$), but a majority are actually at other positions, with slightly higher energies. Angular distribution functions for water molecules at the hydrogen end of H_2CO (not reproduced here) fully support the radial distribution results, illustrating that there is less structure at the hydrogen end. Taken together, the radial and angular distribution functions show a strong solute–solvent structure at the oxygen end of H_2CO, including both first and second solvation shells. The first shell has several water molecules in a range of angles about the formaldehyde, all of which allow good hydrogen bonding with the oxygen atom.

An internal energy analysis of the solute–solvent system also demonstrates that there are significant formaldehyde–water interactions. The average potential energy for the entire system is -2101 ± 10 kcal/mol, of which -26 ± 2 kcal/mol is due to solute–solvent interactions. Hence the average potential energy for each of the 209 SPC waters is approximately -10 kcal/mol, and the average binding energy for a SPC water is -20 kcal/mol, which is significantly less than the formaldehyde binding energy of -26 kcal/mol. Thus, not only is the H_2CO strongly attracted to the surrounding water molecules, but also the interaction energy is far too strong to correspond to only a single, even optimal, hydrogen bond. This is in agreement with the structural results from the simulation, which require a more complicated model to fully explain the solvation.

The molecular dynamics results from the excited-state simulation show that the changes in the atomic charges on the solute engendered by the electronic excitation have a large effect on the solute–solvent structure. The $H_2CO(O)-SPC(O)$ and $H_2CO-(O)-SPC(H)$ radial distribution functions corresponding to solvation of formaldehyde with the excited-state charge distribution are shown in Figure 4, parts a and b, respectively. Figure 4a has a barely noticeable feature at ~ 3.0 Å, dramatically reduced in intensity and moved to larger distance compared to the sharp first maximum present in Figure 2a; similarly, Figure 4b has only a very small peak near 1.9 Å. The reduction of net charge on oxygen from $-0.58e$ ($^1A_1$) to $-0.24e$ ($^1A_2$) has almost completely destroyed the strong local binding of water molecules to the formaldehyde oxygen present in ground-state H_2CO. This loss of solute–solvent structure is similar to the result obtained by Jorgensen et al.[49] during a series of Monte Carlo simulations in which the negative charge on methanol oxygen was reduced as the methanol was "perturbed" to become ethane. In our excited-state simulation, there is still no definite intermolecular structure developed at the hydrogen end of the formaldehyde, despite the fact that the formal charge on the hydrogens has increased to almost $+0.2e$ in the $^1A_2$ state. Excited-state angular distribution functions (not reproduced here) also indicate that the reduced charge on oxygen has greatly reduced the tendency for water molecules to be located at specific angles. In accord with these structural results, the formaldehyde binding energy has changed substantially in the excited state. The averaged total potential energy is -2091 ± 11 kcal/mol in the excited-state simulation with the net solvent–solute interaction accounting for only -11 ± 1 kcal/mol, a dramatic binding energy decrease of ~ 15 kcal/mol relative to the ground-state value. The electrostatic interactions have been increased by 18 kcal/mol (to -8 ± 1 kcal/mol), but this loss is partially compensated by the net change in the sum of Lennard–Jones interactions (-3 kcal/mol). In the ground-state simulation, the strong electrostatic interactions pull the first shell of water molecules in close to the H_2CO molecule where they have repulsive Lennard–Jones interactions, and the sum of Lennard–Jones interactions for the entire system is approximately zero. In the excited-state simulation, the weaker electrostatic attractions cause the first shell water molecules to be farther away from the H_2CO species, in the attractive region of the Lennard–Jones potential.

The solvent-induced blue shift for the first optical absorption band of formaldehyde in water may be estimated from differences

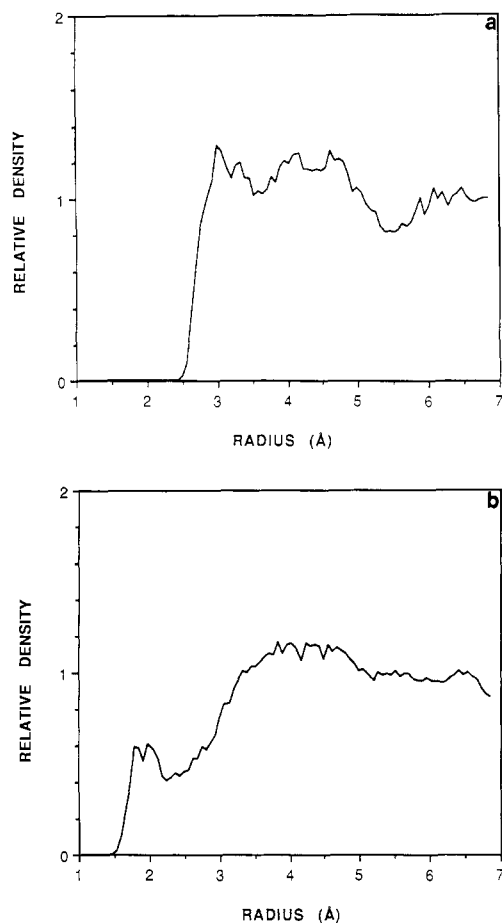(49) Jorgensen, W. L.; Ravimohan, C. *J. Chem. Phys.* **1985**, *83*, 3050.

Solvent Effects on Optical Absorption Spectra

J. Am. Chem. Soc., Vol. 111, No. 18, 1989 6953

Figure 4. (a) $H_2CO(O)-SPC(O)$ radial distribution function from the excited-state simulation. (b) $H_2CO(O)-SPC(H)$ radial distribution function from the excited-state simulation.

in solute interaction energies between the two purely classical simulations of the ground- and excited-state formaldehyde. The reduction in formaldehyde–water interaction energy (~ 15 kcal/mol) is larger than the measured blue shift (2–5 kcal/mol), and so is the change in total energy (+10 kcal/mol). Therefore, although the results from this simple molecular mechanics/dynamics model are in qualitative agreement with the standard explanation that the experimental blue shift is caused by the destruction of hydrogen bonding between water molecules and the excited formaldehyde molecule, the completely classical model does not quantitatively reproduce the magnitude of the blue shift. It is known that for ions with a small ionic radius, ion solvation energies are overestimated by point charge models,[50] and a similar effect would lead to an overestimation of the blue shift. However, considering the magnitude of the formaldehyde partial charges, and the delocalization of these charges, this effect is unlikely to be the cause of the overestimated blue shift in the classical simulation.

The results presented in this section demonstrate that a decrease of the electronic charge on the formyl oxygen by 0.34e upon excitation leads to a large change in the solvation of formaldehyde. Since the formaldehyde partial charges appear as input parameters in the simulations, it is relevant to consider the accuracy we attribute to the partial charges used for the ground- and excited-state simulations. First, there is the question of assigning atomic partial charges from molecular orbital calculations, noting that these charges are not quantum mechanical observables. It is well-known that electronic population analysis is notoriously basis set and method dependent. To estimate the formaldehyde partial charges needed for the simulations, we used the natural atomic net charges computed at the Hartree–Fock level with a split-va-

lence plus polarization basis set. Net charges obtained from natural population analysis[46] have been shown to be less basis set dependent than, for example, charges obtained with the standard Mulliken[51] partitioning procedures. Dipole moments, which are physical observables, reflect the electronic charge distribution, although they depend on more than just one-center charge terms. For comparison, we compute a ground-state dipole moment in H_2CO of 2.66 D, somewhat larger than the experimental value of 2.33 D,[33] and for the excited state at the ground-state equilibrium geometry, we compute a dipole moment of 1.27 D. An experimental value of 1.57 D[32] has been reported for the $^1A_2$ state, but this value refers to the relaxed excited-state geometry. We obtain a value of 1.70 D at the calculated excited-state equilibrium geometry ($R_{CO} = 1.355$ Å, $R_{CH} = 1.078$ Å, $\angle HCH = 118.2°$, $\phi = CH_2$ rocking angle $= 40.3°$). Second, we have considered both electron correlation and basis set effects on the calculated partial charges. Computations with the 6-31G+d basis set including all singly and doubly excited configurations relative to the single determinant (RHF or ROHF) description lead to net charges on the formyl oxygen similar to those at the HF level. At the correlated level they are −0.496 in the ground state (−0.576 at the RHF level) and −0.250 in the excited state (−0.238 at the ROHF level), giving a reduction of 0.25e in charge at the oxygen. The dipole moments calculated at the correlated level (2.30 D in the ground state and 1.67 D in the vertical excited state) are somewhat closer to the experimental values than those calculated at the HF level, and it is possible that the atomic charges calculated at the correlated level could also represent formaldehyde slightly more accurately. In fact, we did carry out limited simulations (8000 steps) on both the ground- and excited-state H_2CO with the net atomic charges obtained from the correlated calculations. Qualitatively, the radial distribution functions obtained were very similar to those produced by the full simulations with the HF charges, including the dramatic change in the first solvation shell. Similar or even smaller changes are obtained at the HF level with a change of basis sets through, e.g., the addition of an extra set of s and p functions to O and C (6-311G+d) or the addition of a second set of d functions to O and C and a set of p functions to both hydrogens. The changes in dipole moments at different computational levels appear to be associated more with the charge polarization terms than with the net charges. Third, the solvation of the formaldehyde increases the polarization of the electron distribution. This effect occurs in both ground and excited states but is more pronounced in the ground state. For the 70 configurations on which 6-31G+d calculations were performed in the presence of all 209 water molecules, the average net charge on the oxygen was −0.699 in the ground state and −0.307 in the excited state, giving a net reduction of 0.39e upon excitation. Thus, the decreased polarization due to electron correlation is partially cancelled by the increased polarization due to solvation. The fluctuations in net atomic charges are small compared to the changes upon electronic excitation; for the 70 configurations the computed oxygen charges had a standard deviation of 0.024e in the ground state and 0.013e in the excited state. Hence the use of a fixed set of atomic charges for the ground state and another fixed set of atomic charges for the excited state is not a bad approximation. Overall, we judge that the natural atomic charges used have realistic "converged" values and present a faithful picture of the charge distribution of the system. They are unadjusted values from ab initio calculations, rather than arbitrary parameters adjusted so the results will agree with experiment. Thus our results described above do show fundamental aspects associated with the solvation of formaldehyde in water.

(B) Quantum Mechanics: Solvent Effects on the $^1A_1 \rightarrow {}^1A_2$ Vertical Electronic Energy. For the $^1A_1 \rightarrow {}^1A_2$ vertical transition in H_2CO, all Hartree–Fock (HF) level calculations predict an energy lower than the experimental value due to the differences in correlation energy between the ground (eight doubly occupied orbitals) and the excited state (seven doubly occupied and two

(50) Chandrasekhar, J.; Spellmeyer, D.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 903.

(51) Mulliken, R. S.; Ermler, W. C. *Diatomic Molecules: Results of Ab Initio Calculations*; Academic: New York, 1977; p 33.
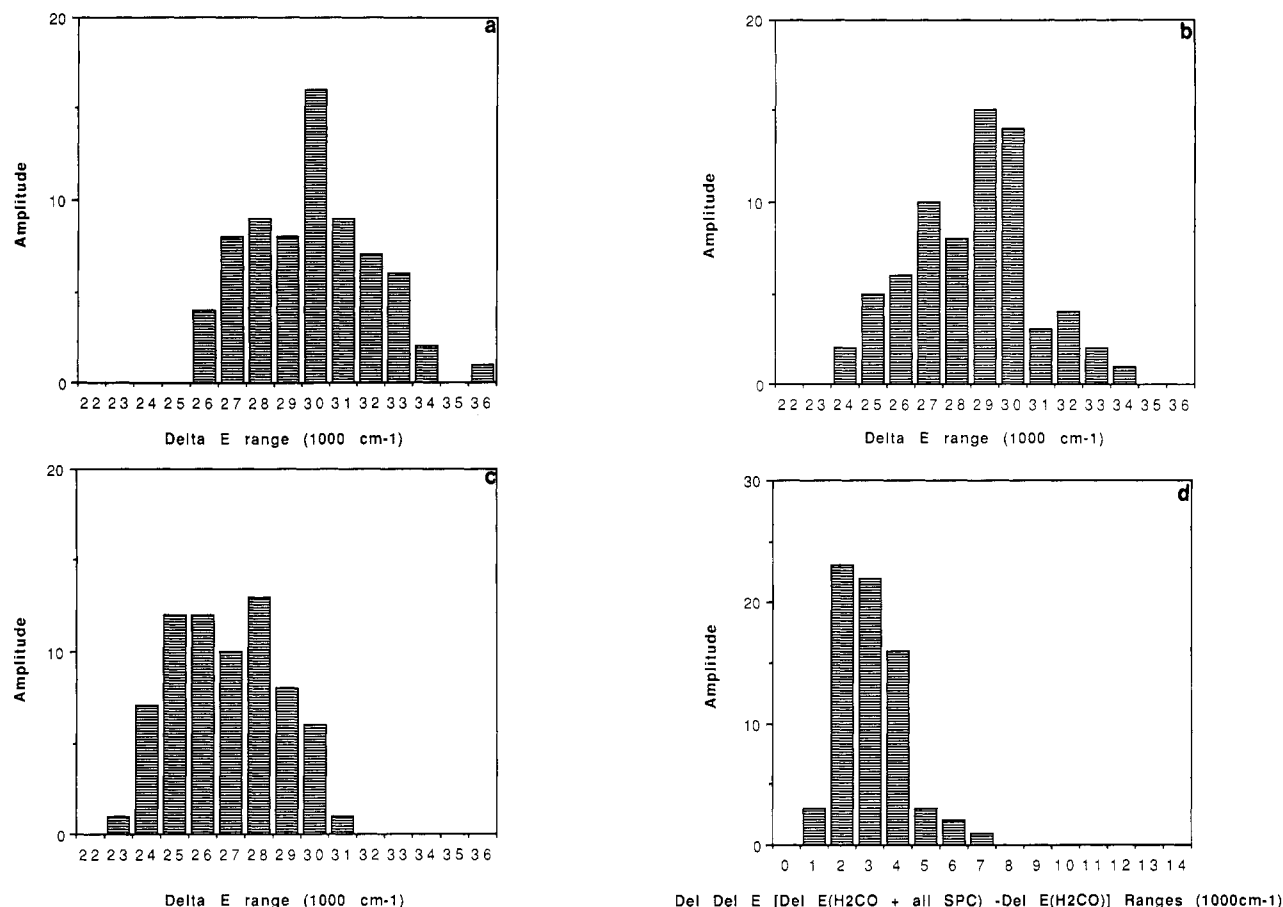
Figure 5. (a) Histogram of transition energies computed for H_2CO in the presence of 209 water molecules. Each bar represents an energy spread of 1000 cm^{-1}. (b) Histogram of transition energies computed for H_2CO in the presence of water molecules from the first solvation shell. Each bar represents an energy spread of 1000 cm^{-1}. (c) Histogram of transition energies computed for H_2CO without water molecules but with distorted geometries. Each bar represents an energy spread of 1000 cm^{-1}. (d) Histogram of differential transition energies. The difference between the transition energy with all water molecules present (a) and the transition energy without any water molecules (c) is plotted for each configuration. Each bar represents an energy spread of 1000 cm^{-1}.

singly occupied orbitals). The value computed with the 6-31G+d basis set for the vertical transition is 28 000 cm^{-1}, some 6000 cm^{-1} below the experimental gas-phase maximum.[21] The adiabatic transition energy is computed to be 19 550 cm^{-1}, some 8650 cm^{-1} below the experimental value (28 200 cm^{-1} [52]). Larger basis sets do not substantially modify these discrepancies but partial recovery of the correlation energy does. Thus, at the correlated CISD/6-31G+d level the transition energy is computed too high at 38 000 cm^{-1}, but extension of the basis set to 6-311G+d at the CISD level brings the computed vertical transition energy (33 900 cm^{-1}) into very close agreement with the experimental value.[20] However, such correlated calculations with large basis sets, although desirable, are still too costly to carry out in a routine manner for many points. We have therefore limited ourselves to the HF level and the 6-31G+d basis set, assuming that the changes in transition energy are reproduced well even if the absolute value is not. The computed results for the vertical vs adiabatic energy difference quoted above lend some support to this contention.

The quantum mechanical calculations on formaldehyde and the SPC water molecules using the 70 sets of configurational coordinates obtained from the molecular dynamics simulations produced distributions of $^1A_1 \rightarrow {}^1A_2$ transition energies, which are presented in graphical form in Figure 5a–d. In order to obtain a more detailed understanding of the structural basis for the solvent spectral broadening, the quantum calculations were carried out in three ways: (1) including all 209 solvent molecules, (2) including only the solvent molecules within the first solvation shell, and (3) excluding all solvent molecules. Because the internal

vibrations of the formaldehyde molecule are included in the classical molecular dynamics simulations, intramolecular distortions lead to a spread in transition energies even when all the solvent molecules are excluded from the quantum calculation. This is considered further below.

Figure 5a is a histogram showing the computed transition energies of H_2CO in the presence of all 209 water molecules. These ΔE values range from 26 000 to 36 250 cm^{-1}, with an average of 29 900 ± 2200 cm^{-1}. Relative to the computed gas-phase value, this average value represents a blue shift of 1900 cm^{-1} induced by the presence of the water molecules, at the high end of what may be inferred from the experimental data. This may reflect the fact, mentioned above, that the changes in net natural atomic charges between the ground and the excited state probably are slightly too large at the HF level. The standard deviation in ΔE values corresponds to a "bandwidth" of 4400 cm^{-1}, in good agreement with experimental results. In general, the electrostatic field produced by the water molecules increases the dipole moment in both the ground and excited states, in some configurations by more than 1.0 D. The average increase is 0.3 D larger in the ground state than in the excited state and larger in those configurations where the water molecules induce large blue shifts. The ground state already possesses the larger dipole moment of the two states, and the additional induced dipole moment preferentially favors the ground state. The excited state is therefore less stabilized by interactions with a polar solvent (water) and the transition energy is increased relative to the gas-phase value. Further decomposition of the factors contributing to the overall blue shift is revealing.

Figure 5b is a histogram showing the computed transition energy values of H_2CO in the presence of only first solvation shell

(52) Moule, D. C.; Walsh, A. D. *Chem. Rev.* **1975**, *75*, 67, and references therein.

Solvent Effects on Optical Absorption Spectra

J. Am. Chem. Soc., Vol. 111, No. 18, 1989 6955

water molecules (see Computational Methods). These ΔE values range from 24 150 to 34 200 cm^{-1}, with an average of 28 600 ± 2200 cm^{-1}. This average computed blue shift of 600 cm^{-1} produced by only the first solvation shell around the formaldehyde oxygen is much smaller than the average blue shift produced by the entire ensemble of 209 water molecules (1900 cm^{-1}) and at the very low end of values inferred from the experimental data. Thus, many water molecules contribute to the change in transition energy (including those near the hydrogen end of H$_2$CO), not just those within the immediate vicinity of the oxygen comprising the primary solvation shell. These results demonstrate that cluster models consisting of solute plus a layer of water molecules are inadequate for studying solvent spectral shifts.

The histogram in Figure 5c shows the computed H$_2$CO transition energies at the geometries sampled during the simulation but without any water charges explicitly present. These ΔE values range from 23 300 to 30 800 cm^{-1}, with an average of 26 850 ± 1900 cm^{-1}. The average value represents a red shift of 1150 cm^{-1} relative to the computed reference gas-phase value of 28 000 cm^{-1}. The majority of transitions in distorted formaldehyde are at lower energies (red shift) than the vertical transition energy, although a significant number of transitions are shifted in the opposite direction. This result is exactly opposite to the suggestion put forth by Taylor as the origin of the blue shift.[37] The major differences between the relaxed ground- and excited-state geometrical structures are the pyramidalization around C($C_{2v} \rightarrow C_s$) and the lengthening of the CO bond in the excited state. Our reference value of 28 000 cm^{-1} is a vertical Franck–Condon transition energy obtained at the equilibrium, ground-state geometry (C_{2v} symmetry). The empirical parameters were adjusted so that the H$_2$CO equilibrium geometry from IMPACT was identical with the reference ground-state geometry from the ab initio calculations (see Computational Methods). However, the simulations were run at 298 K and all the H$_2$CO configurations generated by IMPACT are distorted (C_1 symmetry). Thus the ab initio ground-state energy for each configuration is always higher than that for the reference structure. All configurations used are bent several degrees away from planarity, which will tend to lower all computed excited-state energies. In addition, many configurations will have a CO bond length larger than the equilibrium ground-state value, again lowering the excited-state energy. The intramolecular distortions of formaldehyde due to molecular vibrations and collisions with water molecules will always increase the ground-state energy relative to the vacuum equilibrium geometry reference, but they will usually decrease the excited-state energy due to distortion toward the excited-state equilibrium geometry. The net result is almost always a decrease in the transition energy relative to the idealized gas-phase vertical transition energy. We note, from Figure 5c, that some distorted formaldehyde geometries clearly lead to a blue shift even in the absence of solvent. These distorted structures have compressed C=O bonds, i.e., they involve displacements away from the excited-state equilibrium geometry. We also note that the vibrational distortions of the molecules are very small, e.g., the root mean square deviation of the C=O bond is 0.019 Å.

Figure 5c demonstrates that within the model considered here, intramolecular distortions of the ground-state formaldehyde, although small in magnitude, make a significant contribution to spectral features as compared with the reference vacuum calculation using the frozen ground-state geometry. While the results shown in Figure 5c are of interest in their own right, they can be misleading. A proper treatment of vibrational distortion contributions to the line shapes requires an analysis of Franck–Condon vibrational overlap factors, which have been neglected in the present calculations. In this regard, we note that a novel and appealing approach to the problem would be to carry out a three-part simulation in which the solvent is treated classically, the solute vibrational motion is treated semiclassically, and the electronic transitions are treated fully quantum mechanically. In any case, as a first approximation, we expect the neglect of the Franck–Condon overlaps to be reasonable for studying solvent effects on optical absorption, because solvent broadening will
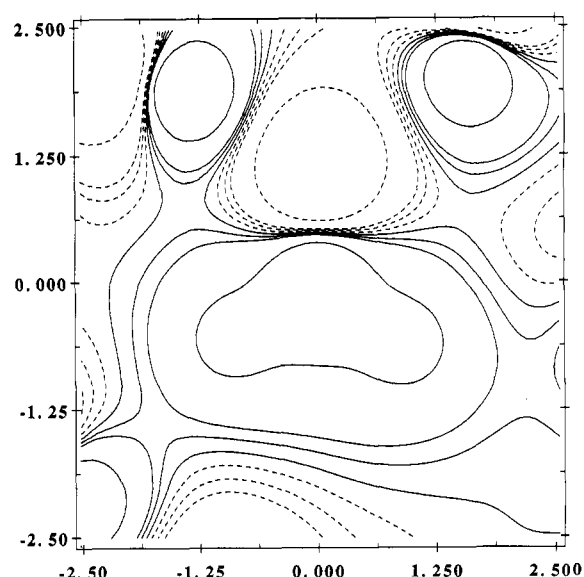

Figure 6. Contour map of electrostatic potential in the region around H$_2$CO for the configuration that gives the largest blue shift. Contours are at $-100, -25, -15, -5$ (dashed lines), $+5, +15, +25$, and $+100$ (solid lines) kcal/mol. The electrostatic potential is due to charges of all water and formaldehyde molecules. Note the two hydrogen atoms (solid oval contours at the top of the figure) bonding to the formaldehyde oxygen.

normally smear out the Franck–Condon fine structure.

To separate the contributions of solvent broadening to the absorption from the effects of intramolecular distortion, we have in Figure 5d calculated a "difference spectrum". For every molecular configuration the transition energy of unsolvated H$_2$CO (Figure 5c) has been subtracted from the transition energy of H$_2$CO with all water molecules included (Figure 5a). The changes are always positive, ranging from 750 to 6600 cm^{-1}, with an average value of 3050 ± 1100 cm^{-1}. In certain configurations the water molecules are arranged so that the interaction with H$_2$CO in its ground state is very favorable, thus producing a large blue shift. In other configurations, the water molecule interactions with ground-state H$_2$CO molecule are less favorable and a smaller blue shift results. However, in our sampling of configurations not a single water configuration produced a red shift relative to the transition energy for unsolvated H$_2$CO, although such a high-energy configuration will occur occasionally. In connection with our previous model work,[20] we had performed a few calculations where two water molecules were structurally frozen with their dipole moments aligned opposite to that of H$_2$CO. In these cases the water molecules raise the energy of the ground state more than that of the excited state, hence leading to a red-shifted transition energy. Distortions within the formaldehyde solute (Figure 5c) will tend to lower the average transition energy and produce a fairly wide range of transition energies. Addition of the energetic effects from the full set of water molecules increases all transition energies so that the majority of transitions are at higher energies than the gas-phase value, but the range of possible transition energies is further broadened. The greatest net blue shift encountered is 8250 cm^{-1} (Figure 5a), in a situation where both the intramolecular and solvent effects act in the same direction. However, a significant minority of transitions are red shifted compared to the gas-phase transition, the greatest red shift being 2050 cm^{-1}.

To further investigate the nature of solvent–solute coupling, we examined classical electrostatic potential contours in the H$_2$CO region of the cubic box. The electrostatic potential contours provide a visual method of examining the classical charge interaction term in the Hamiltonian. From the 70 configurations examined we have chosen the ones that produced the largest (Figure 6) and the smallest (Figure 7) effect upon addition of water charges (i.e., the two extreme configurations from Figure 5d). The contours shown in Figures 6 and 7 represent the electrostatic potential from all 209 water molecules and the form-
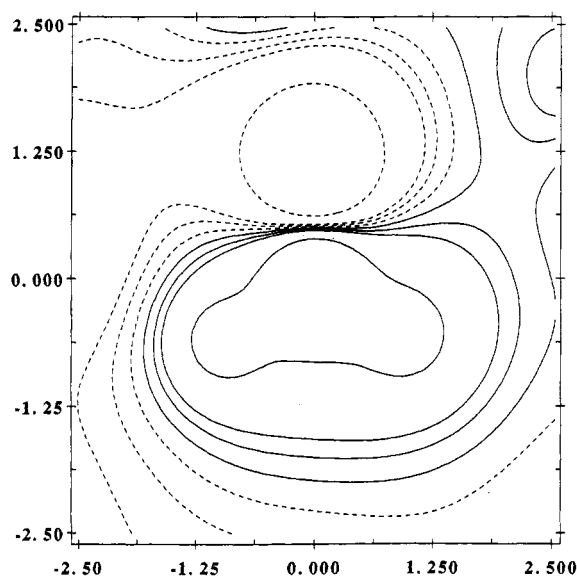
Figure 7. Like Figure 6, except calculated for the configuration that gives the smallest blue shift.

aldehyde molecule. In both figures, the formaldehyde molecule is essentially in the plane of the figure (the H atom near $y = -1.2$ Å in both figures is slightly below the plane). Figures 6 and 7 indicate some of the important electrostatic effects in the water–formaldehyde system. In the ground state of H_2CO, the oxygen atom has a high electron density (large net negative charge) so the system energy will in general be lowered when the oxygen atom overlaps regions of positive electrostatic potential (shown by solid contour lines). Conversely, the electron deficient H_2C end of the molecule will be stabilized when it overlaps regions of negative potential (dashed contour lines). In Figure 6 the oxygen has strongly stabilizing electrostatic interactions with the hydrogens of two nearby waters (indicated by the two solid oval contours at the top of the figure, which are hydrogens that are hydrogen bonded to the carbonyl oxygen). Thus the H_2CO ground state, with the larger net charge on oxygen, is preferentially stabilized and there is a large blue shift induced by this specific water configuration. The H_2C end has both stabilizing and destabilizing interactions and slightly lowers the system energy in both the ground and excited states. In Figure 7 the formaldehyde oxygen has a stabilizing interaction with the electrostatic field and the H_2C end has both stabilizing and destabilizing interactions; thus the overall effect is small, both the ground- and excited-state energies are somewhat decreased. It is interesting to note that, in the configuration with the smallest blue shift (Figure 7), no water molecule is in a position to form a strong hydrogen bond with the H_2CO, in contrast to the configuration with the largest blue shift (Figure 6), where there are two water molecules coplanar with the H_2CO molecule in positions to be able to form strong hydrogen bonds. The largest calculated transition energy occurs in a configuration where the H_2CO geometry is distorted away from the equilibium excited-state geometry ($R_{CO} = 1.163$ Å). In addition, the water molecules are arranged so that they greatly increase the ground-state dipole moment and further blue shift the already large transition energy. For the strongly red-shifted configuration, the H_2CO geometry is distorted toward the equilibrium excited-state geometry ($R_{CO} = 1.224$ Å) and the solvation structure corresponding to this configuration produces only a slight increase in transition energy; hence the net effect is a red shift.

IV. Summary and Conclusions

A classical dynamics simulation of ground ($^1A_1$) state H_2CO in water shows strong local solvation structure around the formaldehyde oxygen with 2.6 water molecules present in the first solvation shell. This ordered structure is largely, but not completely, destroyed when the charges on H_2CO are changed to those of the excited singlet state, where the net oxygen charge becomes

too small to support a distinct solvation shell. In contrast, the water molecules do not appear to be highly ordered at the hydrogen end of formaldehyde in either electronic state. The solvation of the molecule in its ground state is accompanied by a large solute–solvent binding energy, which is significantly reduced in the excited state.

A series of ab initio molecular orbital calculations on solute–solvent configurations generated from a molecular dynamics simulation of ground-state formaldehyde in water produces a distribution of transition energies. On average, these transition energies are blue shifted 1900 cm^{-1} relative to the gas-phase vertical transition energy, with a spread of more than 2000 cm^{-1}. Detailed analysis shows that the spread is due to both geometric distortions of the formaldehyde solute and to electrostatic interactions of the formaldehyde with the water molecules, in about equal amounts. However, the net blue shift is primarily due to electrostatic interactions, since the small deformations of the formaldehyde solute will most often produce a red-shifted transition energy. A large number of water molecules around the entire formaldehyde are responsible for the total blue shift; the first solvation shell only accounts for one-third of the full shift. Excitation of aqueous formaldehyde samples a variety of solvated formaldehyde molecules, each with their individual local environments. The cumulative effect of all these microenviroments produces a blue shift and an inhomogeneous contribution to the spectral broadening. For electronic transitions in polar solvents this appears to be the dominant broadening mechanism. An important implication is that full quantum mechanical calculations on solute–solvent clusters are unlikely to succeed in producing realistic descriptions of the differential solvation between ground and excited states, since investigation of too many geometrical configurations with too many solvent molecules are required.

The differential interactions of formaldehyde with solvent between the ground and excited state are probably slightly overestimated due to the likely overestimate in the changes of the net atomic charges upon excitation. This might be corrected by using correlated wave functions throughout, at considerable expense. However, the induced polarization of the solute by the solvent will increase the magnitude of the atomic charges relative to the gas-phase values, and the two effects will tend to cancel. The hybrid quantum-classical calculations have successfully described the formaldehyde–water interactions, the induced blue shift in the formaldehyde $^1A_1 \rightarrow {}^1A_2$ vertical transition energy, and the inhomogeneous spectral broadening. These calculations also give detailed molecular information on the solute–solvent interactions. The time-determining factor is the ab initio electronic structure calculations on the solute. However, if one remains close to the HF level of approximation, it is certainly possible to extend this approach to the study of solvation in different electronic states for considerably larger molecular systems. Alternatively, an appropriately parameterized semiempirical treatment of the electronic transitions should be sufficiently fast computationally to permit the simulation of the real time dynamical relaxation of the solute and solvent following excitation. Careful attention must be given to the detailed shapes of the potential energy surfaces involved. Such calculations are underway in our laboratory.

Registry No. H_2CO, 50-00-0; water, 7732-18-5.