

SIMPLE MODELS FOR SOLVATION EFFECTS ON ELECTRONIC TRANSITION ENERGIES: FORMALDEHYDE AND WATER

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We have calculated the vertical $S_0 \rightarrow S_1$ transition energy for formaldehyde in vacuo and formaldehyde complexed by one or two water molecules using a combination of molecular orbital (ab initio) and molecular mechanics (SPC model) type methods. Excellent agreement between the computed (33750 cm^{-1}) and observed (34000 cm^{-1}) transition energy is obtained for formaldehyde with augmented split-valence plus polarization basis sets and configuration interaction including single and double excitations. The increase in the transition energy measured in water relative to the gas phase (blue-shift) is reproduced using a few water molecules (ab initio or SPC) to solvate the formaldehyde in idealized cluster configurations. The role of solvent hydrogen bonding in the observed blue-shift and the need for simulating bulk water properties are discussed.

1. Introduction

Accurate modeling of molecular properties in condensed phases is a most difficult but highly important topic for computational chemists to address. If microscopic descriptions of solvation effects are sought, then the use of solvent continuum models must be discarded. However, purely quantum mechanical treatments of the solute-solvent system rapidly become unwieldy as the solute size and/or number of solvent molecules increases. When the interest is centered upon properties associated with electronically excited states, added complexity arises from treating just the solute electronic structure properly.

A polar solvent induces a shift to higher energy in the $S_0 \rightarrow S_1$ transition of formaldehyde and similar molecules containing a carbonyl group. The physical origin of this blue-shift has been investigated previously within an ab initio context, starting with the early work of Morokuma [1] and Del Bene [2]. Molecular orbital calculations were carried out on small formaldehyde: water complexes with minimal basis sets, primarily with the aim of studying hydrogen bonding. The suggestion was put forth that an optimal hydrogen bond formed in the ground state was completely [2] or essentially [1] broken in the ex-

cited state and that the difference in hydrogen bond energies was reflected in the blue-shift, supporting traditional views of the effect [3]. This argument was later rejected by Taylor [4], who provided evidence from large basis set ab initio calculations that substantial hydrogen bonding still remained in the excited state of the optimal 1:1 complex. Similar conclusions were reached by Tomasi et al. using a set of mixed ab initio, point charge, and continuum models [5]. As an alternative, Taylor [4] suggested that the blue-shift was related to geometry changes induced in the component molecules by hydrogen bonding [6].

We are at present engaged in a series of hybrid calculations on electronically excited states that incorporate advantages from both ab initio and molecular mechanics type calculations. The energetics of solvation must ultimately be treated as a statistical mechanical problem, involving calculations on formaldehyde-water configurations with many solvent water molecules present to simulate the fluctuating environments experienced by the solute formaldehyde molecules. Approximations in the physical representation of the solute-solvent system will have to be made and small cluster calculations may lend insight into the adequacy of such approximations. In this Letter, we present results, obtained at higher

computational levels than previously employed, for the $S_0 \rightarrow S_1$ transition energy in formaldehyde (H_2CO) and the energy shift induced by one or two solvating water (H_2O) molecules.

2. Computational details

Ab initio molecular orbital calculations have been carried out on isolated formaldehyde and small formaldehyde-water clusters using the standard basis sets developed by Pople and coworkers (6-311G and 6-31G* ($\alpha_d(C) = \alpha_d(O) = 0.80$)) [7] as well as modified polarized basis sets labelled 6-31G+d and 6-311G+d ($\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$) [8]. Geometry optimization of the formaldehyde-water clusters were made with the GAUSSIAN 86 series of programs [7] and the 6-31G* basis set; all other calculations utilized a locally modified version of the GAMESS package [9]. Closed shell ground states (S_0) were calculated in the single determinant, restricted Hartree-Fock (HF) approximation [10], followed by configuration interaction (CI) involving configurations singly and doubly excited (CISD) relative to the HF determinant using the GUGA formalism [11]. The singlet excited state (S_1) was calculated using restricted open-shell Hartree-Fock theory (ROHF) [12], followed by CISD based on the ROHF determinant or by singly excited configuration interaction (CIS) based on the closed shell, ground state HF determinant. The core orbitals on C and O were always frozen in the CI calculations and in some cases (specified individually later) a few high-lying unoccupied orbitals were also excluded.

Calculations were also made with the water molecules represented classically via the SPC model [13], i.e. as a set of point charges (+0.41 on H, -0.82 on O) separated by $OH = 1.00 \text{ \AA}$ and $\angle HOH = 109.47^\circ$. The Coulombic effects of these point charges are included in the one-electron Hamiltonian used in the ab initio calculations. In addition, solute-solvent interaction energies contain nonbonded Lennard-Jones-type terms between the SPC waters and the H, C, and O atoms of H_2CO [14]. Since we calculate the ground and excited state energies at the same fixed nuclear distances, these terms do contribute to the binding energies but not to the computed excitation energies.

3. Results

3.1. H_2CO

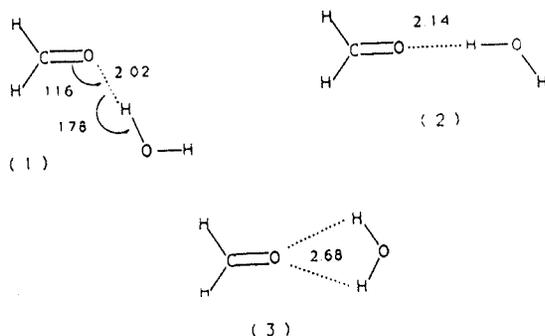
The lowest excited singlet state (1A_2 in C_{2v} symmetry) is normally considered as the result of a $n_O \rightarrow \pi_{CO}^*$ transition although the excited state charge distribution indicates that the excitation more properly should be considered as a localized oxygen $p \rightarrow p$ transition [15]. In the gas phase, the absorption band maximum occurs near 295 nm (33900 cm^{-1}) and Brand reports the most intense line at 34035 cm^{-1} [16]. Presumably, this transition approximates the vertical Franck-Condon transition and 34000 cm^{-1} is thus the proper experimental energy for comparison to our computed energies.

The 6-31G+d basis set produces at the HF level the following equilibrium geometry for the ground state of formaldehyde (C_{2v} symmetry, 1A_1): $R(CO) = 1.184 \text{ \AA}$, $R(CH) = 1.093 \text{ \AA}$, and $\angle HCH = 115.5^\circ$, in good agreement with the experimental r_e structure: $R(CO) = 1.203 \text{ \AA}$, $R(CH) = 1.099 \text{ \AA}$, and $\angle HCH = 116.5^\circ$ [17]. The HF/6-31G+d S_0-S_1 separation ($=\delta E$) is calculated to be 28000 cm^{-1} . It increases to 38600 cm^{-1} at the CIS level and at the CISD level (two highest lying unoccupied orbitals frozen) the transition energy is calculated as 38350 cm^{-1} . The different number of electron pairings in the 1A_1 state (eight doubly occupied orbitals) and 1A_2 state (seven), the neglect of electron correlation and overestimation of electron repulsion in a HF treatment makes the HF ground state energy too high relative to the excited state, open-shell energy, i.e. too low a transition energy is computed at the HF level. This is particularly notable in calculations on H_2CO with non-polarized basis sets [18]. Addition of a complete set of diffuse valence-type functions (6-311G+d) gives $\delta E = 27900 \text{ cm}^{-1}$ at the HF level, 38350 cm^{-1} at the CIS level but 33750 cm^{-1} at the CISD level (four highest unoccupied orbitals frozen). The total energies obtained for the two states at this CISD/6-311G+d//6-31G+d level (1A_1 : -114.19435 au ; 1A_2 : -114.04059 au) are lower than any previously reported in the literature for the determination of the transition energy [15,18], and it is pleasing to note that the resulting computed (33750 cm^{-1}) and experimental (34000 cm^{-1}) values (fortuitously?) are in extremely close agreement.

For larger molecular systems and/or repetitive calculations, a 6-311G+d type basis set becomes prohibitively expensive to use. We will be limiting ourselves to the 6-31G+d basis set in all the single point cluster calculations. The charge distributions provided by the two types of basis sets are very similar for H_2CO and energetic shifts should, in particular, be faithfully reproduced by either basis set.

3.2. $\text{H}_2\text{CO} + \text{H}_2\text{O}$, 1:1 complexes

Three 1:1 complexes of formaldehyde and water, which feature a near-linear (1) or linear (2) hydrogen bond (1, C_s ; 2, C_s , COHO collinear) and bifurcated, symmetrical hydrogen bonds (3, C_{2v}), respectively, have been investigated; a few geometrical features of the optimized geometries are illustrated below. 1 is computed to be 1.2 and 1.4 kcal/mol lower in energy than 2 and 3, respectively, and configuration 1 has indeed been located as the most stable 1:1 $\text{H}_2\text{CO}-\text{H}_2\text{O}$ complex in previous studies [1,2,19] (2 and 3 undoubtedly do not represent minima on the potential energy surface). We have then replaced the water molecules with the classical SPC representation and the Lennard-Jones parameters, but kept the 6-31G+d basis set on H_2CO . The internal formaldehyde structure and the hydrogen bond distances were fixed at their respective values in 1-3. 1 is computed to be 1.6 (2.2) kcal/mol more stable than 2 (3) at this mixed level of calculation, in reasonable agreement with the pure ab initio values.



Turning now to the calculation of the $S_0 \rightarrow S_1$ transition energy in the presence of a SPC-type water molecule, we obtain for 1 a δE of 28900 cm^{-1} at the HF level, 39650 cm^{-1} at the CIS level, and 38900 cm^{-1} at the CISD level. This represents shifts to

higher energy of 900, 1000, and 600 cm^{-1} , respectively, relative to the results obtained on isolated H_2CO at the same computational levels (vide supra). For 2 (3), the corresponding shifts (in cm^{-1}) are HF: 200 (300); CIS: 450 (450); and CISD: 100 (150). For comparison purposes, we have carried out CIS calculations on 1-3 with the 6-31G+d basis set on both H_2CO and H_2O . The transition energies obtained are 39900 cm^{-1} for 1, 39250 cm^{-1} for 2, and 39200 cm^{-1} for 3, implying shifts towards higher energy of 1300 (1), 650 (2), and 600 (3) cm^{-1} , respectively.

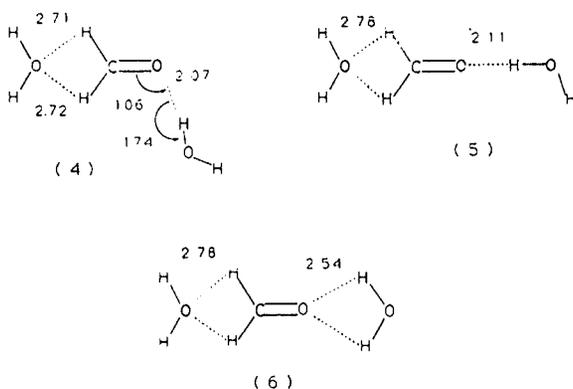
It is unfortunately difficult to obtain an accurate, experimental value for δE in water due to the formation of oligomers and/or ketals. The maximum absorption in dilute formaldehyde-water solution has been reported at temperatures over the range 54-64°C with an average value at 34650 cm^{-1} [20], implying a solvent shift relative to the maximum in vacuo of approximately 600 cm^{-1} . In a more recent extensive investigation by Becker et al. [21], this absorption was attributed to oligomeric formaldehyde with a maximum at 290 nm (34500 cm^{-1}) reported at room temperature. The solvent shift for monomeric acetone ($\text{CH}_3)_2\text{CO}$) in water is close to 1900 cm^{-1} [22], and the values reported for "formaldehyde" are thus likely to represent lower limits for the true solvent shift exhibited by monomeric formaldehyde.

All three hydrogen-bonded 1:1 formaldehyde-water complexes thus produce blue-shifts in the $S_0 \rightarrow S_1$ transition energy. The value obtained for 1 is substantial and typically twice as large as those for 2 or 3. The ab initio super-molecule shifts obtained at the limited level of CIS consistently exceed corresponding values obtained with the SPC representation for the water molecule by $\approx 200 \text{ cm}^{-1}$.

3.3. $\text{H}_2\text{CO} + \text{H}_2\text{O}$, 1:2 complexes

We have investigated three 1:2 complexes (4 (C_s), 5 (C_s), 6 (C_{2v})) formed by adding a second water molecule to 1-3, symmetrically hydrogen bonding in the CH_2 part of the H_2CO molecule; features of the optimized HF/6-31G* structures are illustrated below. It is noteworthy that the second water molecule exerts a small effect on the position of the first, carbonyl-solvating water molecule. In 5 and 6, this latter solvent molecule is in closer proximity to the car-

bonyl oxygen than in 2 and 3. In contrast, the hydrogen bond distance increases in 4 relative to that in 1 and the water molecule orientation changes. Analogous cooperativity effects have been noted before in e.g. water trimers [23]. The energy difference between 4 and 5 is 1.4 kcal/mol and 6 is merely 0.1 kcal/mol above 5 at this level of theory. Replacing the quantum mechanical water description with the SPC charges and Lennard-Jones parameters in a fashion entirely analogous to that described above for the 1:1 complexes, we compute an energetic preference for 4 of 1.2 and 1.5 kcal/mol, respectively, relative to 5 and 6, in very good agreement with the pure ab initio values



For configuration 4 we obtain the following $S_0 \rightarrow S_1$ transition energies with the SPC water molecules and the 6-31G+d basis set on formaldehyde: 29200 cm^{-1} at the HF level, 39900 cm^{-1} at the CIS level, and 38900 cm^{-1} at the CISD level representing shifts of 1200, 1300, and 600 cm^{-1} , respectively. The analogously computed shifts towards higher energy for 5 (6) are HF: 1000 (1150) cm^{-1} ; CIS: 950 (1100) cm^{-1} , and CISD: 450 (600) cm^{-1} . For comparison, the computed δE 's and shifts at the CIS level using the 6-311G+d basis set on the super-molecule are 40300 (1700) cm^{-1} for 4, 39600 (1000) cm^{-1} for 5 and 39650 (1050) cm^{-1} for 6.

These energies show that addition of the second water molecule exerts considerable influence on the computed shift, whether the waters are represented by classical or quantum mechanical means. All the computed shifts fall within the broad range expected to apply for monomeric formaldehyde (600–1900 cm^{-1}). Generally, the magnitude of the shift tends to be slightly smaller for the classical representation,

and at most levels an increased blue-shift of 350–450 cm^{-1} is computed for 4–6 relative to 1–3. However, the computed increases range from 0 cm^{-1} (CISD on 4) to 650 cm^{-1} (CIS on 6) and there are no clear "additivity" trends within either representation or within a particular level of computation.

4. Concluding remarks

We have computed the shift in the $S_0 \rightarrow S_1$ transition of formaldehyde induced by the presence of one or two water molecules using strictly ab initio techniques on the entire solute-solvent cluster or a mixture of ab initio and classical techniques for the solute and solvent, respectively. The cluster configurations were chosen in an ad hoc fashion based on constrained geometry optimizations of intuitive initial guesses. There is clearly no reason to believe, however, that only two water molecules actually solvate the formaldehyde molecule. For example, solvation above and below the molecular plane in the region of the carbonyl π -bond appears inevitable. It is furthermore likely that many configurations other than the ones chosen here are important in a description of the overall solvation process, cf. the energetic proximity of the test configurations chosen above.

The treatment of the water molecules via ab initio or molecular mechanics type methods does not influence the relative stabilities of the clusters or the computed shifts greatly. Although the computed frequency shifts in the 1:1 and 1:2 complexes always are towards higher energy, they are consistently considerably smaller at the CISD level than at the HF (or CIS) levels. A qualitative explanation for this may be obtained from the computed charge distributions and dipole moments. The measured ground and excited state dipole moments are 2.33 [24] and 1.56 D [25], respectively, although this excited state moment corresponds to the equilibrium, non-planar geometry. The decrease in dipole moment implies decreased solvation strength in the excited state relative to the ground state, thus a shift towards higher energy for the transition energy going from in vacuo to bulk water. The calculated dipole moment is too large in the ground state at the HF level (2.66 D with the 6-31G+d basis set) and too small in the excited state (1.27 D). The values obtained at the CISD/6-

31G+d level are closer to the experimental values (2.30 and 1.67 D) and to each other. Hence, the computed blue-shifts induced by solvation are less at the CISD level than at the HF (or CIS) level. Similar arguments may be made on the basis of the computed ground and excited state charge distributions at the various levels of calculation.

It is possible to obtain reasonable numerical agreement with the limited experimental data available from just one water positioned at the optimal location for H-bonding (1), but it is also found that adding one more water molecule may strongly influence the difference in electronic energies between the two states and thus the shift. Solvation is a dynamic process, probably with no static hydrogen bond maintained at room temperature and principally responsible for the blue-shift. Rather, formaldehyde-solvent stabilizing and destabilizing interactions occur continuously and require a large ensemble of molecules for their description. Many solvent configurations will give rise to a blue-shift; some will give rise to a red-shift but they will not be as energetically favorable due to poor dipole alignment and will not occur as often in a formaldehyde-water mixture. However, they will contribute to the line width of the absorption spectrum in solution.

The need for considering many water molecules in numerous configurations requires that simplifications be made in the Hamiltonian for the solute-solvent interaction. Based on the data presented here, we have shown that the SPC representation provides a reasonable description for the formaldehyde-water interaction in both the ground and excited state at a moderate computational cost. This model allows for the necessary inclusion of many solvent molecules into the calculation via the techniques of computational statistical mechanics and has the promise of producing detailed dynamical information about the actual solvation in the two electronic states. Calculations along these lines are in progress.

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