The $n \rightarrow \pi^*$ Electronic Transition in Microsolvated Formaldehyde. A Coupled Cluster and Combined Coupled Cluster/Molecular Mechanics Study[†]

Jacob Kongsted,* Anders Osted, Thomas Bondo Pedersen,[‡] and Kurt V. Mikkelsen

Department of Chemistry, H. C. Ørsted Institute, University of Copenhagen,Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark, and Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Ove Christiansen

Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Received: February 2, 2004; In Final Form: March 17, 2004

In this article, we study the $n \rightarrow \pi^*$ electronic transition in aqueous microsolvated formaldehyde using the coupled cluster (CC) and coupled cluster/molecular mechanics (CC/MM) methods. The CC models used are the coupled cluster singles and doubles (CCSD) and the coupled cluster second-order approximate singles and doubles (CC2) methods. The CC/MM model includes electrostatic and mutual polarization effects on the calculated electronic excitation energies. The CC/MM shifts of the lowest electronic excitation energy compare successfully to the corresponding shifts as defined in the supermolecular approach. Finally, we include, in addition to the explicit water molecules in the supermolecular calculations, a dielectric medium to account for the long-range interactions. The result for the shift in electronic excitation energy compares well with both other theoretical approaches and available experimental data.

I. Introduction

Understanding and accurately modeling chemical phenomena in the condensed phase is crucial for providing improved and fundamental insight into a plenitude of experiments within biology, chemistry, and physics. An obvious way of treating, e.g., solvent effects on molecular properties would be to include the solute and solvent molecules explicitly in the quantum mechanical calculation. However, because of the very steep increasing computational effort with the system size for standard ab initio methods, only a few solvent molecules may be included directly in the quantum mechanical calculation. Thus, methods that model the *effect* of the solvent molecules on the solute, rather than the use of explicit solvent molecules, are good candidates for describing environmental effects on the chemical and physical properties of molecules in condensed phases.

In this article, we describe the solvatochromism of the $n \rightarrow \pi^*$ electronic transition of formaldehyde in aqueous solution. Solvatochromism consists of the phenomena where solvents influence the position, shape, and intensity of the UV absorption (or emission) spectra, relative to the corresponding gas-phase quantities. The $n \rightarrow \pi^*$ electronic transition causes an intramolecular electronic charge transfer from the carbonyl oxygen lone pair into the antibonding π^* orbital localized over the carbonyl group. This excitation leads to a reduction of the dipole moment of formaldehyde in the electronic excited state,[1] and, consequently, a differential solvation of the electronic ground and excited states occurs. Thus, the solute is more favorably solvated in the electronic ground state, which leads to an increase in the electronic excitation energy, as compared to the gas-phase. Thereby, a blue shift is expected for the transition energy.

Experimentally, solvent shifts are difficult to measure for formaldehyde in aqueous solutions, because of the formation of oligomers. However, experimental results for the electronic spectrum of formaldehyde in aqueous solution do exist,[2] but only at very high formaldehyde concentrations. This experimental spectrum exhibits a maximum at 4.28 eV. The corresponding gas-phase measurements gives a maximum at 4.07 eV,[3] leading to a blue shift of $\simeq$1700 cm^{-1}. The solvent shift for the similar transition in the carbonyl group of acetone is directly measurable and known to be[4,5] $\simeq$1700−1900 cm^{-1} and is expected to be comparable to the corresponding shift in formaldehyde. (See, for example, the discussion in the work of Jaffe and Orchin[5] and Kawashima et al.[6])

Theoretically, at least four different schemes have been used to model the shift in the $n \rightarrow \pi^*$ electronic transition. First, the shift for the vertical transition has been calculated on the basis of molecular dynamics (MD) simulations by instantaneously shifting the partial charges from the electronic ground-state values to those of the π^* excited state, followed by calculating the difference in solvation energy.[7] This purely classical method yielded a shift of 4000 cm^{-1}. Note that only the change in solute−solvent energy is used to define the shift; i.e., the quantum mechanical change of the solute's energy is neglected. Also, DeBolt et al.[8] used MD and statistical mechanical free-energy perturbation methods to obtain a shift of 1530 cm^{-1}.

Second, dielectric continuum models have been used to estimate the shift. In the dielectric continuum model, all specific interactions between the solvent molecules and the solute are neglected. Furthermore, the dielectric continuum model requires the use of cavities that range from spherical-shaped to molecular-shaped cavities. However, the size of the cavity is particularly

---

[†] Part of the "Gert D. Billing Memorial Issue".

* Author to whom correspondence should be addressed. E-mail: kongsted@theory.ki.ku.dk.

[‡] Present address: Department of Theoretical Chemistry, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden.

10.1021/jp049540z CCC: $27.50

problematic. Bader et al.[9] compared the solvent shift of the $n \rightarrow \pi^*$ excitation of formaldehyde obtained by MD simulations, using the fluctuating charge model of polarizable water (i.e., charges are allowed to flow between different sites on each molecule) and the dielectric continuum model. Here, Bader et al.[9] found that no unique cavity radius is suitable for formaldehyde in both the ground and π^* electronic states.

Mikkelsen et al.[10] calculated the shift to be $\simeq$589 cm^{-1}, using a multiconfigurational self-consistent-field (MCSCF) wave function, together with a nonequilibrium description of the solvent. Later, Mennucci et al. calculated the same shift for formaldehyde using the polarizable continuum model.[11] Here, a result of 944 cm^{-1} was reported, using a MCSCF wave function, in combination with a nonequilibrium description of the solvent.

Through supermolecular calculations, Canuto and Coutinho[12] obtained a shift of 2200 cm^{-1}, using Monte Carlo (MC) simulations, combined with the semiempirical (intermediate neglect of differential overlap/singly excited configuration interaction (INDO/CIS)[13]) theory, including up to 80 water molecules in the quantum calculations.

Also, Fukunaga and Morokuma[14] performed supermolecular calculations of interaction energies between water and formaldehyde in both the ground and π^* electronic excited state. Based on these results, intermolecular potential functions were derived, and, on the basis of MC simulations, they obtained a blue shift of $\simeq$3100 cm^{-1} for formaldehyde in aqueous solution, whereas smaller shifts were obtained by including only 1, 2, or 3 water molecules in the simulations. Supermolecular calculations on formaldehyde-(x) water clusters (x = 1,2,3) have also been presented by Dimitrova and Peyerimhoff,[15] using self-consistent field (SCF) or configuration interaction (CI) theories. Here, values of $\sim$3800 cm^{-1} (CI) and 4200 cm^{-1} (SCF) were reported for the largest cluster.

Finally, very popular methods for studying the shift are the hybrid quantum mechanical/molecular mechanical (QM/MM) methods. Here, Thompson[16] calculated the shift to be 1150 cm^{-1} (using different structures for the gas- and liquid-phase geometry of formaldehyde) by semiempirical theory. Blair et al.[17] obtained a shift of 1900 cm^{-1}, using SCF theory, combined with MD simulations. In the work of Blair et al.,[17] the water molecules were described at the simple point charge (SPC) level, i.e., no polarization effects were considered. Also, different geometries for the gas- and liquid-phase structure of formaldehyde were used. Naka et al.[18] used the reference interaction site model (RISM) at the SCF level of theory (see the earlier work by Tenno et al.[19]) and obtained a shift of 1998 cm^{-1}. Naka et al.[18] used different geometries for the gas- and liquid-phase structures of formaldehyde. Martin et al.[20] used the method based on the averaged solvent electrostatic potential (ASEP), combined with MCSCF electronic structure calculations, and obtained a shift of 1470 cm^{-1}, using different geometries for the gas- and liquid-phase structures of formaldehyde.

Finally, Kawashima et al.[6] performed MC simulations of formaldehyde in water, combined with MCSCF/MM electronic structure theory calculations of the $n \rightarrow \pi^*$ electronic excitation. Here, a shift of 2660 cm^{-1} was reported, using the largest cluster and a polarizable model for water. Although the shift in electronic excitation energy compares well with experimental observations, they obtained a value of 4.86 eV for the absolute value of the excitation energy for the $n \rightarrow \pi^*$ transition of solvated formaldehyde. As compared to experimental data, this value is overestimated, which probably is due to the neglect of dynamical correlation in the electronic structure method used by Kawashima et al.[6]

A successful method for describing solvation of excited states should not only give an accurate value for the shift in electronic excitation energy (as compared to vacuum), but should also provide an accurate value for the absolute value of the electronic excitation energy. With this in mind, we have, in the past years, developed a method that combines coupled cluster and molecular mechanics (CC/MM) models (for properties up to quadratic response, see ref 21 and references therein). In the CC/MM model, we use CC response theory[22,23] to calculate electronic excitation energies. This has the advantage that only the ground electronic state must be known and no excited states need to be calculated explicitly. This allows for simple calculation of vertical excitation energies.

It is well-known that formaldehyde, when excited to the π^* state, undergoes significant geometrical changes. However, in this work, we will focus on the vertical excitation and no adiabatic excitation energies are calculated. Thus, we intend to obtain an accurate determination of the $n \rightarrow \pi^*$ electronic excitation, together with the shift, as compared to that obtained in vacuum. Furthermore, we wish to compare the results using a supermolecular coupled cluster and a combined CC/MM approach.

In the present work, we will only consider the microsolvated approach. However, for the description of the bulk structure of the system, we include, in the supermolecular calculations, a dielectric continuum that implicitly includes the effect of a dynamical solvent. The reason for this choice of microsolvation is that we intend to keep the solvated system so small that complete ab initio approaches may be used to check the validity of the hybrid model. We note that such a static approach to solvation may be a crude approximation and that a proper description requires sampling over many solvent configurations, including hundreds of solvent molecules.

This paper has the following structure. In section II, we outline the methodology and present a method for obtaining the coupling parameters. Section III contains the computational details, and, in section IV, we present the results. Finally, a summary ends the paper.

II. Method

A. The Combined Coupled Cluster/Molecular Mechanics Model. The theoretical framework and implementational aspects of the CC/MM method have been presented in previous papers (for electronic excitation energies and linear response properties, see the work of Kongsted et al.[24] and references therein). However, previous calculations on aqueous solutions using the CC/MM model have assumed an isotropic polarizability of the classically treated molecules. In this work, we also investigate the effect of introducing distributed polarizabilities to define the classical molecules. Here, we briefly mention the main characteristics of the CC/MM model.

The CC/MM model is a hybrid quantum-classical method where the two subsystems (quantum and classical) are coupled semiclassically. As in most hybrid QM/MM methods, the total energy of the system is defined as

$$E = E_{\mathrm{QM}} + E_{\mathrm{QM/MM}} + E_{\mathrm{MM}} \tag{1}$$

which implies an analogous separation of the Hamiltonian. The term E_{QM} is the usual quantum mechanical energy described by the many-body vacuum Hamiltonian ($\hat{H}_{\mathrm{QM}}$) and $E_{\mathrm{QM/MM}}$ represents the interaction between the QM and MM systems.

Finally, E_{MM} describes the classically treated portion of the total system. Using a mean-field description[25,26] of the coupling between the two subsystems, we may, according to the theory of intermolecular interactions, decompose the QM/MM energy into different contributions. These contributions account for (i) electrostatic interactions, (ii) dispersion and short-range interactions, and (iii) polarization of the MM system by the QM system and vice versa. The electrostatic interactions are modeled by assigning partial point charges to the MM nuclei, which are introduced into the one-electron part of the many-body vacuum Hamiltonian. Dispersion and short-range effects are, as in most hybrid QM/MM methods, described by the introduction of a potential independent of the QM electronic degrees of freedom. Alternatively, direct methods have been proposed in which dispersion is accounted for directly in the optimization of the electronic wave function.[25,27] Finally, polarization effects are introduced semiclassically using the QM/MM polarization Hamiltonian

$$\hat{H}^{\mathrm{pol}} = -\frac{1}{2}\sum_{a=1}^{A} \boldsymbol{\mu}_a^{\mathrm{ind}} \cdot (\hat{\boldsymbol{R}}\mathbf{r}_a + \boldsymbol{E}^n(\vec{R}_a)) \qquad (2)$$

where $\boldsymbol{\mu}_a^{\mathrm{ind}}$ is the induced dipole moment at the center a, $\hat{\boldsymbol{R}}\boldsymbol{r}_a$ is the QM electronic electric field operator, and $\boldsymbol{E}^n(\vec{R}_a)$ is the QM nuclear electric field both at the center a. In a linear approximation (and neglecting contributions of magnetic character), $\boldsymbol{\mu}_a^{\mathrm{ind}}$ is related to the *total* electric field at the center a as

$$\boldsymbol{\mu}_a^{\mathrm{ind}} = \alpha_a \boldsymbol{E}_a^{\mathrm{total}} \qquad (3)$$

where α_a is the electric dipole−dipole polarizability at the center a. Insertion of eq 3 into eq 2 allows for a determination of the effective operator accounting for the polarization effects. We note that this treatment of polarization effects includes all terms linear in α_a and, thereby, the relaxation of the induced moments due to an external perturbation. For a detailed discussion of this issue, we refer to ref 24. The electric dipole−dipole polarizability in eq 3 is approximated as the frequency-independent electric dipole−dipole polarizability. Because our intent is to make a comparison between a full CC description (excluding all vibrational contributions) and a CC/MM description of the system, the electric dipole−dipole polarizability includes only the purely electronic contribution, i.e., $\alpha_a = \alpha_a^{\mathrm{el}}$. Introducing the effects of vibrations on the specific properties would lead to the added inclusion of the vibrational contribution in the electric dipole−dipole polarizability.

The above-discussed interaction terms may be introduced into the time-dependent CC quasi-energy Lagrangian, and, following the method outlined in ref 22, the linear and higher-order response functions are derived. A pole analysis of the CC/MM linear response function yields expressions for excitation energies, and, in the CC and CC/MM method, the eigenvalues of the CC Jacobian defines the electronic excitation energies. For a detailed discussion, we refer to ref 24.

B. Ab Initio Determination of Hybrid Coupling Parameters. As described previously, the classical and quantum subsystems are coupled semiclassically. The specific coupling defines a variety of models. Common for all the CC/MM models is the assignment of a set of partial charges to each of the water nuclei. Furthermore, in the calculations including the mutual polarization of the two subsystems, we also assign either an isotropic point polarizability (at the center of mass of each water molecule) or a distributed polarizability (located at the O and H atoms).

The partial charges are obtained in the following way. Using the intramolecular geometry of liquid water (R(OH) = 0.9572 Å, ∠(H−O−H) = 104.49°, and C_{2V} symmetry),[28] a CCSD/aug-cc-pVQZ calculation of the dipole moment is performed. Orienting the water molecule with the C_2 axis along the $\boldsymbol{z}$-axis and with the oxygen in the origin of the coordinate system leads to a unique determination of the partial charges on the H atom (q_{H}) and the constraint $2q_{\mathrm{H}} + q_{\mathrm{O}} = 0$ enables a unique determination of the partial charge on the O atom (q_{O}). In this way, we can determine $q_{\mathrm{H}} = 0.331$ and $q_{\mathrm{O}} = -0.662$, and these charges hence reproduce a water dipole moment of 1.865 D. (In passing, we note that the experimental result is 1.855 D,[29] obtained using a *gas-phase* structure.)

The isotropic polarizability is also determined using ab initio CCSD/aug-cc-pVQZ theory. Here, a value of 9.501 au for the isotropic portion of the dipole−dipole polarizability is observed, which compares well with the best results reported in ref 30 (9.56 au), based on CC3/CCSD and large basis set calculations. Experimentally, the static dipole−dipole polarizability is found to be 9.83 au. This value is found from a quadratic extrapolation of refractivity data and, therefore, does exclude most of the pure vibrational contributions. The zero-point vibrational average (ZPVA) contribution has, on the basis of second-order Møller−Plesset perturbation (MP2) theory, been reported to be 0.29 au.[31] Adding the ZPVA contribution to the pure electronic contribution, we obtain $\bar{\alpha}(0;0) = 9.79(1)$ au, which compares well with the experimental value. Note that the effect of geometrical changes between the liquid- and gas-phase geometries of water have been neglected in the aforementioned discussion.

The distributed polarizabilities were taken from the work of Jensen et al.[32] (the Thole-A model), and, accordingly, we assign the following atomic polarizabilities to the water nuclei: $\alpha_{\mathrm{H}} = 0.0690$ au and $\alpha_{\mathrm{O}} = 9.3005$. These polarizabilities reproduce the full molecular polarizability tensor of water, calculated at the CCSD(T)[33] ($\bar{\alpha} = 9.62$ au) level of theory.

III. Computational Details

A. Determination of the Microsolvated Structures. All the formaldehyde−water clusters are optimized by applying the Gaussian 98 program package,[34] using density functional theory (DFT) and the standard B3LYP[35−37] approach. The basis set used is the cc-pVTZ basis set of Dunning.[38] Harmonic frequencies are also calculated (which are all positive and real), to ensure a true minimum on the potential energy surface. We have tried several initial configurations for the geometry optimizations. The choice of DFT, using the B3LYP functional in combination with the cc-pVTZ basis set, is based on the analyses presented in the work of Helgaker et al.[39] and Jensen,[40] where it was shown that MP2 or DFT/B3LYP, combined with the cc-pVTZ basis set, yield satisfactory results for bond distances, whereas, for example, the cc-pVDZ basis set is not sufficient for describing radial and angular electron correlations. The DFT approach is much less expensive (in terms of computer processing unit (CPU) time); therefore, we have used the B3LYP/cc-pVTZ method in the optimization of formaldehyde and the formaldehyde−water clusters. We note that the B3LYP functional has been determined to be very effective in systems with hydrogen bonding.[41−43] Thus, we conclude that the B3LYP/cc-cpVTZ method would give reliable geometries for the formaldehyde−water clusters.

B. Property Calculations. The calculation of electronic excitation energies (and linear response properties) described within the CC/MM method has been implemented in a local version of the Dalton program package[44] at the coupled cluster singles and doubles (CCSD) and the coupled cluster second-order approximate singles and doubles (CC2)[45] level of theory. The implementation has been described in detail in ref 24. The advantage of the CC2 model is attributed to the computational scaling, which is only N^5, as compared to the N^6 scaling of the CCSD model, with N being the number of basis functions. In passing, we mention that the MP2 method also scales as N^5; however, the MP2 linear response function has poles at the SCF response excitation energies and, therefore, this model cannot be used in the calculation of correlated electronic excitation energies.

The shift in electronic excitation energy is defined as $\delta E_{ex} = E_{ex}(\text{solvated}) - E_{ex}(\text{vacuum})$. However, it is well-known that the shift in electronic excitation energy, as defined in the supermolecular calculations, suffers from basis set superposition errors (BSSEs). Thus, we report both shifts in electronic excitation energy that have been corrected and not corrected for BSSE. To correct for BSSE, we use the counterpoise correction (CPC) of Boys and Bernardi.[46] We note that, using the CC/MM method, the problem concerning BSSE is naturally eliminated, because no basis sets are introduced for the classically treated molecules.

All the property calculations use the correlation consistent aug-cc-pVXZ (X = D,T) basis sets[38] for formaldehyde and the aug-cc-pVDZ basis set for water. Increasing the basis set on water to aug-cc-pVTZ changes the absolute value of the electronic excitation energy by $<0.1\%$. However, as will become clear later, basis set effects are rather small, and for the largest cluster, we therefore only consider the aug-cc-pVDZ basis set also for formaldehyde. When correcting for BSSE, a “ghost” basis set is introduced, which is denoted by Gh-aug-cc-pVDZ. In all the property calculations, the lowest orbitals of 1s character on C and O were frozen.

In addition to accounting for explicit water molecules in the supermolecular calculations, we also study the effect of including a dielectric continuum (DC) in the supermolecular calculations. These results are denoted by DC. The calculations that use the (spherical and nonequilibrium) coupled-cluster/dielectric-continuum (CC/DC) model[47] are assigned the following parameters: a maximum of $L_{max} = 10$ in the spherical multipole moment, a static dielectric constant of $\epsilon_{st} = 78.54$, and an optical dielectric constant of $\epsilon_{op} = 1.778$, whereas the radius of the cavity is $R_{cav} = 6.961$, 7.647, and 9.256 au, including 1, 2, and 4 water molecules, respectively. These cavity radii are obtained as the maximum distance between the center of mass of the formaldehyde−water clusters to the atoms plus the van der Waals radius of the specific atoms.

IV. Results and Discussion

A. Coupled Cluster Results. The optimized intramolecular geometry of CH_2O in a vacuum is (C_{2V} point group symmetry) $R(\text{CH}) = 1.100$ Å, $R(\text{CO}) = 1.211$ Å, $\angle(\text{OCH}) = 121.9°$, and $\angle(\text{HCH}) = 116.2°$, which compares well with the experimental geometry of ref 48 ($R(\text{CH}) = 1.12 \pm 0.01$ Å, $R(\text{CO}) = 1.21 \pm 0.01$ Å, and $\angle(\text{HCH}) = 118° \pm 2°$).

In the microsolvated structures, we include one, two, or four water molecules. The internal C_{2V} symmetries of the individual molecules are not locked during the geometry optimization. Figures 1, 2, and 3 show the formaldehyde−water clusters for the CH_2O:1W, CH_2O:2W, and CH_2O:4W clusters, respectively, and Table 1 gives some information about bond lengths and angles. The atoms labeled 5, 6, and 7 belong to water molecule number 1, the atoms labeled 8, 9, and 10 belong to water molecule number 2, and so forth. All the microsolvated structures possess C_1 point-group symmetry. Furthermore, as seen from Table 1, the distance between the formaldehyde oxygen and the nearest hydrogen-bonded water hydrogen is 2.017, 1.891, and 1.799 Å for the one-water, two-water, and four-water microsolvated systems, respectively.

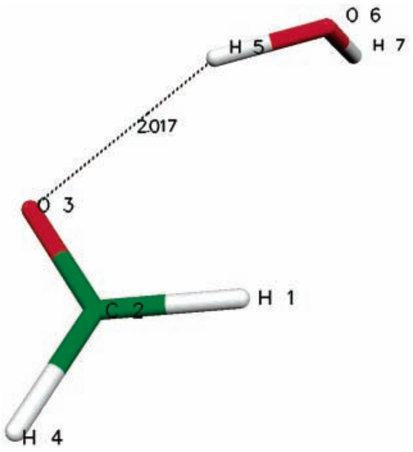

Figure 1. Geometry of the CH_2O:1W cluster, as obtained by a B3LYP/cc-pVTZ geometry optimization. The indicated distance (in Angstroms, Å) is the nearest water hydrogen, as measured from the carbonyl oxygen.

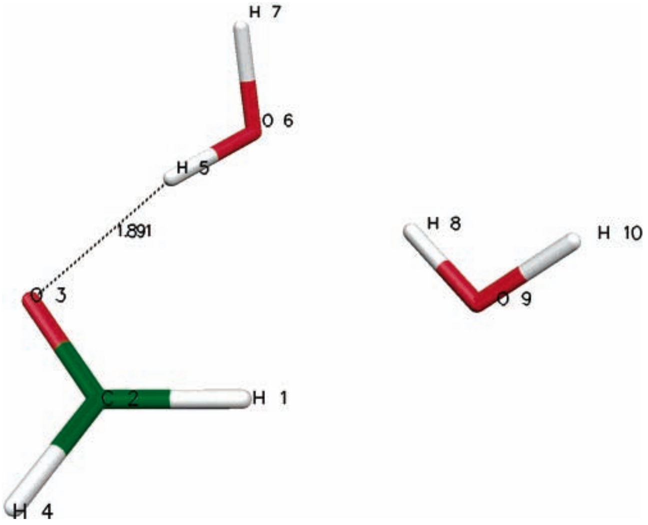

Figure 2. Geometry of the CH_2O:2W cluster, as obtained by a B3LYP/cc-pVTZ geometry optimization. The indicated distance (in Angstroms, Å) is the nearest water hydrogen, as measured from the carbonyl oxygen.

The first water molecule forms a hydrogen bond with the formaldehyde oxygen. However, subsequent water molecules primarily form hydrogen bonds to other water molecules. Thus, in the larger clusters, formaldehyde is surrounded by more water molecules; however, the gas-phase clusters do not provide an obvious full solvation shell. Nevertheless, we expect the clusters to be sufficiently realistic to, first of all, test the CC/MM method versus supermolecular calculations and, second, to give reasonable solvent shifts.

In Table 2, we report the lowest electronic excitation (E_{ex}), in electron volts (eV) ($^1A_2$) for formaldehyde in a vacuum, using the structures for formaldehyde as obtained from the geometry optimization of the clusters (i.e., the water molecules have been removed). Calculations are performed using the CCSD and CC2 models. These electronic excitation energies are used to calculate the shifts, as defined in the CC/MM model. Furthermore, if no BSSE corrections are considered, the shifts in the supermolecular

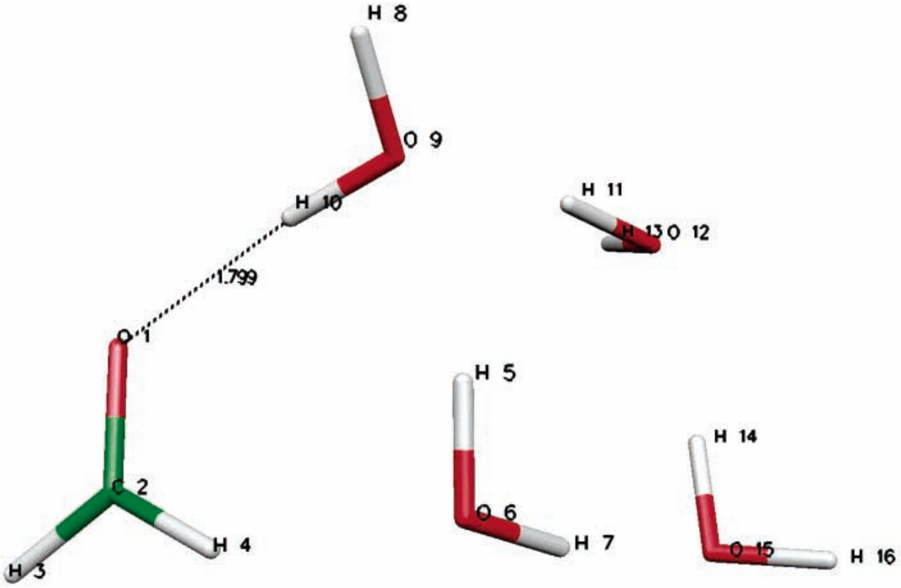

Figure 3. Geometry of the CH_2O:4W cluster, as obtained by a B3LYP/cc-pVTZ geometry optimization. The indicated distance (in Angstroms, Å) is the nearest water hydrogen, as measured from the carbonyl oxygen.

TABLE 1: Geometrical Parameters for the Three Clusters Used in This Work[a]

	water molecule 1	water molecule 2	water molecule 3	water molecule 4
		CH_2O:1W		
$R(O_F-H_{Wn})$	2.017 Å 3.356 Å			
$R(O_F-O_{Wn})$	2.897 Å			
$\angle(C_F-O_F-H_{Wn})$	101.3°			
		CH_2O:2W		
$R(O_F-H_{Wn})$	1.891 Å 3.281 Å	3.332 Å 4.430 Å		
$R(O_F-O_{Wn})$	2.842 Å	3.691 Å		
$\angle(C_F-O_F-H_{Wn})$	114.0°	79.8°		
		CH_2O:4W		
$R(O_F-H_{Wn})$	3.365 Å 4.036 Å	1.799 Å 3.236 Å	3.803 Å 4.609 Å	4.811 Å 5.950 Å
$R(O_F-O_{Wn})$	3.617 Å	2.774 Å	4.594 Å	5.086 Å
$\angle(C_F-O_F-H_{Wn})$	74.7°	116.6°	108.5°	82.0°

[a] According to the Figures 1, 2, and 3, the atoms labeled 5, 6, and 7 belong to water molecule 1, those labeled 8, 9, and 10 belong to water molecule 2, and so forth. The index F refers to formaldehyde, whereas the index W refers to water. The angle $\angle(C_F-O_F-H_{Wn})$ is defined in terms of the C and O atoms in formaldehyde and the nearest hydrogen-bonded water H atom.

TABLE 2: Lowest (Dipole-Forbidden) Electronic Excitation ($^1A_2$) for CH_2O in a Vacuum, Using the Structures for CH_2O as Obtained from the Geometry Optimization of the Clusters Calculated Using CCSD and CC2

geometry optimization	E_{ex} (eV)			
	CH_2O[a]	CH_2O:1W	CH_2O:2W	CH_2O:4W
CCSD/aug-cc-pVDZ	4.006	4.041	4.012	3.990
CC2/aug-cc-pVDZ	4.077	4.112	4.083	4.063
CCSD/aug-cc-pVTZ	3.995	4.032	4.004	3.984
CC2/aug-cc-pVTZ	4.053	4.089	4.064	4.043

[a] Using CC3/aug-cc-pVTZ, we obtain a value of 3.951 eV.

calculations are defined relative to the electronic excitation energies for CH_2O in this table. From this table, we find that the CC2 model overestimates the electronic excitation energy compared to CCSD. Also, we observe that the deviations in electronic excitation energies between different structures (using the same method and basis set) are small, i.e., only ~1%. The difference between CC2 and CCSD is larger than the basis set effects. To estimate the effects of triples excitations (on the vacuum result), we have used the CC3 method,[49] together with the aug-cc-pVTZ basis set, and obtained a value of 3.951 eV for the lowest excitation. Thus, the effect of triples excitations is found to slightly reduce the excitation energy.

In Table 3, we show the lowest electronic excitation (in eV) ($^1A_2$) for formaldehyde microsolvated by water, using CCSD and CC2. The basis sets listed horizontally are those for water (W), whereas the basis sets listed vertically are for formaldehyde. In the first column in Table 3 (denoted Gh-aug-cc-pVDZ), we have included a "ghost" basis set for water (i.e., only the electrons formally assigned to formaldehyde are treated in the CC calculation). These numbers serve as the basis for the BSSE corrected results for the shift in electronic excitation energies. From this first column, we observe a modest decrease in the electronic excitation energy upon enlargement of the basis set.

The second column of Table 3 contains the lowest electronic excitation energy as obtained in supermolecular calculations. For all the formaldehyde−water clusters, we observe a blueshift of the lowest electronic excitation. As for formaldehyde in a vacuum, we find that the CC2 versus CCSD differences are more pronounced than the basis set effects and the CC2 model is again found to give a higher electronic excitation energy than CCSD.

The second column of Table 3 also contains results obtained by, in addition to accounting for, explicit water molecules, including the effect of a dielectric continuum in the supermolecular calculations (denoted the semi-continuum model).

TABLE 3: Lowest (Dipole-Forbidden) Electronic Excitation ($^1A_2$) in CH_2O Microsolvated by Water, Using CCSD and CC2[a]

geometry optimization	E_{ex} (eV)		$\boldsymbol{\mu}_{tot}{}^{b}$ (D)
	Gh-aug-cc-pVDZ	aug-cc-pVDZ	
	CH_2O:1W		
CCSD/aug-cc-pVDZ	4.044	4.195	2.405
CC2/aug-cc-pVDZ	4.116	4.259	2.309
CCSD/aug-cc-pVDZ/DC		4.236	2.740
CC2/aug-cc-pVDZ/DC		4.301	2.654
CCSD/aug-cc-pVTZ	4.037	4.183	2.422
CC2/aug-cc-pVTZ	4.097	4.233	2.309
CCSD/aug-cc-pVTZ/DC		4.224	2.761
CC2/aug-cc-pVTZ/DC		4.275	2.658
	CH_2O:2W		
CCSD/aug-cc-pVDZ	4.012	4.182	2.444
CC2/aug-cc-pVDZ	4.084	4.235	2.373
CCSD/aug-cc-pVDZ/DC		4.204	2.742
CC2/aug-cc-pVDZ/DC		4.257	2.681
CCSD/aug-cc-pVTZ	4.005	4.171	2.449
CC2/aug-cc-pVTZ	4.064	4.209	2.370
CCSD/aug-cc-pVTZ/DC		4.193	2.751
CC2/aug-cc-pVTZ/DC		4.223	2.680
	CH_2O:4W		
CCSD/aug-cc-pVDZ	3.991	4.211	2.506
CC2/aug-cc-pVDZ	4.063	4.257	2.437
CCSD/aug-cc-pVDZ/DC		4.220	2.558
CC2/aug-cc-pVDZ/DC		4.264	2.640

[a] All results use the microsolvated geometries of CH_2O. The basis sets listed horizontally are for water (W), whereas the basis sets listed vertically are for CH_2O. The geometries of CH_2O:xW ($x = 1, 2, 4$) are obtained using B3LYP/cc-pVTZ. The calculations using the CC/DC model are assigned the following parameters: $L_{max} = 10$, $\epsilon_{st} = 78.54$, $\epsilon_{op} = 1.778$, whereas $R_{cav} = 6.961$, 7.647, and 9.256 au for $x = 1$, 2, and 4, respectively. [b] The term $\boldsymbol{\mu}_{tot}$ is the total dipole moment of the formaldehyde−water clusters.

These results are denoted by the abbreviation "DC". The DC accounts for the bulk structure and thereby introduces the effects of long-range interactions on the calculated excitation energies. Table 3 shows that the effect of the DC is most important for the small clusters and almost negligible for the larger ones. This is also what we would expect, because the first solvation shell clearly accounts for most of the environmental effects. Also, for the larger CH_2O:4W cluster, the distance to the most distinct atoms, defining the cavity radius, is quite large, which obviously reduces the effect of the DC. In passing, we note that, for a single formaldehyde molecule enclosed by a DC, we have obtained a lowest electronic excitation energy of 4.079 eV, using the CCSD/DC model, together with the aug-cc-pVTZ basis set and the same set of parameters as outlined in the section on computational details (cavity radius equal to 5.123 au). Clearly, this shows that including only the effects of the DC in the condensed-phase calculations has a tendency to underestimate the effects of solvation.

Table 3 also shows the total dipole moments of the formaldehyde−water clusters. Table 3 shows that the effect of the DC on these clusters is always to increase the total dipole moment. For a single formaldehyde molecule in a vacuum, we obtain a dipole moment of 2.225 and 2.242 D, using the aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively. Thus, the effect of the discrete water molecules and the DC is to increase this value. In regard to the DC calculations, we note, that the reaction-field is crucially dependent on the dimensions of the cavity. This means that, even though the total dipole moment for the formaldehyde and formaldehyde−water clusters only varies over a range of 2.225−2.761 D, the reaction field has a tendency to have a small effect on the properties for the larger clusters. This is indeed also what we observe from Table 3. The aforementioned discussion was made solely in terms of the dipole moments leading to the Onsager approach to solvation.[50] In passing, we note that, in the DC results that we presented in Table 3, we have included a multipole expansion of the charge distribution up to $L_{max} = 10$.

In Table 4, we report the calculated shifts in the lowest electronic excitation ($^1A_2$) energy of microsolvated formaldehyde, as defined in the supermolecular calculations, using CCSD and CC2. The numbers given in parentheses refer to the shifts as calculated using the (nonequilibrium) semi-continuum CC/DC model, whereas the corresponding numbers without parentheses exclude the effect of the DC. All the shifts are reported in reciprocal centimeters (cm^{-1}).

Table 4 shows that the BSSE correction is ∼10−140 cm^{-1}. The differences between CC2 and CCSD are in the interval of 60−220 cm^{-1} (5%−13%), being generally larger for the larger clusters. The CC2 model is found to systematically underestimate the shifts in electronic excitation energy, compared to CCSD.

Table 4 also shows that the effect of introducing a DC in the supermolecular calculations is only ∼50−70 cm^{-1} for the largest cluster but is considerably more important for the smaller clusters. In all cases, we note that the effect of the DC is to enhance the blue-shift, which is also what we would expect.

In the last block of Table 4, we have reported the shift in electronic excitation energy, as defined relative to the vacuum-optimized structure. Thus, no BSSE is considered in these shifts. From this last block, we find that, including this type of geometrical effect but neglecting the BSSE, the shifts are, for

TABLE 4: Calculated Shifts in the First Electronic Excitation ($^1A_2$) in CH_2O Microsolvated by Water, Using CCSD and CC2

geometry optimization	Calculated Shift, δE_{ex} (cm^{-1})[a]		
	CH_2O:1W	CH_2O:2W	CH_2O:4W
CCSD/aug-cc-pVDZ BSSE, corrected	1215 (1549)	1370 (1549)	1775 (1846)
CC2/aug-cc-pVDZ BSSE, corrected	1149 (1494)	1215 (1391)	1563 (1624)
CCSD/aug-cc-pVTZ BSSE, corrected	1180 (1511)	1338 (1517)	
CC2/aug-cc-pVTZ BSSE, corrected	1100 (1438)	1309 (1336)	
CCSD/aug-cc-pVDZ, no BSSE correction	1240 (1574)	1378 (1557)	1783 (1854)
CC2/aug-cc-pVDZ, no BSSE correction	1176 (1520)	1222 (1399)	1567 (1628)
CCSD/aug-cc-pVTZ, no BSSE correction	1223 (1554)	1343 (1522)	
CC2/aug-cc-pVTZ, no BSSE correction	1160 (1495)	1168 (1339)	
CCSD/aug-cc-pVDZ, relative to vacuum optimization	1524 (1857)	1421 (1600)	1660 (1731)
CC2/aug-cc-pVDZ, relative to vacuum optimization	1464 (1808)	1270 (1447)	1449 (1510)
CCSD/aug-cc-pVTZ, relative to vacuum optimization	1515 (1846)	1415 (1594)	
CC2/aug-cc-pVTZ, relative to vacuum optimization	1453 (1788)	1255 (1426)	

[a] Numbers in parentheses refer to the shifts as calculated using the CC/DC model, whereas the corresponding numbers excluding the effect of the dielectric continuum are shown without parentheses.

TABLE 5: Results of the Lowest (Dipole-Forbidden) Electronic Excitation ($^1A_2$) in CH_2O Microsolvated by Water, Using CCSD/MM and CC2/MM

	Electronic Excitation (eV)[a]				Shift in E_{ex} on solvation (cm^{-1})[b]	
	E^a_{ex}	E^b_{ex}	E^c_{ex}	E^d_{ex}	δE_{ex}(ms)	δE_{ex}(vs)
CH_2O:1W						
CCSD/aug-cc-pVDZ	4.182	4.182	4.182	4.173	1142	1426
CC2/aug-cc-pVDZ	4.253	4.253	4.253	4.243	1129	1417
CCSD/aug-cc-pVTZ	4.174	4.173	4.173	4.163	1145	1437
CC2/aug-cc-pVTZ	4.231	4.231	4.230	4.221	1140	1433
CH_2O:2W						
CCSD/aug-cc-pVDZ	4.190	4.189	4.188	4.167	1448	1491
CC2/aug-cc-pVDZ	4.257	4.254	4.253	4.231	1402	1450
CCSD/aug-cc-pVTZ	4.183	4.178	4.177	4.154	1439	1511
CC2/aug-cc-pVTZ	4.235	4.228	4.227	4.204	1382	1470
CH_2O:4W						
CCSD/aug-cc-pVDZ	4.229	4.229	4.229	4.192	1922	1799
CC2/aug-cc-pVDZ	4.294	4.295	4.294	4.257	1869	1750
CCSD/aug-cc-pVTZ	4.221	4.222	4.221	4.183	1911	1822
CC2/aug-cc-pVTZ	4.272	4.272	4.272	4.233	1847	1766

[a] E^a_{ex} is obtained using $\bar{\alpha} = 9.501$ au, and E^b_{ex} is obtained using $\bar{\alpha} = 9.620$ au. For E^c_{ex}, a distributed polarizability, $\alpha_H = 0.0690$, and $\alpha_O = 9.3005$ is used. Finally, for E^d_{ex}, the polarization effect is neglected. [b] The term δE_{ex}(ms) is defined as the shift relative to CH_2O, using the microsolvated structure, and E_{ex}(vs) is defined as the shift relative to CH_2O, using the vacuum structure. For all reported shifts, $q_O = -0.662$ and $q_H = 0.331$. Shifts are only reported relative to E^a_{ex}.

the smallest cluster, changed by ≃25%. However, the deviations, as compared to the corresponding results, excluding geometrical effects, are less pronounced for the larger clusters (≃100 cm^{-1}).

Table 4 shows that our best supermolecular result for the shift in electronic excitation energy is 1775 cm^{-1} and, including the effect of the DC, we obtain a shift of 1846 cm^{-1}. In comparison, we note that, for a single formaldehyde molecule enclosed by a DC, we have observed a shift of 669 cm^{-1}, using the CCSD/DC model together with the aug-cc-pVDZ basis set and the same set of parameters as outlined in the section on computational details (cavity radius equal to 5.123 au).

B. Combined Coupled Cluster/Molecular Mechanics Results. Table 5 contains the CC/MM results of the lowest electronic excitation in eV ($^1A_2$) in formaldehyde microsolvated by water, using CCSD/MM and CC2/MM. Also shown are the shifts in electronic excitation energy upon solvation (in cm^{-1}). The term δE_{ex}(ms) is defined as the shift, relative to CH_2O, using the microsolvated structure and E_{ex}(vs) is defined as the shift relative to CH_2O, using the vacuum-optimized structure. The excitation energy E^a_{ex} is obtained using $\bar{\alpha} = 9.501$ au, for E^b_{ex}, we have $\bar{\alpha} = 9.620$ au, and for E^c_{ex}, a distributed polarizability, $\alpha_H = 0.0690$, and $\alpha_O = 9.3005$ is used (the isotropic value equals 9.620 au). Finally, for E^d_{ex}, the polarization effect is neglected. Shifts are only reported relative to E^a_{ex}.

From Table 5, we first observe that the CC/MM models including polarization effects in the three different ways (a, b, and c) almost give results of similar quality. This illustrates that the CC/MM model is not very sensitive to the absolute value of the polarizability. Also, from a comparison of E^b_{ex} and E^c_{ex}, we find that the effect of using a distributed polarizability is almost negligible. This is also what we would expect for a molecule as small as water. Neglecting the polarization effects (E^d_{ex}) leads to a minor reduction of the electronic excitation energies. However, this change is small, which has previously been noted by Dupuis et al.[51] and Bader et al.[9]

As for the supermolecular calculations, the differences between CC2 and CCSD are larger than the differences between the different basis sets. The absolute values of the CC/MM electronic excitation energies compare excellently with the corresponding results obtained using the supermolecular approach. The deviations are <1% and are typically ~0.3%. Comparing the shifts in electronic excitation energy (δE_{ex}(ms)), we also find excellent agreement between the CC/MM and supermolecular results. The deviations are ~20−300 cm^{-1} but typically <100 cm^{-1}. Thus, the deviations between the CC/MM and supermolecular results are only slightly larger than the BSSE introduced in the supermolecular calculations.

In Table 5 we also show the shifts in electronic excitation energy as defined relative to the vacuum-optimized formaldehyde molecule (E_{ex}(vs)). These numbers should be compared to those in the last block of Table 4. For the CC/MM calculations of E_{ex}(vs) we find the same trends as for the super-molecular calculations, i.e., an overestimation of the shifts for the smallest clusters and an underestimation for the larger cluster.

Table 5 shows that, excluding geometrical effects, the best CC/MM result for the shift in the lowest electronic excitation energy is ~1900 cm^{-1} (1922 cm^{-1}, using the aug-cc-pVDZ basis set, and 1911 cm^{-1}, using the aug-cc-pVTZ basis set). However, introducing geometrical effects in the calculation of the shift leads to the most-accurate CC/MM results of 1822 cm^{-1}, using CCSD/aug-cc-pVTZ, and 1799 cm^{-1} using CCSD/aug-cc-pVDZ. Hence, the introduction of geometrical effects reduces (for the largest cluster) the blue shift. In fact, it also compares better with the experimental value, which, naturally, also includes geometrical effects; however, this may be fortuitous, in particular, in view of the uncertainty in the experimental value. The change in the blue shift when introducing geometrical effects is of the same magnitude as that found by Dupuis et al.[51]

As discussed in Section II.A, we approximate the electric dipole−dipole polarizability of the water molecules by its static value. However, introducing a simple iterative procedure allows for determination of excitation energies using the electric dipole−dipole polarizability of the water molecules at the frequency of the electronic excitation. First, we calculate the electronic excitation energy using the static value of the electric dipole−dipole polarizability. Second, we perform ab initio calculations of the frequency-dependent electric dipole−dipole polarizability of water at the frequency of the electronic excitation. We then perform another calculation of the electronic excitation energy, using the *dynamical* electric dipole−dipole polarizability. This procedure is continued until convergence in the electronic excitation energy is attained. Usually, only few iterations are needed (i.e., in the cases we have studied, only three iterations are necessary in order to obtain converged values). However, the changes in the electronic excitation energies are also very small. For the largest cluster studied in this work, we obtain an extra blue shift of ≃32 cm^{-1} independent of method and basis set (aug-cc-pVDZ or aug-cc-pVTZ). Thus, neglecting the frequency dependence of the electric dipole−dipole polarizability is clearly a good approximation.

C. Discussion of Other Hybrid Theoretical Approaches and Comparison with Available Experimental Data. As discussed in the Introduction, the experimental solvent shift for formaldehyde in aqueous solutions is expected to be ≃1700 cm^{-1}. Thus, we obtain a good agreement with available experimental data for the shift in electronic excitation energy. However, the absolute value is also predicted very accurately with the CC methodology. For this state of formaldehyde, we have, for example, a CCSD/aug-cc-pVTZ vacuum electronic excitation of 3.995 eV. The experimental frequency of maximum absorption is 4.07 eV. Although this type of comparison of theory and experiment is approximate, it, together with the previously discussed small triples corrections, lends some support to the relatively high accuracy of the CC vertical excitation energies.

To our knowledge, this work represents the first study of the $n \rightarrow \pi^*$ electronic transition in formaldehyde including environmental effects as modeled at the CC level of theory. Other theoretical hybrid approaches have used either semiempirical electronic structure calculations, SCF theory or MCSCF theory. However, in SCF theory, electronic correlation is totally ignored, and, in MCSCF theory, only the static electronic correlation is taken into consideration. It is well-known that dynamical electron correlation is crucial to describe molecular properties accurately and, as noted by Kawashima et al.[6] in a study of the same transition, a dynamically correlated description of the QM portion of the system represents an improvement, as compared to the MCSCF description. Also, as found by Mennucci et al.,[11] using the polarizable continuum model (PCM), the shifts calculated using the SCF method have a tendency to be overestimated, as compared to methods including electronic correlation. Previously, we have shown that an SCF/MM description for water overestimates the solvation effects.[26,52,53] For formaldehyde, the dipole moment is smaller in the $^1A_2(\pi^*)$ electronic state, as compared to the ground electronic state. Hence, the solvent effect on the ground electronic state is more significant than in the $^1A_2(\pi^*)$ electronic state. Therefore, when using a SCF description, the solvent effects are probably even more overestimated for the ground electronic state than for the $^1A_2(\pi^*)$ electronic state, leading to an overestimation in the shift.

Generally, the results obtained by Thompson[16] for the shift in excitation energy for microsolvated formaldehyde are much smaller than our results. On the other hand, we obtain reasonably good agreement, as compared to the work of Dupuis et al.,[51] using the MCSCF method combined with molecular mechanics, despite the fact that the absolute value for this excitation is predicted somewhat too high using MCSCF.

In a study similar to this one, Blair et al.[54] calculated the $n \rightarrow \pi^*$ electronic excitation energies and shifts, relative to microsolvated formaldehyde using SCF and configuration interaction including singles (CIS) and singles and doubles (CISD). They used a hybrid method where the water molecules were represented as SPC water molecules and compared the results with full ab initio calculations. Generally, Blair et al. obtained shifts smaller than our results and poorer agreement between hybrid and full ab initio calculations. This may partly be attributed to the neglect of polarization effects in the hybrid model and to the neglect of correcting the supermolecular calculations for BSSE.

V. Summary

In this article, we have presented the first study of the $n \rightarrow \pi^*$ electronic transition in microsolvated formaldehyde using coupled cluster and combined coupled cluster/molecular mechanics methods. The structures are obtained from DFT geometry optimization. In addition to including explicit water molecules in the supermolecular calculations, we have also embedded the clusters in a dielectric continuum. When comparing the results obtained from supermolecular calculations with the corresponding CC/MM results, we find that deviations are only slightly larger than the BSSE introduced in the supermolecular calculations. When comparing our CC/MM results with those obtained by embedding a single formaldehyde molecule in a dielectric continuum, we observe remarkable improvement. Our results for both the absolute value of the electronic excitation energy and the shift (based upon vacuum calculations) compare well with the available experimental data. For instance, using the CC/MM method and the aug-cc-pVTZ basis set, we obtain a shift of 1822 cm^{-1}, including geometrical effects.

Thus, the primary conclusion of this work is that the CC/MM method is a cost-efficient and reliable alternative to supermolecular calculations for the study of solvent effects on the $n \rightarrow \pi^*$ electronic excitation energy of formaldehyde. The CC/MM method can be used in calculations with a substantial number of solvent molecules. Although CC2 is less accurate than CCSD, it was found to give fairly reasonable results, supporting CC2/MM as a computationally cheaper alternative to CCSD/MM.

However, even though the effect of the first solvation shell has a crucial role in the process of solvation,[6] a main drawback is that, in this study, because of the use of only one solvent configuration, we have not been able to calculate either the statistical error in the reported results or the bandwidth of the studied excitation. Also we note that the use of minimum-energy optimized structures almost certainly will lead to differences in the effect of the first solvation shell, compared to the average obtained for structures found from a dynamical approach. The ground-state formaldehyde−water interactions will probably be maximized by the use of minimum-energy optimized structures. In this study, the cluster structures are also only partly providing a first solvation shell. The issue of a dynamical versus static solvent approach, as described in the CC/MM model, is currently being developed and will be presented in a forthcoming paper.

Acknowledgment. O.C. acknowledges support by Statens Naturvidenskabelige Forskningsråd (SNF) and Danish Center for Scientific Computing (DCSC). K.V.M. thanks SNF, Statens Teknisk Videnskabelige Forskningsråd, DCSC, and the EU networks MOLPROP and THEONET II for support.

References and Notes

(1) Freeman, D. E.; Klemperer, W. *J. Chem. Phys.* **1966**, *45*, 52.

(2) Bercovici, T.; King, J.; Becker, R. S. *J. Chem. Phys.* **1972**, *56*, 2956.

(3) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1985; Vol. III.

(4) Bayliss, N. S.; Wills-Johnson, G. *Spectrochim. Acta, Part A* **1968**, *24A*, 551.

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

(6) Kawashima, Y.; Dupuis, M.; Hirao, K. *J. Chem. Phys.* **2002**, *117*, 248.

(7) Levy, R. M.; Kitchen, D. B.; Blair, J. T.; Krogh-Jespersen, K. *J. Phys. Chem.* **1990**, *94*, 4470.

(8) DeBolt, S. E.; Kollman, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 7515.

(9) Bader, J. S.; Cortis, C. M.; Berne, B. J. *J. Chem. Phys.* **1997**, *106*, 2372.

(10) Mikkelsen, K. V.; Cesar, A.; Ågren, H.; Jensen, H. J. Aa. *J. Chem. Phys.* **1995**, *103*, 9010.

(11) Mennucci, B.; Cammi, R.; Tomasi, J. *J. Chem. Phys.* **1998**, *109*, 2798.

(12) Canuto, S.; Coutinho, K. *Int. J. Quantum Chem.* **2000**, *77*, 192.

(13) Zerner, M. C. *ZINDO: A Semiempirical Program Package*; University of Florida: Gainesville, FL, 1997.

(14) Fukunaga, H.; Morokuma, K. *J. Phys. Chem.* **1993**, *97*, 59.

(15) Dimitrova, Y.; Peyerimhoff, S. D. *J. Phys. Chem.* **1993**, *97*, 12731.

(16) Thompson, M. A. *J. Phys. Chem.* **1996**, *100*, 14492.

(17) Blair, J. T.; Krogh-Jespersen, K.; Levy, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 6948.

(18) Naka, K.; Morita, A.; Kato, S. *J. Chem. Phys.* **1999**, *110*, 3484.

(19) (a) Ten-no, S.; Hirata, F.; Kato, S. *Chem. Phys. Lett.* **1993**, *214*, 391. (b) Ten-no, S.; Hirata, F.; Kato, S. *J. Chem. Phys.* **1994**, *100*, 7443.

(20) Martín, M. E.; Sánchez, M. L.; del Valle, F. J. O.; Aguilar, M. A. *J. Chem. Phys.* **2000**, *113*, 6308.

(21) Kongsted, J.; Osted, A.; Mikkelsen, K. V.; Christiansen, O. *J. Chem. Phys.* **2003**, *119*, 10519.

(22) Christiansen, O.; Jørgensen, P.; Hättig, C. *Int. J. Quantum. Chem.* **1998**, *68*, 1.

(23) Christiansen, O.; Mikkelsen, K. V. *J. Chem. Phys* **1999**, *110*, 1365.

(24) Kongsted, J.; Osted, A.; Mikkelsen, K. V.; Christiansen, O. *J. Chem. Phys.* **2002**, *118*, 1620.

(25) Kongsted, J.; Osted, A.; Mikkelsen, K. V.; Christiansen, O. *Mol. Phys.* **2002**, *100*, 1813.

(26) Kongsted, J.; Osted, A.; Mikkelsen, K. V.; Christiansen, O. *J. Phys. Chem. A* **2003**, *107*, 2578.

(27) Thole, B. T.; van Duijnen, P. Th. *Chem. Phys.* **1982**, *71*, 211.

(28) Billing, G. D.; Mikkelsen, K. V. *Chem. Phys.* **1994**, *182*, 249.

(29) Lovas, F. J. *J. Phys. Chem. Ref. Data* **1978**, *7*, 1445.

(30) Christiansen, O.; Gauss, J.; Stanton, J. F. *Chem. Phys. Lett.* **1999**, *305*, 147.

(31) Russell, A. J.; Spackman, M. A. *Mol. Phys.* **1995**, *84*, 1239.

(32) Jensen, L.; van Duijnen, P. Th.; Snijders, J. G. *J. Chem. Phys.* **2003**, *118*, 514.

(33) Maroulis, G. *Chem. Phys. Lett.* **1998**, *289*, 403.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.2; Gaussian, Inc.: Pittsburgh, PA, 1998.

(35) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(36) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(37) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(38) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(39) Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic Structure Theory*; Wiley: New York, 2000.

(40) Jensen, F. *Introduction to Computational Chemistry*; Wiley: New York, 1999.

(41) Latajka, Z.; Boutellier, Y. *J. Chem. Phys.* **1994**, *101*, 9793.

(42) Lee, H. M.; Suh, S. B.; Kim, K. S. *J. Chem. Phys.* **2001**, *114*, 10749.

(43) Velardez, G. F.; Ferrero, J. C.; Beswick, J. A.; Daudey, J. P. *J. Phys. Chem. A* **2001**, *105*, 8769.

(44) Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Auer, A. A.; Bak, K. L.; Bakken, V.; Christiansen, O.; Coriani, S.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Fernandez, B.; Hättig, C.; Hald, K.; Halkier, A.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Pedersen, T. B.; Ruden, T. A.; Sanchez, A.; Saue, T.; Sauer, S. P. A.; Schimmelpfennig, B.; Sylvester-Hvid, K. O.; Taylor, P. R.; Vahtras, O. Dalton, an ab Initio Electronic Structure Program, release 1.2, 2002.

(45) Christiansen, O.; Koch, H.; Jørgensen, P. *Chem. Phys. Lett.* **1995**, *243*, 409.

(46) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(47) Christiansen, O.; Mikkelsen, K. V. *J. Chem. Phys.* **1999**, *110*, 8348.

(48) Lawrence, R. B.; Strandberg, M. W. P. *Phys. Rev.* **1951**, *83*, 363.

(49) Christiansen, O.; Koch, H.; Jørgensen, P. *J. Chem. Phys.* **1995**, *103*, 7429.

(50) Böttcher, C. J. F. *Theory of Electronic Polarization*; Elsevier Scientific: Amsterdam, 1973.

(51) Dupuis, M.; Kawashima, Y.; Hirao, K. *J. Chem. Phys.* **2002**, *117*, 1256.

(52) Poulsen, T. D.; Kongsted, J.; Osted, A.; Ogilby, P. R.; Mikkelsen, K. V. *J. Chem. Phys.* **2001**, *115*, 2393.

(53) Mikkelsen, K. V.; Ågren, H.; Jensen, H. J. Aa.; Helgaker, T. *J. Chem. Phys.* **1988**, *89*, 3086.

(54) Blair, J. T.; Westbrook, J. D.; Levy, R. M.; Krogh-Jespersen, K. *Chem. Phys. Lett.* **1989**, *154*, 531.