

# Ab Initio Study of the Electronic Spectrum of Formamide with Explicit Solvent

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**Abstract:** Of the many roles that solvent plays, its influence on molecular electronic structure is perhaps one of the more challenging phenomena to study. In this study, the effect of solvation on the electronic spectrum of formamide is investigated. Ab initio complete-active-space self-consistent field (CASSCF) and multiconfigurational second-order perturbation theory (CASPT2) methods are used to compute the ground- and excited-state energies of formamide complexed with one, two, and three water molecules. In addition, a semicontinuum approach is employed, in which formamide-(H<sub>2</sub>O)<sub>n</sub> (*n* = 1, 2, 3) complexes are studied within a continuum solvent model. The presence of the explicit water molecules destabilizes the Rydberg states of formamide by approximately 0.5 eV. In the case of the  $\pi_{\text{nb}}\pi^*$  transition, a red shift from 7.41 eV (gas phase) to 7.16 eV is observed, and its oscillator strength increases by ~10%. The  $n\pi^*$  transition undergoes a blue shift which is dependent on the O-H formamide-water hydrogen bond distance. The physical origin of these solvatochromic shifts is investigated. The former effects have been well reproduced in a previous ab initio study with a continuum model. In contrast, at least one explicit water molecule is needed to observe the blue shift in the  $n\pi^*$  transition. The semicontinuum approach provides a description of the electronic spectrum of solvated formamide that captures important local and bulk solvent effects.

## Introduction

Solvation modulates many phenomena. The structure and function of proteins are influenced by their aqueous environment.<sup>1</sup> Solvent can have a significant effect on chemical equilibria, for example, in keto-enol tautomerism reactions.<sup>2</sup> The presence of a solvent may also alter electronic spectra, sometimes changing the shape, intensity, and position of the spectral bands.<sup>3</sup> Such solvatochromic shifts are a consequence of unequal effects of the solvent on the ground and excited states of the solute, arising from differences in electrostatics, exchange, dispersion, and correlation.

The study of the electronic structure of solvated systems is more difficult than their gas-phase counterparts, because of the complex nature of the solute-solvent interaction.<sup>3</sup> However, several theoretical approaches exist. One may use classical ensemble treatments, such as molecular dynamics simulations and Monte Carlo statistical methods, to sample solvent configurations using parameters that describe the solute excited state.<sup>4-6</sup> These parameters are usually derived from ab initio calculations on small solute-solvent clusters. In these methods, a large number of solvent molecules may be considered explicitly. The accuracy and applicability of these methods is,

generally, dependent on sampling procedures and the quality of potential energy functions. For a more detailed description of electronic structure, ab initio techniques may be employed in conjunction with molecular dynamics simulations in hybrid methods.<sup>7</sup> Within such schemes, it is possible to simulate the effect of solvent configuration on the absorption spectra.<sup>4,8</sup> However, these methods are computationally demanding, and consequently only a small number of systems have been studied.

This study is concerned with the changes induced by the solvent on the electronic structure of the solute. This requires a large number of electronic states to be accurately calculated. Consequently, we have used a correlated ab initio method that is able to evaluate excited-state energies and has been employed successfully to describe amide electronic spectra.<sup>9</sup> The increased computational effort in the description of the solute means that extensive sampling of the solvent configuration space is, currently, computationally prohibitive. However, one is able to obtain a general picture of the effect of solvent on the electronic structure. Furthermore, parameters derived from the study of these model systems can provide the basis for large-scale simulations.

Using a purely ab initio approach there are three general strategies:<sup>10</sup> the continuum model, the discrete model, and the semicontinuum model. In the continuum model, the solute lies in a cavity surrounded by a continuum dielectric of a given macroscopic dielectric constant. The charge distribution inside the cavity induces a reaction field in the dielectric and a

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polarization energy results from the interaction of the induced field with the charge distribution inside the cavity.<sup>11</sup> This approach provides a general treatment of the bulk solvent with relatively little additional computational effort. In the discrete model, explicit solvent molecules are included within the ab initio treatment. This gives a detailed description of short-range interactions between the solute and solvent, such as hydrogen bonding, charge transfer, and exchange effects, which are absent in the continuum model. The steep rise in computational cost with size makes it unlikely that sufficient solvent can be included to reflect genuine bulk behavior. This computational cost may be reduced by the introduction of effective fragment potentials to describe the solvent molecules.<sup>12</sup> A third option is to combine the two procedures in a semicontinuum model, whereby a solvation shell of explicit solvent molecules is embedded within a continuum dielectric.

In this paper, we investigate the effect of solvation on the electronic spectrum of formamide within discrete and semicontinuum ab initio treatments. Calculations that include one, two, and three explicit water molecules are presented. Further calculations on the formamide-(H<sub>2</sub>O)<sub>n</sub> (*n* = 1, 3) complexes within a continuum dielectric are described. Formamide is an important model of the peptide bond. A further motivation for this study on formamide is our interest in the circular dichroism spectra of proteins based on the parametrization of the individual chromophoric groups.<sup>13–16</sup> A detailed knowledge of the electronic structure of the constituent monomers is a prerequisite to understanding the optical spectroscopy of proteins.

In vacuo, the absorption spectrum<sup>17,18</sup> of formamide is typical of amides, comprising five bands, labeled W (a weak  $n\pi^*$  transition), V<sub>1</sub> (an intense transition from the nonbonding  $\pi$  orbital  $\rightarrow \pi^*$  orbital,  $\pi_{nb}\pi^*$ ), R<sub>1</sub> and R<sub>2</sub> (Rydberg transitions), and Q. The original assignment of the Q band as the  $\pi_b\pi^*$  transition (bonding  $\pi$  orbital  $\rightarrow \pi^*$  orbital)<sup>19</sup> has been questioned by recent experiments.<sup>18</sup> In acetonitrile<sup>17</sup> the absorption spectrum is less structured and consists of three bands, a weak W band, the V<sub>1</sub> band, and a strong absorption in the Q band region. This high-energy band has been linked with a red-shifted deep valence shell excitation, in addition to the  $\pi_b\pi^*$  transition.<sup>17</sup> The V<sub>1</sub> band is subject to a large red shift of 0.5 eV, and there is no evidence of the R<sub>1</sub> and R<sub>2</sub> bands. The experimental data are summarized in Table 1.

The electronic spectra of formamide<sup>9,20,21</sup> and other amides<sup>9,22,23</sup> in vacuo are, in general, well understood. For an accurate theoretical treatment, correlated methods and basis sets containing diffuse functions are required. The electronic spectrum of formamide in condensed phases has not been studied exten-

**Table 1.** Experimental Data for the Electronic Spectrum of Formamide

band	acetonitrile <sup>a</sup>		gas phase <sup>b</sup>	
	$\Delta E$ (eV)	<i>f</i>	$\Delta E$ (eV)	<i>f</i>
W ( $n\pi^*$ )	5.58	0.002	5.82	0.002
R <sub>1</sub>			6.35	N/A <sup>c</sup>
V <sub>1</sub> ( $\pi_{nb}\pi^*$ )	6.81	0.30	7.36	0.37
R <sub>2</sub>			7.72	N/A
Q ( $\pi_{br}\pi^*$ )	>8.6	0.1	9.23	N/A

<sup>a</sup> Refs 9, 17. <sup>b</sup> Refs 17, 18. <sup>c</sup> N/A = not available.

sively. Experimental studies have shown solvent to have a profound effect on the electronic structure of formamide.<sup>17</sup> In this paper we investigate the effect of hydrogen bonds on the electronic spectrum. In addition, the physical origin of the observed solvatochromic shifts is discussed. This should provide some insight into the approximations made within a continuum model of the solvent. Another feature of many electronic spectra in solution is the apparent absence of transitions to Rydberg states. In a previous study<sup>24</sup> we have shown, within a continuum model, that the more diffuse Rydberg states are destabilized by the Pauli repulsion (exchange interaction) of the solvent. Understanding the importance of Rydberg states in condensed phases is an active area of research. Experimental studies on NO have found blue shifts of 0.4–1 eV and broadening of the absorption bands of the Rydberg states in rare gas matrixes.<sup>25</sup> This was attributed to the repulsive overlap of the Rydberg electron with electron cloud of the rare gas atoms. There has also been interest in this issue recently with respect to amides.<sup>26</sup> In the present study this feature is examined in more detail.

The ground state of formamide in solution has been extensively studied, by a variety of theoretical techniques. Its structure and geometry have been investigated in the presence of many explicit solvent molecules, using Monte Carlo techniques,<sup>27,28</sup> and with a small number of solvent molecules using ab initio methods.<sup>29–34</sup> The cyclic formamide–water complex has been identified as the most stable small cluster, and furthermore, in solution, bonding to the carbonyl group is stronger.<sup>34</sup> Hydrogen bonding between two formamide molecules has also been studied.<sup>30,35–37</sup> The variation of hydrogen bond strength with configuration was explained in terms of steric effects.<sup>37</sup> Hydrogen bonds appear to be more easily broken in water than in apolar solvents.<sup>36</sup> The barrier to internal rotation about the C–N

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bond in formamide increases in solution.<sup>38</sup> Studies employing both continuum<sup>39,40</sup> and explicit<sup>41–43</sup> solvent methods have predicted this trend, which saturates at about four water molecules.<sup>43</sup> The tautomerization of formamide is an example in which the inclusion of an explicit solvent molecule can provide additional theoretical insight into a reaction. Bulk solvent is found to stabilize the keto tautomer relative to the enol form because of the higher dipole moment of formamide.<sup>44,45</sup> However, studies that included explicit solvent molecules have shown that this trend can be offset by the formation of stronger hydrogen bonds in the enol form.<sup>46,47</sup> In addition, the reaction mechanism changes to a solvent-assisted scheme, lowering the activation energy.<sup>46,48–50</sup>

The focus of this paper is the electronic spectrum of formamide, and hence its electronic excited states. Studies of the excited states of formamide in solution are relatively few. In an early study<sup>51</sup> of formamide complexed with one and two water molecules, Del Bene observed a blue shift in the  $n\pi^*$  energy in self-consistent field (SCF) calculations using a STO-3G basis set. The magnitude of the blue shift was correlated with the strength of the hydrogen bond, which weakened in the excited state. An alternative origin, namely, changes in solute geometry induced by the hydrogen bonding,<sup>52</sup> has been suggested for a similar blue shift in the  $n\pi^*$  transition observed in formaldehyde.

More recently, Sobolewski<sup>53</sup> performed calculations on the formamide–(H<sub>2</sub>O)<sub>1</sub> complex using the CASSCF/CASPT2 method within a double- $\zeta$  plus polarization basis set. Transition energies and oscillator strengths (shown in parentheses) of 6.03 eV (0.01) and 7.52 eV (0.34) were reported for the  $n\pi^*$  and  $\pi_{nb}\pi^*$  states, respectively. The  $n\pi^*$  state was blue shifted by 0.18 eV, while the  $\pi_{nb}\pi^*$  state was red shifted by 0.15 eV relative to the gas phase. This study focused on the valence states and did not investigate the Rydberg states. Krauss and Webb<sup>54</sup> investigated formamide in the presence of three water molecules using the multiconfigurational self-consistent field method. Full geometry optimizations were performed for the ground state and the first excited singlet and triplet states. Full geometry optimizations for higher valence energy states were not possible. This was attributed to the coupling between these states and the Rydberg series in which they are embedded. An excitation energy of 6.14 eV was reported for the  $n\pi^*$  state. The water molecules were also found to significantly polarize the formamide

molecule. At the restricted Hartree–Fock level, the dipole moment of the ground state increased from 4.23 to 5.16 D.

Recently, we have investigated the electronic spectrum of formamide within a continuum model.<sup>24</sup> Although the electrostatic contribution is a major component of the solute–solvent interaction, other interactions are also important for a complete model of solvation,<sup>55</sup> in particular, the Pauli repulsion between solute and solvent. In our previous study, a repulsive potential<sup>56,57</sup> was used to describe this interaction. This potential lies outside the cavity and is essentially zero within the cavity. Our calculations agreed well with the available experimental data. Excitation energies of 5.54, 6.95, 9.83, and 10.42 eV were found for the  $n\pi^*$ ,  $\pi_{nb}\pi^*$ ,  $n'\pi^*$ , and  $\pi_{nb}\pi^*$  states, respectively. The ground-state dipole moment was calculated to be 4.49 D compared to 4.08 D in gas-phase calculations.<sup>9</sup> The larger Rydberg states were significantly destabilized by the Pauli repulsion and did not appear in the lower energy region of the spectrum. One Rydberg state was observed, a  $\pi_{nb}3s$  state, which was significantly blue shifted. However, the Rydberg state energies are sensitive to the choice of cavity size, and for a slightly smaller cavity no Rydberg states were observed below 10 eV.

In this study a more complete description of the effect of water molecules on the electronic spectrum is presented. Calculations are performed that describe vertical excitations to both Rydberg and valence states. This includes valence states of higher energy, such as the  $n'\pi^*$  and  $\pi_{nb}\pi^*$  transitions. In previous work the effect of explicit solvent molecules on the Rydberg states has not been studied. Furthermore, it has been shown<sup>9</sup> that it is important to account for the Rydberg states in order to obtain accurate valence-state transition energies, particularly for the  $\pi_{nb}\pi^*$  state. One purpose of the present study is to investigate, using explicit solvent and ab initio methods, the physical basis for the empirical repulsive potential used previously to model Pauli repulsion within the continuum model. The current study also addresses the particular effect of water hydrogen bonding on the electronic structure of formamide. More generally, our work seeks to provide theoretical evidence to help resolve the questions regarding the importance of Rydberg states in condensed phases.

## Computational Details

In this study, we have followed the procedure with which Serrano-Andrés and Fülischer<sup>9</sup> successfully described the gas-phase electronic spectra of a number of small amides, including formamide. This should enable a direct comparison with the gas-phase spectra and allow the effect of the presence of water molecules on the excited states to be better quantified. Full geometry optimizations were performed at the MP2 level using a 6-31G\* basis set within the Gaussian<sup>94,58</sup> suite of programs. No symmetry constraints were imposed, and nonplanar structures of C<sub>1</sub> symmetry were obtained. These structures are very similar to those found using SCF and effective fragment potential methods.<sup>43</sup> The water molecules do not surround formamide but form

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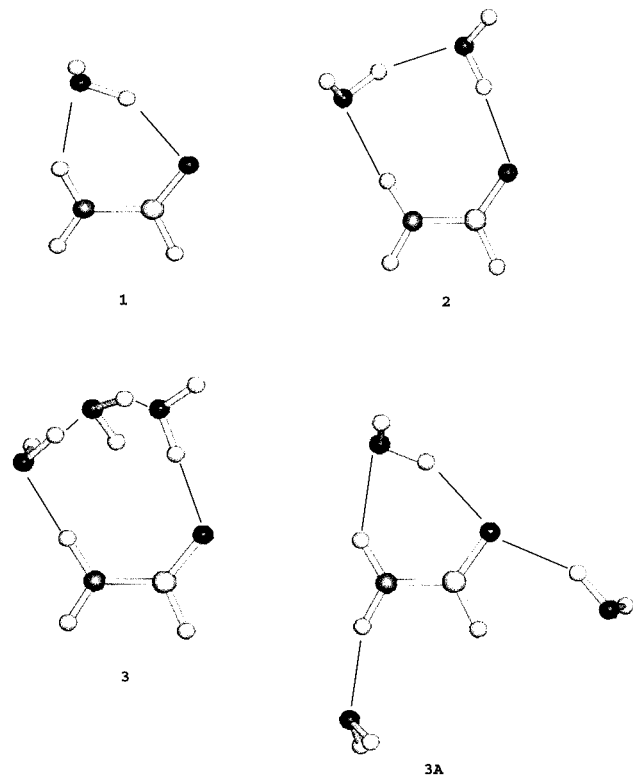
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**Table 2.** Hydrogen Bond Lengths of the Formamide–Water Complexes

no. of water molecules	bond length (Å)			
	O - - H	NH - - O	(O - - H)'	(NH - - O)'
1	2.017	1.948		
2	1.829	1.863		
3	1.779	1.810		
3A	2.042	1.938	1.929	1.982

**Figure 1.** Minimum energy structures of the formamide–water complexes. Hydrogen bonds are depicted by thin lines.

a ring of solute–solvent and solvent–solvent hydrogen bonds. The formamide molecule itself is involved in two hydrogen bonds, as a proton donor and a proton acceptor. The lengths of these hydrogen bonds are given in Table 2. As alluded to earlier, there are most likely many low-energy configurations. To give a complete picture of solvent, all of these configurations should be sampled. The present calculations are too computationally intensive to make this a practical option. However, for the cluster containing three water molecules an additional configuration, denoted formamide–(H<sub>2</sub>O)<sub>3A</sub>, in which there are four solute–solvent hydrogen bonds, is considered. The structures are shown in Figure 1.

There are two steps to the subsequent calculations. First, a state-averaged complete-active-space SCF (CASSCF)<sup>59</sup> calculation is performed. This calculation, typically, includes all the states of interest equally weighted and uses reference orbitals from a SCF calculation. The second step is a multiconfigurational second-order perturbation theory (CASPT2)<sup>60,61</sup> calculation. This accounts for dynamic correlation and was performed for each root of the CASSCF wave function individually. In the present work we have employed a version of CASPT2 which has a level shift facility to reduce the problem of intruder states.<sup>62</sup> In the reported calculations a level shift of 0.3 au was used, following Serrano-Andrés and Fülischer.<sup>9</sup> The only minor exceptions are in the cases of the  $n'\pi^*$  states (see below) and the  $np$  Rydberg

states in the formamide–(H<sub>2</sub>O)<sub>2</sub> complex, where a level shift of 0.35 au was used. The valence states are sensitive to mixing with the Rydberg states.<sup>9,63</sup> Consequently, further CASSCF/CASPT2 calculations were performed in order to determine the valence state properties. In these calculations the reference orbitals are the CASSCF orbitals from the original CASSCF calculation but with the Rydberg orbitals removed. This procedure reduces the mixing between valence and Rydberg states and has been successfully applied to a variety of systems.<sup>63–65</sup>

Generally contracted basis sets of atomic natural orbitals (ANO) type<sup>66</sup> were used with the following contractions: C,N,O 4s3p1d and H 2s. This basis set was supplemented with an additional 1s1p1d set of diffuse Rydberg functions. For a more complete description the reader is referred to the original gas-phase calculation.<sup>9</sup> The Rydberg basis functions are placed at the average charge centroid of both the <sup>2</sup>A' and <sup>2</sup>A'' cations. The internal geometry of the formamide molecule undergoes very little change in the presence of the water molecules. The location of the Rydberg basis functions, however, was adjusted so its position relative to the heavy atoms was preserved. The MOLCAS4<sup>67</sup> ab initio package was used to perform the calculations.

The gas-phase study reported results for an active space of 8 a' orbitals and 7 a'' orbitals, denoted (8,7). This active space included the  $\pi_b$ , n, and  $\pi_{nb}$  orbitals, which are doubly occupied in the ground state. It was reported that excitation energies for a (5,5) active space differed by less than 0.05 eV.<sup>9</sup> This indicates that the excitation energies are fairly insensitive to the choice of active space. In the present study we have chosen an active space of 10 orbitals. This should be comparable to the (5,5) active space. However, even though the size of the active space is the same, due to the change of symmetry and presence of the solvent molecules, exactly the same orbitals may not be included. The 1s orbitals of the heavy atoms in formamide and the 1s and 2s orbitals of the solvent oxygen atoms were kept frozen after the initial SCF calculation. The CASSCF calculation was equally weighted over 11 roots. This included Rydberg s and p states in addition to the  $n\pi^*$  and intense  $\pi_{nb}\pi^*$  transitions. For the formamide–(H<sub>2</sub>O)<sub>1</sub> and formamide–(H<sub>2</sub>O)<sub>3A</sub> clusters 12 roots were included in order to obtain well-described distinct p states. For the valence-state calculation, four Rydberg orbitals, one 3s and three 3p, were deleted and the second lone pair on oxygen ( $n'$ ) was included, giving an active space of seven orbitals and eight electrons. A CASSCF calculation equally weighted over five roots was then performed, followed by CASPT2 calculations for each root.

In solution a formamide molecule would be surrounded by a large number of solvent molecules. A better approximation to this than the purely explicit model may be a semicontinuum approach, which combines the effects of bulk solvent with the local interactions between solute and solvent. In the present study further calculations were performed that treated the formamide–(H<sub>2</sub>O)<sub>1</sub> and formamide–(H<sub>2</sub>O)<sub>3A</sub> complexes within a continuum model. A different procedure is required for the semicontinuum calculations. The CASSCF with a self-consistent reaction field (CASSCF–SCRF) method<sup>68,69</sup> separates the response of the reaction field into electronic and nuclear components. The response of the nuclear degrees of freedom is assumed constant during an electronic excitation because of the slow relaxation times. The fast relaxation times of the electronic degrees of freedom require them to be optimized for each state, so they remain in equilibrium with the molecular charge distribution. A CASPT2-RF<sup>56,57</sup> calculation then follows for each root. Cavity sizes were chosen on the basis of van der Waals radii.<sup>70</sup> Spherical cavities with radii of 8.5 and 11.0  $a_0$  were

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**Table 3.** Excitation Energies of the Formamide–Water Complexes

state	$\mu^{a,b}$	transition energies (eV)							
		gas <sup>b</sup>	1	2	3	3A	SC <sup>c</sup> -1	SC-3A	continuum <sup>d</sup>
n $\pi^*$	2.12	5.61	5.97	6.09	6.11	6.24	5.89	5.99	5.54
$\pi_{nb}3s$	4.00	6.52	6.92	6.93	7.00	7.19			8.23
n3s	3.67	6.59	6.89	6.89	7.28	7.31			
$\pi_{nb}3p_y$	1.70	7.04	8.06	8.11	8.06	8.00			
n3p <sub>y</sub>	0.59	7.31	8.12	8.15	8.12	8.07			
$\pi_{nb}\pi^*$	6.12	7.41	7.26	7.26	7.16	7.18	7.12	6.77	6.95
$\pi_{nb}3p_z$	4.06	7.72	8.20	7.82	7.93	8.01			
n3p <sub>x</sub>	4.05	7.73	7.80	8.11	8.34	8.24			
n3p <sub>z</sub>	2.09	7.81	8.40	8.54	8.44	8.33			
$\pi_{nb}3p_x$	6.31	7.97	7.86	8.15	8.21	8.26			
n' $\pi^*$	N/A <sup>e</sup>	N/A	10.13	10.25	10.11	9.92	10.18		9.83
$\pi_b\pi^*$	5.24	10.50	10.71	10.73	10.61	10.65	10.58	10.42	10.42

<sup>a</sup> Gas-phase dipole moments (D). <sup>b</sup> Ref 9. <sup>c</sup> SC = semicontinuum calculation. <sup>d</sup> Ref 24. <sup>e</sup> N/A = not available.

chosen and surrounded by a continuous dielectric characterized by a macroscopic dielectric constant  $\epsilon = 80.0$  and a refractive index  $\eta = 1.33$ , corresponding to water. A repulsive potential which lies outside the cavity was included.<sup>56,57</sup> This potential models the exchange repulsion of the solvent and maintains the charge distribution within the cavity. Excitations to Rydberg states were not observed below 10 eV, because of the destabilizing effect of the repulsive potential. Thus, only valence states are reported. As in the calculations of the valence-state properties, an active space of seven orbitals was used.

## Results and Discussion

**Rydberg States.** Excitation energies are presented in Table 3. Comparison of the gas-phase excitation energies with those for the formamide–(H<sub>2</sub>O)<sub>1</sub> complex shows that the presence of the water molecule causes a clear increase in the excitation energies for all but one the Rydberg states. This increase varies from 0.3 to 1.0 eV. In addition, throughout the study excitations to d states are not observed, even in the calculations in which the Rydberg s and p orbitals are removed. This suggests that they lie above 10.7 eV. As discussed in the Introduction, the solvatochromic shift arises from the interaction of the solvent with the lower (ground) state and the excited state being dissimilar. The electrostatic, exchange, and dispersion interactions are three components of the solute–solvent interaction that are likely to differ between electronic states. Although it is difficult to calculate the contribution to the solvatochromic shift from the different types of interaction accurately, it is possible to make some estimation.

The dipole moments of the Rydberg states in the gas phase vary from much lower to significantly higher than the ground state value of 4.08 D. Even for states with a dipole moment similar to that of the ground state, a blue shift of about 0.4 eV is observed. This suggests that the blue shift for the Rydberg states is not purely electrostatic in nature. The dispersion interaction between a solute *M* and solute *S* separated by distance *d* can be expressed in terms of the solute and solvent polarizabilities:<sup>3</sup>

$$E_{\text{disp}} = -\frac{3\alpha_M\alpha_S}{2d^6} \left( \frac{I_M I_S}{I_M + I_S} \right) \quad (1)$$

in which  $\alpha$  and *I* represent polarizabilities and ionization potentials, respectively. The polarizability of a diffuse Rydberg state will be larger than for the ground state. So there will be a more favorable dispersion interaction for the excited state, resulting in a red shift in the corresponding transition energy. Table 4 shows the CASSCF polarizabilities of the lower energy electronic states of formamide calculated using the finite field

**Table 4.** Calculated Polarizabilities and Contribution to the Solvatochromic Shifts from Dispersion

state	$\alpha$ (au)	$\Delta E$ (eV)
ground	27.17	
n $\pi^*$	21.12	+0.01
$\pi_{nb}3s$	517.75	−0.82
n3s	892.94	−1.44
$\pi_{nb}3p_y$	237.69	−0.35
n3p <sub>y</sub>	406.09	−0.63
$\pi_{nb}\pi^*$	11.82	+0.03
$\pi_{nb}3p_z$	230.52	−0.34
n3p <sub>x</sub>	66.74	−0.07
n3p <sub>z</sub>	245.23	−0.36
$\pi_{nb}3p_x$	45.75	−0.03

method.<sup>71,72</sup> In this method  $\alpha$  is calculated from the perturbation in the dipole moments of the electronic states which result from applying an electric field *F* (0.001 au).

$$\alpha = \frac{\mu_F - \mu_0}{F} \quad (2)$$

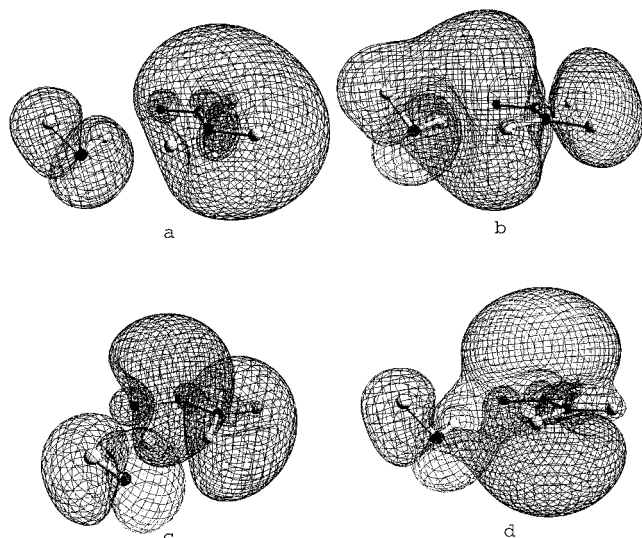
The estimated shift in the transition energies is also shown. The distance between the oxygen atom in water and the carbon atom in formamide in the formamide–(H<sub>2</sub>O)<sub>1</sub> complex provides an estimate for *d*. Values of 10.08 and 12.61 eV are used for the ionization potentials of formamide and water, and the polarizability of water is taken to be 10.0 au.<sup>73</sup> The results show that the dispersion interaction causes a red shift in the transition energies of the Rydberg states. This shift can be large, particularly for the n3s and p<sub>nb</sub>3s states. This is not surprising because one would expect the large diffuse 3s orbital to have a greater dispersion interaction. However, this contribution is not the dominant one, because overall a blue shift is observed in the Rydberg transition energies. The ground state and valence states have similar polarizabilities, and thus dispersion has little effect on the valence transition energies.

The destabilizing effect of the solvent molecules on the diffuse Rydberg states originates from the exchange contribution. This is illustrated in Figure 2, which depicts the Rydberg orbitals along with the orbitals from the water molecule. The Rydberg orbitals begin to overlap spatially with the solvent molecule, which will result in a repulsive exchange interaction in addition to the electrostatic interaction. This interaction is sufficient to overcome the favorable dispersion contribution. This is in

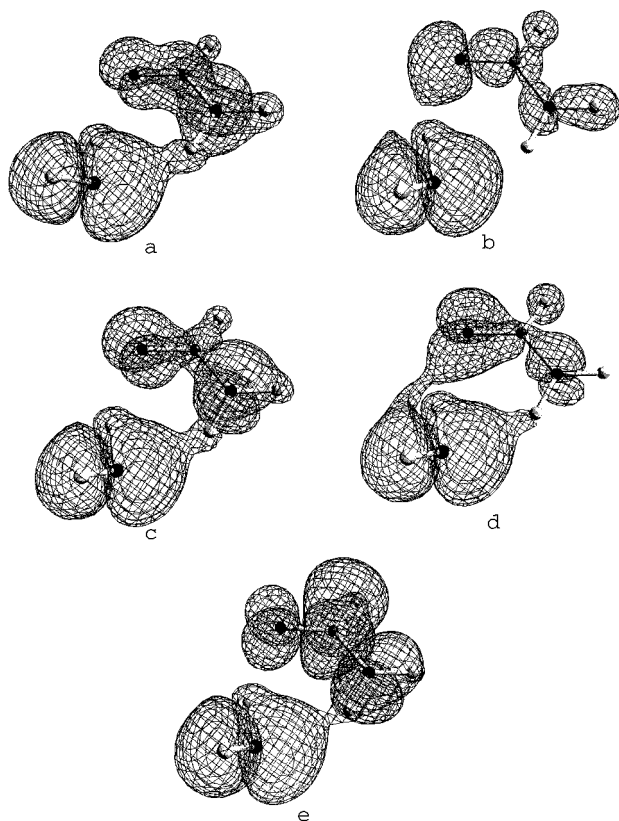
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**Figure 2.** Rydberg orbitals of formamide-(H<sub>2</sub>O)<sub>1</sub> gas-phase cluster contoured at  $\pm 0.012$  au, from a CASSCF calculation averaged over 12 roots: (a) 3s orbital, (b) 3p<sub>x</sub> orbital, (c) 3p<sub>y</sub> orbital, and (d) 3p<sub>z</sub> orbital.



**Figure 3.** Valence orbitals of formamide-(H<sub>2</sub>O)<sub>1</sub> gas-phase cluster contoured at  $\pm 0.012$  au, from a CASSCF calculation averaged over 5 roots with the Rydberg orbitals removed: (a)  $\pi_b$  orbital, (b)  $n'$  orbital, (c)  $\pi_{nb}$  orbital, (d)  $n$  orbital, and (e)  $\pi^*$  orbital.

contrast to the valence orbitals, depicted in Figure 3, which at the same contour value are not interacting spatially with the solvent. For excited states in which there is little difference between ground- and excited-state dipole moments, the electrostatic contribution to the solvatochromic shift will be approximately zero. Thus, for these states it is possible to estimate the magnitude of the blue shift arising from the exchange contribution, assuming that the net contribution from other sources, such as correlation, will be relatively small. For the  $\pi_{nb}$  3s state the exchange contribution is large,  $\sim 1.3$  eV. For

the  $\pi_{nb}3p_z$  and  $n3p_x$  states exchange makes a smaller contribution; values of  $\sim 0.4$ – $0.7$  eV and  $0.2$ – $0.7$  eV, respectively, are observed.

On the basis of electrostatics, a blue shift would be predicted for states with a lower dipole moment than the ground state. In the case of these states, large blue shifts of  $0.6$ – $1.0$  eV are observed, suggesting that the electrostatic and exchange effects are acting in concert to destabilize the excited state relative to the ground state. The one Rydberg state ( $\pi_{nb}3p_x$ ) with a higher dipole moment than the ground state shows a slight red shift in excitation energy. This suggests that the favorable electrostatic interaction is being offset by the destabilizing exchange interaction.

As the number of surrounding solvent molecules is increased, one would expect the Rydberg states to be destabilized further. This trend is generally reflected in the transition energies. The magnitude of these energy shifts is similar to those observed for NO in rare gas matrixes.<sup>25</sup> The largest number of water molecules considered in this study represents only a fraction of the first solvation shell. In solution the formamide solute would be surrounded in three dimensions by solvent molecules, so it is reasonable to expect this trend would continue until, as observed experimentally, the Rydberg states no longer appear in the condensed phase electronic spectrum. Another factor that may contribute to the absence of Rydberg states is broadening of the spectral bands. Thus this broadening and energy shift may result in the Rydberg spectral bands being absorbed into the broad valence bands present in the condensed phase spectra. The results suggest that considering only electrostatic interactions within a continuum model will not give an accurate picture for excited states. It is important to take account of exchange interactions, and this can be qualitatively achieved by a repulsive potential placed outside an appropriate cavity. From the results of this study it is not possible to determine whether the repulsive potential, as it is currently parametrized, is quantitatively correct. In fact, it is probably unlikely that it would reproduce accurately condensed phase Rydberg state energies. However, the results do suggest that it is qualitatively correct. For many applications this is sufficient, since it is generally valence state properties that are of interest.

**Valence States.** The valence-state energies also show some interesting trends. The  $n\pi^*$  transition is calculated to be 5.97 eV for the formamide-(H<sub>2</sub>O)<sub>1</sub> complex. This represents a blue shift of 0.36 eV. As the number of water molecules increases, the blue shift increases. A similar trend has been observed in calculations on formaldehyde.<sup>74</sup> There is good agreement with the blue shifts calculated by Sobolewski<sup>53</sup> and by Krauss and Webb,<sup>54</sup> who reported values of 0.18 and 0.44 eV for one and three water molecules, respectively. The increasing blue shift is matched by a decrease in the length of the hydrogen bonds in the formamide-water complexes. This is consistent with the findings of Del Bene<sup>51</sup> and Taylor<sup>52</sup> that there is an important relationship between hydrogen bonding and the  $n\pi^*$  transition. This relationship is, perhaps, not surprising because the hydrogen bond to the carbonyl oxygen will have a large effect on the lone pair orbital which is localized on the formamide oxygen atom, as illustrated for the  $n$  orbital in Figure 3. In our calculations the overall change in the ground-state geometry is small. However, these changes do increase with decreasing hydrogen bond length. There is a lengthening of the C=O bond length by 0.003 Å, a shortening of the C–N bond by 0.010 Å, and a shortening of the N–H bond to the hydrogen-bonded

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hydrogen by 0.043 Å. The largest blue shift is calculated for the formamide-(H<sub>2</sub>O)<sub>3A</sub> complex in which there are two hydrogen bonds to the carbonyl oxygen.

Within the pure continuum model, no blue shift was predicted for the  $n\pi^*$  transition, even though one would be expected from the gas-phase dipole moments. However, the predicted transition energy is in good agreement with the available experimental data. One reason for this may be that the experimental spectrum was measured in acetonitrile, where the formamide-solvent hydrogen bond is relatively weak.<sup>47</sup> Experimental work on similar amides suggests that the  $n\pi^*$  state does undergo a blue shift in water. Nielson and Schellman<sup>75</sup> report that the  $n\pi^*$  band lies at about 5.9 eV for most amides in aqueous solution.

The  $\pi_{nb}\pi^*$  band dominates electronic spectrum of formamide. In solution this band undergoes a significant red shift.<sup>17</sup> The explicit water molecules induce a red shift of the  $\pi_{nb}\pi^*$  band, which is greatest for the three-water-molecule complex. The magnitude of the red shift is less than that predicted by the continuum model, but it would presumably increase on addition of further water molecules. Figure 3 shows all three  $\pi$  orbitals have a significant hydrogen-bonding interaction between the amide hydrogen and the solvent water molecule. The transition energies, however, appear to be dominated by the electrostatic interaction. The trend observed for the  $\pi_b\pi^*$  transition energy is less clear. The gas-phase  $\pi_b\pi^*$  state has a dipole moment that is greater than the ground state, but less than the  $\pi_{nb}\pi^*$  state. Thus a small red shift would be expected, as observed in the continuum calculation. The explicit solvent calculations predict a blue shift, although this decreases for the formamide-(H<sub>2</sub>O)<sub>3</sub> complex. This may again be due to a hydrogen-bonding interaction. However, the differences may be within the error of the calculation.

The calculations within the semicontinuum framework should provide a better model of formamide in aqueous solution, combining both local and bulk solvent effects. The results show no transition to Rydberg states below 10 eV, in accordance with the experimental picture. This is a direct result of the repulsive potential included outside the cavity. The  $n\pi^*$  transition energies obtained are similar to those from the gas-phase complexes. A larger blue shift is observed for the formamide-(H<sub>2</sub>O)<sub>3A</sub> complex. Comparison of the semicontinuum model with the pure continuum model shows the  $n\pi^*$  state undergoes a blue shift of 0.35–0.45 eV. Again this shift is similar to that previously obtained. The small change in basis set and active space between the continuum study and the present study does not significantly affect the result. The  $n'\pi^*$  state also undergoes a blue shift 0.35 eV. For the formamide-(H<sub>2</sub>O)<sub>3A</sub> complex the  $n'\pi^*$  state was not accessible with the 7a active space, because of the presence of the lone pair orbitals on water. The red shift in the  $\pi_{nb}\pi^*$  transition energy is underestimated when only one water molecule is included in the cavity. The larger cavity leads to an underestimation of the electrostatic effects. However, a greater red shift results when additional water molecules are placed in the cavity. A transition energy of 6.77 eV is obtained, which is close to the experimentally observed 6.81 eV in acetonitrile.

**Oscillator Strengths.** The calculated oscillator strengths of the valence states are presented in Table 5. The  $n\pi^*$  and  $n'\pi^*$  transitions are weak. The  $n'\pi^*$  oscillator strength appears to decrease with increasing number of water molecules. The spectra are dominated by the  $\pi_{nb}\pi^*$  and  $\pi_b\pi^*$  transitions. The presence of one water molecule has little effect on the  $\pi_{nb}\pi^*$  oscillator

**Table 5.** Oscillator Strengths

state	oscillator strengths							
	gas <sup>a</sup>	1	2	3	3A	SC <sup>b</sup> -1	SC-3A	continuum
$n\pi^*$	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
$\pi_{nb}\pi^*$	0.371	0.378	0.395	0.422	0.396	0.353	0.384	0.230
$n'\pi^*$	N/A <sup>c</sup>	0.040	0.021	0.010	0.018	0.005		0.017
$\pi_b\pi^*$	0.131	0.150	0.149	0.166	0.148	0.140	0.113	0.149

<sup>a</sup> Ref 9. <sup>b</sup> SC = semicontinuum calculation. <sup>c</sup> N/A = not available.

strength. However, addition of further water results in an increase. The oscillator strengths of the two largest clusters differ significantly. This indicates some sensitivity of the oscillator strength to the local arrangement of the solvent. The increase contradicts the continuum calculation, which predicts a decrease in the  $\pi_{nb}\pi^*$  oscillator strength. The oscillator strengths for the  $\pi_b\pi^*$  transition show a small increase compared with the gas phase and are similar to those calculated from the continuum model. The oscillator strengths for the Rydberg states show small increases over gas-phase values but remain small (less than 0.05).

The oscillator strengths predicted by the semicontinuum calculations for the  $n\pi^*$ ,  $n'\pi^*$ , and  $\pi_b\pi^*$  states are close to those from the continuum model calculation. The oscillator strength for the  $\pi_{nb}\pi^*$  transition shows a decrease compared with the appropriate gas-phase calculation, indicating that the reduction is electrostatic in nature. However, this oscillator strength is still significantly larger than for the continuum model calculation. We note that while the transition energies are insensitive to small changes in basis set, the  $\pi_{nb}\pi^*$  oscillator strength is more sensitive. An oscillator strength of 0.285 is obtained for the  $\pi_{nb}\pi^*$  transition for the semicontinuum calculation when the Rydberg functions are removed. This is closer to the previous calculation. The remaining difference may be consequence of the influence of the water molecule(s) or the larger cavity for the semicontinuum calculation, resulting in an underestimation of the electrostatic effects.

## Conclusions

The electronic spectra of formamide with one, two, and three water molecules have been studied using high-level correlated ab initio methods that have been shown to describe the electronic structure of many systems accurately. Although these complexes will not provide a complete model of formamide in aqueous solution, a greater understanding of the local interactions with solvent has been obtained. In addition, calculations on small solute-solvent clusters can provide information that may be incorporated into larger scale simulations of excited states. The diffuse Rydberg states are destabilized by the surrounding solvent, and this effect can overcome favorable electrostatic and dispersion interactions. This demonstrates the importance of other components of the solute-solvent interaction besides the electrostatic component for excited-state calculations. The  $\pi_{nb}\pi^*$  transition undergoes a red shift which is dominated by an electrostatic interaction. These effects are reproduced well by the previous study with a continuum model. In addition, an increase is observed in the  $\pi_{nb}\pi^*$  and  $\pi_b\pi^*$  oscillator strengths. However, the blue-shift induced in the  $n\pi^*$  transition energy requires at least one explicit water molecule. This blue shift is also found to be dependent on the formamide-water hydrogen bond distance. In an attempt to capture all these features, within one model, a semicontinuum approach was adopted. This model can predict the main features of the spectrum, the absence of Rydberg states, a blue shift in the  $n\pi^*$  transition energy, and a

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red shift in the  $\pi_{\text{nb}}\pi^*$  transition energy. However, this red shift is underestimated when only one water molecule is included in the cavity. When additional water is placed in the cavity, a larger red shift is obtained, which agrees with experiment. The remaining valence transition energies are predicted to be at energies greater than 10 eV.

This study has shown that to compute electronic spectra in solution accurately, one may have to go beyond a simple continuum model. First, dispersion and exchange effects are important, particularly for Rydberg states. Furthermore, short-range interactions, such as hydrogen bonding, are also significant. Our calculations show that the semicontinuum approach is capable of describing most of these features.

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**Supporting Information Available:** Atomic coordinates of the optimized formamide–water clusters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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