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Specific Microsolvation Triggers Dissociation-Mediated Anomalous Red-Shifted Fluorescence in the Gas Phase

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Abstract: Ion-depletion IR spectroscopy has revealed that at least two water molecules are required in complexes with 4-(dimethylamino)benzoic acid methyl ester (DMABME) for anomalous red-shifted fluorescence to occur in the gas phase. Through the use of high-level quantum-chemical calculations, two experimentally observed isoenergetic isomers are assigned to complexes in which a water dimer is hydrogen-bonded either to the carbonyl oxygen of the ester function or to the amino nitrogen. Surprisingly, computed IR spectra reveal that the N-bonded isomer is responsible for the observed red-shifted fluorescence. For an explanation, the mechanism of twisted intramolecular charge-transfer (TICT) formation and energy dissipation is investigated in detail. In general, for red-shifted fluorescence to occur, the N-bonded complexes must be able to dissipate energy, which in the gas phase can only happen nonradiatively via fragmentation. Arguments are given that only the N-bonded isomer photodissociates rapidly enough into free DMABME and a water dimer as a result of the immediate repulsion between the amino nitrogen and the water dimer in the TICT state. The O-bonded isomer, on the other hand, stays intact because the hydrogen bond is strengthened by additional electrostatic attraction in the ICT state. Furthermore, an experiment to further corroborate that mechanism is suggested.

Introduction

After the first discovery of the dual fluorescence of 4-(dimethylamino)benzonitrile (DMABN) in polar solvents,[1] much experimental and theoretical effort has been undertaken to clarify the underlying molecular mechanism. At present, it is well-established that the formation of a photoinduced intramolecular charge-transfer (ICT) state is responsible for the red-shifted additional fluorescence in polar environments,[2,3] since back-electron transfer is suppressed as a result of large structural changes in the ICT state. However, the detailed molecular structure of the fluorescing ICT state has been a matter of long-standing debate. To date, several different ICT mechanisms suggesting that the additional red-shifted fluorescence occurs from a twisted ICT (TICT),[4−6] a planar ICT (PICT),[7,8] a rehybridized ICT (RICT),[9,10] or a wagged ICT (WICT)[11] state have been proposed. The most promising candidates appear to be the TICT and PICT models.

Recent high-level ab initio calculations on the excited states of DMABN revealed that the initially excited S_2 state, also designated as the L_a or charge-transfer (CT) state, decays rapidly into the S_1 state [also called the locally excited (LE) or L_b state] via a conical intersection.[12] Conical intersections are special but ubiquitous topologies of excited-state potential energy surfaces, and in general, they are responsible for ultrafast nonradiative decay processes of excited states.[13] They are thus also often called photochemical funnels. Indeed, it has been shown that an S_2/S_1 conical intersection is spatially and energetically very close to a planar minimum on the S_2 surface of DMABN,[12] which allows for an ultrafast radiationless transition from the S_2 to the S_1 potential energy surface. On the S_1 surface, two minima are then accessible: a planar structure and a TICT structure. These two states hence correspond to two structural isomers on the same electronic S_1 state. In fact, the local planar minimum of the S_1 state has been assigned to a PICT state, combining the PICT and TICT models in one general mechanism for dual fluorescence in DMABN.[12] The

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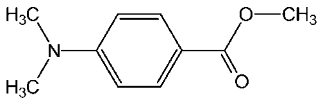
10.1021/ja800528p CCC: $40.75

Scheme 1. 4-(Dimethylamino)benzoic Acid Methyl Ester (DMABME)



occurrence of dual fluorescence in related push–pull systems finally depends on the relative energies of the two minima and the height of the energy barrier connecting them. Accordingly, aromatic push–pull systems can be classified into four groups, depending on the relative vertical excitation energies of the CT and LE states as well as on the stabilization energy of the ICT.[14]

However, most of the experimental studies have been performed in solution and only a few in the gas phase, while most of the theoretical works neglect the environment or treat it as dielectric medium.[2,3] In principle, this is justified when the influence of the solvent on the ICT mechanism is that of a dielectric medium without direct influence on structural or electronic properties of the molecules. Traditionally it is assumed that the electrostatic field of a polar solvent stabilizes the formed ICT state because of its large dipole moment, thereby reducing the energy barrier between the LE state and the ICT state, leading to dual fluorescence. An apolar solvent, on the other hand, does not open the ICT channel (at least in DMABN), and hence, dual fluorescence is not observed. Nevertheless, solvent molecules can have a direct influence on ICT,[15−17] i.e., on dual fluorescence. Especially when the solvent is polar, protic, or basic, the solvent molecules can form solute–solvent complexes or larger structured clusters via, for instance, dative bonds or hydrogen bonds.[17,3] As a consequence, the geometric or electronic structure of the reacting species may be significantly changed, thereby affecting the ICT mechanism.

Indeed, recent progress in chemical kinetics has unveiled the fact that so-called "elementary reactions" such as proton and electron transfer are often controlled by interactions of the reagent with the solvent, which often occur in a very specific way that governs the underlying reaction mechanisms.[17] Along these lines of thought, an experimental study of the dual fluorescence of 4-(dimethylamino)benzoic acid methyl ester (DMABME) (Scheme 1) employing high-resolution laser-induced fluorescence excitation spectroscopy revealed that red-shifted fluorescence does occur in DMABME complexes with only a few water molecules. It was suggested that TICT formation is the key mechanism for the observed red-shifted fluorescence and that this process is facilitated by microsolvation and mixing of the low-lying electronic states.[18] This was also supported by early calculations.[19] To corroborate these findings, an IR depletion study of jet-cooled clusters of DMABME with one and two water molecules was performed to study the direct influence of water microsolvation, i.e., of individual water molecules, on the onset of dual fluorescence.[20,21] It was found that two water molecules are necessary to induce red-shifted fluorescence in DMABME. Moreover, the IR spectra clearly revealed that two different isomers are formed under the experimental ultracold conditions in a supersonic jet beam. However, only one of these isomers exhibits anomalous red-shifted fluorescence. Unfortunately, an unambiguous assignment of the vibrational bands to the different isomers was not possible on the basis of the experiments alone, and thus, the isomer responsible for the observed red-shifted fluorescence could not be identified.

In this work, we present the results of our computational study of the IR spectra and fluorescence properties of different isomers of DMABME·2H$_2$O employing high-level quantum-chemical methodology. The two energetically equivalent isomers that are formed in the experiment are identified to be those in which a water dimer is bound either to the amino nitrogen of the DMA group (isomer **1**) or to the carbonyl group of the ester function (isomer **2**). Furthermore, it is shown that isomer **1** of DMABME·2H$_2$O is responsible for the observed red-shifted fluorescence, which originates from isolated DMABME in its TICT state. The latter can only be reached via dissociation of the precursor DMABME·2H$_2$O complexes, since otherwise the molecules cannot dissipate their excess energy in the gas phase efficiently to emit a strongly red-shifted fluorescence photon.

Computational Approach

The equilibrium geometries and harmonic frequencies of the DMABME–water clusters were calculated using second-order Møller–Plesset perturbation theory (MP2) with the 6-31G** basis set and employing the counterpoise (CP) correction for the basis-set superposition error (BSSE) in the energies and potential energy surfaces, as implemeted in Q-Chem 3.0.[22] For the computation of relative energies and stabilization energies of the different DMABME·2H$_2$O isomers, zero-point vibration was also taken into account at the MP2/6-31G** level. We extensively tested the accuracy and reliability of this theoretical level by benchmark calculations on small model clusters, including the formic acid–water and ammonia–water complexes as well as the water dimer. We chose these model complexes because they contain all of the types of hydrogen bonds (carbonyl–water, amino–water, hydroxy–water) that are also present in the investigated DMABME·2H$_2$O clusters. For these small systems, theoretical levels up to CP-corrected CCSD/cc-pVTZ and MP2/cc-pVQZ were used (details are provided in the Supporting Information). These calculations revealed that the energetic ordering of the relevant OH stretch vibrations is nicely conserved at all levels of theory. Therefore, we were able to rely on CP-corrected MP2 calculations with a moderate 6-31G** basis set in the interpretation of the experimental IR spectra of the DMABME·2H$_2$O clusters. To allow for a direct comparison of the computed frequencies with the measured ones, we empirically scaled the calculated frequencies by a factors of 0.946 and 0.940 for isomers **1** and **2**, respectively. These factors were derived by comparison of computed OH vibrations of two DMABME·H$_2$O isomers at the CP-MP2/6-31G** level with their experimental values (see the Supporting Information). After application of these shift factors to the computed OH stretch vibrations of DMABME·2H$_2$O, we obtained an excellent agreement between experiment and theory that was certainly sufficient to assign the experimental IR spectra in this case.

For the investigation of the optical properties of DMABME·2H$_2$O, the two lowest excited electronic states of the

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DMABME−water clusters were calculated at the RI-CC2/TZVP[23] and TDDFT/B3LYP/TZVP[24,25] levels of theory. The equilibrium structures on the S_1 potential energy surface were optimized employing time-dependent density functional theory (TDDFT) at the TDDFT/B3LYP/TZVP level, and for consistency, the ground-state was also reoptimized at the DFT/B3LYP/TZVP level of theory using TURBOMOLE 5.7.[26] Comparison of the ground-state geometries of isomer **1** calculated at the CP-MP2/6-31G** and DFT/B3LYP/TZVP levels revealed that the change in geometrical parameters, including the relevant hydrogen bonds, was very small (maximum deviation of only 0.05 Å). However, one generally cannot expect the TDDFT/B3LYP method to yield reliable excited-state structures with large CT character. Therefore, we studied the influence of Hartree−Fock (HF) exchange in the exchange correlation (XC) functional on the geometrical parameters of the TICT structure by optimization of the TICT equilibrium structure using the B3LYP and BHLYP XC functionals. The geometrical parameters were practically independent of HF exchange when at least 20% HF exchange is included in the XC functional, i.e., when at least B3LYP is employed. The largest difference was found in the length of the CN bond connecting the amino group to the benzene ring. This bond had lengths of 1.44 and 1.40 Å when the B3LYP and BHLYP XC functionals, respectively, were used for the optimization of the TICT structure. With an increasing amount of HF exchange, the bond length becomes shorter as a result of the improved description of the electrostatic interaction between the separated charges in the CT state. However, manual changes of this bond length had no effect on the relative positions and shapes of the computed excited-state surfaces, and thus, one can rely on the TDDFT/B3LYP-optimized geometries.

In general, the calculated excitation energies agree very favorably at the TDDFT/B3LYP and RI-CC2 levels for planar geometries and deviate only for the TICT states; the deviation is ~0.8 eV and is clearly due to the well-known CT failure of TDDFT,[27−29] which results in a strong underestimation of excitation energies of CT excited states.

The minimum-energy paths for TICT formation in the most stable DMABME·$2H_2O$ isomers were computed at the TDDFT/B3LYP level on the excited-state surface along the dihedral angle describing the twisting of the DMA group. However, because of the CT failure of TDDFT for the vertical excitation energies and the resulting too-low de-excitation energies at the pronounced TICT geometries, we performed RI-CC2 single-point calculations along the TDDFT/B3LYP-optimized reaction pathway.

Results and Discussion

Assignment of the Infrared Spectra of DMABME·$2H_2O$ Complexes. DMABME (Scheme 1) is a prototypical aromatic push−pull system that is known to exhibit anomalous red-shifted fluorescence in aqueous solution.[2] Traditionally, the solvent is seen as a dielectric medium or polar environment that stabilizes the CT state and thereby makes TICT formation and red-shifted fluorescence energetically feasible. An immediate question to ask is whether spatially close water molecules have a direct influence on the structural and electronic properties of DMABME. From such a microscopic perspective, one may equally well ask how many water molecules are necessary to observe red-shifted fluorescence of DMABME. As already mentioned in the Introduction, these questions have recently been addressed in an IR depletion study of jet-cooled clusters of DMABME with one and two water molecules,[20,21] which showed that in fact at least two water molecules are necessary to induce dual fluorescence of DMABME at wavelengths of 325 and 425 nm. The recorded IR ion-depletion spectrum of the complexes with two water molecules exhibits four distinct bands (at 3466, 3514, 3525, and 3550 cm^{-1}) corresponding to H-bonded OH stretch vibrations and two bands (at 3718 and 3724 cm^{-1}) representing free OH stretches (Figure 1). Hence, two structural isomers of DMABME·$2H_2O$ must be present in the molecular beam in approximately equal amounts. However, the cluster responsible for the CT emission exhibits bands only at 3466, 3525, and 3718 cm^{-1}, giving evidence that only one of the two structural isomers is capable of the observed red-shifted CT emission at 425 nm.

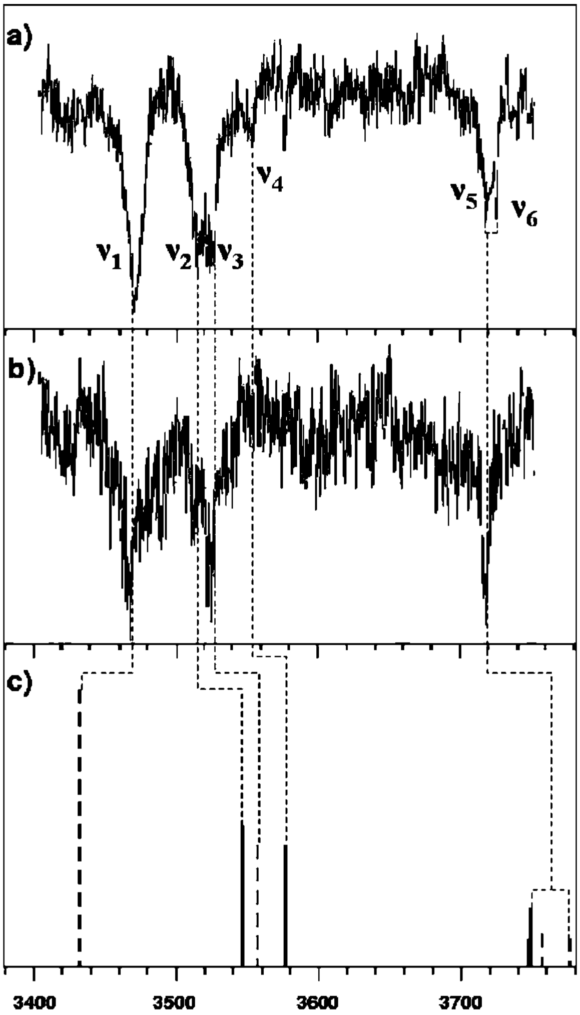

Figure 1. (a) IR ion-depletion spectrum of a mixture of two isomers of DMABME·$2H_2O$. (b) IR depletion spectrum of the species responsible for CT emission, measured as the depletion of the red-shifted fluorescence. (c) Calculated IR spectrum at the CP-corrected MP2/6-31G** level. Dashed lines correspond to isomer **1** and solid lines to isomer **2**.

To identify the two structural isomers of DMABME·$2H_2O$ that are present in the experimentally determined IR spectra (Figure 1a), we studied the structural and electronic properties of five isomers of DMABME·$2H_2O$ by means of high-level quantum-chemical computations. The investigated isomers vary

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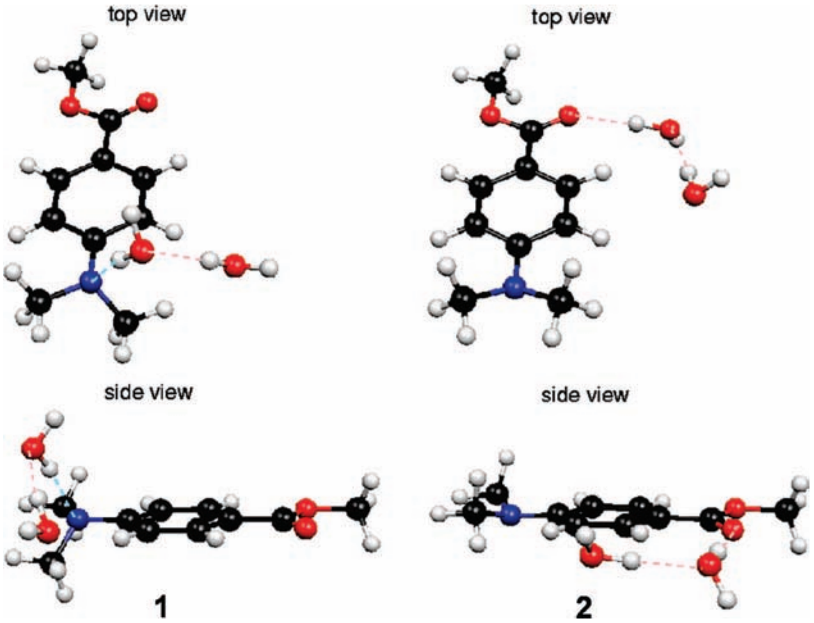

Figure 2. Equilibrium structures of the energetically most stable and essentially degenerate isomers **1** (left) and **2** (right) of the DMABME·2H_2O cluster in the electronic ground state.

Table 1. Relative Energies and Stabilization Energies of the Investigated Isomers of DMABME·2H_2O Obtained at the CP-Corrected MP2/6-31G** and MP2/cc-pVTZ Levels of Theory[a]

	Isomer				
	1	2	3	4	5
			Relative Energies (kcal mol^{-1})		
MP2/6-31G**	0.00/0.00	0.51/−0.08	2.56/1.93	3.77/2.70	7.02/5.45
MP2/cc-pVTZ	0.00	0.01	2.18	2.99	6.10
			Stabilization Energies (kcal mol^{-1})		
MP2/6-31G**	−13.50/−9.04	−12.99/−9.11	−10.94/−7.11	−9.73/−6.33	−6.94/−3.59
MP2/cc-pVTZ	−13.08	−13.07	−10.90	−10.10	−6.98

[a] At the MP2/6-31G** level, values given after the slash were obtained when zero-point energy was also included. The energy of isomer **1** is set to zero.

in the binding pattern of the two water molecules to the DMABME molecule. In Isomer **1**, a water dimer is bound to the amino nitrogen (Figure 2, left), while in isomer **2**, it is connected to the carbonyl oxygen of the ester function (Figure 2, right). A third alternative is to attach the water dimer to the ether oxygen of the ester function, which was realized in isomer **3** (not shown). However, one can also split the water dimer and attach one water molecule to the carbonyl oxygen and one to the nitrogen (isomer **4**, not shown) or one to the ether oxygen and one to the nitrogen (isomer **5**, not shown).

At the optimized equilibrium structures, which were all verified by analyses of their harmonic frequencies, isomers **1** and **2** are practically degenerate in energy and are the two most stable isomers of the series (Table 1). At the MP2/6-31G** level and employing the CP correction and taking zero-point energy into account, **2** is slightly more stable than **1** by 0.08 kcal/mol, while at the MP2/cc-pVTZ level using the MP2/6-31G** equilibrium geometry, it is 0.01 kcal/mol^{-1} higher in energy. Isomer **3** is ~2 kcal/mol less stable at both levels of theory, while isomers **4** and **5** are 3 and 6 kcal/mol, respectively, higher in energy than isomers **1** and **2** (Table 1). Since isomers **1** and **2** are practically energetically degenerate and clearly the energetically lowest isomers, it can be concluded that these are the ones observed in equal amounts in the jet-cooled beam of the above-described IR depletion experiment.

The optimized structures of isomers **1** and **2** of DMABME·2H_2O are displayed in Figure 2. Although the geometrical parameters of the DMABME molecules within the complexes are essentially identical, hydrogen bonding to the DMA group leads to a strong pyramidalization of the nitrogen and a pretwist of the amino group in **1** (Figure 2, left). In contrast, in free DMABME and in complexes in which water is bound to the carbonyl group, the DMA group is essentially planar and only very slightly pyramidalized. This also holds for the corresponding 1:1 complexes.

For the assignment of the vibrational bands of the IR depletion spectra to the identified most stable isomers, the IR spectra of **1** and **2** were calculated at the CP-corrected MP2/6-31G** level of theory. The calculated harmonic frequencies of **1** and **2** were furthermore scaled by constant factors of 0.946 and 0.940, respectively, to account for BSSE and missing electron correlation and anharmonicity. The scaling factors were derived from the calculated harmonic frequencies of the hydrogen-bonded OH vibrations of the corresponding 1:1 complexes and their known experimental values.

The comparison of the experimental IR spectra with the calculated harmonic frequencies of **1** and **2** (Figure 1 and Table 2) finally clarifies that the strong bands at 3466 and 3525 cm^{-1}, which are visible in both the ion-depletion IR spectrum and the IR depletion spectrum of the red-shifted fluorescence (Figure

Table 2. Assignment and Comparison of Scaled Calculated Harmonic Frequencies of the DMABME Isomers **1** and **2** at the CP-Corrected MP2/6-31G** Level with the Measured IR Ion-Depletion Spectrum of the Mixture and the CT Emission Depletion Spectrum

	OH stretch frequencies (cm^{-1})				
	calculated		experimental		
	isomer **1**	isomer **2**	IR depletion	CT emission	character
ν_1	3432		3466	3466	N···HO
ν_2		3546	3514		C=O···HO
ν_3	3557		3525	3525	H_2O···HO
ν_4		3576	3550		H_2O···HO
ν_5	3747/3749		3718	3718	free OH
ν_6		3757/3776	3724		free OH

1), are due to the N···HO and O···HO hydrogen bonds, the latter one in the water dimer in **1**. The bands at 3514 and 3550 cm^{-1}, which are only present in the ion-depletion IR spectrum, are due to the O···HO carbonyl−water and water-dimer hydrogen bonds in **2** (Table 2). Thus, it is clear that the isomer of DMABME·$2H_2O$ that exhibits red-shifted fluorescence is isomer **1**, in which a water dimer is bound to the DMA nitrogen (Figure 2).

It is highly surprising and contradictory to chemical intuition that isomer **1** is responsible for the observed red-shifted CT emission, because hydrogen bonding to the DMA group, i.e., the electron donor, increases the ionization potential (IP), which makes electron transfer energetically less favorable. This should destabilize the ICT state. On the other hand, hydrogen bonding to the carbonyl oxygen, the electron acceptor, increases its electron affinity (EA) and stabilizes the ICT state (see, for example, refs 30−32). Calculations of the IPs and EAs of the isomers corroborate this picture, and indeed, the vertical excitation energy of the CT state is also higher for isomer **1** than for isomer **2**. From this point of view, the opposite behavior of the DMABME·$2H_2O$ isomers **1** and **2** should be expected, i.e., isomer **2** would naively be expected to exhibit red-shifted fluorescence. However, as we will show, it is not the excitation energies but rather the details of the electronic and molecular structure that are essential for an explanation of the occurrence of red-shifted fluorescence. The properties of the excited states and their dynamics in the gas phase will be discussed in the following sections.

Vertical Excited States of DMABME·$2H_2O$. As a first step in the investigation of the excited-state properties of the energetically most stable isomers **1** and **2** of DMABME·$2H_2O$, their vertical excited states were calculated at the RI-CC2 and TDDFT/B3LYP levels of theory employing the standard TZVP basis set. For this objective, the geometries of the ground S_0 and excited S_1 states were optimized at the DFT/B3LYP and TDDFT/B3LYP level of theory, respectively. All of the equilibrium structures were confirmed by analyses of their harmonic frequencies. The vertical excitation energies for the ground-state equilibrium structure are directly comparable to experimentally observed absorption spectra, while the vertical excited states computed at the equilibrium structure of the electronic S_1 state directly relate to the observed fluorescence wavelengths. The computed vertical excitation and de-excitation energies are summarized in Table 3. The RI-CC2 calculations are more reliable than the TDDFT results, since they do not suffer from problems with CT excitations, and we will thus focus on those results in the following discussion.

Table 3. RI-CC2 and TDDFT/B3LYP Excitation Energies and Static Dipole Moments of Isomers **1** and **2** of DMABME·$2H_2O$ Calculated at the DFT- and TDDFT-Optimized Equilibrium Geometries on the Ground S_0 and Excited S_1 Surfaces

	S_0^{eq}		$S_1^{PICT,TS}$			S_1^{TICT}		
	E_{ex} (eV)		E_{ex} (eV)			E_{ex} (eV)		
state	TDDFT	RI-CC2	TDDFT	RI-CC2	μ (D)	TDDFT	RI-CC2	μ (D)
				Isomer **1**				
LE	4.75	4.78	4.20	4.32		3.26	3.94	
CT	4.52	4.86	3.49	3.65	6.0	2.01	2.76	11.1
				Isomer **2**				
LE	4.57	4.59	4.47	4.50		3.80	4.46	
CT	4.25	4.41	4.03	4.15	7.5	2.28	3.05	12.5
				Isolated DMABME				
LE	4.55	4.57	4.36	4.45		3.88	4.56	
CT	4.43	4.64	3.60	3.82	9.05	2.56	3.37	14.0

At the ground-state equilibrium geometry of **1**, the S_1 and S_2 states are almost degenerate, with excitation energies of 4.78 and 4.86 eV at the RI-CC2 level. While the S_1 state corresponds to the locally excited state, the S_2 state is identified as the typical intramolecular CT state exhibiting an oscillator strength of 0.18. In this CT state, an electron is transferred from the DMA group to the ester function, resulting in a strongly positively charged amino nitrogen and a strongly negatively charged carbonyl oxygen. At the TDDFT/B3LYP level, the order of states is reversed, with the LE and CT states exhibiting excitation energies of 4.75 and 4.52 eV, respectively; this is due to the typical underestimation of CT excited states by TDDFT.[25,27−29] Comparison with the vertical excited LE and CT states of isolated DMABME (Table 3), which have excitation energies of 4.57 and 4.64 eV, respectively, reveals that the CT excited state is destabilized by the water dimer in the N-bonded isomer **1** by 0.22 eV. This is caused by the hydrogen bonding of the water dimer to the amino nitrogen, which increases the IP.

Unconstrained geometry optimization using TDDFT/B3LYP in the S_1 (CT) state of isomer **1** leads directly to a twisted equilibrium structure with value of 90° for the dihedral angle between the essentially planar DMA group and the phenyl ring (Figure 3) and a large static dipole moment of 11.1 D (Table 3). This structure is commonly identified as the TICT state. The TICT geometry is the only minimum that could be identified on the potential energy surface of the CT state at the TDDFT level. Concomitant with the charge transfer, i.e. the change from negative to positive partial charge at the nitrogen, and the twisting of the DMA group, the hydrogen bond from the water dimer to the amino nitrogen breaks up during the course of the geometry optimization. Eventually, the water dimer turns around such that the oxygen of the spatially closest water molecule interacts with the now positively charged amino nitrogen. Loosely speaking, the water dimer switches from hydrogen bonding to ion solvation. In the TICT equilibrium structure, the CT state of isomer **1** exhibits an excitation energy of only 2.76 eV.

Constrained geometry optimization in the CT state, in which the DMA group is not allowed to twist, leads to a planar structure that exhibits typical properties of a PICT state. However, this state corresponds to a transition state at the level of TDDFT/B3LYP, as revealed by a single imaginary harmonic vibrational frequency. Also, the static electric dipole moment

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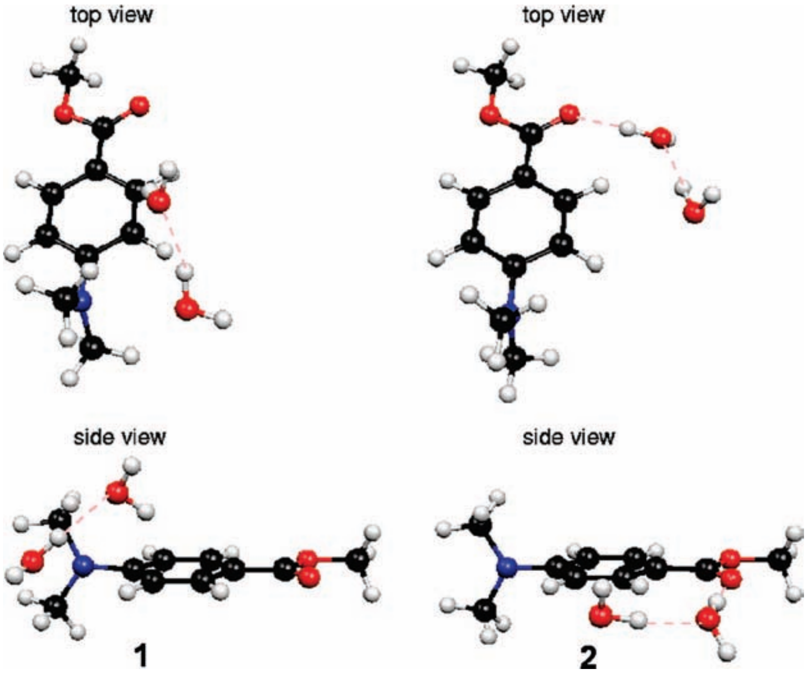

Figure 3. Equilibrium geometries of the TICT states of isomers **1** (left) and **2** (right) on the S_1 potential energy surfaces.

of only 6.0 D is not as large as that in the TICT structure at TDDFT/B3LYP level. Nevertheless, in this planar arrangement, the hydrogen bond between the water dimer and the amino nitrogen is already broken and the water dimer rearranged in the above-described way. At the geometrically relaxed planar saddle point, the DMABME$\cdot$2H_2O isomer **1** exhibits an excitation energy of 3.65 eV at the RI-CC2 level. It should be noted that at this geometry, the LE (S_2) state is already 0.7 eV higher in energy than the CT state. At the equilibrium geometry of the ground state, i.e., at initial excitation, the CT state has been found to possess a slightly higher energy than the LE state. Since a conical intersection has been found for DMABN,[12] it is justified to assume that a conical intersection is also present in DMABME in the vicinity of the ground-state equilibrium structure, allowing for an efficient radiationless transition.

The O-bonded isomer **2** of DMABME$\cdot$2H_2O exhibits vertical excited states at lower excitation energies than **1**, with values of 4.41 and 4.59 eV for the CT and LE states, respectively, at the RI-CC2 level of theory. In particular, the excitation energy of the CT state is 0.45 eV lower in **2** than in **1**, making this the lowest excited state for the ground-state equilibrium structure. This is mainly due to the above-mentioned effect that the hydrogen bond to the carbonyl oxygen increases the EA and stabilizes the CT state in comparison to the LE state. This effect is further underlined by a comparison with the vertical excitation energy of 4.64 eV for the CT state in free DMABME, which is 0.23 eV higher than that in isomer **2**, which lacks the stabilization by the water dimer. Therefore, no state crossing between the CT and LE states is present in isomer **2**.

In analogy to isomer **1**, unconstrained geometry optimization of the S_1 (CT) state of isomer **2** results in a twisted equilibrium structure (Figure 3) with a static dipole moment of 12.5 D, thus representing a TICT state. The vertical excitation energy of the TICT minimum is strongly red-shifted and exhibits a value of only 3.05 eV at the RI-CC2 level of theory. Also in analogy to isomer **1**, a planar transition state with a vertical excitation energy of 4.15 eV is found. It is important to note that in contrast to isomer **1**, the hydrogen bond does not break up during the course of the geometry optimization but instead becomes even stronger. This is manifested by a decrease of its bond length from 1.84 Å in the ground state to 1.72 Å in the TICT state. This is easily understood in terms of the increase of negative charge on the carbonyl oxygen in the CT excited state, which of course strengthens the hydrogen bond because of the additional electrostatic attraction.

To summarize briefly our computational results for the vertical excitation energies of the CT and LE states of isomers **1** and **2** for the ground-state equilibrium structure as well as for the TICT structure, the two isomers exhibit very similar properties. The discovered structural differences alone do not explain the observed anomalous red-shifted fluorescence of only isomer **1**, but they will become important in the discussion of possible TICT formation mechanisms.

To receive a more detailed picture of the TICT formation mechanism, the potential energy surfaces of the CT excited states of isomers **1** and **2** were computed along the dihedral angle between the DMA group and the phenyl group, which represents TICT formation. Along this path, all of the other geometrical parameters were allowed to relax freely at the TDDFT/B3LYP level. The curves obtained for the N-bonded isomer **1** and the O-bonded isomer **2** representing the minimum-energy pathways are displayed in Figure 4.

Surprisingly, the minimum-energy pathways for TICT formation in the two isomers exhibit no significant differences. Both isomers can in principle form a TICT structure along a direct pathway from the initially excited structure of the electronic ground state with no energy barriers present. Once the system has arrived in the TICT state, the computed barrier height for complete rotation of the DMA group via the planar transition state is 0.25 eV for both isomers. However, the Franck−Condon points of **1** and **2**, i.e., the total energies of the CT states at the equilibrium geometries of the respective ground states, are energetically above the rotation barrier by 0.85 and 0.25 eV, respectively. Therefore the DMA group can rotate freely in both isomers upon photoexcitation unless the energy is dissipated and the molecules are cool enough to form stable TICT

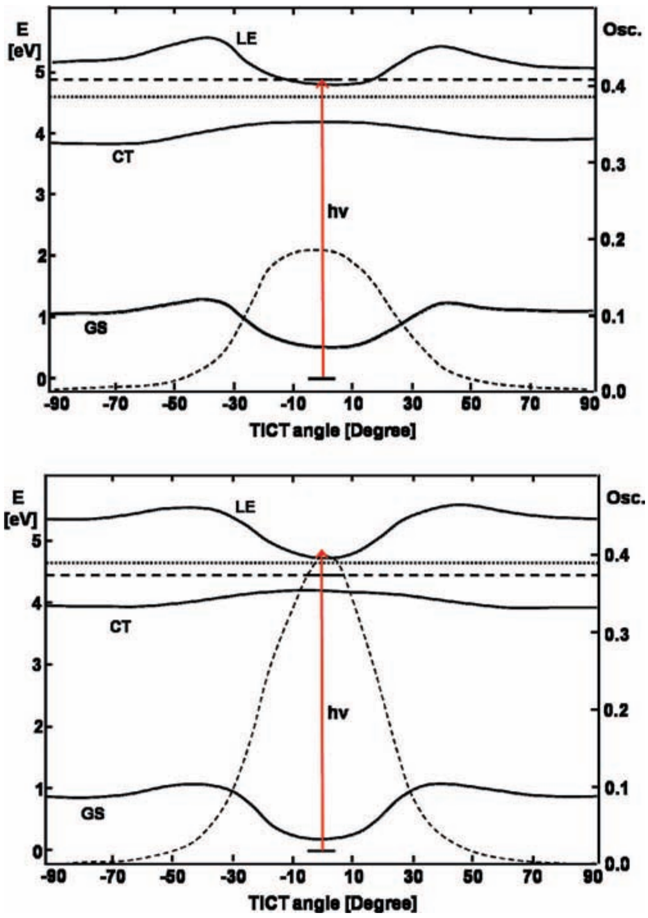

Figure 4. Potential energy surfaces of the ground (GS), locally excited (LE), and charge-transfer (CT) states for isomers **1** (top) and **2** (bottom) calculated at the RI-CC2 level along the TDDFT/B3LYP-optimized pathway on the surface of the CT state along the TICT dihedral angle. The vertical excitation energies of the CT states as well as their dissociation energies are given as horizontal dashed and dotted lines, respectively. The energy of the ground-state equilibrium structures is set to zero. The dependence of the oscillator strength of the CT states on the TICT angle is plotted as dashed line. The vertical arrow represents the experimentally observed excitation energy.

structures that eventually decay radiatively by emission of red-shifted fluorescence.

Since the minimum-energy pathways for TICT formation are again very similar for the two isomers **1** and **2**, they do not provide an explanation for the difference in their observed fluorescence behaviors. The only remaining possible explanation can be given by differences in the mechanism of energy dissipation, since the latter is a necessary prerequisite for red-shifted fluorescence.

Dissociation-Mediated TICT Formation in DMABME. According to our assignment of the IR spectra and the conclusion that both isomers exist but only the N-bonded isomer exhibits red-shifted fluorescence, energy is obviously more efficiently dissipated in the N-bonded isomer **1** than in the O-bonded isomer **2** of DMABME•$2H_2O$. Thus, the crucial question to answer now is how the molecules can lose their excess internal energy.

The IR and fluorescence depletion experiments described above were performed in the gas phase, and both DMABME•$2H_2O$ isomers were excited with the same laser wavelength, which was tuned to the red edge of the observed broad absorption spectrum.[21,18] Our calculations reveal that the CT state has a much larger oscillator strength than the LE state, and since both isomers are observed in the IR depletion spectrum, the laser energy must thus at least correspond to the higher vertical excitation energy of the CT state of the N-bonded isomer **1**, which is marked with vertical arrows in Figure 4. Photoexcitation at the same laser wavelength deposits into each isomer approximately the same amount of excess internal energy (~0.25 eV) with respect to the dissociation energy. It should be noted that on the basis of our calculation, a peak that is red-shifted by an additional ~0.4 eV should exist in the absorption spectrum of DMABME•$2H_2O$, corresponding to the CT state of the O-bonded isomer. However, this peak is not detectable employing one-color, resonant two-photon ionization (R2PI), since two photons of the required excitation energy are not sufficient for ionization. Possibly two-color R2PI, which is currently not available, would allow for its observation.

To return to the initial question, the only possibility for isolated DMABME•$2H_2O$ complexes to dissipate sufficient energy to allow them to emit red-shifted fluorescence in the gas phase is by fragmentation of the complex. Thus, since the N-bonded isomer **1** exhibits red-shifted fluorescence while the O-bonded isomer **2** does not, isomer **1** obviously dissociates while **2** stays stable during the experiment. The latter can then emit only regular fluorescence. In fact, our geometry optimizations of the TICT structures of **1** may provide a possible explanation of that observed phenomenon. As we have seen, the hydrogen bond between the amino nitrogen and the water dimer in isomer **1** breaks up immediately upon photoexcitation into the CT excited state, leaving a twisted CT monomer and a water dimer. During the geometry optimization, the water dimer is at first repelled and moves away but then rearranges and finally returns to the DMABME molecule, thereby switching from hydrogen bonding to ion solvation (see above). Experimentally, this quantum-chemical geometry optimization would correspond to nonphysical conditions, i.e., zero temperature and no kinetic energy of the nuclei (and thus, infinite time for the molecules to adopt equilibrium structures). In the experiment, the initial immediate repulsion between the amino nitrogen and the water proton leads to an instantaneous dissociation of the DMABME•$2H_2O$ complexes into isolated twisted DMABME and a water dimer. In the experiment, the remaining internal energy in the isolated DMABME after dissociation is not larger than 0.2 eV (Figure 5).

Calculation of the potential energy curve of the CT state of isolated DMABME produced by fragmentation of the water dimer along its TICT formation pathway revealed that this curve is practically identical to the ones of its complexes: it also exhibits a TICT minimum and a planar transition state with excitation energies of 3.37 and 3.82 eV, respectively (Table 3 and Figure 5). However, the remaining internal energy of ~0.2 eV in the fragmented DMABME molecule is not sufficient for rotation of the DMA group. As a consequence, the generated free DMABME molecules are trapped in a TICT structure, from which they can decay only via red-shifted fluorescence. Hence, excited N-bonded DMABME•$2H_2O$ complexes can act as precursors of twisted isolated DMABME molecules, which decay via red-shifted fluorescence.

In the experiment described above, the O-bonded isomer **2** is excited with the same laser wavelength as isomer **1**, and thus, enough energy should also be present to dissociate **2** and dissipate its energy, similar to the mechanism outlined for isomer **1**. However, the experiment did not reveal red-shifted fluorescence originating from isomer **2**. In this case, a rationalization

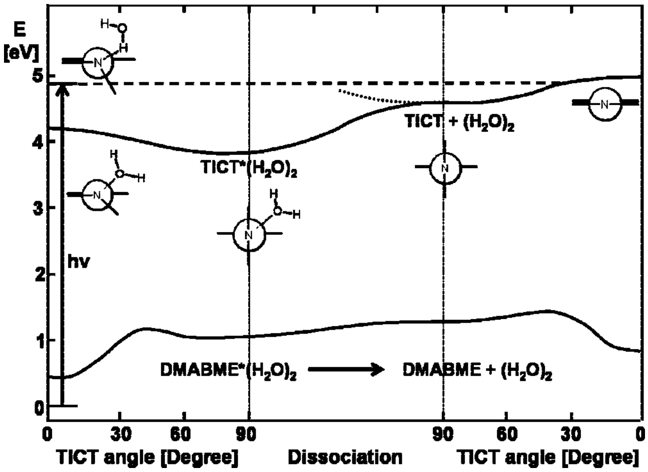

Figure 5. Potential energy surfaces of the CT states of the N-bonded isomer **1** along the TICT angle and dissociation pathway going from the 1:2 complexes to isolated DMABME and a free $(H_2O)_2$ dimer. The vertical energy of isomer **1** is given as dashed horizontal line, and the energy of the ground state equilibrium structure is set to zero.

is again provided by the geometry optimization of the TICT structures of **2**. In fact, it is seen in this isomer that the hydrogen bond between the carbonyl oxygen of the ester group and the water dimer does not break up but is instead substantially strengthened upon photoexcitation. Calculation of the strength of the hydrogen bond reveals that it amounts to ~0.7 eV in the CT state, which is unusually strong compared to typical hydrogen bonds exhibiting binding energies of ~0.1−0.25 eV. The equilibrium bond length of the DMABME·$2H_2O$ hydrogen bond is also shorter in the ICT state than in the electronic ground state (see above). This strongly enhanced hydrogen bond in the TICT structure of isomer **2** can simply be explained by the increase of negative partial charge on the carbonyl oxygen in the CT state and the resulting additional electrostatic attraction between the carbonyl oxygen and the hydrogen atom. Therefore, a direct dissociation of the water dimer in isomer **2** can be excluded.

Nevertheless, fragmentation is in principle energetically possible, since the internal energy upon photoexcitation is 0.25 eV above the dissociation threshold. It can occur when the internal energy is redistributed such that sufficient energy is channelled into the coordinate for dissociation of the intermolecular hydrogen bond. From a statistical point of view, though, it seems unlikely that almost the complete internal energy is employed to dissociate the water dimer from the DMABME. In fact, it has been demonstrated previously that photoexcitation with energies of 0.25 eV above the dissociation threshold can lead to delayed or metastable dissociation in much weaker van der Waals clusters.[33,34] However, quantitative conclusions about the details of the mechanism of internal vibrational energy redistribution (IVR) of isomer **2** are at present simply not feasible on the basis of our static calculations alone.

In brief, the photoinduced CT from the DMA group to the ester group in DMABME leads to a positively charged nitrogen atom and negatively charged carbonyl oxygen. This results in a strong electrostatic repulsion between the amino nitrogen and the bound hydrogen atom in the N-bonded isomer **1** of DMABME·$2H_2O$ but a strong electrostatic attraction between the carbonyl oxygen and the water dimer in isomer **2** that leads to an unusually strong hydrogen bond. As a consequence, the former isomer **1** dissociates instantaneously while the dissociation of the latter is strongly suppressed, if it occurs at all. Since dissociation is required in order to dissipate energy to allow the red-shifted fluorescence to occur in the gas phase, this difference provides an explanation for why only the N-bonded isomer is found experimentally to exhibit red-shifted fluorescence.

The depicted mechanism is at first glance in contradiction to the results of a recent investigation of hydrogen-bonded phenol complexes, where it has been demonstrated that the efficiency of hydrogen-bond dissociation is independent of the hydrogen-bond strength.[35] However, in that experiment, the OH stretch vibration of phenol was selectively excited with IR light, and as a consequence, the internal energy was from the start directly pumped into the hydrogen-bond dissociation coordinate. Furthermore, the investigated hydrogen bonds (with energies of 0.25 eV at most) are substantially weaker than the one in the TICT state of isomer **2** (with an energy of 0.7 eV). Therefore, on the basis of the arguments given above, one cannot a priori expect a photoexcited O-bonded DMABME·$2H_2O$ complex to dissociate into DMABME and a water dimer as a result of efficient IVR, even when the energy present in the complex is in principle enough for hydrogen-bond dissociation.

To further clarify the suggested mechanism of red-shifted fluorescence in DMABME·$2H_2O$ complexes, we suggest IR and fluorescence depletion experiments in which the O-isomer **2** is excited with its individual vertical excitation energy of 4.41 eV (obtained at the RI-CC2 level), which is about 0.4 eV lower than that of isomer **1**. According to our calculations, the binding energy of isomer **1** is ~0.7 eV in the excited CT state for the TICT equilibrium structure (Figure 4). However, the Franck−Condon point of isomer **1** is only 0.5 eV above the TICT minimum, i.e., the internal vibrational energy present is not enough for dissociation to occur, and thus, this energy dissipation channel is closed. In that experiment, one should hence not be able to observe red-shifted fluorescence at all, since the excited O-bonded isomers should exhibit only regular fluorescence and the N-bonded isomers are not excited because the photon energy is too low.

A final question to address is why one hydrogen-bonded water molecule at the amino nitrogen is not sufficient to induce red-shifted fluorescence in DMABME·H_2O.[19] Indeed, such an isomer exists and possesses a structure essentially identical to that of **1**; not surprisingly, a barrierless decay into a TICT state is possible, and thus, red-shifted fluorescence could in principle be observed. In the IR ion-depletion experiment, however, only one isomer is observed for the DMABME·H_2O clusters. Our calculations at the MP2/cc-pVTZ level reveal that the O-bonded isomer of DMABME·H_2O (analogous to **2**) is thermodynamically more stable by 0.5 kcal/mol than the N-bonded one. The computed IR spectra of these isomers confirm that the one present in the molecular beam experiment is the O-bonded isomer. Thus, for the same reasons as for isomer **2** of DMABME·$2H_2O$, red-shifted fluorescence is not observed for the O-bonded DMABME·O isomer.

Summary and Conclusions

In this work, high-level ab initio calculations have been used to assign the vibrational bands of experimental IR and fluores-

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cence depletion spectra of DMABME$\cdot$2H_2O to two different but isoenergetic isomers: an O-bonded isomer, in which a water dimer is bound to the carbonyl oxygen of the ester function, and an N-bonded isomer, in which the water dimer is hydrogen-bonded to the nitrogen of the DMA group. Moreover, our assignment proves that only the N-bonded isomer results in unusual red-shifted fluorescence in the gas phase. This finding is surprising, since ICT formation can be expected to be energetically less favorable in the N-bonded isomer than in the O-bonded one because hydrogen bonding of the DMA nitrogen increases the ionization potential, i.e., destabilizes ICT, while hydrogen bonding of the ester function increases the electron affinity, i.e. stabilizes ICT. Indeed, this is corroborated by the vertical excitation energies of the two isomers of DMABME$\cdot$2H_2O.

To understand this surprising behavior of the two isomers, the potential energy surfaces of the two DMABME$\cdot$2H_2O isomers as well as of the isolated DMABME molecule were studied along the TICT formation coordinate, represented by the dihedral angle between the DMA group and the phenyl ring. Astonishingly, all of the molecules possess TICT equilibrium structures on the CT excited-state surface. In addition, barrierless formation of the TICT state is in principle possible for all of them. However, the experiment was performed on isolated complexes in the gas phase, and under these conditions, excited molecules cannot easily dissipate excess internal energy and localize in equilibrium structures, specifically the TICT geometry in this case. The only possible way to lose excess internal energy radiationlessly is by fragmentation. Indeed, this is energetically feasible for both isomers in the conducted experiments. However, upon photoexcitation into the CT state, the hydrogen bond immediately breaks up in the N-bonded isomer as a result of strong electrostatic repulsion between the now positively charged amino nitrogen and the hydrogen atom. In the O-bonded isomer, the opposite effect is observed: the hydrogen bond is substantially strengthened because of the increased negative charge on the carbonyl oxygen, leading to an unusually strong hydrogen bond that suppresses dissociation of the complex. The isolated DMABME molecules stemming from the dissociated N-bonded DMABME$\cdot$2H_2O complexes can finally form stable TICT equilibrium structures on the CT surface and eventually decay via red-shifted fluorescence. In the end, it is the detailed electronic structure of the CT state that explains the different fluorescence behaviors of the N-bonded and O-bonded DMABME$\cdot$2H_2O complexes.

The example of DMABME$\cdot$2H_2O demonstrates an important but often forgotten property of solvent molecules: their ability to serve as energy acceptors allowing chemical reactions to occur in specific ways along well-defined minimum-energy pathways. Moreover, in our example, even the specific binding pattern of the water dimer to DMABME determines the fate of the photoexcited species. Whether the carbonyl oxygen or the amino nitrogen is hydrogen-bonded steers the photochemistry toward either regular or red-shifted fluorescence. Since hydrogen bonds are ubiquitous in nature, we expect the identified mechanism of energy dissipation via hydrogen-bond fission to be not a scarce peculiarity but rather of general importance for many chemical and biological processes. Our findings underline once more the importance of specific solvation models derived from sophisticated studies combining cluster spectroscopy and ab initio calculations.

Acknowledgment. A.D. acknowledges financial support by the Deutsche Forschungsgemeinschaft as an Emmy Noether Fellow. M.Z. is grateful to Dr. Pedro Salvador for valuable references on BSSE. Computer time was generously provided by the Center of Scientific Computing of the University of Frankfurt.

Supporting Information Available: Benchmarking of the calculations of the IR spectra of the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

JA800528P