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# Energetics of the Gas Phase Hydrates of *trans*-Formanilide: A Microscopic Approach to the Hydration Sites of the Peptide Bond

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The energy of binding a water molecule to two H-bonded sites of *trans-N*-phenyl formamide (formanilide), an amide molecule that mimics the planar −NH−CO− peptide bond, has been measured in the gas-phase and calculated by an ab initio study. For the first time, the $D_0$ dissociation energy of two 1:1 complexes, simultaneously observed in a supersonic expansion, is measured experimentally. They are found to be very similar. At the CO site, the water molecule acts as a proton donor and the H-bond has a energy of 5.40 ± 0.28 kcal/mol. At the NH site, the water acts as an acceptor and the binding energy is 5.65 ± 0.30 kcal/mol. Comparison of IR shifts with binding energies shows that they do not always correlate when the donor groups are different.

## 1. Introduction

The use of supersonic expansion, sometimes coupled to desorption systems, has enabled spectroscopists to study the structures and energetics of small biomolecules isolated in the gas phase[1−8] as well as their van der Waals complexes with various solvents, in particular water.[9,10] Model molecules have also been used to explore molecular interactions involving the key subunits of large biomolecules,[10−23] for example, aromatic residues or the peptide bond in proteins.[15−23] Recently, several aromatic molecules (benzene, phenol, and indole) have been used to mimic the solvation properties of the residues of the three aromatic amino acids (phenylalanine, tyrosine, and tryptophan). Their cooling in the free jet expansion and the stabilization of successively solvated molecular complexes has allowed molecule-solvent interactions to be studied in a controlled manner. Binding energy measurements, in particular, have provided a key set of data for precise modeling of the protein interacting with its solvent environment.[18−22]

The aim of the present work is to report binding energy measurements of a water molecule to two of the alternative amide sites in *trans-N*-phenyl formamide (formanilide), a molecule that mimics the planar −NH−CO− peptide bond. Two distinct UV spectral signatures have been detected recently in the R2PI spectra of the 1:1 complex of *trans*-formanilide with water.[15,16] Their independent existence was initially confirmed by means of UV hole burning spectroscopy[15] and subsequently through infrared ion-dip measurements.[17] An unambiguous assignment was provided by the comparison between the experimental rotational contours and simulations deduced from ab initio calculations.[15] In complex I, formanilide acts as a proton donor, via its NH site, to the oxygen atom of water; in complex II, the water acts the proton donor to the oxygen atom of formanilide (see Figure 1).

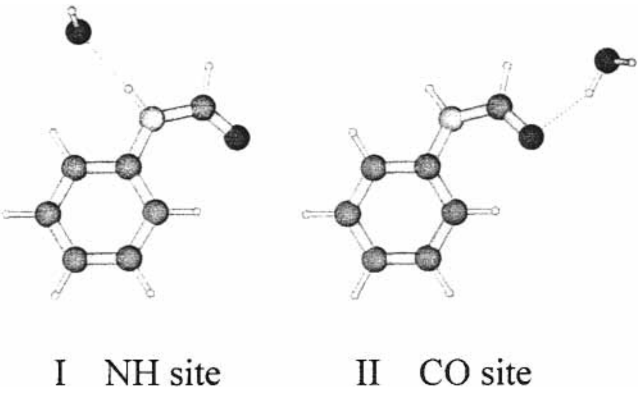

**Figure 1.** ab initio geometries of the two 1:1 hydrates of *trans*-formanilide, predicted by MP2/6-311+G** calculations.

Using a technique based on the fragmentation of these complexes following two-color photoionization, already successfully applied to other systems,[18,20,22] the binding energies of these two complexes of formanilide with water have been measured. The results obtained are discussed and compared to the energies computed ab initio, as well as to those of other similar hydrogen bonds recently studied experimentally.

## 2. Methodology

The experimental setup, already described elsewhere,[18,20,22] combined a supersonic beam, tunable lasers, and a reflectron-type TOF mass spectrometer. Neutral complexes of formanilide with water were formed in a pulsed expansion generated by a heated pulsed valve (General Valve) of 0.4 mm diameter operating at a frequency of 10 Hz. Formanilide and water were vaporized in temperature-controlled reservoirs (100 and 0 °C, respectively) located upstream of the valve. Helium was used as the carrier gas at backing pressures of 2−3 bar. The jet was skimmed before entering the mass spectrometer chamber (pressure less than $10^{-6}$ Torr during operation) parallel to the spectrometer axis.

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The complexes were initially excited by the output of an excimer-pumped (Lambda Physik EMG 201) dye laser (Lambda Physik FL 3002) and then ionized using the frequency-doubled beam of a visible (640−470 nm) optical parametric oscillator (YAG-pumped VEGA, 7 ns pulse duration, 1 cm$^{-1}$ spectral width, BMI Corp.). The two pulsed laser beams were electronically synchronized in order to cross simultaneously the pulsed molecular beam in the interaction chamber of the mass spectrometer. The ions formed were extracted, accelerated in the spectrometer source and deflected from the jet axis in order to separate them from the neutral beam as well as to send them to the electrostatic mirror entrance. After reflection and drift in a second field-free region, ions were detected by a microchannel plate detector. The mass spectra were averaged on a numeric oscilloscope (LeCroy 9350) and then processed with a LabView-based computer program. The fragmentation ratio was carefully measured, by integrating the parent and daughter ion signals and subtracting the signal baseline. Laser intensities were kept low enough to have negligible one-color $\nu_1 + \nu_1$ R2PI signal as well as to minimize ion photoexcitation (by either $\nu_1$ or $\nu_2$) after ionization.

Energetic and structural properties of *trans*-formanilide$(H_2O)_1$ clusters were also investigated by performing a series of ab initio calculations using Gaussian 94.[24] Full ab initio optimizations were carried out at the HF/6-31G*, B3LYP/6-31+G* and MP2/6-311+G** levels of theory. Basis set superposition errors (BSSE) were calculated to include the fragment relaxation energy

$$E_{\mathrm{BSSE}} = E^{\alpha}_{\mathrm{AB}}(\mathrm{A}) - E^{\alpha|\beta}_{\mathrm{AB}}(\mathrm{A}) + E^{\beta}_{\mathrm{AB}}(\mathrm{B}) - E^{\alpha|\beta}_{\mathrm{AB}}(\mathrm{B}) \qquad (1)$$

where $E^{\alpha|\beta}_{\mathrm{AB}}(\mathrm{A})$ is the electronic energy of fragment A in the geometry of the complex AB with the complex basis set $\alpha \cup \beta$. Force fields were also calculated at the HF/6-31G* and B3LYP/6-31+G* levels to obtain vibrational frequencies and zero-point energy corrections.

## 3. Experimental Results

**3.1. Principle of the Binding Energy Measurements.** The principle behind the binding energy measurements, already given in detail elsewhere,[18,20] rests on the possibility of accessing the vibrational predissociation threshold in the ionic complex. The complexes (M−S) are photoionized selectively (M$^+$−S) in a two-color resonant two-photon ionization process. The second color is then scanned in the dissociation region of the complex until fragmentation into M$^+$ + S can be monitored in the time-of-flight mass spectrometer. The binding energy $D_0$ is deduced from the difference between the appearance potential AP of the M$^+$ ion and the ionization energy IP of the molecule M:

$$D_0 = \mathrm{AP}\,(\mathrm{M}^+{-}\mathrm{S} \rightarrow \mathrm{M}^+ + \mathrm{S}) - \mathrm{IP}\,(\mathrm{M}) \qquad (2)$$

The experiment can be conducted only for those systems in which the Franck−Condon distribution of ion vibrational levels encompasses the fragmentation limit. Keeping this in mind, one-color experiments on aromatic molecules are useful to test the feasibility of the measurement. Owing to the energy of the $S_1$ state of these species, the two-photon energy of the 1C R2PI process usually overcomes the upper limits of the Franck−Condon region in the ion, so that one-color experiments produce all the vibrational levels accessible in the ion.

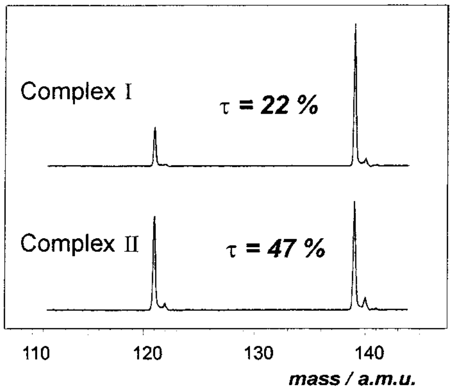

**Figure 2.** Time-of-flight mass spectra obtained after one-color R2PI selective excitation of the complexes I (NH site) and II (CO site) of *trans*-formanalide with water, showing the parent (FA$^+$−water: $m$ = 139 amu) and daughter (FA$^+$: $m$ = 121 amu) ions. Different fragmentation ratios ($\tau$) are observed (see text).

Previous experiments on several hydrates of aromatic molecules have shown that significant intermolecular geometry changes between the neutral $S_1$ state and the ion shift the Franck−Condon accessible region reached in the ion toward high energies.[18,20,22] In particular, when the aromatic molecule is a proton donor (e.g., phenol), the geometry change between the neutral and the ion is essentially a simple shrinkage of the intermolecular bond, and the fragmentation yield in the one-color experiment is small (10%). However, when the aromatic molecule is a proton acceptor (e.g., benzene), the ionic and neutral structures are so different that the majority of the cluster-ions formed are dissociative and their fragmentation yield can reach large values (85% for benzene−water). The main reason for this behavior is the additional charge-permanent dipole interaction in the ion, compared to the neutral: (the charge is mainly localized on the benzene ring and therefore the electric field is directed radially from the ring). The extra interaction will stabilize or destabilize the ion depending on the orientation of the water molecule relative to the electric field. In this respect, a proton accepting water molecule will give rise to stabilization whereas a proton donor molecule will be destabilized. Despite its qualitative nature, such an argument can be used as a clue to the gross structure of the complexes. In summary, the information carried in one-color R2PI spectra helps to establish the feasibility of two-color binding energy measurements.

**3.2. One-Color Mass Spectra.** The UV and IR spectroscopy of the two 1:1 complexes of *trans*-formanalide with water has been recently reported by Simons and co-workers[15] and by Robertson.[17] Mass spectra of these complexes have been obtained by pumping their $S_1 \leftarrow S_0$ origin bands, which are displaced −219 cm$^{-1}$ and +113 cm$^{-1}$ from the corresponding monomer origin. As shown in Figure 2, very different fragmentation ratios are measured for the two complexes (22% and 47% respectively). Given the considerations discussed above, these fragmentation ratios suggest that the water molecule acts as the proton acceptor in the red-shifted complex, and as the donor in the blue-shifted species. This fragmentation behavior is consistent, therefore, with the known structures established through rotational band contour analysis[15] and infrared spectral measurements.[17]

**3.3. Photoionization Threshold of *trans*-Formanilide.** The photoionization threshold of the trans isomer of the formanilide molecule was determined by two-color resonant two-photon ionization, with the first photon tuned to the $S_1 \leftarrow S_0$ origin transition, as determined in refs 15 and 16. The onset for ion signal in the 2C-R2PI experiment was found to be sharp, indicating its adiabatic character, i.e., corresponding to a transition toward the vibrationless level of the ion. The ionization potential, corrected for the effect of electric field ionization,[25]

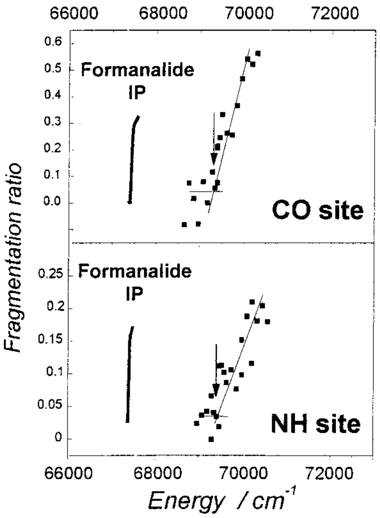

**Figure 3.** Fragmentation efficiencies of the two photoionized hydrates of *trans*-FA as a function of the total photon energy in the 2C-R2PI experiment. The adiabatic 2C-R2PI sharp ionization threshold of *trans*-FA is also given as a reference. The energy scale is corrected for the electric field ionization.

was found to be 67430 ± 20 $cm^{-1}$ (8.360 ± 0.002 eV). Additional steplike features have been observed at higher energies, indicating a significant geometry change between neutral and ion molecular species. This probably explains the significant difference between the present ionization potential value and that obtained from a previous photoelectron experiment (8.60 eV),[26] in which the vibrational structure was not resolved.

**3.4. Binding Energy Measurement.** Figure 3 shows the fragmentation efficiency of the $FA^+(H_2O)$ complex ions, formed by photoionization of both complexes I and II. In each case, the fragmentation ratio was found to increase near linearly from a well-defined onset. The appearance energy has been taken as the intersection of the extrapolated, linearly increasing, ionization signal with the constant background signal recorded below threshold (which is assigned to undesired three-photon processes). The ionization energy of the bare *trans*-formanilide molecule, measured under the same experimental conditions, in particular with the same extraction electric field, allowed a determination of the ground-state binding energies of the two complexes. The best values were 245 ± 13 meV (5.65 kcal/mol) for complex I (NH site) and 234 ± 12 meV (5.40 kcal/mol) for complex II (CO site). These values result from an average over several fragmentation spectra, illustrated by those presented in Figure 3. When these data are combined with the positions of the complex $S_1 \leftarrow S_0$ origins, the $D_0$ binding energies in the $S_1$ state may also be calculated: 272 ± 13 meV (6.27 ± 0.30 kcal/mol) for complex I (NH site) and 220 ± 12 meV (5.08 ± 0.30 kcal/mol) for complex II (CO site).

**3.5. Calculations.** $D_0$ and $D_e$ binding energies, calculated at the HF/6-31G*, B3LYP/6-31+G* and MP2/6-311+G** levels, are given in Table 1. When BSSE is ignored, the $D_0$ binding energies are ca. 5 kcal $mol^{-1}$ with complex I (NH site) being slightly preferred, in reasonable agreement with experiment even for the most primitive calculation (HF/6-31G*). When BSSE is included, however, the $D_0$ energies are underestimated by a considerable margin, even at the highest level of present theory (MP2/6-311+G**). Clearly the 6-311+G** basis set is not adequate for convergence of the BSSE corrections. A recent study found that basis sets larger than cc-pVTZ are required for BSSE to become systematically small.[27] For complexes involving molecules the size of formanilide, such calculations present major practical difficulties, which further highlights the need for reliable experimental measurements such as those presented here.

**TABLE 1: Experimental Binding Energy $D_0$ Compared to the ab Initio Calculations ($D_0$ and Well Depths $D_e$) for the Two Neutral Complexes of *trans*-Formanilide with Water**

| FA-$H_2O$ | units | $D_e$ | $D_0$[a] |
|---|---|---|---|
| site NH (complex I) | | | |
| experimental $S_1$ | meV | | 272 ± 13 |
| | kcal $mol^{-1}$ | | 6.27 ± 0.30 |
| experimental $S_0$ | meV | | 245 ± 13 |
| | kcal $mol^{-1}$ | [7.0][b] | 5.65 ± 0.30 |
| HF/6-31G* | kcal $mol^{-1}$ | 6.65 | 5.36 |
| HF/6-31G* (with BSSE) | kcal $mol^{-1}$ | 5.54 | 4.25 |
| B3LYP/6-31+G* | kcal $mol^{-1}$ | 6.56 | 5.20 |
| B3LYP/6-31+G* (with BSSE) | kcal $mol^{-1}$ | 5.42 | 4.05 |
| MP2/6-311+G**[a] | kcal $mol^{-1}$ | 7.64 | 6.28 |
| MP2/6-311+G** (with BSSE) | kcal $mol^{-1}$ | 5.41 | 4.05 |
| site CO (complex II) | | | |
| experimental $S_1$ | meV | | 220 ± 12 |
| | kcal $mol^{-1}$ | | 5.08 ± 0.30 |
| experimental $S_0$ | meV | | 234 ± 12 |
| | kcal $mol^{-1}$ | [7.2][b] | 5.40 ± 0.28 |
| HF/6-31G* | kcal $mol^{-1}$ | 6.48 | 4.68 |
| HF/6-31G* (with BSSE) | kcal $mol^{-1}$ | 4.79 | 2.99 |
| B3LYP/6-31+G* | kcal $mol^{-1}$ | 6.73 | 4.93 |
| B3LYP/6-31+G* (with BSSE) | kcal $mol^{-1}$ | 6.09 | 4.28 |
| MP2/6-311+G** | kcal $mol^{-1}$ | 6.82 | 5.02 |
| MP2/6-311+G** (with BSSE) | kcal $mol^{-1}$ | 5.24 | 3.44 |

[a] Ab initio values for $D_0$ include scaled zero point corrections (factor 0.90 for HF/6-31G*, 0.97 for B3LYP/6-31+G*). For MP2 energies, the B3LYP correction was applied. [b] On the basis of the experimental $D_0$ values, combined with the B3LYP zero-point corrections.

The HF and B3LYP calculations are in good agreement concerning the zero point corrections (1.29 and 1.36 kcal/mol for complex I, and 1.80 and 1.80 kcal/mol for complex II). Combining them with the experimental $D_0$ values leads to an estimate of the well depths, $D_e \approx 7.2$ kcal/mol for complex I and ≈ 7.0 kcal/mol for complex II. The slight energetic preference for complex I reflected in the experimental $D_0$ values is reversed for $D_e$.

## 4. Discussion

The two hydrogen-bonded hydrates of trans formanilide are observed simultaneously in the expansion, with similar relative abundances. Only a few similar situations with well-characterized complexes have been reported so far; for instance the two 1:1 hydrates of 2-phenyl ethanol,[12,28] or the three conformers of the *para*-chloro-fluorobenzene-methanol complex.[29] It suggests a priori that the two complexes have very similar binding energies. The present result, indicating equal binding energies within the experimental precision, pleasingly confirms this intuitive guess.

As a comparison, the indole−water complex also has two possible structures, but the $\pi$-type hydrogen-bonded complex in which the water is proton donor to the aromatic rings of indole is *not* observed experimentally.[22,23] Its binding energy, deduced by comparison with the $\pi$-type hydrogen-bonded complex of 1-methylindole with water, is estimated to be 0.7 kcal/mol less than that of the NH-bonded complex which is observed. The barrier to isomerization toward the absolute minimum was calculated to 0.63 kcal/mol.[22]

The present binding energies can be usefully compared with those already measured for similar systems as well as with the other indicators of the H bond strength like the IR data of the chromophores engaged in the H bond, see Table 2.

**TABLE 2: Ab Initio and Experimental Characteristics of the Hydrogen Bonds A−H···B of Formanalide, Phenol and Indole with Water (Figures in Parentheses Are the Shift Relative to the Unsolvated Molecule)**

| | units | formanilide (I) | formanilide (II) | phenol | indole |
|---|---|---|---|---|---|
| AH···B | | $NH\cdots O_{water}$ | $OH_{water}\cdots O$ | $OH\cdots O_{water}$ | $NH\cdots O_{water}$ |
| $D_0$ | | | | | |
| experiment | kcal mol$^{-1}$ | 5.65 | 5.40 | 5.60[a] | 4.84[b] |
| B3LYP/6-31+G* | kcal mol$^{-1}$ | 4.05 | 4.28 | 4.46 | 3.36[c] |
| $\nu_{\text{AH stretch}}$ | | | | | |
| experiment | cm$^{-1}$ | 3402 (−61)[d] | 3527 (−130)[d] | 3524 (−133)[e] | 3436 (−89)[c] |
| B3LYP/6-31+G* | cm$^{-1}$ | 3509 (−84) | 3584 (−151) | 3571 (−180) | 3558 (−109)[c] |
| $r_{AH}$ | | | | | |
| MP2/6-311+G** | pm | 101.60 (+0.46) | 96.85 (+0.90) | | |
| B3LYP/6-31+G* | pm | 101.88 (+0.57) | 97.97 (+1.08) | 97.98 (+0.99) | 101.6 (+0.7)[c] |
| $R_{H\cdots B}$ | | | | | |
| MP2/6-311+G** | pm | 199 | 193 | | |
| B3LYP/6-31+G* | pm | 199 | 189 | 186 | 197[c] |

[a] Reference 18. [b] Reference 22. [c] Reference 23. [d] Reference 17. [e] Reference 33.

The experimental binding energy of complex II (5.40 kcal/mol) is very similar to that of other complexes containing an $OH\cdots O$ bond, namely, phenol−water ($OH\cdots O_{water}$, 5.60 kcal/mol)[18] and 1-naphthol−water ($OH\cdots O_{water}$, 5.82 kcal/mol).[30] Presumably the fact that water is a weaker H-bond donor than phenol (it is at least less acidic, $\Delta H_{acid.} = 391$ vs 350 kcal/mol),[31] is balanced by the amide being a stronger acceptor (the proton affinity of *N*-methylformamide is 204 kcal/mol, compared to water 165 kcal/mol for water).[32] The binding energies of these $OH\cdots O$ complexes happen to mirror quite well the shifts in their donor OH stretch frequencies: −130, −133, and −148 cm$^{-1}$ respectively.[17,33,34]

The correlation breaks down when complex I ($NH\cdots O_{water}$, 5.65 kcal/mol) and indole−water ($NH\cdots O_{water}$, 4.84 kcal/mol)[22] are considered, both of which have water as the H-bond acceptor. First, the shifts in their donor NH stretch modes are considerably less than in the $OH\cdots O$ complexes, reflecting the different behavior of NH and OH donors. Second, the formanilide complex exhibits a shift (−61 cm$^{-1}$)[17] which is less than the shift for indole (−89 cm$^{-1}$),[23] although its binding energy is greater. Apparently, the aromatic NH of indole also behaves differently from the amide NH. This may be related in part to differing proton-transfer acidities (indole 350 kcal/mol, *N*-methylformamide 360 kcal/mol);[29] as the $A^-\cdots HB^+$ state increases in energy, it has less effect on the $A-H\cdots B$ potential in the region of the lowest vibrational levels. In any case, it appears that a direct correlation of IR shifts with binding energies may be valid only if the donor group remains the same or very similar. A similar conclusion was drawn from the comparison between experimental IR data and calculated binding energies by Maes and co-workers.[35,36]

In connection to this, we note that, although the measured binding energies are dominated by the H-bond interaction, the contribution of other smaller interactions are suggested by examination of the MP2/6-311+G** structures. In FA−water (II), the $OH_{water}\cdots O_{amide}$ H-bond is distorted 25° from linearity, so that the $O_{water}\cdots HC_{amide}$ distance is only 271 pm, suggesting the influence of a dispersive $CH\cdots O$ interaction. In FA−water (I) the oxygen of water is situated just 273 pm from the nearest ring hydrogen and the orientation of the water molecule is favorable for such an interaction. Analogous structures in phenol−water, 1-naphthol−water and indole−water imply that they too benefit from some additional stabilization due to $CH\cdots O$ interactions, although the effect might be weaker in the case of indole because of the location of the nitrogen atom in a five-membered ring.

Two aspects of the ab initio calculations are worth noting in this overall context. First, while the IR shift does not correlate with the binding energy for all the H-bonded complexes (determined experimentally or computationally), it does correlate very well with the extension of the A−H bond, which reflects the change in the A−H *potential*. Second, when the amide NH is bound to water it is not only the N−H bond length that changes (MP2: +0.46 pm) − the entire amide group is affected. The amide C−N bond contracts (MP2: −0.57 pm) and the C=O bond stretches (MP2: +0.34 pm), reflecting stabilization of the $RHN^+=CH-O^-$ resonance form. The same is true of the C=O bound complex of formanilide.

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