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**S<sub>0</sub>, S<sub>1</sub>, and Ion I<sub>0</sub> Binding Energies of the p-Methoxyphenethylamine(H<sub>2</sub>O)<sub>1–4</sub> Complexes****Jose A. Fernández, Iñigo Unamuno, Asier Longarte, and Fernando Castaño\****Departamento de Química-Física, Facultad de Ciencias, Universidad del País Vasco,  
Apart. 644, 48080 Bilbao, Spain**Received: July 31, 2000; In Final Form: October 19, 2000*

Binding or dissociation energies of the ground state, S<sub>0</sub>, the first electronic excited state, S<sub>1</sub>, and the ion ground state, I<sub>0</sub>, of the p-methoxyphenethylamine(H<sub>2</sub>O)<sub>1–4</sub> complexes, referred to henceforth as either MPEA(H<sub>2</sub>O)<sub>1–4</sub> or by their stoichiometric ratios 1:1–4, have been analyzed by threshold ion fragmentation. MPEA(H<sub>2</sub>O)<sub>1–4</sub> complexes were prepared by the supersonic expansion of premixed samples containing appropriate amounts of MPEA and water molecules into carrier gas He. A number of isomers, with characteristic 0<sub>0</sub><sup>0</sup> transition energies, have been identified: two for MPEA(H<sub>2</sub>O)<sub>1</sub> at 35 676 and 35 689 cm<sup>−1</sup>, one for MPEA(H<sub>2</sub>O)<sub>2</sub> at 35 687, one for MPEA(H<sub>2</sub>O)<sub>3</sub> at 35 571 and two for MPEA(H<sub>2</sub>O)<sub>4</sub> at 35 419 and 35 422 cm<sup>−1</sup> respectively. The ionization energy and fragmentation thresholds, the latter defined as the onset energy of the process MPEA(H<sub>2</sub>O)<sub>n</sub><sup>\*</sup> + *hν* → MPEA(H<sub>2</sub>O)<sub>n−1</sub><sup>+</sup> + H<sub>2</sub>O, have been determined, and from them the dissociation energies for the set of MPEA(H<sub>2</sub>O)<sub>1–4</sub> isomers in their ground state, first electronic excited states, and ion ground states were readily obtained. The set of values are compared with those computed for the water association complexes.

**I. Introduction**

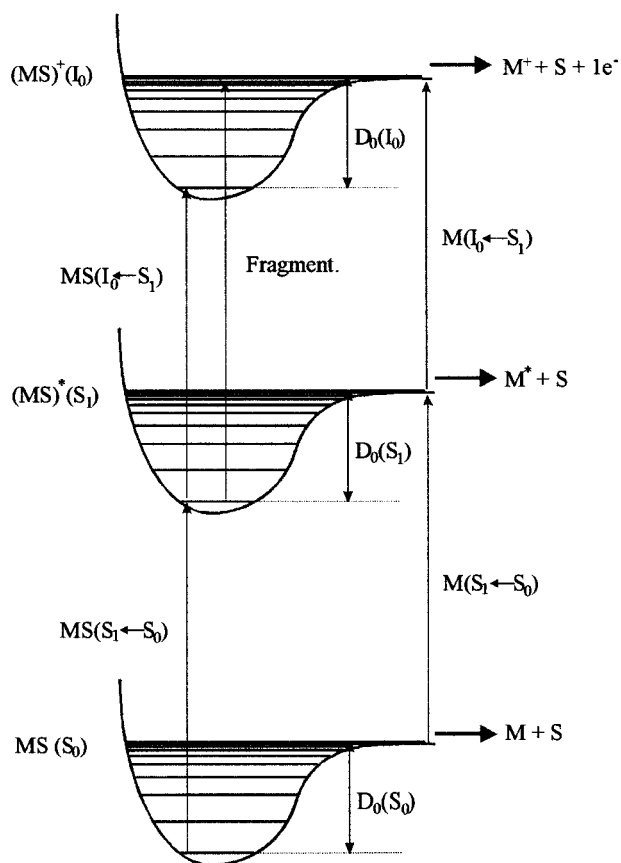
Gas-phase spectroscopy studies of chemical size hydrogen bond (H-bond) complexes have developed rapidly in the past few years; as a consequence, a substantial amount of information has been accumulated on the solvation of ground- and excited-state neutrals,<sup>1</sup> radicals,<sup>2</sup> and ions.<sup>3</sup> Structural information drawn from these studies includes<sup>4</sup> the knowledge of the solvated geometries, 0<sub>0</sub><sup>0</sup> transition energies, relative solvation site preferences, ground and excited-state binding energies, complexes stiffness or floppiness, characteristic intermolecular vibrations, etc., and this body of knowledge constitutes a firm basis for the modeling of large molecules with intramolecular H-bond interactions. Among the collected information, the elusive binding energy is claimed to be, after geometry, the second most significant parameter to aid in the quantitative understanding of the H-bond intermolecular forces and the starting point to work out synthetic potentials to describe the solute–solvent interactions.<sup>5</sup> A detailed knowledge of the binding energies for a variety of complexes would allow one to optimize the computational procedures used to describe the H-bond properties. Once the binding energies of a complex are known, the computation by standard quantum chemical methods, such as HF, MP2, DFT, CASSCF, etc., with appropriate basis set would permit the finding of the basic requirements to describe the structures and properties with the desirable accuracy. Unfortu-

nately, only a few binding energies of weakly bound complexes have been reported so far, largely because of experimental difficulties.<sup>5</sup>

Binding energies (D<sub>0</sub>) of complexes are experimentally determined by a number of methods: extension of the diatomic RKR inversion to intermolecular complex progressions;<sup>6</sup> vibrational predissociation to obtain the upper limit and the less certain lower limit on the S<sub>0</sub> and S<sub>1</sub> states; stimulated emission pumping R2PI,<sup>7</sup> and the threshold ion fragmentation.<sup>8</sup> Most weakly bound complexes show few progressions in the intermolecular vibrations, and their vibrational predissociation, when observed, yields only upper limits, so that the scope of the first two methods is limited. Stimulated emission pumping R2PI applies essentially to the complex ground state, and the threshold ion fragmentation requires a good coupling between the complex intra- and intermolecular modes to be applied successfully.

In the present paper, we have applied the threshold ion fragmentation method to determine the dissociation energies of MPEA(H<sub>2</sub>O)<sub>1–4</sub> conformers (also referred to hereafter by their stoichiometry, i.e., as 1:n). MPEA is a member of the phenethylamine family, known to be an efficient neurotransmitter.<sup>9–12</sup> In a previous paper<sup>13</sup> a battery of experimental techniques, including laser induced fluorescence, LIF, resonance enhanced multiphoton ionization, REMPI, two-color, REMPI referred to here as R2PI, fluorescence dispersed emission and ionization energy thresholds, IE, in conjunction with ab initio calculations at the B3LYP/6-31+G\* and the B3LYP/6-311+G\* levels were used to identify the 0<sub>0</sub><sup>0</sup> transitions of the MPEA seven experimental conformers. The seven conformers are formed by internal

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**Figure 1.** Schematic representation of the one-dimensional potential energy for the ground, first electronic excited states and ion ground state of a weakly bound isomer, MS. Dissociation or binding energies are indicated by  $D_0$  followed by the state considered and transitions as MS (final  $\leftarrow$  initial state) and M (final  $\leftarrow$  initial state), respectively.

rotation around the  $C_\alpha-C_\beta$  and  $C_\alpha-NH_2$  bonds. From the chemical viewpoint, the conformers are interesting examples of species stabilized by intramolecular interactions, i.e., between the  $\pi$ -system electronic cloud and the amino group. Interactions of this type are found in many biomolecules and are thought, together with the hydrogen bond, to play a central role in the formation of the secondary and tertiary structure of large biological molecules, including proteins and DNA. In the ionization process extensive fragmentation from  $MPEA(H_2O)_n$  complexes were detected in the  $MPEA(H_2O)_{n-1}$  mass-channel and, as will be discussed later, the addition of one water molecule to MPEA results in a severe reduction of the number of isomers from seven to two, revealing that the solvent preferably stabilizes some conformers. Furthermore, the addition of successive water molecules has specific effects noticeably observed by the number of isomers: two for the 1:1 complex, one for the 1:2 and 1:3 and two for the 1:4. The behavior of the binding energies with the addition of solvent molecules and the comparison with reported aromatic/water and water/water complexes prompts us to suggest structures for all of the conformers studied.

## II. Method and Experimental Set-up

The method used in this work is based on the knowledge of the bare molecule and the ionization energy differences of the isomers and is referred to as threshold ion fragmentation<sup>14,15</sup> (Figure 1). In Figure 1 the one-dimensional potential energy curves of the ground, first electronic excited, and the ion ground

states are schematically shown, as well as the correlated dissociation solute states, M,  $M^*$ , and  $M^+$  and the solvent, S. The dissociation energies of the three states considered are related to the following measured ionization energies (see Figure 1 for nomenclature):

$$D_0(I_0) = MS(\text{fragment}) - M(I_0 \leftarrow S_1) \quad (1)$$

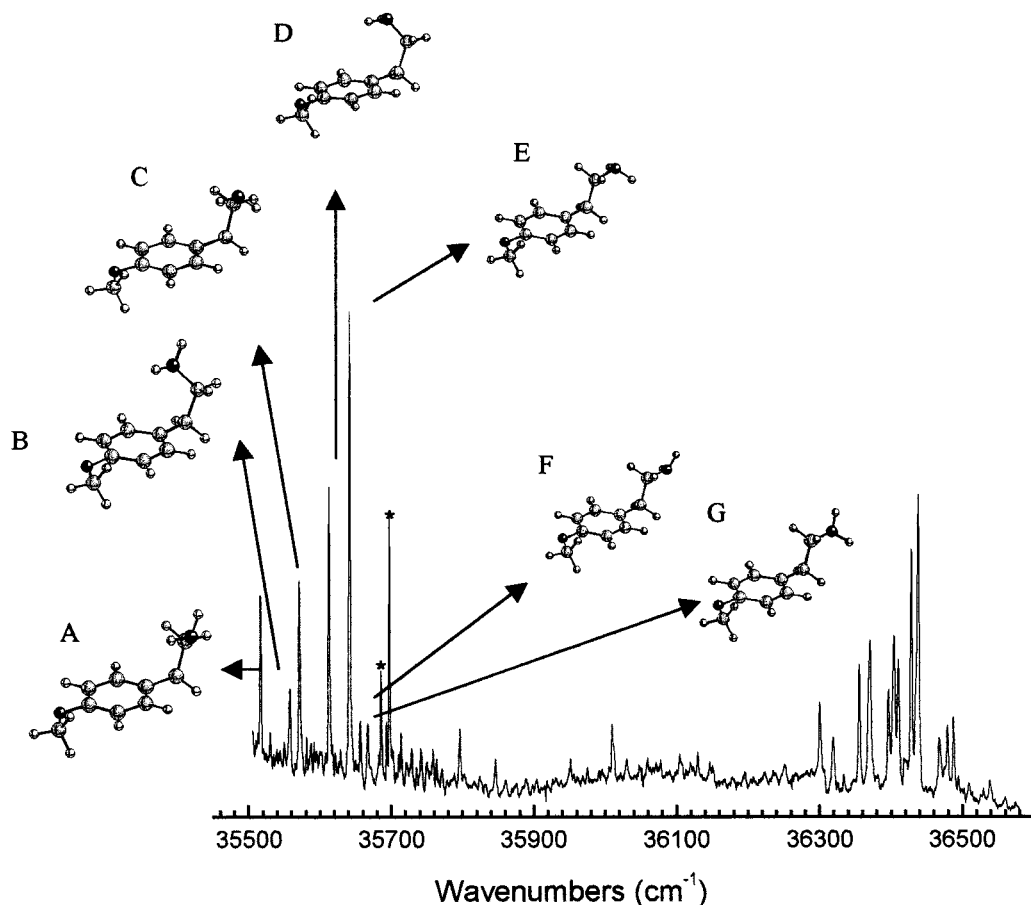
$$D_0(S_0) = MS(\text{fragment}) + MS(S_1 \leftarrow S_0) - M(I_0 \leftarrow S_1) - M(S_1 \leftarrow S_0) \quad (2)$$

$$D_0(S_1) = D_0(S_0) + M(S_1 \leftarrow S_0) - MS(S_1 \leftarrow S_0) \quad (3)$$

where  $M(S_1 \leftarrow S_0) - MS(S_1 \leftarrow S_0)$  is the complex origin band shift with respect to that of the bare molecule  $0_0^0$  transition and "fragment" stands for the energy necessary to ionize the  $MS^*$  species and to simultaneously evaporate one solvent molecule. We shall refer to this quantity as the fragmentation energy. According to eqs 1–3, a knowledge of the solvent and the complex, MS,  $S_1 \leftarrow S_0$  transition energies, the ionization and the fragmentation energy thresholds of  $MS^+$  to  $M^+$  and S, allows one to determine the ground  $MS(S_0)$ , first electronic  $MS(S_1)$ , and ion  $MS(I_0)$  binding energies. The method has some difficulties and drawbacks in its application. First, if the  $I_0 \leftarrow S_1$  transition is associated with a large geometry change, the ionization threshold is not well-defined, due to the uncertainties introduced by the characteristic slow slope. In addition, the chromophore intramolecular and the complex intermolecular vibrations must be strongly coupled in order to get a fast energy transfer to the vibrations that drive the system to dissociation. If these conditions are fulfilled, the complex three states binding energies can be determined to a satisfactory accuracy.

The experimental setup used has been partially described elsewhere,<sup>16</sup> and thus only a complementary account will be provided here. The system shares a number of lasers; one-laser experiments, LIF and DE, use an Nd:Yag/dye laser coupled system, frequency doubled with a KDP crystal, to cross 1–2 cm downstream, a supersonic beam expansion created with the aid of a heated electromagnetic valve (Iota One, General Valve) in a vacuum chamber ( $6 \times 10^{-5}$  mbar), and the complexes emitted light focused with a mirror/aspherical lens device onto a PM detector placed outside the chamber. In two-laser studies, both an excimer/dye and an Nd:Yag/dye coupled laser system, appropriately delayed and intensity controlled, were used in a counterpropagating configuration perpendicular to the jet beam and the ions produced analyzed with a time-of-flight mass system (TOF-MS R:M. Jordan). Isomer preparation was carried out on pulsed valves fed with buffer gas He at a stagnation pressure of 2–5 bar and seeded with suitable MPEA vapor and water in a flowing mixture. In the mass detection experiments the beam was skimmed downstream with an 0.8 mm  $\phi$  skimmer to select the central section of the beam. The pump–probe ionized species are drawn out by suitable electric fields and driven to the flight tube with an MCP detector at the far end; the electrical signals produced by the MCP detector, as well as those yielded in one laser experiments by the PM detector, are routed to a Tektronix 2430A digital oscilloscope, where they are integrated, averaged and sent to a PC computer for further analysis and storage.

Two-color experiments use TOF mass detection and include R2PI spectroscopy, ionization and fragmentation thresholds and "hole burning" (HB) spectroscopy. In R2PI, the pump laser is



**Figure 2.** Laser induced fluorescence, LIF, spectrum of a supersonic expansion of seeded MPEA in He. The structures of the seven conformers (four gauche and three anti) are indicated on their 0<sub>0</sub><sup>0</sup> transitions.

set at the 0<sub>0</sub><sup>0</sup> transition of the chosen isomer and the probe laser is scanned while the desired mass is detected and integrated. In ionization and fragmentation energy measurements, the pump laser excites the selected isomer to the S<sub>1</sub> state while it is spatially and temporally overlapped with the scanned probe laser and the detection is carried out at the mass of either the complex pumped 1:*n*, yielding the ionization energy (IE), or that with one water molecule less, 1:*n*−1, providing the fragmentation energy (FE). Ionization hole burning spectroscopy is used to identify the number of isomers, their 0<sub>0</sub><sup>0</sup> transitions and vibrational features and is carried out by burning a hole in the complexes mixture and scanning to ionization the remaining isomers.

Laser tuning was accomplished with the aid of either Rhodamine 590 or Fluoresceine 548 dyes (Exciton) and monitored in real time by a Fizeau wavelength meter (New Focus model 7711). MPEA was purchased from Sigma–Aldrich Chemicals and used as available; its vapor pressure and concentration to seed the He mixture was attained by heating the sample at 120 °C and the pulsed valve at ca. 70 °C.

### III. Results

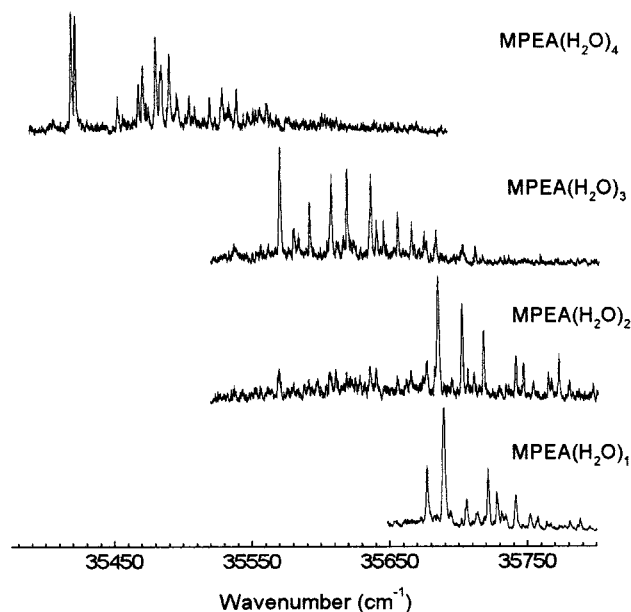
Binding energy determination of complexes by the threshold ion fragmentation method requires, to begin with, the knowledge of the bare molecule and the S<sub>1</sub> ← S<sub>0</sub> transition energies of the isomers (Figure 1). Bare MPEA has seven experimental conformers,<sup>13,17</sup> and in principle, any of them may be the MPEA(H<sub>2</sub>O)<sub>1</sub> isomer precursors. Figure 2 shows the MPEA LIF spectrum in the 35 500–36 550 cm<sup>−1</sup> region, where the seven

**TABLE 1: S<sub>1</sub>←S<sub>0</sub>, I<sub>0</sub>←S<sub>1</sub> Transitions and Ionization Energies (IE) in cm<sup>−1</sup> for the Set of Seven MPEA Conformers<sup>13</sup>**

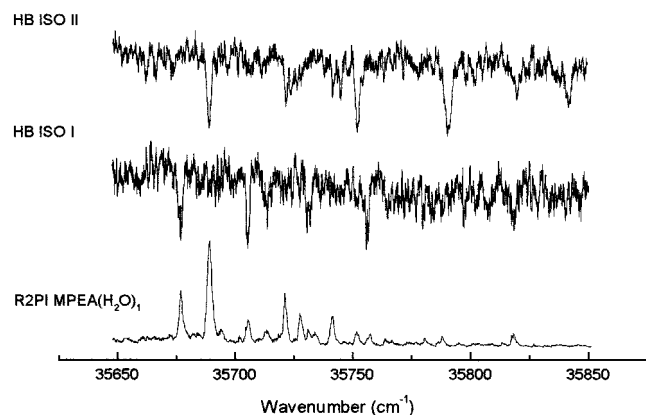
	Origin						
	A	B	C	D	E	F	G
S <sub>1</sub> ←S <sub>0</sub>	35 505	35 546	35 559	35 601	35 630	35 645	35 655
I <sub>0</sub> ←S <sub>1</sub>	28 493	28 166	28 468	28 248	28 148	28 091	28 125
I. E.	63 998	63 712	64 027	63 849	63 778	63 736	63 780

conformer origin bands have been labeled with the structures,<sup>13</sup> and Table 1 collects their 0<sub>0</sub><sup>0</sup> transitions and ionization energies. The two peaks marked with an asterisk correspond to MPEA(H<sub>2</sub>O)<sub>1</sub> complexes. To discriminate between peaks due to species of different stoichiometry, two-color mass-resolved spectroscopy (R2PI) has been used and the results for MPEA-(H<sub>2</sub>O)<sub>*n*</sub>, *n*=1–4 setting the ionization laser at 21 860, 28 000, 27 970, and 27 950 cm<sup>−1</sup> for the 1:1, 1:2, 1:3, and 1:4 complexes, respectively, are shown in Figure 3. It is easily appreciated that under these experimental conditions, no fragmentation from MPEA(H<sub>2</sub>O)<sub>2</sub> to MPEA(H<sub>2</sub>O)<sub>1</sub> mass-channel is observed. However, there is some fragmentation from higher order complexes in the 1:2 mass-channel, as indicated by noisy background to the red of the MPEA(H<sub>2</sub>O)<sub>2</sub> origin (35 687 cm<sup>−1</sup>). In any case, the comparison is good enough to identify the peaks belonging to each stoichiometry.

The number of isomers of each complex has been determined by HB spectroscopy, setting the probe laser to the most prominent features of the analyzed spectrum. The results of the HB experiments for the 1:1 and 1:4 complexes are shown in Figures 4 and 5, respectively. For each of these stoichiometries



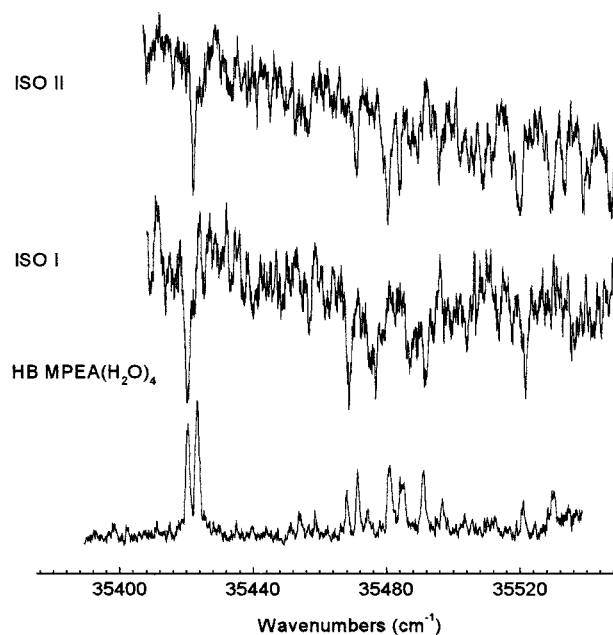
**Figure 3.** R2PI spectra of the MPEA(H<sub>2</sub>O)<sub>1–4</sub> complexes in the 35 400–35 600 cm<sup>−1</sup> region.



**Figure 4.** Hole burning spectra of the MPEA(H<sub>2</sub>O)<sub>1</sub> isomers. The isomers are distinguished as I and II for reference. To make the comparison easy, the R2PI spectrum is shown underneath.

two isomers have been observed, with origin bands at 35 676 and 35 689 cm<sup>−1</sup> for the 1:1 complex and at 35 419 and 35 422 cm<sup>−1</sup> for the 1:4 complex. For the other stoichiometries, only one isomer has been found, with origin band at 35 687 cm<sup>−1</sup> for the 1:2 and at 35 571 cm<sup>−1</sup> for the 1:3 complex. The poor s/n ratio of the HB spectra is due to the existence of large fragmentation patterns, unavoidable in one-color ionization experiments, although the results lead us to unequivocally settle two origin bands, associated with the existence of two and only two MPEA(H<sub>2</sub>O)<sub>1</sub> isomers, and similarly another two for the 1:4 complex. Therefore, the binding of one water molecule to MPEA results in a drastic reduction of the number of species from seven in the bare molecule to two in the 1:1 complex, indicating at the same time that the binding process increases the energy difference between the conformers. Table 2 shows the isomers vibrational mode wavenumbers relative to their 0<sub>0</sub><sup>0</sup> transitions. Owing to low signal intensities, only a few clearly distinguishable vibrations of each isomer have been identified.

Isomer binding energies are computed from MPEA(H<sub>2</sub>O)<sub>1–4</sub> experimental ionization (IE) and fragmentation energies (FE), and their measured values are collected in Figures 6 and 7. The traces are noisy and therefore, to improve the final results and



**Figure 5.** Hole burning spectra of the MPEA(H<sub>2</sub>O)<sub>4</sub> isomers. The isomers are distinguished as I and II for reference. To make the comparison easy, the R2PI spectrum is shown underneath.

estimate measurement uncertainties, a number of traces were recorded for each complex and their IE and FE values averaged (Table 3). The dispersion in the experimental energy values is less than  $\pm 30$  cm<sup>−1</sup>, and this error limit will be assumed henceforth as that of the dissociation energy. To find out the 1:1 complex binding energy, it is mandatory to identify the MPEA conformer that originates each of the MPEA(H<sub>2</sub>O)<sub>1</sub> isomers. As this is unknown so far, the calculations were carried out as if any of the seven conformers were possible precursors for each of the two 1:1 isomers. Similarly, any of the two 1:1 isomers may originate the single 1:2 complex, and therefore two binding energies are obtained. However, only one ion dissociation energy,  $D_0(I_0)$ , is obtained, no matter which conformer is chosen (see Figure 1 and eq 1). Table 4 shows the binding energy  $D_0$  values obtained for the formation of a 1:1 complex from each conformer, and Table 5 lists the binding energy  $D_0$  values obtained for the 1:2, 1:3, and 1:4 complexes.

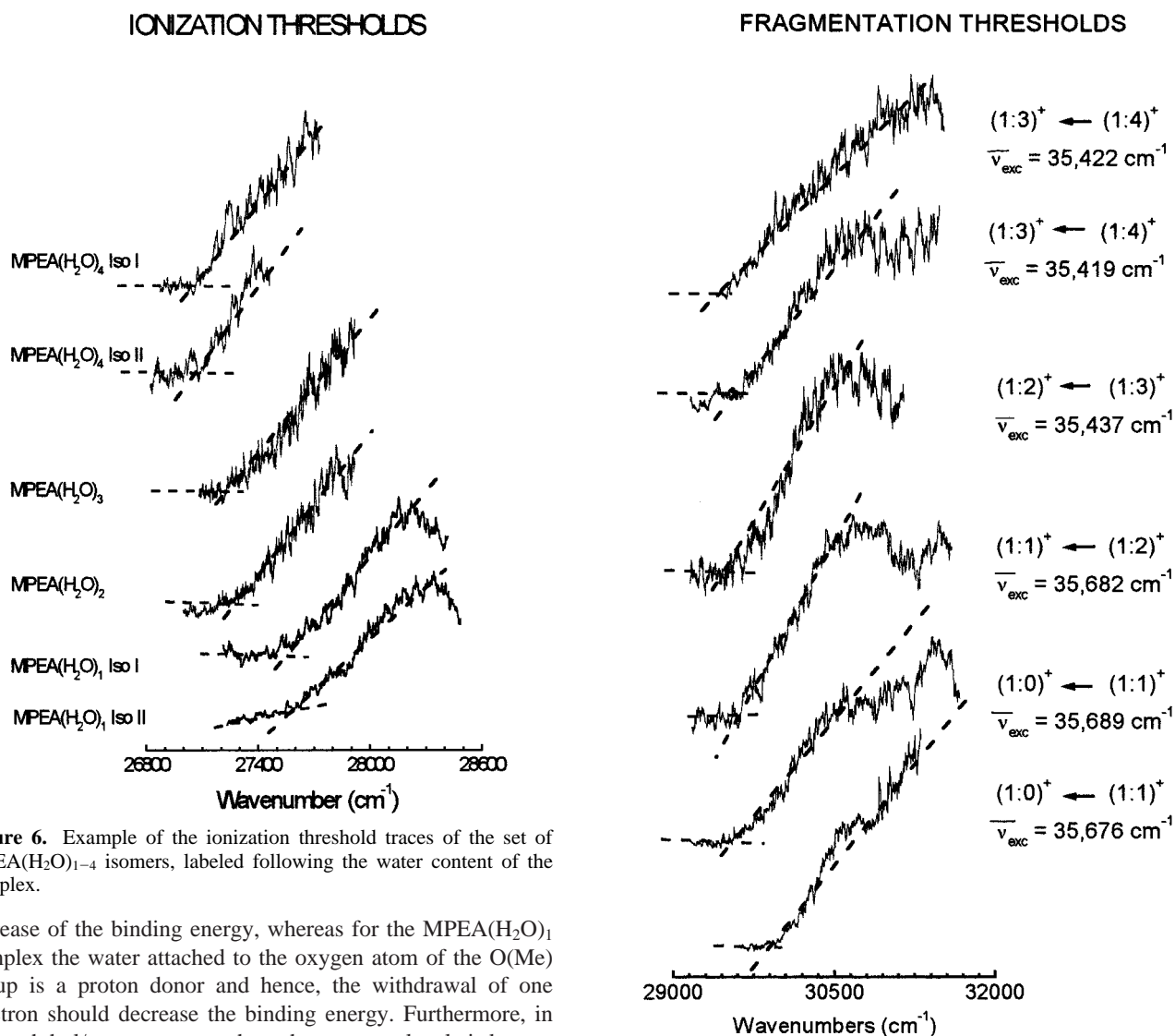
#### IV. Discussion

The MPEA(H<sub>2</sub>O)<sub>2</sub> isomers experimental dissociation energies collected in Table 4 raise two questions: which MPEA conformer is the precursor of the observed complexes and what is the actual complex geometry. MPEA itself has three solvation sites: the amino hydrogen atoms, the amino nitrogen atom and the oxygen lone pairs. If the latter were the solvation site, one would expect the electronic excitation to substantially affect the binding energy. Furthermore, removal of one electron from the aromatic ring would significantly decrease the binding energy, because some of the oxygen atom electronic density would be shifted to the aromatic ring to compensate the positive charge. However, the ground neutral and ground ion dissociation energies,  $D_0(S_0)$  and  $D_0(I_0)$ , are not that different, in contrast with those found in other systems. In fact, phenol/water has a ground dissociation energy,  $D_0(S_0)$ , of  $1960 \pm 40$  cm<sup>−1</sup> ( $5.60 \pm 0.11$  kcal/mol)<sup>18</sup> increasing to  $6489 \pm 40$  cm<sup>−1</sup> ( $18.45 \pm 0.09$  kcal/mol) for the ion state. In a proton acceptor water system, the removal of one electron is associated with an



TABLE 2: Low Vibrational Modes in Wavenumbers Observed in the MPEA(H<sub>2</sub>O)<sub>1-4</sub> Isomers

1:1		1:2	1:3	1:4	
origin at 35,676 cm <sup>-1</sup> (Iso I)	origin at 35,689 cm <sup>-1</sup> (Iso II)	origin at 35,687 cm <sup>-1</sup>	origin at 35,571 cm <sup>-1</sup>	origin at 35,419 cm <sup>-1</sup> (Iso I)	origin at 35,422 cm <sup>-1</sup> (Iso II)
28	32	18	10	34	35
37	38	34	14	49	49
64		57	22		59
75	74	62	38		62
791	810	70	48	72	74
		80	66		
		83	70		
		88	75		
			86		
			96		
			105		
			113		

Figure 6. Example of the ionization threshold traces of the set of MPEA(H<sub>2</sub>O)<sub>1-4</sub> isomers, labeled following the water content of the complex.

increase of the binding energy, whereas for the MPEA(H<sub>2</sub>O)<sub>1</sub> complex the water attached to the oxygen atom of the O(Me) group is a proton donor and hence, the withdrawal of one electron should decrease the binding energy. Furthermore, in the naphthol/water system, where the water molecule is known to solvate the proton-donor >N-H group, the system binding energy changes from  $1632 \pm 15$  cm<sup>-1</sup> (ref 19) to  $1694 \pm 81$  cm<sup>-1</sup> (ref 20) in the neutral ground state, to  $4790 \pm 10$  cm<sup>-1</sup> (ref 19) –  $4855 \pm 39$  cm<sup>-1</sup> (ref 20) in the ion. In consequence, the water is expected to H-bonded to the NH<sub>2</sub> group.

Amines are good proton-acceptors, in contrast with water, which is usually a proton-donor. As a consequence, MPEA-(H<sub>2</sub>O)<sub>1</sub> has an expected complex geometry with water attached to the N atom. However, because of the folded configuration of some conformers, the geometry with a proton-acceptor water

Figure 7. Example of the fragmentation threshold traces of the set of MPEA(H<sub>2</sub>O)<sub>1-4</sub> isomers, labeled following the water content of the complex.

interacting both with the amino hydrogen atom and the aromatic ring compares favorably with the geometry just described above. In this case, the water–aromatic ring interaction is expected to cause a significant stabilization energy difference between the neutral and the ion binding energies, which is not observed. In addition, the stabilization energy provided by the OH<sub>2</sub>⋯π bonding is balanced by the absence of the NH⋯π interaction.

**TABLE 3:  $S_1 \leftarrow S_0$  Transition Energies, Ionization and Fragmentation Energy Thresholds, in  $\text{cm}^{-1}$ , of the Set of  $\text{MPEA}(\text{H}_2\text{O})_{1-4}$  Complexes<sup>a</sup>**

		$S_1 \leftarrow S_0$	$I_0 \leftarrow S_1$	fragmentation
1:1	isomer I	35 676	27 622	29 901
	isomer II	35 689	27 580	29 039
1:2		35 687	27 284	29 962
1:3		35 571	27 269	29 875
1:4	isomer I	35 419	26 924	30 877
	isomer II	35 422	26 937	29 808

<sup>a</sup> Note that the ionization energy is the sum of  $S_1 \leftarrow S_0$  and  $I_0 \leftarrow S_1$  transition energies. Fragmentation energies are defined in Figure 1.

**TABLE 4: Dissociation Energy,  $D_0$ , of the Two  $\text{MPEA}(\text{H}_2\text{O})_1$  Isomers Observed in a Pulsed Supersonic Expansion of He Seeded with MPEA and  $\text{H}_2\text{O}$ <sup>a</sup>**

	conformer						
	A	B	C	D	E	F	G
origin band at 35,676 $\text{cm}^{-1}$ (Isomer I)							
$D_0(S_0)$	1579	1865	1550	1728	1799	1841	1797
shift <sup>b</sup>	171	130	117	75	46	31	21
$D_0(S_1)$	1408	1735	1433	1653	1753	1810	1776
$D_0(I_0)$	2279						
origin band at 35 689 $\text{cm}^{-1}$ (Isomer II)							
$D_0(S_0)$	1730	2016	1701	1879	1950	1992	1948
shift <sup>b</sup>	193	152	139	97	68	53	43
$D_0(S_1)$	1546	1873	1571	1791	1891	1948	1914
$D_0(I_0)$	2459						

<sup>a</sup>  $\text{MPEA}(\text{H}_2\text{O})_1$  origin band shift respect to the MPEA conformers  $0_0^0$  transition. According to the MPEA conformer chosen, the ground and electronic excited states binding energies,  $D_0(S_0)$  and  $D_0(S_1)$ , vary slightly, but the binding energy of the ion,  $D_0(I_0)$ , is unaffected.

<sup>b</sup>  $\text{MPEA}(\text{H}_2\text{O})_1$  origin band shift respect to the MPEA conformers  $0_0^0$  transition.

The recent study on phenethylamine/water complexes<sup>9</sup> also confirms the identification proposed. Therefore, we conclude that the water is the proton-donor in an  $\text{HO}-\text{H}\cdots\text{N}$  hydrogen bond.

The geometry of the complex, however, does not provide any clues on the precursor molecule conformation from which it derives. A mass-resolved high-resolution spectroscopy<sup>21</sup> and ab initio calculations study of 2-phenylethylamine (PEA)—a molecule only differing from MPEA in the absence of the O(Me) group—led to the conclusion<sup>22</sup> that the single isomer detected has the core of one of the PEA folded conformations. Moreover, the O(Me) group of MPEA, on one hand, splits the number of conformers of PEA into two and, in addition, is not expected to significantly change the energy of the complex formation, allowing us to conclude that the two observed  $\text{MPEA}(\text{H}_2\text{O})_1$  isomers have MPEA folded conformations as precursors, simply differing in the relative orientation of the  $\text{NH}_2$  and O(Me) groups. Therefore, only bands labeled as A, B or C, D in Figure 2 can be regarded as suitable precursors. As a rough approach, one can use the intensity pattern to aid in the identification. As the C and D bands are the most intense and the band intensity pattern of the  $\text{MPEA}(\text{H}_2\text{O})_1$  isomers band origins are very similar (cf. Figures 2 and 3), one could establish  $\text{MPEA}(\text{H}_2\text{O})_1$  Isomer I as deriving from the bare molecule conformer C core and Isomer II from conformer D. Accordingly, the splitting of 42  $\text{cm}^{-1}$  between the bare molecule conformers diminishes to only 13  $\text{cm}^{-1}$  in the  $\text{MPEA}(\text{H}_2\text{O})_1$  complex. The plausible arguments used in the identification are expected to be confirmed by the accurate ab initio calculations in progress.

From Table 4 it is also clear that the isomer I ( $0_0^0$  transition

**TABLE 5: Dissociation Energies of the  $\text{MPEA}(\text{H}_2\text{O})_{2-4}$  Isomers, Calculated by Eqs. 1 and 3 and the Experimental Data Listed in Table 1<sup>a</sup>**

		precursor	
		1:1 isomer I	1:1 isomer II
1:2			
	$D_0(S_0)$	2351	2380
	shift	+11	−2
	$D_0(S_1)$	2340	2382
	$D_0(I_0)$	2678	2678
1:3			
	$D_0(S_0)$	2475	
	shift	−116	
	$D_0(S_1)$	2591	
	$D_0(I_0)$	2606	
1:4 Isomer I			
	$D_0(S_0)$	2456	
	shift	−152	
	$D_0(S_1)$	2608	
	$D_0(I_0)$	2953	
1:4 Isomer II			
	$D_0(S_0)$	2390	
	shift	−149	
	$D_0(S_1)$	2539	
	$D_0(I_0)$	2871	

<sup>a</sup> Note that any of the two isomers of  $\text{MPEA}(\text{H}_2\text{O})_1$  can be the precursor of  $\text{MPEA}(\text{H}_2\text{O})_2$ , and therefore the calculation has to be made for both.

at 35 676  $\text{cm}^{-1}$ )  $S_0$ ,  $S_1$ , and  $I_0$  binding energies are lower than those of the blue isomer and that, while the ground to excited-state binding energy difference is small, it is larger if the electron is removed from the aromatic ring. The  $\text{HO}-\text{H}\cdots\text{N}$  H-bond is reinforced by the existence of an  $\text{HN}-\text{H}\cdots\pi$  interaction in the bare molecule. This interaction is weaker in the excited state, due to the delocalization of the  $\pi$  electron density, and the effect is transmitted back to the water solvent H-bond, that becomes weaker, resulting in a blue shifted  $0_0^0$  transition with respect to the bare molecule band origin. The increasing of the binding energy in the ion must be due to a large reorganization of the complex structure that would need ab initio calculations to be fully understood.

The addition of a second water molecule to  $\text{MPEA}(\text{H}_2\text{O})_1$  yields a single isomer, with the new molecule linked to the water of the complex, because of the high water–water binding energy.<sup>23–26</sup> In this structure, with the water chain end bonded to MPEA at the amino group, there still exists a molecular asymmetry caused by the relative orientation of the  $\text{NH}_2$  and the O(Me) groups. However, that the split decreases from the bare molecule (43  $\text{cm}^{-1}$ ) to the 1:1 complex (13  $\text{cm}^{-1}$ ) would explain an overlap between the two 1:2 isomers at the experimental resolution used.

The addition of the second water molecule is expected to strengthen the 1:1 H-bond, as mirrored in the binding energy increase. Tables 4 and 5 quantitatively show an increase of over 500  $\text{cm}^{-1}$  in the process; cf. >2300  $\text{cm}^{-1}$  for the 1:2 complex compared to 1550–1879  $\text{cm}^{-1}$  for the 1:1, depending on the isomer chosen. The water–water bond energy has been estimated to be approximately 1645  $\text{cm}^{-1}$  (4.7 kcal/mol),<sup>27–31</sup> some 700  $\text{cm}^{-1}$  (ca. 2 kcal/mol) lower than the measured energy for the addition of the second water molecule to the 1:2 complex. The extra energy accounts for the cooperative effects between water–water and water– $\text{NH}_2$  H-bonds.

Following the above argument, the 1:3 isomer ought to have the three water molecules linked in a chain. Extrapolation of the structures observed in the addition of water for other

systems<sup>32–36</sup> leads one to suggest a structure in which the three water molecules form a ring (both ends of the chain bonded), linked to the bare molecule by the HO–H···NH<sub>2</sub> H-bond. The binding energy increase by adding the third water molecule is not as large as for the second –2475 cm<sup>–1</sup>, compared with 2351–2380 cm<sup>–1</sup>, and indicates that the formation of the ring, with an extra H-bond, is partially compensated by structure stress, since the chain is short enough to get the most favorable angles and distances. Mó et al.<sup>37</sup> estimated the water trimer extra stabilization energy, to be due to the creation of a cycle, in 126 cm<sup>–1</sup> (0.36 kcal/mol, MP2/6-311+G(2d,2p)), in excellent agreement with the energy difference to remove one water molecule between 1:3 and 1:2 complexes (124 or 95 cm<sup>–1</sup>, depending on the 1:1 isomer core chosen). A direct comparison between the energies to remove the second and the third water molecules, that is, (2,351 or 2380) + 2475 cm<sup>–1</sup> ~ 4841 cm<sup>–1</sup> (13.83 kcal/mol) and the calculated binding energy for the water trimer is not straightforward, due to the data dispersion of the theoretical value (from 13 to 17 kcal/mol, ref 38), but it is obvious that the reported experimental value is in the lower end of the calculated range.

Finally, with the addition of the fourth water molecule, the solvents are expected to build a stable ring attached to the amino group, as already observed in other aromatic 1:4 complexes. Two isomers result from either the molecular asymmetry or the existence of two structures with slightly different orientations of the water ring. The binding energies of the addition of the third and fourth water molecules to the complex are very close and their difference lies within the experimental error. A decrease in the stabilization energy due to water addition has been recently reported<sup>39</sup> in the phenol(H<sub>2</sub>O)<sub>3</sub>/phenol(H<sub>2</sub>O)<sub>4</sub> system and justified by arguing that the first three water molecules saturate the solvation site and the solvation limit is reached by addition of more molecules. When compared with the calculated energy of the water tetramer<sup>40</sup> (25.35 kcal/mol computed at the MP2/aug-cc-pVDZ level), a larger value for the addition of the fourth water molecule is found than the per-bond binding energy in the (water)<sub>4</sub> complex: ~2400 cm<sup>–1</sup> compared to 2219 cm<sup>–1</sup> for the water tetramer. As in other MPEA complexes, the difference is due to the presence of one extra H-bond and the weak interaction of the water chain with other parts of the bare molecule. These qualitative aspects require further calculations for their assessment.

## V. Conclusions

MPEA(H<sub>2</sub>O)<sub>1–4</sub> complexes formed in the pulsed supersonic expansion of a mixture of He conveniently seeded with MPEA and water have been investigated by LIF, R2PI, and HB spectroscopies, identifying two isomers in both 1:1 and 1:4 stoichiometry complexes, and one single isomer in both 1:2 and 1:3 complexes. Two-color laser experiments have also been carried out in order to measure the ionization and the fragmentation energy thresholds of the set of isomers. The knowledge of these energies and the set of the origin band transitions of the bare molecule yielded the determination of the ground state, D<sub>0</sub>(S<sub>0</sub>), the first electronic excited state, D<sub>1</sub>(S<sub>1</sub>), and the ion state, D<sub>0</sub>(I<sub>0</sub>), binding energies, the most relevant features of the weakly bound complexes. Although the binding energies provide clues about the geometries of the complexes, only plausible conclusions have been suggested, on the understanding that the quantitative ab initio calculations in progress will settle the interpretations. The comparison between the experimental

binding energies of the states studied and other chromophore/water complexes allows us to establish the contribution of binding energy due to the H-bonds and to other interactions. The estimation of the energy to create the cycle in the 1:3 complex is of ~100 cm<sup>–1</sup>.

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