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A Computational Study of the Structures of the *p*-Methoxyphenethylamine(H₂O)_{2–4} Complexes

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A computational investigation of the hydrated complexes of *p*-methoxyphenethylamine(H₂O)_{2–4} (hereafter referred to as either MPEA(H₂O)_{2–4} or simply 1:2–4) has been conducted at the B3LYP/6-31+G* level in order to find out the stable structures and the isomer binding energies (BEs). As expected, the calculations supply a large number of stable geometries, built up from one of the seven MPEA conformers and a chain of solvent molecules attached to a number of sites of the chromophore molecule. Within each complex stoichiometry, some isomers have very close binding energies, in fact, smaller than that of the basis set superposition error (BSSE). Despite the seven MPEA conformer precursors, the number of complex isomers recognized in two-color mass-resolved time-of-flight (TOF) and “hole burning” spectra are scarce: one for both 1:2 and 1:3 complexes, and two for the 1:4 complex. Notwithstanding the difficulty to identify the participant conformer within a specific complex, the computation shed light on a number of significant features of their structures, for example, that the first water molecule is always bound to the nitrogen atom of the NH₂ group; in the 1:2 complex, the last arrived solvent attaches to the water already bound and to the hydrogen atom of the NH₂ pointing away from the aromatic ring; the addition of the third solvent results in the formation of a water daisy chain around the NH₂ moiety, and the addition of the fourth water gives rise to two structures of close stability. These results are interpreted as the systematic presence of two isomers for all 1:1–4 complexes but that their spectra overlap for 1:2 and 1:3 at the resolution of the experiments. The calculated energies for the addition of one water molecule at a time to the 1:*n* complex match fairly well the experimental measurements (within ~200–300 cm⁻¹, <1 kcal/mol).

I. Introduction

The *p*-methoxyphenethylamine (MPEA) chromophore is an analogue of the neurotransmitter mescaline.¹ The molecules of the family are characterized by flexible ethylamino chains that give rise to a variety of stable conformers: five in the simplest molecule phenethylamine,^{2–6} nine in MPEA,⁷ and presumably a higher number in larger-size members. Some conformers have been observed in supersonic expansions by mass-resolved ionization spectroscopy.^{2–7} As the perturbation produced by the orientations of the flexible chain on the S₁←S₀ transition energy is small, the spectra of the conformers are expected to be very close and even to overlap. The assignment of the spectra is by no means simple, and some have recently been reported.^{2,3–5,8} In the following, and to avoid misunderstandings, we use the word “conformer” to refer to one stable geometry of the chromophore and apply “isomer” to one specific structure of a complex or cluster of fixed stoichiometry.

Supersonic expansions of seeded water and MPEA molecules into a carrier gas produce a mixture of complexes of assorted stoichiometry, of which the 1:1 has been the most studied.^{1,9} Studies of two-photon resonance enhanced ionization (R2PI) and hole burning (HB) spectroscopies⁹ have provide arguments to assess the existence of two isomers in the 1:1 complex, one in the 1:2 and the 1:3 complexes, and two in the 1:4 complex. The small number of isomers contrasts with the large number of precursor conformers (see Figure 1) and it points out that

either the solvation process selectively stabilizes some conformers or the complex formation energy is used to overcome the potential energy barriers, producing a more stable conformer.

Although the binding energies (BEs) of the complexes have been determined by the ionization threshold method^{1,9–12} and provide useful information, they do not supply a clear picture on the structure of the complexes. Such information is presumably obtained by quantum chemistry *ab initio* calculations. With the aim to know the geometry and the BEs and also to find out the smallest basis set to describe accurately enough these properties, the computations were initiated on the 1:1 complex, MPEA(H₂O)₁, and conducted with the B3LYP functional and four basis sets, namely, 6-31G, 6-31+G*, 6-311+G*, and AUG-cc-pVDZ.^{1,9} The BEs calculated with the largest basis set are in very good agreement with the experimental values, but the accord is also good for the 6-31+G* basis set. It is also concluded that for the four basis sets tried, the solvent preferred solvation site is the nitrogen atom of the NH₂ group and that the complexes built with gauche conformers are more stable than those with anti. As expected, the interaction between the NH₂ moiety and the aromatic π -electrons leads to an electron density increase on the N atom. Hence, the solvation produces an increase in the energy difference between gauche and anti derived conformers, in favor of the gauche. Further, it was also confirmed that the comparison between experimental and calculated ionization thresholds is a powerful tool to assign these complexes.

In the present work we extend the synergy of the experimental and computational analysis already applied to the 1:1 complex

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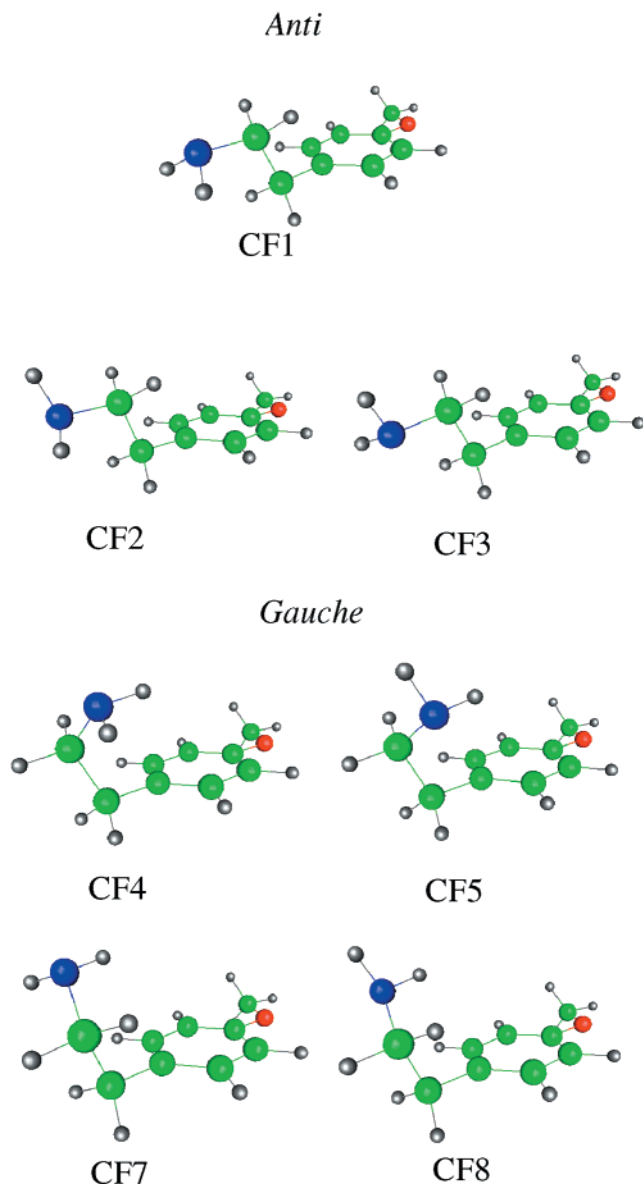


Figure 1. Optimized structures of the seven observed conformers of the *p*-methoxyphenethylamine molecule. Note that [CF2, CF3] and [CF5, CF8] conformer pairs have the same NH₂ orientation but match the [trans, cis] pairs according to the relative orientation of NH₂ and O(Me) groups.

to the MPEA(H₂O)_{2–4} complexes. In turn the computed BEs provide a good assessment to confirm that the ionization threshold method yields excellent experimental BEs of complexes with high solvent content. The experimental method, based on the calculation of the energy required to evaporate one solvent molecule at a time, assumes that the evaporation process drives the 1:*n* complex into the bottom of the 1:*n*–1 potential energy surface (see Figure 2a). However, if evaporation is accompanied by a large reorganization of the 1:*n*–1 complex, the BEs may be affected by a large systematic error (Figure 2b), and the ground-state BE, $D_0(S_0)$, can no longer be obtained from the equation

$$D_0(S_0) = (\text{fragmentation} \leftarrow S_1) + MS(S_1 \leftarrow S_0) - M(I_0 \leftarrow S_1) - M(S_1 \leftarrow S_0) \quad (1)$$

We will show that the computed BEs faithfully reproduce the experimental values. In addition, we address two issues that

are unresolved with the experimental data alone, namely, the determination of the most stable geometry for a fixed complex stoichiometry and the dependence of the increase of the energy difference between gauche precursor conformers with the number of solvent molecules.

II. Ab Initio Calculations

It has been shown¹ that the four gauche conformers CF4, CF5, CF7, and CF8 (Figure 1), are the precursors of most stable 1:1 complexes, and thereby only they are taken into account to work out the higher solvent content structures. In addition, it was also concluded that the properties of interest of the 1:1 complex are satisfactorily described at the B3LYP/6-31+G* level.¹ As the systems studied contain a considerable number of electrons, a concomitant basis function is required and, presumably, the complexes with higher solvent content are expected to be described even better. In consequence, the study was conducted at the B3LYP/6-31+G* level, using Gaussian 98W¹³ on a number of PCs. All the stable structures reported have been tested by a normal mode computation, seeking for the lack of negative frequencies. The calculated BEs were corrected for the zero-point energy (ZPE) and the basis set superposition error (BSSE), calculated with the full counterpoise procedure of Boys and Bernardi.^{14,15}

III. Results

The MPEA chromophore has several feasible solvation sites, namely, the aromatic π -electrons, the oxygen atom lone pairs, and the NH₂ group, which may be proton donor or acceptor. According to the calculations on the 1:1 complex, the N atom is by far the preferred solvation site of the bare molecule. In general terms, the NH₂ moiety is a good proton acceptor, whereas the water is a good proton donor. In addition, the HN–H $\cdots\pi$ intramolecular interaction increases the N atom partial charge, strengthening the H₂N \cdots H–OH hydrogen bond. Figure 3 shows the geometry of the two most stable conformers of the 1:1 complex, calculated at the B3LYP/6-31+G* level and assigned to the two experimental isomers.¹ The next two most stable 1:1 isomers have CF4 and CF7 as precursors. These two structures and the pair shown in Figure 3 are the departing geometries for the calculations of the 1:2 isomer structures.

MPEA(H₂O)₂. In the calculations of the 1:2 most stable isomers the following assumptions are made: (a) the water molecules of the 1:1 complex attach to the nitrogen atom of the NH₂ group by an H₂N \cdots H–OH hydrogen bond and (b) the second water molecule binds to the end water site of the 1:1 complex. The latter assumption is justified by the high water–water association energy and the strength of the 1:1 hydrogen bond due to two-body effects. We limit our calculations to the gauche conformers (Figure 1) as they yield the most stable 1:1 structures.¹

In the prospective of finding stable 1:2 complexes by adding water one molecule at a time, the second water molecule was attached to the four most stable 1:1 isomers, resulting two structures for each isomer (Figure 4), one with the water bound to both the hydrogen atom of the NH₂ group and the aromatic π -electrons (the “internal” H atom), and other with the water bound to the hydrogen atom of the NH₂ group pointing away from the aromatic ring (the “external” H atom). The BEs depend on the conformer chosen as precursor but are similar for the four conformers. For the internal hydrogen atom structure the BE is ca. 3700 cm^{–1}, whereas for the external hydrogen atom the BE is ca. 4000 cm^{–1}.

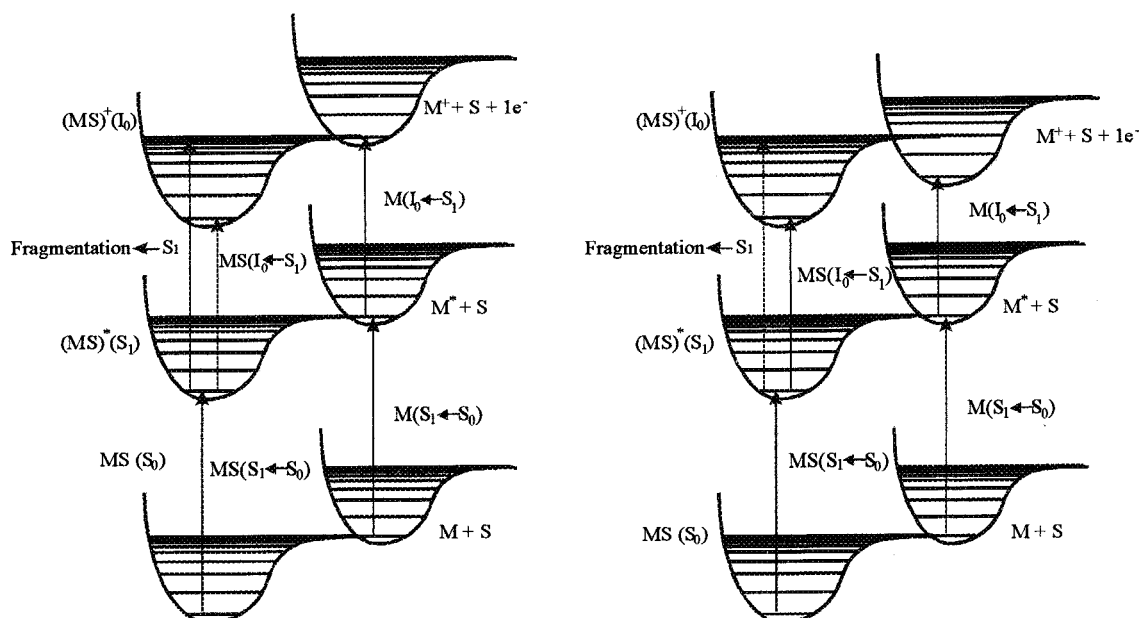
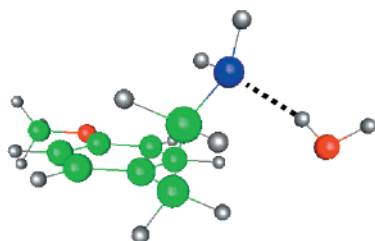
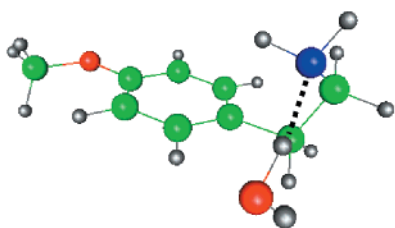


Figure 2. Schematic drawing of the one-dimensional wells for the ground state S_0 , first electronic excited state, S_1 , and the ground-ion I_0 state of the complex MS and the chromophore M . If the evaporation of one solvent molecule evolves $(MS)^+(I_0)$ into $M^+(I_0)$ ground vibronic level (a), the ground-state binding energy, $D_0(S_0)$, is readily computed from eq 1. Otherwise (b) the determination of $D_0(S_0)$ will include an error equal to the vibronic energy with which $M^+(I_0)$ appears.

MPEA(H₂O)₁



CF8
BE 1951 cm⁻¹



CF5
BE 1877 cm⁻¹

Figure 3. Two of the four most stable MPEA(H₂O)₁ structures, as calculated at the B3LYP/6-31+G* level. CF8 and CF5 refer to the bare MPEA conformer within the complex and BE stands for the binding energy corrected from ZPE and BSSE. The two structures are identified as the two observed isomers.

While energy arguments provide grounds to identify the solvation site chosen by the second water molecule, it is not simple to distinguish the precursor from which the complex is built. The 1:2 most stable structures built with the CF4, CF7, CF5, and CF8 gauche conformers have the following BEs:

TABLE 1: Experimental and Calculated Vibrational Wavenumbers of the Most Stable 1:2 Isomers Built Up on the Four Gauche Precursors CF4, CF7, CF5, and CF8

exptl	bare molecule conformation			
	CF7	CF4 ^a	CF8 ^a	CF5 ^a
18 m	21 (ν_1)	21	22	19
26 vw	26 (ν_2)	25	25	25
34 m	32 (ν_3)	38	28	27
57 w	53 (ν_4)	51	61	60
62 w	$\nu_2 + \nu_3$	$\nu_2 + \nu_3$	$\nu_2 + \nu_3$	$\nu_2 + \nu_3$
70 w	71 (ν_5)	73	66	65
80 w	$\nu_1 + \nu_2 + \nu_3$	$\nu_1 + \nu_2 + \nu_3$	$\nu_1 + \nu_2 + \nu_3$	79
83 vw	$\nu_2 + \nu_4$	84	82	$\nu_2 + \nu_4$
88 w	89 (ν_6)	$\nu_1 + \nu_5$	$\nu_1 + \nu_5$	$\nu_1 + \nu_5$
132 vw	125 (ν_7)	126	145 (ν_8)	147 (ν_8)
171 vw	170 (ν_9)	172	160 (ν_9)	165 (ν_9)

^a Same normal mode numbering as for CF7, except if indicated otherwise.

4050, 4081, 3957, and 3948 cm⁻¹, respectively. It is worth noting that the orientation of the hydrogen atoms of the NH₂ group and the relative cis–trans orientation have a marginal influence on the binding energies (10–30 cm⁻¹).

The comparison between experimental and calculated vibrational modes has proven to be useless for assignment purposes. Indeed, the abundance and similarity for the four complexes of vibrational bands in the low 200 cm⁻¹ region precludes a safe identification. The suggested assignment reported in Table 1 should be regarded with suspicion, particularly in the case of multiple choices.

MPEA(H₂O)₃. The calculations of the 1:3 most stable structures departing from the already established 1:2 structures yield three types of isomers, with the water molecules as a daisy chain (2-fold) and as a three-water ring. In the latter structures, the water molecules and the NH₂ group simultaneously have hydrogen bonds with proton-donor and proton-acceptor character (see Figure 5). As for the 1:2 complexes, the linear chain is bound to the nitrogen atom of the NH₂ group and either the external or the internal hydrogen atom of the NH₂. The last structure is ca. 500 cm⁻¹ less stable and consequently is not

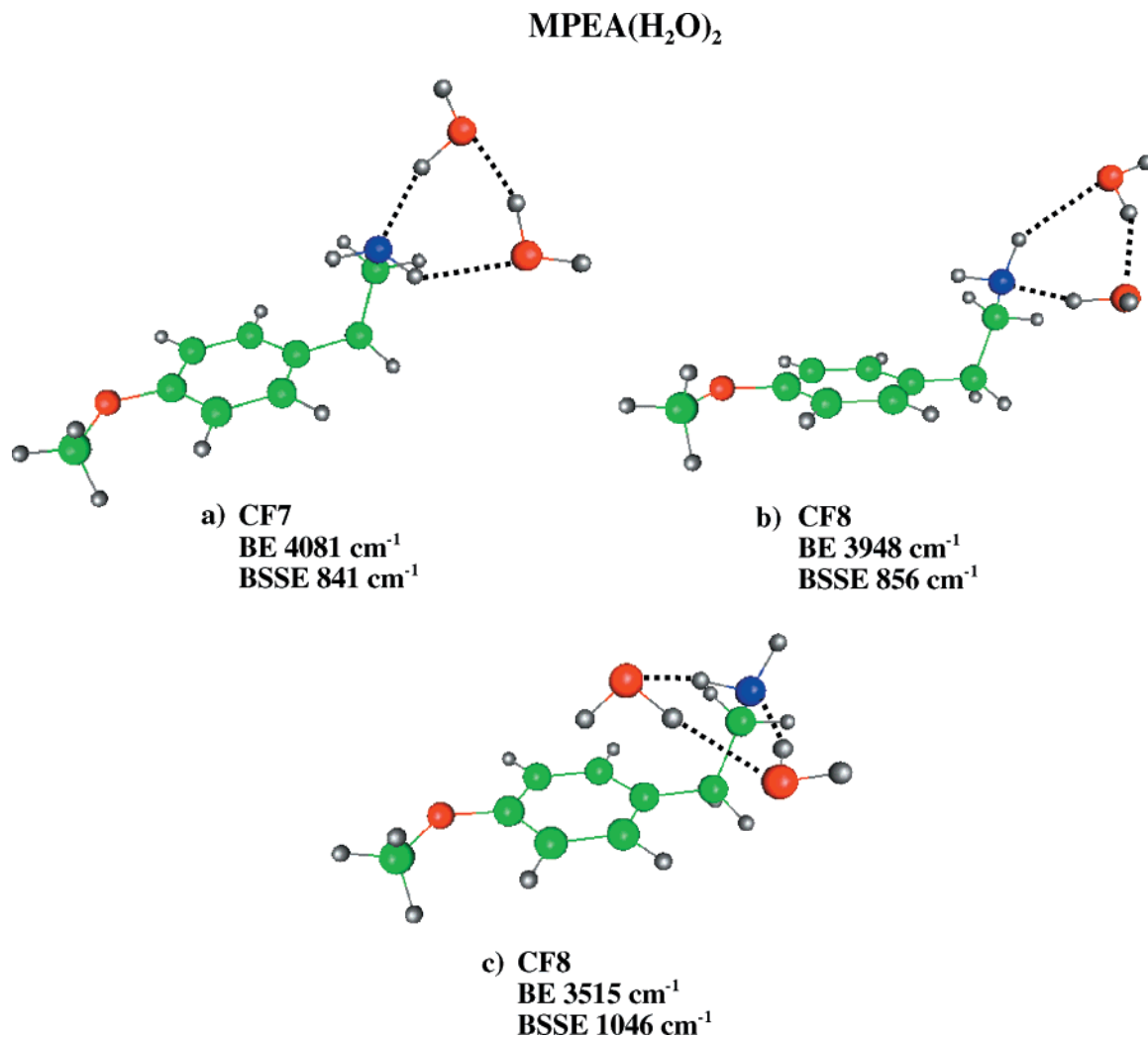


Figure 4. Three examples of 1:2 isomer structures as calculated at the B3LYP/6-31+G* level. In structures (a) and (b), the second water molecule interacts with the hydrogen atom of the NH₂ that is “external” with respect to the ring, while in structure (c), the second water molecule interacts with the “internal” H atom with respect to the aromatic ring. BE stands for binding energy corrected from ZPE and BSSE. The structure (a) is the most stable of the 1:2 complex.

TABLE 2: Experimental and Calculated Vibrational Wavenumbers of the Most Stable 1:3 Isomers Built Up on the Gauche Precursors CF7, CF4, and CF8^a

exptl	bare molecule conformer		
	CF7	CF4	CF8
10 vw	16 (ν_1)	16	19
14 vw	20 (ν_2)	21	20
22 w	25 (ν_3)	34	25
38 m	41 (ν_4)	43	41
48 m	55 (ν_5)	52	64
66 m	79 (ν_6)	76	67
70 w	$\nu_3 + \nu_5$	$\nu_3 + \nu_5$	$\nu_3 + \nu_5$
75 w	$2\nu_4, 79 (\nu_7)$	$2\nu_4, 80$	$2\nu_4, 81$
86 w	$\nu_4 + \nu_5$	$\nu_4 + \nu_5$	$\nu_4 + \nu_5$
96 w	$2\nu_5$	$2\nu_5$	$2\nu_5$
105 w	$106 (\nu_8), \nu_4 + \nu_6$	$105, \nu_4 + \nu_6$	$106, \nu_4 + \nu_6$
113 w	$3\nu_4, 2\nu_6$	$3\nu_4, 2\nu_6$	$3\nu_4, 2\nu_6$

^a The most stable structures have water daisy chains joined to the “external” H atom (Figure 3).

considered. The structure with a ring of three water molecules attached to the N atom is stable only for precursors CF4 and CF7, but in any case it is less stable than the daisy chain (with a BE of ca. 1200 cm⁻¹ lower than the daisy chain around the external H atom). Therefore, the experimentally observed feature probably corresponds to the daisy chain type structure. However,

as noted for the 1:2 complex, it is uncertain what is the structure of the conformer within the complex. Actually, the orientation of the NH₂ group gives rise to an energy difference of ~150 cm⁻¹, which compares with the calculated BE. The orientation of the O(Me) with respect to the ethylamino group results in an even smaller energy difference (ca. 50 cm⁻¹), and therefore there are no arguments to figure out the orientation of the amino group in the complex.

Table 2 shows a comparison between observed and calculated vibrational modes of the 1:3 complex based on CF7, CF4, and CF8 conformers. As for the 1:2 complex, the large number of modes and their narrow spacing make the assignment tentative and do not provide any arguments on the conformer structure inside the complex.

MPEA(H₂O)₄. As already mentioned, the two-color mass-resolved and HB spectra provide neat evidence of the occurrence of two isomers.¹ From the computational viewpoint it is expected that the larger the number of solvent molecules, the higher the variety of structures. Further, the potential energy landscape is so involved that a change in the position of one hydrogen atom of the water shifts the energy by ~100–200 cm⁻¹. However, the isomerization barrier between most isomers is necessarily small, as only two isomers are observed. The method to explore the structures with lowest minima of the 1:4 complex departs

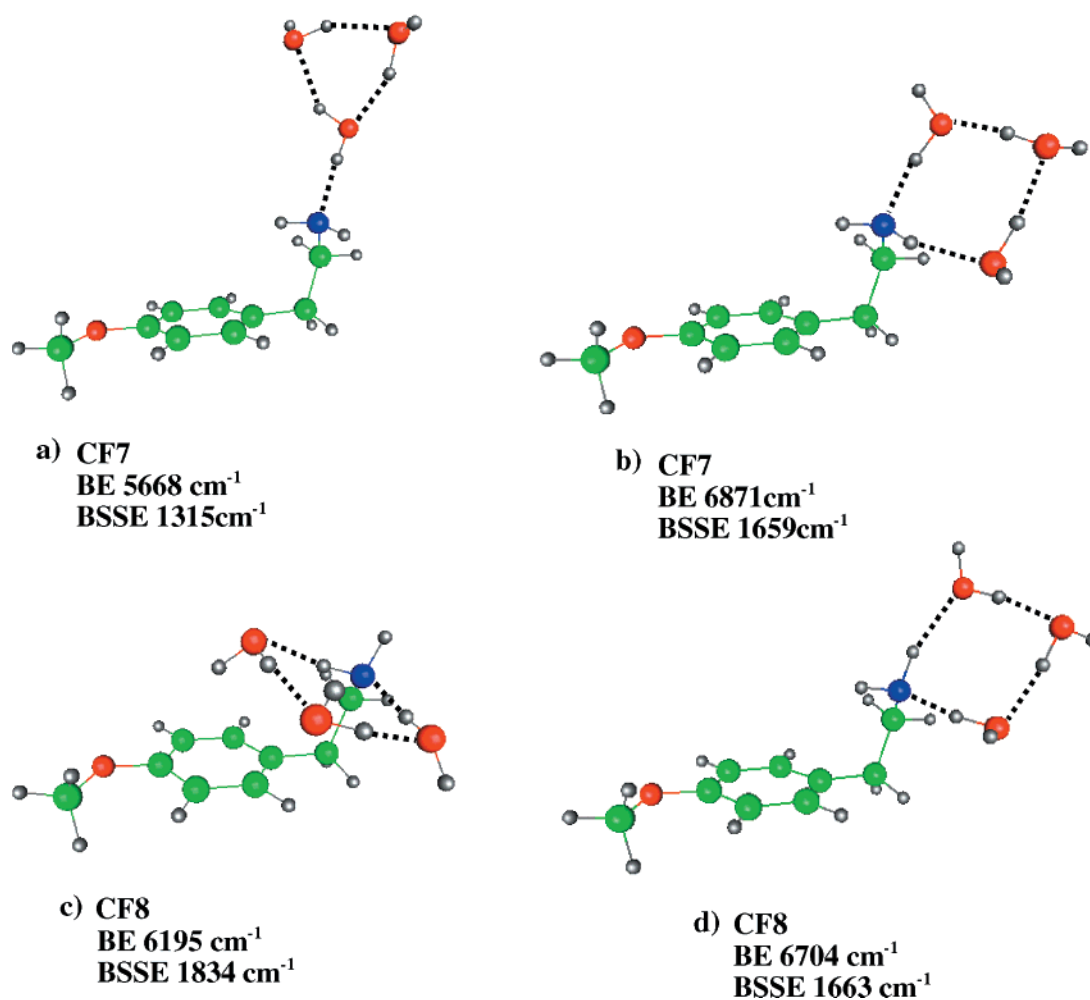
MPEA(H₂O)₃

Figure 5. Four selected 1:3 isomers structures calculated at the B3LYP/6-31+G* level, build up from precursors CF7 and CF8 (see Figure 1). BE stands for the binding energy corrected from ZPE and BSSE. The upper right geometry is the most stable structure of the 1:3 complex.

TABLE 3: Experimental and Calculated Vibrational Wavenumbers of the Most Stable 1:4 Isomers Built Up on the Gauche Precursor CF4^a

exptl		freq no.	CF4	
isomer I	isomer II		internal H	external H
		1	13	16
		2	19	17
		3	25	34
		4	38	41
48 m	49 m	5	46	48
55 vw	58 w	6	60	70
56 vw	61 w	7	76	74
71 m	73 m	8	88	86
101 m	98 m	9	98	88
142 vw	107 m	10	110	100
		11	140	141

^a The structures have daisy chains of water molecules ending in the external H atom (most stable) and in the internal H atom of the NH₂ group. Note the similarity between both sets of calculated frequencies, despite the considerable difference in geometries.

from the three optimized stable isomers of the MPEA(H₂O)₃ complex and add one molecule of solvent to the daisy chain or the water ring site, optimizing the resulting structure. The procedure is repeated for each of the four conformers of the bare molecule.

Figure 6 shows a few of the most stable structures and their binding energies calculated at the B3LYP/6-31+G* level. Once more, there are two types of structures: one with a daisy chain of water molecules attached to one side of the NH₂ moiety and other with a crown of four water molecules, with one of its solvents bound to the NH₂ group. The energy difference between both structures is ~500 cm⁻¹. There are a number of additional structures, for example, a four water molecule ring attached to the NH₂ by an HO—H...NH₂ hydrogen bond and interacting with the aromatic ring, with a binding energy ~300 cm⁻¹ less stable than the most stable structure (Figure 6a).

Table 3 shows the vibrational modes observed in the hole-burning spectrum of the 1:4 isomers. For the purpose of comparison, the table also depicts the calculated vibrational modes of the two most stable calculated species based on the CF4 conformer, i.e., the structures with the daisy chain of water molecules attached to either the external (Figure 6c) or the internal hydrogen atom of the NH₂ (Figure 6b). It is worth noting the close energy of the vibrational modes of both isomers. In addition, the large number of vibrational bands hampers the formal assignment, or even the decision whether the internal H atom structure is one of the experimental isomers.

IV. Discussion

The overall analysis presented thus far prompts to the conclusion that the preferred geometry of the complexes studied

MPEA(H₂O)₄

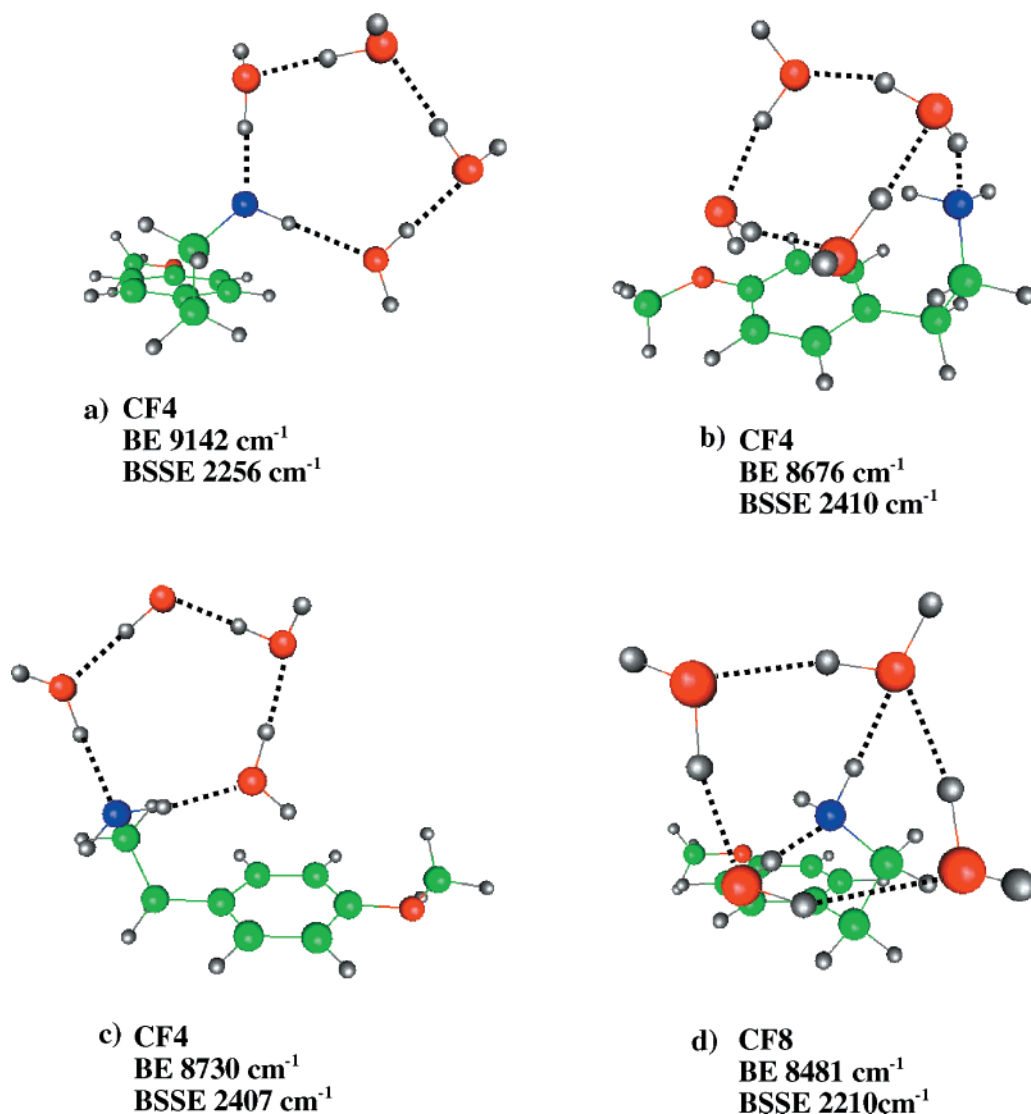


Figure 6. Four selected 1:4 isomer structures calculated at the B3LYP/6-31+G* level, built up from precursors CF4 and CF8 (see Figure 1). BE stands for the binding energy corrected from ZPE and BSSE. The upper left geometry is the most stable structure of the 1:4 complex.

has the chain of water molecules linking the N atom to the external H atom (of the NH₂) and, presumably, the observed complex has this structure. The energy difference between isomers with water daisy chains bound to internal and external H atoms is independent of the number of water molecules; in fact, ~400 cm⁻¹ for the 1:2 complex, ~500 cm⁻¹ for the 1:3, and ~400 cm⁻¹ for the 1:4. Further, the BSSE correction for the internal H atom structures of any stoichiometry is ~200 cm⁻¹ larger than that for the external, a likely consequence of the spatial overlapping of the aromatic ring and the water molecule basis functions. A similar effect is observed in the chromophore, where gauche conformers are more affected by a structural BSSE than the anti ones.¹⁶

Addition of the third water molecule to the 1:2 isomers built from precursors CF4 and CF7 originates a new type of structure, namely a ring of water molecules attached to the NH₂ group by a single hydrogen bond (Figure 5a). In the case of precursors CF5 and CF8, the orientation of the NH₂ group precludes the formation of water-ring type structures, or at least the barrier

connecting these minima with the more stable daisy chain structures are very small, as we have been unable to optimize the structures. In addition, the ring of water molecules is ca. 1200 cm⁻¹ less stable than the daisy chain. This energy difference decreases to only 500 cm⁻¹ for the 1:4 complexes.

It should be noted that the structure of the conformers within the complex has a small effect on the complex BE, and the feature applies to all the stoichiometries. For example, the energy difference between complexes based on the pairs [CF4, CF7] or [CF5, CF8] are ca. ~150 cm⁻¹, and the same applies to the energy difference between cis and trans conformer pairs, ~50 cm⁻¹. The small size of energy differences avoids the safe identification of the precursors of the experimental isomers.

Inspection of Table 4 helps to address the influence of the change in ion geometry on the experimental binding energies. Table 4 shows a comparison between the experimental and calculated energy release on the addition of one water molecule (Δ BE) to the 1:1 to 1:4 complexes, and between the calculated and experimental BEs obtained from the most stable geometry

TABLE 4: Experimental and Calculated Energies for the Addition of One Water Molecule to the Most Stable 1:*n* Complex (Δ BE) and Binding Energies of the 1:*n* Complex (BE) as a Function of the Number of Solvent Molecules of the Complex (both energies are corrected from BSSE and ZPE)

MPEA/H ₂ O	Δ BE		BE	
	exptl	calcd	exptl	calcd
1:1 ^a	1865/1730 ^b	1877/1951	1865 ^c	1951 ^c
1:2	2351	2130	4216	4081
1:3	2475	2790	6691	6871
1:4	2456/2390 ^b	2270	9147 ^c	9142

^a From ref 1. ^b Two isomers are observed. ^c Mean values.

for each stoichiometry. Both reported energies are BSSE and ZPE corrected. The difference between calculated and experimental BEs is less than 300 cm⁻¹ (i.e., <1 kcal/mol), and thus the agreement may be considered as excellent. There exists a correlation between the calculated and the experimental Δ BE with the number of water molecules. In fact, the addition of the second water to the 1:1 complex increases the BE more than the addition of the first solvent to the chromophore, as expected from the large water–water interaction energy and the cooperative effects. The addition of the third water molecule results in the largest Δ BE, due to a relaxation of the ring stress, yielding bond angles and distances close to the optimum values.¹⁷ Therefore, the comparison between experimental and calculated BEs confirms that the experimental isomer has a structure with a chain of water molecules around the NH₂ group. The addition of the fourth water molecule does not have such a large increase in BE since the chain is already relaxed, but both calculations and experiments point to a Δ BE larger than that for the addition of the second water molecule. This is justified by the cooperative effects, which are larger than for the 1:2 species.

The experimental and calculated total BEs are in excellent agreement, in particular for the 1:4 species, for which they differ in some 5 cm⁻¹, possibly as a consequence of errors cancellation. The source of uncertainties between both sets of values stems from the errors inherent to the calculation and experimental inaccuracies (the experimental values are known to ± 100 cm⁻¹) and thus, the experimental determination is not affected by a large change in the ion structure. This is not to say that the change is not produced, but that the minimum potential energy of the ion is accessible from the S₁ state, providing a precise determination of the complexes BEs. Furthermore, the agreement leads to assess that despite the large number of isomer structures, it is likely that the most stable species have been found. Alternatively, if there were some other stable structures, their energy difference would only differ from the proposed ones by less than ~ 1 kcal/mol.

The data in Table 4 also provide a clue to the 1:4 complex assignments. The experimental BEs of the two existing isomers are within 66 cm⁻¹, which is of the order of the BE difference between the cis and trans pairs. Therefore, the existence of two 1:1 isomers and two 1:4 isomers seems to be due to the relative orientation of NH₂ and O(Me) groups, and not different water structures, sharing the same conformer.

In summary, with the well identified two isomers for the 1:1 and 1:4 complexes, we are tempted to propose an overall picture for the MPEA(H₂O)_{2–4} complexes. In fact, the two isomers of the 1:1 complex, have origin bands shifted by 13 cm⁻¹ and structures with the proton-donor water hydrogen bonded to the nitrogen atom of the NH₂ and arising from precursors CF5 or CF8 (i.e., the two cis–trans pairs of a NH₂ orientation). It is likely that the 1:2 and 1:3 complexes also have two isomers each, based on a cis–trans pair of conformers, but with origin bands separated by less than 1 cm⁻¹, and thereby observed as a single isomer in our REMPI and hole-burning experiments. The addition of the fourth water to the 1:3 complex leads again to an observable isomer shift of ~ 3 cm⁻¹, splitting the origin bands in the REMPI spectrum. These assignments are confirmed by the comparison between experimental and calculated BEs.

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- No hydrogen bond structural parameter data are included in the text. The data are available from the corresponding author.