A Theoretical and Experimental Study of Water Complexes of *m*-Aminobenzoic Acid MABA·$(H_2O)_n$ ($n = 1$ and 2)

Yonggang He, Chengyin Wu, and Wei Kong*

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

Received: August 31, 2004; In Final Form: November 15, 2004

We report studies of supersonically cooled water complexes of *m*-aminobenzoic acid MABA·$(H_2O)_n$ ($n = 1$ and 2) using two-color resonantly enhanced multiphoton ionization (REMPI) and UV−UV hole-burning spectroscopy. Density functional theory calculations are also carried out to identify structural minima of water complexes in the ground state. For the most stable isomers of both complexes, water molecules bind to the pocket of the carboxyl group in a cyclic hydrogen bond network. Vibrational frequency calculations for the first electronically excited state (S_1) of these isomers agree well with the experimental observation. The addition of water molecules has a major impact on the normal mode that involves local motion of the carboxyl group, while negligible effects are observed for other normal modes. On the basis of the hole-burning experiment, two major isomers for each complex are identified, corresponding to the two conformers of the bare compound. Compared with the other two isomers of aminobenzoic acid, the red shifts of the origin bands due to water complexation in MABA are considerably larger. Similar to *p*-aminobenzoic acid and different from *o*-aminobenzoic acid, the existence of the intermolecular stretching mode is ambiguous in the REMPI spectrum of MABA·$(H_2O)_n$.

Introduction

Hydrogen bonding is ubiquitous in chemical and biological systems. Studies of organic chromophores containing competitive multiple hydrogen bonding sites constitute an active area of research.[1−5] The preference of a solvent molecule for a certain binding site on a solute molecule is of general chemical interest. Such information can be obtained from experiments in the gas phase without the interference of the bulk solvent. Using molecular beam techniques, cold, isolated clusters of different solute−solvent compositions can be prepared, and isomeric molecular complexes with solvent molecules "frozen" at different binding sites on the solute can be generated.[6] These complexes can then be interrogated using a variety of high-resolution spectroscopic methods such as mass-resolved resonantly enhanced multiphoton ionization (REMPI). For the identification of different isomeric structures, hole-burning spectroscopy is also routinely employed.

In this paper, we report spectroscopic studies of complexes of *m*-aminobenzoic acid (MABA) containing one or two water molecules. The general interest in aminobenzoic acids and their solvation mechanisms arises from both their biological importance and their chemical properties. They are multifunctional hydrogen bonding molecules, ideal for studies of interactions between water and aromatic chromophores. In protic solvents, they can act both as H acceptors at the O atom of the −C═O group and the N atom of the $-NH_2$ group, and as H donors at the −OH group and the $-NH_2$ group. They can also form hydrogen bonds through their aromatic π electrons. In nonpolar solvents, MABA exists predominantly as a neutral molecule. In the solid state or in aqueous solutions, it exists as a zwitterion, unlike the other two isomers.[7,8] On the biological aspect, aminobenzoic acids are antimetabolites of sulfanilamide. MABA is also of great importance in pharmaceutical and chemical industries; it is used in synthesis of analgesics, antihypertensives, and vasodilators.[9]

In our previous effort on bare MABA, we observed two conformational isomers, as shown in Figure 1, on the basis of results from resonantly enhanced multiphoton ionization and zero kinetic energy photoelectron spectroscopy (ZEKE).[10] Our hole-burning experiment further revealed that the transition energies to the first electronically excited state (S_1) differ by 27 cm^{-1} for the two conformers. The frequencies of the vibrational modes, however, were independent of the molecular conformation.[10] In this study, we extend our investigation to the structural and spectroscopic properties of MABA·$(H_2O)_n$ complexes with $n = 1$ and 2. We have also performed quantum mechanical calculations to obtain structures and binding energies for a few possible isomers in the ground state and vibrational frequencies of these species in the first electronically excited state. These results will be discussed in comparison with another study on the water complexes of *p*-aminobenzoic acid (PABA) and *o*-aminobenzoic acid (OABA) from our own group[11] and a few other groups.[12−15]

Experimental Details

The experimental setup has been described elsewhere.[16,17] Briefly, the apparatus is a standard molecular beam machine with a time-of-flight mass spectrometer (TOF-MS) and a heatable pulsed valve for supersonic cooling. The sample was purchased from Aldrich Co. and used without further purification. The temperature of the nozzle was ~150 °C, and the carrier gas at 2 atm pressure was a mixture of argon and room-temperature water vapor. To optimize for a specific complex, the time delay between the pulsed valve and the laser was adjusted by a delay generator (Stanford Research, DG535).

To resolve the different conformational isomers, we preformed UV−UV hole-burning experiments. At first, a two-color

---

[*] Author to whom correspondence should be addressed. E-mail: Wei.Kong@Oregonstate.edu; phone: 541-737-6714; fax: 541-737-2062.

10.1021/jp0460644 CCC: \$30.25

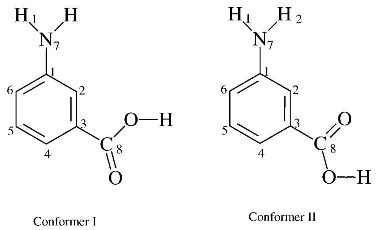

Figure 1. Structural conformers of MABA.

two-photon REMPI spectrum was recorded by scanning the pump laser (Laser Analytical Systems, LDL 20505, pumped by a Nd:YAG laser, Spectra Physics, GCR 190) across the vibronic levels of the S_1 state while using the fourth harmonic of a Nd:YAG laser at 266 nm (Continuum, Powerlite 7010) for further ionization. The intensities of both lasers were minimized so that the ion signal due to either laser was negligible. Then, a third (hole-burning) UV laser (Laser Analytical Systems, LDL 2051, pumped by a Nd:YAG laser, Spectra Physics, GCR 230) was introduced with a time advance of 20 ns. By fixing the third laser on one of the origin bands while monitoring the depletion of the ion signal as the pump laser scanned across the REMPI spectrum, vibronic features of the chosen isomer were identified. The two resonant laser beams were set to counterpropagate, while the ionization laser was set to cross the two resonant laser beams at a 5° angle.

Calculation. Possible structures of MABA and its complexes with one or two water molecules were explored by performing a series of density functional theory (DFT) calculations using the Gaussian 03 suite.[18] The optimized structure of bare MABA was used as the starting point for the complex containing one water molecule (1:1 complex). The water molecule was initially placed alternatively to the different hydrogen bonding sites of MABA, and each structure was then fully optimized using the Becke−Lee−Yang−Parr functional (B3LYP) with a basis set of 6-31+G(d). The convergence of the resulting isomer was confirmed by calculations of vibrational frequencies. The initial structures for complexes with two water molecules (1:2 complex) were generated either with a water dimer bound alternatively to the different hydrogen bonding sites or with each water molecule bound independently to the available sites. The most stable ground-state structures for both the 1:1 and 1:2 complexes were subsequently chosen as the starting point of optimization for the S_1 state at the CIS/6-31G level. Vibrational frequencies of the normal modes at the S_1 state were also calculated at the same level of theory. To obtain a good agreement between theory and experiment in the vibrational assignment, a scaling factor of 0.9 was used.[19]

Results

1. Theoretical Calculations. Our previous UV−UV hole-burning experiment on bare MABA has confirmed the coexistence of two conformational isomers in the gas phase named conformer I and II (Figure 1).[10] Each conformer has six stable structural arrangements with one water molecule. The fully optimized structures together with their relative energies including zero point vibrational energy (ZPVE) corrections are displayed in Figure 2. In the two most stable structures Ia and IIa, the water molecule bridges between the −C═O and the −OH groups, and the resulting extra stability is about 4 kcal/mol compared with the second set of most stable isomers Ib and IIb.[11,20] All higher energy isomers have only one H-bond, and those hydrogen bonded at the −C═O group are the most stable, while those bonded at the −OH group are the least stable.

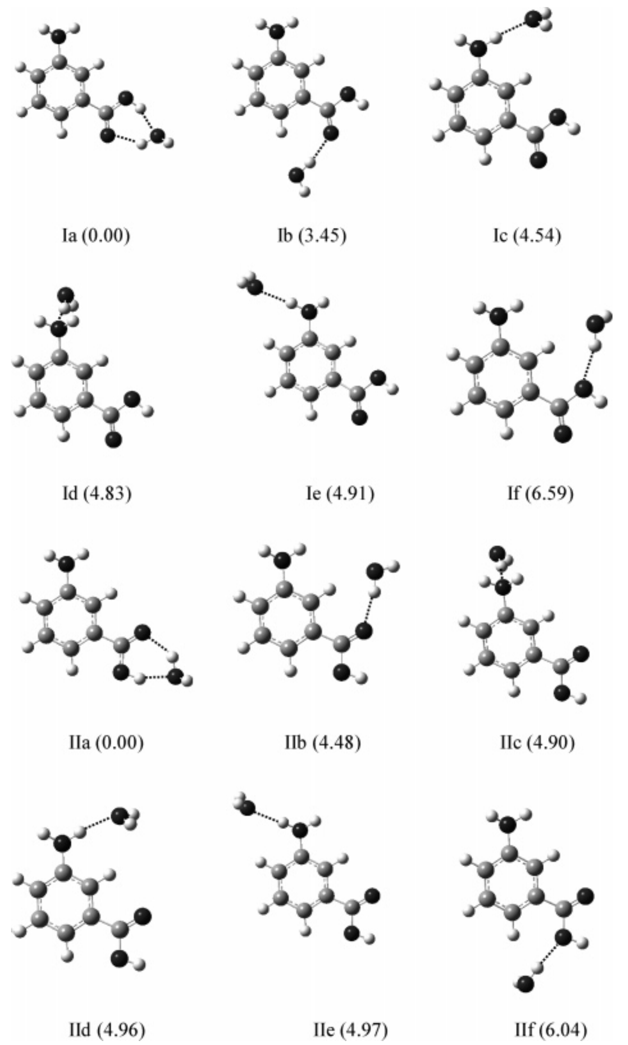

Figure 2. Optimized geometries of the 1:1 water complex of the two conformers of MABA at the B3LYP/6-31+G(d) level. The values in parentheses are relative energies in kcal/mol.

The three structures with water hydrogen bonded to the amino group are of similar binding energies, about 5 kcal/mol compared with those of the most stable structures. The molecular conformation, on the other hand, has essentially no effect on the structural arrangement between water and MABA, and except for an order switch between isomers c and d, a one-to-one correlation between the two sets of isomers can be observed.

For each conformer of bare MABA, more than 20 energy minima were found for the 1:2 complex. Nine of the most stable isomers for conformer I are displayed in Figure 3, and the two most stable structures for conformer II are displayed in Figure 4. Other structures for conformer II are similar to those for conformers Ib−Ih, and they are therefore not reproduced for compactness. The energetically most stable structures incorporate three linear hydrogen bonds and allow each molecule to be both a H-bond donor and a H-bond acceptor. In structures Ii and IIb, water dimer bridges are formed between the $-NH_2$ and the −COOH groups. The energy cost of this bridge, compared with the bridge inside the −COOH group (Isomer Ia and IIa), is about 3 kcal/mol for IIb and 7 kcal/mol for Ii. This difference is consistent with the observation of the 1:1 complex, that is, the O atom of the −C═O group with a higher electron density is a stronger H acceptor than that of the −OH group. Except for this order switch between structures b and i, similar

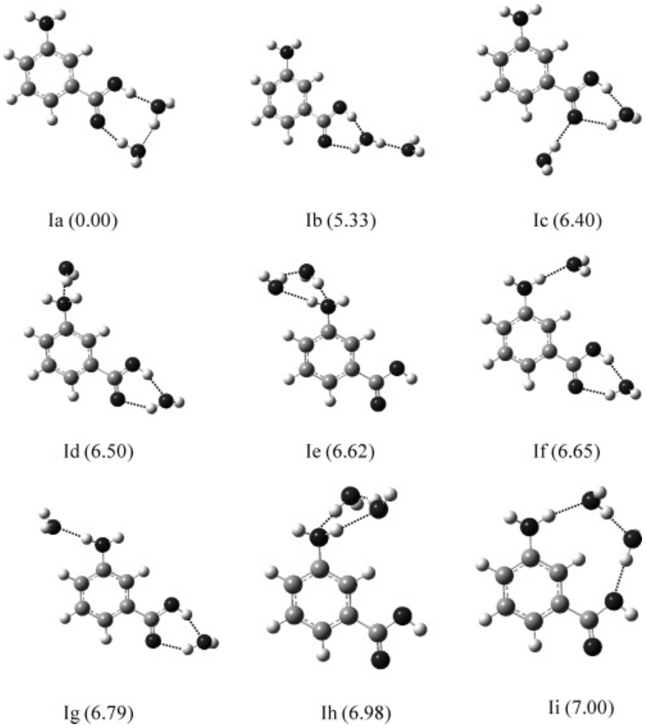
Ia (0.00) Ib (5.33) Ic (6.40)
Id (6.50) Ie (6.62) If (6.65)
Ig (6.79) Ih (6.98) Ii (7.00)

Figure 3. Optimized geometries of the 1:2 water complex of conformer I of MABA at the B3LYP/6-31+G(d) level. The values in parentheses are relative energies in kcal/mol.

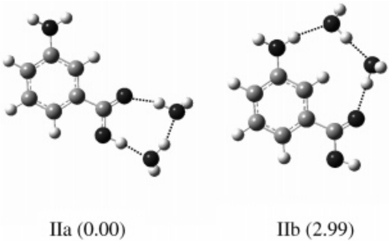
IIa (0.00) IIb (2.99)

Figure 4. Two most stable structures for the 1:2 water complex of conformer II of MABA at the B3LYP/6-31+G(d) level. Higher energy structures are similar to those of Figure 3, Ib−Ih.

to the case of the 1:1 complex, a one-to-one correlation between the two sets of isomers are also observed.

2. Experimental Results. The two-color 1+1′ REMPI spectrum of the 1:1 water complex of MABA is displayed in Figure 5, trace *a*. The intensities of both laser beams were optimized to avoid interference due to nonresonant ionization, and the ion signal due to any single laser was essentially undetectable. On the low-energy side of the spectrum, more than one strong transition is observable, implying the existence of multiple isomers. Hole-burning experiments are therefore necessary to ascertain the nature and number of isomers.

The hole-burning spectra of the two major isomers of the 1:1 complex are shown in the lower two traces of Figure 5, with the hole-burning laser set at positions Ia (30365 cm^{-1}, trace *b*) and IIa (30373 cm^{-1}, trace *c*), respectively. These two isomers are hereafter denoted as Ia and IIa and are tentatively assigned to the corresponding structures shown in Figure 2. The rationale for this assignment will be presented in the following Discussion section. The small shoulder at 30415 cm^{-1} marked by a number sign in the figure also corresponds to a minor isomer. However, the intensity of this isomer was so low that the hole-burning experiment only produced a single feature at the origin, with no vibrational assignment possible. The features marked by asterisks belong to the 1:2 complex, and they will be discussed later. Taking these considerations into account, all the significant features in trace *a* can then be accounted for. We therefore conclude that there are only two major isomers in the molecular beam within our observation window.

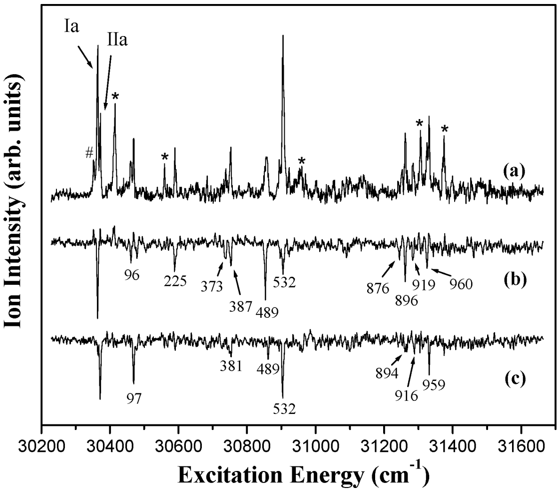

Figure 5. Two-color two-photon REMPI spectrum of jet-cooled MABA·$(H_2O)_1$ (trace *a*) and UV−UV hole-burning spectra with the hole-burning laser fixed at the Ia (30365 cm^{-1}, trace *b*) and IIa (30373 cm^{-1}, trace *c*) positions. The feature marked by "#" represents a minor isomer, while those marked by "*" are from dissociation of the 1:2 complex (see Figure 7 for further details).

TABLE 1: Observed Vibrational Frequencies and Assignments for the S_1 State of the 1:1 Water Complex of MABA

Isomer Ia		Isomer IIa		
expt	calcd[a]	expt	calcd[a]	assignment & description[b]
96	100	97	101	H_0^1, β(−COOH), $\beta(H_2O)$
225	225			C_0^1, β(−COOH)
373	370			$6b_0^1$, β(ring)
387	380	381	376	D_0^1, $\beta(-NH_2)$
489	492	489	484	E_0^1,β(−COOH), $\beta(-NH_2)$ and β(ring)
532	533	532	527	$6a_0^1$, β(ring)
876				$D_0^1E_0^1$
896	877	894	871	$19a_0^1$, β(ring)
919		916		$D_0^16a_0^1$
960	967	959	968	12_0^1, β(ring)

[a] The values include a scaling factor of 0.9. [b] β represents in-plane bending vibrations.

The amount of red shift of the origin band in the 1:1 complex compared with the bare compound is considerably larger for MABA than for OABA and PABA. The difference in transition energy between the two isomers of bare MABA or the two isomers of its 1:1 complex, however, is small. The origin band of the two conformers of MABA only differs by 27 cm^{-1}, and the difference for the water complexes Ia and IIa is less than 10 cm^{-1}. The red shifts due to water complexation, on the other hand, are about 100 cm^{-1} for both Ia and IIa. In comparison, the red shift in the 1:1 complex of OABA is 55 cm^{-1}, while a blue shift of 17 cm^{-1} has been observed in PABA.[11] Additional stabilization in the excited electronic state is implied in the 1:1 complex of MABA.

Table 1 lists the observed vibronic transitions of the two major isomers. To assist with the assignment, we have performed ab initio calculations on the CIS/6-31G level for the vibrational frequencies of the S_1 state. An overall agreement between the calculation and the experiment is obtained when a scaling factor of 0.9 is used for the calculated frequencies. Modes that are associated with the motion of the aromatic ring are labeled using the convention of Varsanyi's nomenclature.[21] Other modes that

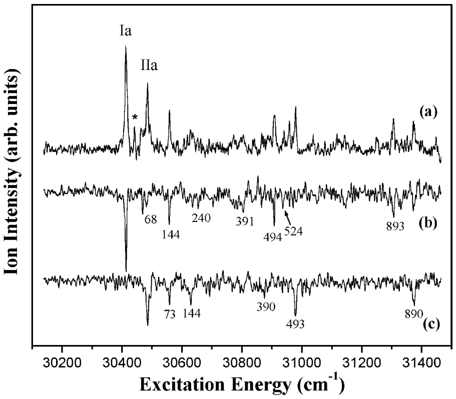

Figure 6. Two-color two-photon REMPI spectrum of jet-cooled MABA·$(H_2O)_2$ (trace *a*) and UV−UV hole-burning spectra with the hole-burning laser fixed at the Ia (30414 cm^{-1}, trace *b*) and IIa (30486 cm^{-1}, trace *c*) positions.

TABLE 2: Observed Vibrational Frequencies and Assignments for the S_1 State of the 1:2 Water Complex of MABA

Isomer Ia		Isomer IIa		
expt	calcd[a]	expt	calcd[a]	assignment & description[b]
68	73	73	72	H_0^1, β(−COOH), $\beta(H_2O)$
144	152	144	152	a_0^1, $\gamma(H_2O$-ring)
240	235			C_0^1, β(−COOH)
391	389	390	392	D_0^1, $\beta(-NH_2)$
494	498	493	497	E_0^1,β(−COOH), $\beta(-NH_2)$ and β(ring)
524	543			$6a_0^1$, β(ring)
893	879	890	874	$19a_0^1$, β(ring)

[a] The values include a scaling factor of 0.9. [b] β represents in-plane bending vibrations.

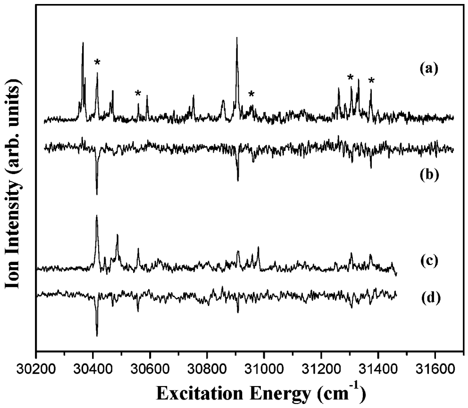

Figure 7. REMPI spectra of the 1:1 and 1:2 complexes of MABA. (a) Two-color two-photon REMPI spectrum of jet-cooled MABA·$(H_2O)_1$; (b) UV−UV hole-burning spectrum of MABA·$(H_2O)_1$ with the hole-burning laser fixed at 30415 cm^{-1}; (c) two-color two-photon REMPI spectrum of jet-cooled MABA·$(H_2O)_2$; (d) UV−UV hole-burning spectrum of MABA·$(H_2O)_2$ with the hole-burning laser fixed at 30414 cm^{-1}.

mainly involve the motion of the $-NH_2$ and the −COOH moieties are named according to the corresponding modes observed in bare MABA.[10] Similar to bare MABA, the spectrum is dominated by in-plane or even quanta of out-of-plane vibrational modes because of symmetry reasons. The normal modes in the 1:1 complex exhibit essentially no dependence on the molecular conformation, and therefore they cannot be used to distinguish between the two isomers Ia and IIa. The transition observed at 96 cm^{-1} (mode *H*) for isomer Ia is assigned as a collective motion of the −COOH group and H_2O. This mode is also observable in the spectrum of isomer IIa. On the basis of our calculation for isomer Ib in Figure 2, the only low frequency in-plane motion below 200 cm^{-1} is the intermolecular stretching mode at 69 cm^{-1}, and this value is too small to be assigned to the above transition at ~100 cm^{-1}. We therefore conclude that there is no obvious intermolecular vibrational activity in Figure 5. The feature at 876 cm^{-1} is tentatively attributed to the combination band of modes *D* and *E*, although it is also close to the theoretical value of mode 19a. The rationale for this assignment is that typically for this type of calculation with a scaling factor of 0.9, we only expect a reasonable agreement between theory and experiment for low frequency modes, while at nearly 1000 cm^{-1}, an exact agreement would be fortuitous. The same argument is also applied in the assignment of the 1:2 complex. The satisfactory assignment in Table 1 further supports the notion that under our experimental conditions, only the most stable isomers Ia and IIa exist in our molecular beam. Normal mode calculations for other structures listed in Figure 2 were considered unnecessary because of the high energies of the corresponding isomers.

Figure 6 shows the two-color 1+1′ REMPI spectrum of the 1:2 complex (trace *a*) together with the two hole-burning spectra (traces *b* and *c*). The origins of the hole-burning spectra are 30414 and 30486 cm^{-1}, about 70 cm^{-1} apart. Between the two major isomers, the weak feature marked by an asterisk was confirmed to be a third isomer, but its intensity was too low for vibrational analysis. With the exception of this weak feature, all the significant features of the REMPI spectrum correlate well with the two hole-burning spectra, and we thus conclude that similar to the 1:1 complex, there are only two major isomers and one minor isomer in our molecular beam for the 1:2 complex. These two major isomers are hereafter denoted Ia and IIa and are tentatively assigned to the corresponding structures shown in Figures 3 and 4. The origins of the two major isomers are red shifted from their respective bare molecules by 65 and 20 cm^{-1}. In contrast, a blue shift of 19 cm^{-1} has been observed in the REMPI spectra of the 1:2 water complexes of both OABA and PABA.[11]

The observed vibronic transitions of both major isomers of the 1:2 complex are listed in Table 2 together with results from ab initio calculations on the CIS/6-31G level. Consistent with Table 1, the scaling factor for the calculated frequencies is also 0.9. Similar mode distributions are observed for both the 1:1 and 1:2 complexes, including mode *H*, which involves a collective motion of the carboxyl group and the two water molecules. Mode *a* represents out-of-plane vibration of the water dimer relative to the ring.

A recalcitrant problem with experimental studies of weakly bound complexes is the possibility of dissociation.[18] Figure 7 compares the REMPI spectra of the 1:1 (trace *a*) and the 1:2 complex (trace *c*), together with a hole-burning spectrum of each complex. All the features marked by asterisks in trace *a* line up with those in traces *b*−*d*. Trace *b* was obtained by setting the hole-burning laser at 30415 cm^{-1} and the mass gate on the 1:1 complex, while trace *d* was obtained by setting the hole-burning laser at the same origin but the mass gate on the 1:2 complex (isomer Ia). The identical locations of all the marked features allude to the possibility that the species of trace *b* is a dissociation product of the 1:2 complex in trace *d*. Some of the marked features in trace *a* only show up once either in trace *b* or in trace *d*, and we attribute this result to mode dependence during dissociation. For example, mode *H* at 68 cm^{-1} and its second harmonic at 144 cm^{-1} must have a low yield for dissociation, since they are barely observable in the hole-burning spectrum of the 1:1 complex (trace *b*), while they are clearly distinguishable in the spectrum of the 1:2 complex (trace *d*). In contrast, the feature near 30962 cm^{-1} should have a high dissociation yield since it is clearly observable from the spectrum of the 1:1 complex (trace *b*) but not observable in the spectrum of the 1:2 complex (trace *d*). This feature is most likely an intermolecular bending mode with a value of 478 cm^{-1} on the basis of our calculation, and it is not included in Table 2 because of its highly dissociative nature. The feature near 30 900 cm^{-1} (trace *a*) contains multiple transitions, including mode 6a of the 1:1 complex, and its intensity is therefore not reproduced in the spectrum of the 1:2 complex.

Discussion

Structural assignment for the two major isomers of the 1:1 complex is based on the transition energy to the S_1 state. According to our CIS calculation, the transition energy is 4.871 eV for isomer Ia and 4.899 eV for isomer IIa. A blue shift observed in the REMPI spectrum of isomer IIa therefore conforms to the above assignment. Although the energy difference from our calculation is larger than the experimental value, we believe that the theory should be qualitatively reliable in predicting the trend in transition energies. In addition, the relative intensities of the origin bands of the two isomers are similar to those of the two conformers of bare MABA, and this assignment is therefore consistent with the conformational assignment of the bare compound. Our DFT calculation, on the other hand, resulted in a more stable structure for isomer IIa by 37 cm^{-1}, including corrections due to zero-point energies. Given the uncertainty of this type of calculations, we prefer not to use this information in this assignment. Due to the insensitivity of the vibrational frequencies on the molecular conformation and the limited amount of information available at present, this assignment is only tentative.

Similarly, for the 1:2 water complex of MABA, the calculated transition energy is 4.884 eV for isomer Ia and 4.908 eV for isomer IIa. Following the same reasoning as above, the lowest transition at 30414 cm^{-1} in Figure 6a can thus be assigned to the water complex of conformer I of MABA, and vide infra. This assignment is also consistent with that of the 1:1 complex and that of the bare compound, that is, the lower energy transition with a higher intensity corresponds to conformer I in Figure 1 and its water complexes.

For both the 1:1 and 1:2 complexes, traces of a third isomer are observed, although in both cases, the transition intensities of the minor isomer are too low for any vibrational assignment. For the 1:1 complex, structure Ib is more stable than structure IIb by almost 1 kcal/mol in Figure 2; thus, this structure is the most logical candidate for the minor isomer. In Figure 4, structure IIb shows substantial stability compared with the rest of the higher energy isomers. We tentatively assign this structure to the minor isomer of the 1:2 complex. This result offers evidence that a ring structure involving both the amino and the carboxyl groups is possible, albeit unfavorable compared with the structure where a water cluster anchors at the carboxyl site. In contrast, our observations of water complexes of OABA and PABA only contained one isomer, with no traces of any minor structures.[11] This difference might be an indication of the weaker electron induction effect in the meta-substituted compound.

The red shifts of the origin bands of the water complexes compared with the bare compound are considerably larger for MABA than for OABA and PABA.[11] For the 1:1 complex of PABA and the 1:2 complexes of PABA and OABA, blue shifts of less than 20 cm^{-1} have been observed. A more tightly bonded excited state than the ground state is thus implied in the water complexes of MABA. On the basis of our DFT and CIS calculations, for the 1:1 complex of MABA, the length of the hydrogen bond $C{=}O\cdots HO_w$ decreases while that of $O{-}H\cdots O_w$ increases upon excitation. The observed additional stabilization in the excited electronic state in the 1:1 water complex is thus a reflection of a stronger hydrogen bonding capability of the carbonyl group than that of the hydroxyl group.

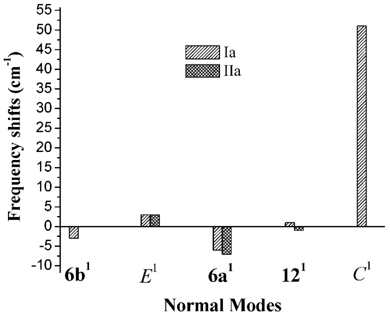

Figure 8. Frequency shifts of a few observed normal modes in MABA·$(H_2O)_1$ relative to the bare compound. The uncertainty for all the values is 3 cm^{-1}.

The vibrational spectroscopy of the water complexes offers information on the initial step of water solvation. The site of water addition can be deduced from the frequency shifts with the addition of water molecules. These shifts are displayed in Figure 8 for the two major isomers of the 1:1 complex. Modes 6b, *E*, 6a, and 12 mainly involve deformation of the aromatic ring, and with the addition of water molecules, they only undergo slight shifts. On the other hand, a large shift is observable for the in-plane bending mode of the carboxyl group: in Figure 8, mode *C* for the Ia isomer increases by ~50 cm^{-1} with the addition of one water molecule. The site of water addition should therefore be the carboxyl group for conformer I of MABA, in excellent agreement with our DFT calculations. Although mode *C* for isomer IIa is too weak for a definitive assignment, the above conclusion should also be applicable, since the normal modes in the water complexes exhibit essentially no dependence on the molecular conformation. Interestingly, the addition of the second water molecule to the 1:1 complex results in marginal changes in the vibrational frequency. Modes D, *E*, and 6a undergo frequency shifts within 10 cm^{-1} of their respective values in the 1:1 complex, and even for the in-plane bending mode *C* of the carboxyl group, the shift is only 15 cm^{-1}. This fact suggests that the second water molecule should be in close proximity to the first water molecule, exerting minimal disturbance to the molecular frame. Limited by available resources, we were unable to perform an IR−UV hole-burning experiment to investigate the vibrational spectroscopy of the ground state of the water complexes. Certainly more information on the frequency shifts of the ground-state complexes would be a tremendous addition to this study.

Similar to the cases of PABA and OABA,[11] in both the 1:1 and 1:2 complexes of MABA, we believe that it is the hydrogen-bonding site on the carboxyl group that water molecules prefer to occupy. The amino group, although typically considered hydrophilic, loses out in the competition even with the availability of two water molecules. Given the high electron density at the carboxyl group, it is no surprise that the first water molecule prefers the carboxyl site. Somewhat surprising is the essentially hydrophobic behavior of the amino group. All aminobenzoic acid molecules contain a pair of electron "push−pull" substituents. In the ground state, a fraction of the electron from the amino group is transferred to the carboxyl group.

According to the Mulliken population analysis, the amino group has a positive charge of $\sim +0.1$ and the carboxyl group has a negative charge of ~ -0.1 for both conformers of MABA. Although the electron-attracting inductive effect of the carboxyl group in MABA is slightly smaller than that in PABA and OABA because of the resonance effect, it is still sufficient to hold on to both water molecules, at least for the major isomers formed in our molecular beam.

Similar to PABA but different from OABA,[11] the assignment of the intermolecular stretching mode in the REMPI spectra of the water complexes of MABA remains ambiguous, although mode *H* and mode *C* both contain contributions from intermolecular bending vibration. On the basis of our calculation, the stretching mode should appear at 178 cm^{-1} above the origin of the 1:1 complex. Given the signal-to-noise ratio of the experimental spectrum (Figure 5), it is difficult to definitively identify this transition.

Conclusions

Spectroscopic properties of the excited state of MABA water complexes have been studied using two-color resonantly enhanced multiphoton ionization and UV−UV hole-burning spectroscopy. Structures and binding energies for several of the most possible isomers in the ground state have been explored on the basis of DFT calculations. The overall analysis of the experimental and theoretical data has led to the identification of two major isomers for both the 1:1 and 1:2 complexes. With the aid of ab initio calculations, vibrational modes of the S_1 state of the observed isomers have been assigned, and a reasonable agreement between theory and experiment has been obtained. From the frequency shifts of some of the observed normal modes upon water addition, we conclude that it is the hydrogen bonding site on the carboxyl group that water molecules prefer to occupy. Different from the water complexes of the other two isomers of aminobenzoic acid, both the 1:1 and 1:2 complexes of MABA show signs of a minor isomer, and in the 1:2 complex the minor isomer may contain a water bridge between the carboxyl group and the amino group. We attribute this result to the weaker electron “push−pull” effect in MABA. Mode-dependent dissociation of the 1:2 complex is also observed, but the assignment of the intermolecular stretching mode remains ambiguous.

Acknowledgment. This work was supported by the National Science Foundation, Division of Chemistry. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Wei Kong is an Alfred P. Sloan research fellow.

References and Notes

(1) Bernstein, E. R. *Atomic and Molecular Clusters*; Elsevier: Amsterdam, 1990.

(2) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer: Berlin, 1991.

(3) Castleman, A. W., Jr.; Wei, S. *Annu. Rev. Phys. Chem.* **1994**, *45*, 685−719.

(4) Zwier, T. S. *Annu. Rev. Phys. Chem.* **1996**, *47*, 205−241.

(5) Wolfenden, R.; Snider, M. J. *Acc. Chem. Res.* **2001**, *34*, 938−945.

(6) *Atomic and Molecular Beam Methods*; Scoles, G., Ed.; Oxford University Press: New York, 1988; Vol. 1.

(7) Gopal, L.; Jose, C. I.; Biswas, A. B. *Spectrochim. Acta* **1967**, *23A*, 513−518.

(8) Théorêt, A. *Spectrochim. Acta* **1971**, *27A*, 11−18.

(9) Palafox, M. A.; Gil, M.; Nunez, J. L. *Spectrosc. Lett.* **1996**, *29*, 609−629.

(10) He, Y.; Wu, C.; Kong, W. *J. Chem. Phys.* **2004**, *121*, 8321−8328.

(11) He, Y.; Wu, C.; Kong, W. *J. Phys. Chem. A* **2004**, submitted.

(12) Stearns, J. A.; Das, A.; Zwier, T. S. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2605−2610.

(13) He, Y.; Wu, C.; Kong, W. *J. Chem. Phys.* **2004**, *121*, 3533−3539.

(14) Wu, C.; He, Y.; Kong, W. *Chem. Phys. Lett.* **2004**, *398*, 351−356.

(15) Southern, C. A.; Levy, D. H.; Florio, G. M.; Longarte, A.; Zwier, T. S. *J. Phys. Chem. A* **2003**, *107*, 4032−4040.

(16) He, Y.; Wu, C.; Kong, W. *J. Phys. Chem. A* **2003**, *107*, 5145−5148.

(17) He, Y.; Wu, C.; Kong, W. *J. Phys. Chem. A* **2004**, *108*, 943−949.

(18) Frisch, M. J., et al. *GAUSSIAN* 03, Revision A. 7; Gaussian, Inc.: Pittsburgh, PA, 2003.

(19) Casida, M. E.; Jamorski, C.; Casida, K. C.; Sulahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439−4449.

(20) Stearns, J. A.; Das, A.; Zwier, T. S. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2605−2610.

(21) Varsanyi, G. *Assignment of Vibrational Spectra of Seven Hundred Benzene Derivatives*; Wiley: New York, 1974.

(22) *Cluster Ions*; Ng, C.-Y., Baer, T., Powis, I., Eds.; J. Wiley & Sons: Chichester, New York, 1993.