Structure and Hydrogen Bonding of Different Isomers of 2-Aminopyridine·NH_3 Studied by IR/R2PI Spectroscopy

Ronghu Wu, Sascha Vaupel, Petr Nachtigall,† and Bernhard Brutschy*

Institut für Physikalische und Theoretische Chemie, Johann Wolfgang Goethe-Universität Frankfurt, Marie-Curie-Str. 11, D-60439 Frankfurt am Main, Germany

Received: August 26, 2003

The electronic and vibrational spectra of the 1:1 clusters of 2-aminopyridine (2AP) with ammonia have been measured using resonant two-photon ionization (R2PI) and IR/R2PI vibrational spectroscopy. Density functional theory calculations were performed to identify structures and assign the vibrational spectra in the NH stretch region. The two lowest-energy isomers have been identified. In isomer I, which is the global minimum energy structure, ammonia forms a strong H bond with the amino group and a weak one with the aromatic nitrogen. The vibrations of the groups involved in this H bonding exhibit red shifts of 110 cm^{-1} for the donating amino N−H and of 69 cm^{-1} for the donating N−H group of ammonia. The degeneracy of the two asymmetrical vibrations of ammonia is removed in the cluster, with the corresponding bands at 3438 and 3406 cm^{-1}. In isomer II ammonia forms an H bond to the N−H group which points away from the aromatic nitrogen. This bond is weaker than the corresponding one in isomer I. The stretching vibration of the H bonded N−H in the amino group exhibits a red shift of 66 cm^{-1}, whereas the vibrations of ammonia are very similar to those of isolated ammonia. This gives evidence that ammonia is a pure H bond acceptor. The exclusiveness of these structural isomers is due to the dominant role of the proton affinity of ammonia in the H bond. The spectroscopic results are well supported by the calculations performed at the density functional level of theory. In a similar spectroscopic study of 2AP with one or two water molecules, water forms in-plane bridges between the ring nitrogen and the amino group. However, the H bond with the ring nitrogen is dominant and only one lowest-energy isomer could be found for each cluster size (Wu et al. *Phys. Chem. Chem. Phys*. **2004**, *6*, 515).

1. Introduction

The study of microsolvated molecules both by spectroscopy and ab initio calculations allows a precise insight into weak solute−solvent interactions and an examination of the accuracy of present theoretical methods. IR/R2PI vibrational spectroscopy, combining both resonant two-photon ionization mass spectroscopy (R2PI) and IR-induced vibrational predissociation spectroscopy, provides a powerful method for investigating the vibrational spectra of clusters, in particular those representing microsolvated molecules with the solvent interacting with a chromophore by hydrogen bonds.[1−7] This vibrational spectroscopy incorporates not only mass and isomer selectivity but also the ultrahigh sensitivity inherent in ion-based spectroscopy. The structure of a cluster may be deduced by comparing its measured vibrational spectrum with the calculated one from ab initio calculations. Most ambiguities which normally complicate an R2PI spectrum, such as bands from isomeric structures, hot bands, and spectral features from fragmenting larger complexes, may be disentangled and often assigned in a straightforward manner. Even in cases where R2PI spectra exhibit broad, congested bands, clear spectroscopic IR fingerprints are often obtained by this method.[8]

2-Aminopyridine (2AP) is a heterocyclic molecule containing two nitrogen atoms. It may be used as a model molecule for understanding biomolecules containing purines and pyrimidines. This molecule has been extensively studied by using a variety of different techniques.[9−12] Hager and Wallace[13,14] studied clusters of 2AP with H_2O and NH_3, respectively, by multiphoton ionization and threshold photoionization spectroscopy. The cluster of 2AP with Ar has been studied by mass-analyzed threshold ionization spectroscopy. [15] We recently investigated clusters of 2AP with one and two water molecules using R2PI and IR/R2PI spectroscopy, in combination with ab initio calculations.[16] Under microhydration, water forms a very strong H bond with the aromatic nitrogen. In the cases of 2AP·H_2O and 2AP·$(H_2O)_2$, this is seen by H bonded OH stretches red shifting by 254 and 413 cm^{-1}, respectively, relative to the symmetric stretching vibration of free water. Whereas one water molecule forms a second H bond with the amino group, two water molecules form a H bonded water dimer bridge between the aromatic and the amino nitrogen. Thus, both clusters exhibit exclusively cyclic structures at very low temperatures. Due to a reduced geometric strain, the H bond to the ring nitrogen is considerably stronger in the 1:2 than in the 1:1 cluster.

In this study, we want to elucidate the interaction of 2AP with ammonia since NH···N hydrogen bonds are very important in biological systems. In 2AP, we must distinguish between two different nitrogen atoms, the aromatic and the amino nitrogen, which are both capable of forming such bonds. Each may act as an acceptor in a H bond with ammonia and in addition compete with the aromatic π system, which also may be a H bond acceptor. Moreover, the amino group may be a H bond donor to ammonia. It should be noted that, despite these different

* To whom correspondence should be addressed. Fax: +49-69-79829560. E-mail: Brutschy@chemie.uni-frankfurt.de.

† Permanent address: Heyrovský Institute of Physical Chemistry of the Academy of Sciences of the Czech Republic and Center for Complex Molecular Systems and Biomolecules, Dolejskova 3, 18223 Praha 8, Czech Republic.

10.1021/jp031012k CCC: $27.50
Published on Web 03/19/2004

binding possibilities of 2AP, with water only one isomer has been found for both the 1:1 and the 1:2 clusters. As will be shown with ammonia, two different 1:1 isomers exist, reflecting the different H bonding sites. The study of clusters of 2AP and ammonia will help us to better understand the characteristics of different types of NH···N bonds.

In this work, the R2PI spectrum of 2AP·NH_3 has been measured near the electronic origin of the $S_1 \leftarrow S_0$ transition. The IR/R2PI spectra of the isomers have been recorded in the region of the NH stretches (3200−3600 cm^{-1}). Two different isomers have been found with characteristic vibrational spectra. Also density functional theory (DFT) calculations have been performed for obtaining the lowest-energy structures, binding energies, and harmonic vibrational frequencies of these clusters in the electronic ground state. The experimentally observed vibrational spectra are assigned by both its characteristic spectral features and a comparison with calculated spectra.

2. Experimental Setup

The experimental setup for obtaining the R2PI and IR/R2PI spectra has been described in more detail elsewhere.[17,18] Clusters are produced in a supersonic expansion utilizing a pulsed nozzle operating at a frequency of 10 Hz. The vapor of 2AP at about 50 °C is mixed with the He seed gas, containing ammonia at a 1 vol. % concentration. The total stagnation pressure is about 3 bar. Typical operating pressures are 5×10^{-6} mbar in the expansion chamber and 2×10^{-7} mbar in the detection chamber. Behind the skimmer, the cluster beam is ionized by one-color R2PI and mass analyzed in a conventional linear time-of-flight mass spectrometer (TOF-MS). Due to the resonant step in the two-photon ionization, the wavelength-dependent yield of an ion reflects the UV absorption spectrum of its neutral precursor (R2PI spectrum). Monomers and clusters are ionized using the frequency-doubled output of an optical parametric oscillator working in the UV (Continuum Sunlite-OPO). The amplified ion signals are collected and analyzed by a transient digitizer (LeCroy 9310), interfaced to a personal computer. To increase the S/N ratio, the spectra are averaged over 150 laser pulses.

For taking an IR/R2PI spectrum, the IR laser pulse of a continuously tunable IR−OPO precedes the UV laser pulse by about 100 ns. The two counter-propagating laser beams are focused and intersect the skimmed molecular beam at a right angle. If a cluster absorbs IR light, ammonia rapidly dissociates. Thus, the absorption is observed as a dip of the R2PI ion signal. The IR/R2PI spectrum of an individual cluster is recorded by scanning the IR wavelength, while the UV wavelength is fixed to a transition specific of the cluster under study. Such a spectrum represents the vibrational spectrum of the neutral cluster in the ground state.

The IR laser light is generated by a home-built, injection-seeded OPO using $LiNbO_3$ crystals. Its wavelength may be tuned in the range from 2.5 to 4.0 μm at a bandwidth of 0.2 cm^{-1}. The typical energy is about 5 mJ/pulse. 2-Aminopyridine (2AP, 99+%) was purchased from Aldrich and used without further purification.

Structures and harmonic vibrational frequencies were calculated at the DFT level, employing the hybrid B3LYP functional and using the 6-311G(d, p) and aug-cc-pVDZ basis sets. The calculated vibrational frequencies were scaled by a factor of 0.965, which minimizes the difference between the experimental and calculated frequencies. For calculating the binding energies, basis set superposition error (BSSE) corrections were calculated using the counterpoise correction method. Calculations have been carried out with the Gaussian 03 program.[19]

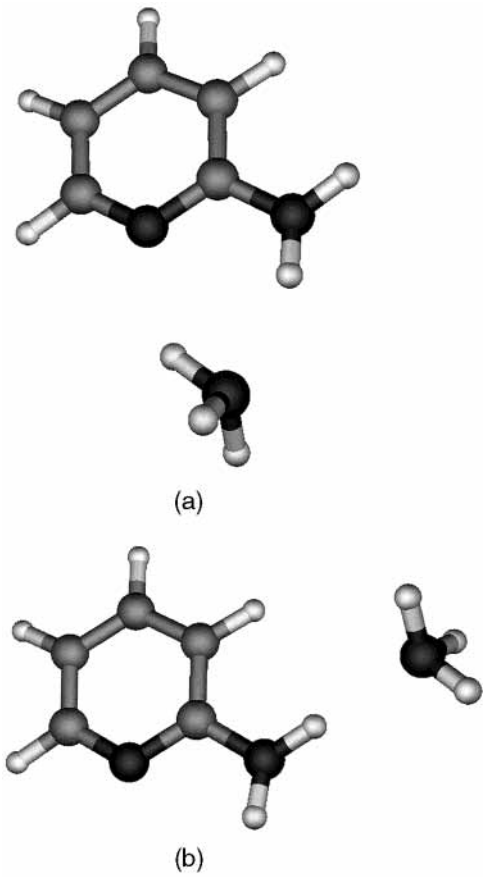

Figure 1. Structures of 2AP·NH_3, calculated at the B3LYP/6-311G-(d, p) level: isomer I (a) and isomer II (b).

3. Results and Discussion

3.1. Calculated Structures and Binding Energies of the Isomers. For the clusters of 2AP with ammonia, the two most stable isomers are shown in Figure 1. Table 1 lists the binding energies and some important structural parameters as obtained at the B3LYP/6-311G(d, p) level.

For isomer I, which is the global minimum energy structure, ammonia forms two hydrogen bonds with 2AP, one with the aromatic nitrogen as a proton donor and one with the amino group as an acceptor. The length and angle of the H bond with the amino group are 2.011 Å and 155.8° and in the H bond with the aromatic nitrogen 2.257 Å and 141.3°. From these structural parameters, we may conclude that ammonia forms a stronger H bond with the amino group than with the aromatic N. This behavior is contrary to the binding of water. In 2AP·H_2O, the length and angle of the H bond with the aromatic N are 1.940 Å and 153.6° and with the amino group 2.025 Å and 147.7°. All data have been obtained at the B3LYP/6-311G(d, p) level.[16]

For isomer II, ammonia binds to the other side of the amino group, as compared with isomer I, and forms a H bond as an acceptor. The length of this H bond is 2.066 Å, and its angle of 178.5° reveals a nearly linear H bond, because no structural strain is imposed contrary to the H bond in isomer I.

The binding energies with the zero-point vibrational energies (ZPE) and the BSSE corrections taken into account are 4.7 and 3.9 kcal/mol for the two isomers, respectively. For comparison, the clusters with one water molecule may form only isomers

TABLE 1: Binding Energies and Some Structural Parameters Obtained at the B3LYP/6-311G(d, p) Level (All Distances in Å)

	2AP	2AP·NH_3 (isomer I)	2AP·NH_3 (isomer II)
binding energy/(kcal/mol)		9.5	7.5
binding energy with ZPE/(kcal/mol) included		7.6	6.0
binding energy with ZPE and BSSE/(kcal/mol)		4.7	3.9
binding energy with ZPE and 50% BSSE/(kcal/mol)		6.2	5.0
R_{C-NH}	1.382	1.365	1.369
R_{CN-H_1}[a]	1.009	1.022	1.008
R_{CN-H_2}[b]	1.008	1.006	1.019
$R_{NH\cdots NH_3}$[c]		2.011	2.066
$R_{N\cdots HNH_2}$		2.257	
$\Phi_{NH\cdots NH_3}$		155.8	178.5
$\Phi_{N\cdots HNH_2}$[d]		141.3	
Φ_{CNH}[a]		117.7	114.4
Φ_{CNH}[b]		118.4	119.6
dipole moment/(*D*)	1.95	0.80	4.89
rotational constants (GHZ)			
A	5.80	3.90	4.27
B	2.73	1.29	1.04
C	1.86	0.98	0.85

[a] The bond length between nitrogen and the hydrogen in the NH_2 group which is close to the aromatic nitrogen. [b] The hydrogen pointing away from the aromatic nitrogen. [c] The distance of H bond between amino group and NH_3; [d] The angle of H bond between aromatic N and NH_3.

with very different binding energies of 5.7 and 2.1 kcal/mol respectively (isomer 1a and 1c in ref 16). The energy difference between the two isomers with ammonia (0.8 kcal/mol) is much less than in the corresponding isomers with water (3.6 kcal/mol).

The full counterpoise correction of the binding energy often causes an underestimation of the real binding energy if small basis sets are used. Often a 50% BSSE correction provides values closer to the experimental binding energies.[20] With a 50% BSSE correction, the binding energies are 6.2 and 5.0 kcal/mol, respectively. It should be pointed out that these binding energies are considerably smaller than the binding energy between 2AP and a water molecule (7.9 kcal/mol).

In addition, the dominant H bond is different. Water forms a strong hydrogen bond with the aromatic nitrogen and a weaker one with the amino group. On the other hand, ammonia in isomer I forms a stronger bond with the amino group than with the aromatic nitrogen. This difference stems from the different characteristics of the two solvents, i.e., from the difference in proton affinity: the proton affinities of ammonia and water are 853.6 and 691.0 kJ/mol, respectively.[21] Ammonia prefers to accept a hydrogen from the amino group in 2AP, whereas water prefers to donate a hydrogen to the nucleophilic aromatic nitrogen in 2AP. Due to this difference, ammonia has a second iomeric structure that is energetically only about 1 kcal/mol above the energy of isomer I, which is structurally similar except for the additional weak interaction with the aromatic nitrogen.

3.2. R2PI Spectra. The R2PI spectrum of the chromophore is shown in Figure 2a. The electronic origin 0_0^0 is assigned to the band located at 33 466 cm^{-1}, which is in good agreement with the values reported in the literature.[11,13] The spectrum of the cluster 2AP·NH_3 is displayed in Figure 2b. As will be discussed in the following, the band at 32 358 cm^{-1} is assigned as the origin band of an isomer of the 1:1 cluster (isomer I, the global minimum energy structure), whereas the minor band located at 32 504 cm^{-1} is assigned to the origin of the second

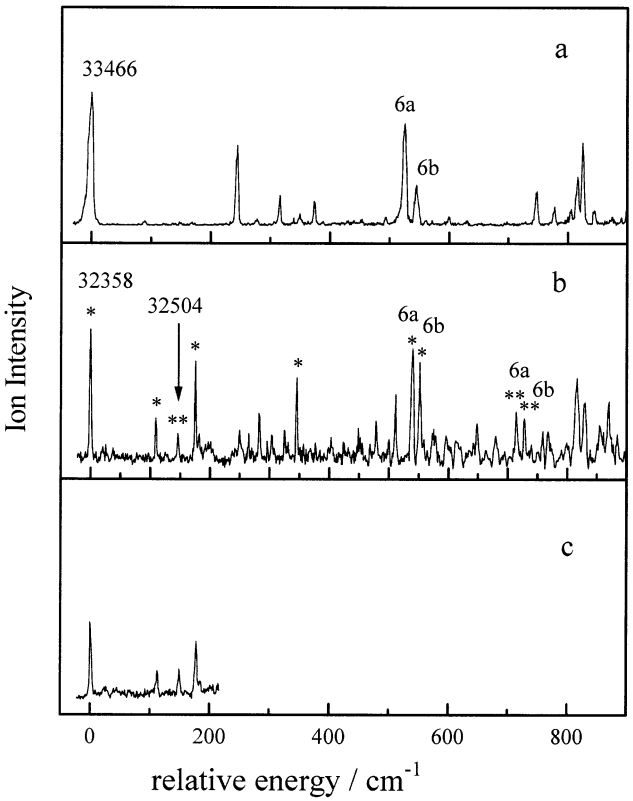

Figure 2. R2PI spectra of 2AP (a), of 2AP·NH_3 (b), and of 2AP·NH_3 with the IR hole burning laser fixed to 3406 cm^{-1} (c), relative to the vibrationless origins of the $S_1 \leftarrow S_0$ transitions of 2AP and isomer I, respectively. One asterisk marks bands of isomer I, and a double asterisk marks those of isomer II.

isomer (isomer II). Both spectral origins exhibit red shifts of 1108 and 962 cm^{-1}, respectively, relative to that of the isolated chromophore. The dipole moment of 2AP increases upon electronic excitation. Thus, the dipolar solvent is more strongly stabilized in the excited state as compared to the ground state, giving rise to the red shift. A further reason could presumably be an enhanced H bond in the excited state. For comparison, 2AP with one and two waters exhibits red shifts of 919 and 1340 cm^{-1}, respectively.[16]

Hager and Wallace reported for the origin of the cluster 2AP·NH_3 a red shift of 392 cm^{-1}.[13] This shift is much smaller than the shifts measured in this study, although nearly the same value was obtained for the origin of the monomer. A similar discrepancy in the assignment of the origin between the work of Hager and Wallace and our measurements occurred for the cluster with water. Our IR/R2PI spectra confirm without any doubt that the bands at 32 358 and 32 504 cm^{-1} are from different isomers of the 1:1 cluster. Additional support provides the good correspondence of the measured IR/R2PI spectra of the clusters with the calculated vibrational spectra, as will be discussed later.

Clear evidence for the existence of two conformers is given by an IR−UV hole burning spectrum. When the IR laser is fixed to one of the vibrational bands of isomer I (3406 cm^{-1}) (see Figure 3), the R2PI spectrum is equally depleted for the three strong bands nearby the origin, whereas the band at 32 504 cm^{-1}, assigned in the following to the origin of isomer II, is not depleted. Moreover, with the UV laser fixed to one of these three R2PI bands one measures the same IR/R2PI spectra. Therefore, they are assigned to isomer I. In Figure 2b, the bands marked with an asterisk belong to isomer I, whereas those marked with a double asterisk belong to isomer II.

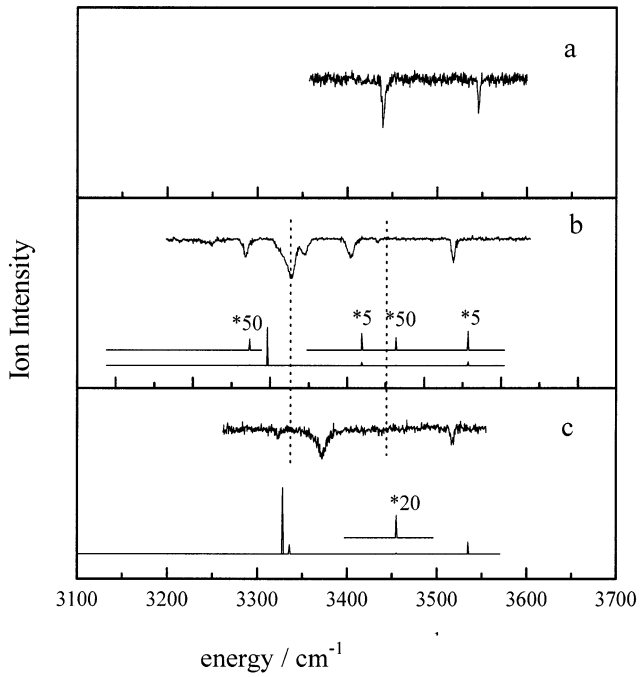

Figure 3. IR/R2PI spectra of 2AP·Ar (a), 2AP·NH_3 (isomer I) (b), and 2AP·NH_3 (isomer II) (c). The spectra were recorded with the UV laser fixed to the 0_0^0 transitions of the clusters. The lower parts in (b) and (c) are the spectra calculated at the B3LYP/aug-cc-pVDZ level. The frequencies are scaled by the factor 0.965. The dashed lines are the positions of the asymmetric and symmetric stretching vibrations of isolated ammonia.

If one compares the single cluster R2PI spectra in Figure 2 with that of the monomer further evidence for the correct assignment of the origin is given by the similar location of the higher vibrational bands measured for the monomer and the 1:1 isomers. It should be noted, that the vibrational bands in the aromatic chromophore exhibit frequency shifts upon complexation. For example, the modes 6a and 6b, corresponding to in-plane ring deformations, appear for the monomer at 525 and 545 cm^{-1}, for isomer I at 540 and 551 cm^{-1}, and for isomer II at 568 and 582 cm^{-1}. For 2AP with water, they appear at 538 and 556 cm^{-1}.[16] However, these differences are mainly due to the variation of the reduced mass in the clusters with water. Hager and Wallace[13] did not find two isomers and they assigned mode 6a of isomer II as the origin of the cluster with ammonia (in our spectrum this band has a red shift of 394 cm^{-1} relative to the origin of the monomer, close to the value of 392 cm^{-1} assigned by Hager and Wallace to the cluster origin band). In addition, beyond mode 6a of isomer II, the shape of our spectrum is similar with that reported by these authors.[13] This correspondence of their spectrum with that of isomer II needs some remarks. In their system, the background pressure in the expansion region during normal operation of the jet is 5 mTorr (about 6×10^{-3} mbar). That is considerably higher than our operating pressures in the expansion chamber (5×10^{-6} mbar). Consequently, the relative amount of isomer II should be increased in their beam due to a presumably higher temperature induced by collisions.

From the intensities of the origin bands in the R2PI spectra (Figure 1), one may evaluate the ratio of population of the two isomers at the temperature of the molecular beam (typically 20 K). The ratio of the peak heights of the origin bands of the two isomers is about 6:1. From the differences in the binding energies one calculates for 20K and thermal equilibrium conditions a negligible relative population probability for isomer II. So either the difference in the calculated binding energies are too large or the clusters are formed under very nonequilibrium conditions.

3.3. Infrared Ion Depletion Spectra of the Clusters. *3.3.1. 2AP·Ar.* To observe the shift in the vibrational frequency of the amino group induced by the cluster formation, we first sampled these vibrations for the isolated monomer. Since predissociation is impossible in this case, depletion can only be induced by depopulation of the ground state by optical pumping. However, in this case, IR/R2PI spectroscopy proved to be very inefficient. One reason for this could be that the structure of the monomer does not differ that much between the ground and excited vibrational state. Hence, the molecule may be ionized by R2PI even though it is vibrationally excited by the IR laser. We tried to get the IR/R2PI spectrum of the monomer this way, but did not succeed.

The chromophore easily shows depletion bands from the vibrations of the amino group if a noble gas atom is bound to the π system. It is then a scavenger or "spy" of the molecule's IR absorption, if it does not change the vibrational frequencies. The infrared dissociation spectra of the phenol·Ar and phenol·Kr clusters were measured by Fujii et al. They found that the perturbation of the vibrational frequencies induced by the rare gas atoms is very small (± 2 cm^{-1}). Thus, the observed frequencies represent those of the monomer.[22]

In the R2PI spectrum of 2AP·Ar (not shown here), the origin is at 33 434 cm^{-1}. This value is consistent with that reported in the literature for this complex.[15] Compared with that of the monomer (33466 cm^{-1}), it is red shifted by 32 cm^{-1}.[13,15] Figure 3a depicts the IR/R2PI spectrum sampled for 2AP·Ar with the UV laser fixed to the origin of the cluster at 33434 cm^{-1}. The symmetric (ν_1) and asymmetric (ν_3) stretching vibration bands of the amino group appear at 3439 and 3546 cm^{-1}, respectively. Compared with those of aniline (3422 and 3508 cm^{-1}),[23] they are blue shifted by 17 and 38 cm^{-1}, respectively. This difference is due to the aromatic nitrogen. Its lone pair electrons disturb the symmetry of the NH bonds. This is also supported by ab initio calculations (B3LYP/6-311G(d,p)). For aniline, the length of the two NH bonds is identical with 1.010 Å. For 2AP, the lengths of both N−H bonds are shortened, but not equally. In the N−H adjacent to the aromatic nitrogen, it is 1.009 Å, whereas in the other N−H bond, it is 1.008 Å. This slight elongation of the N−H group in the neighborhood of the ring nitrogen was also reported in the literature and interpreted as a sign of a weak intramolecular H bond.[24]

3.3.2. Isomer I of 2AP·NH_3. Figure 2b shows the IR/R2PI spectrum of isomer I of 2AP·NH_3 with the wavelength of the ionizing laser being fixed to its 0_0^0 transition (32 358 cm^{-1}). In its lower part is depicted the vibrational spectrum calculated at the B3LYP level employing the aug-cc-pVDZ basis set. The locations of the measured vibrational bands in Figure 2b are summarized in Table 2, together with the calculated values by using the B3LYP functional and 6-311G(d,p) and aug-cc-pVDZ basis sets, respectively. For comparison, we also list other related bands in Table 3 including those of ammonia,[25] aniline,[23] and some related IR absorption bands of 4-aminopyridine (4AP), 4AP·H_2O (>N···O−H) (isomer I), 4AP·H_2O (>N−H···H) (isomer II) measured in an Ar matrix.[26]

The highest frequency band located at 3538 cm^{-1} is assigned to a free stretching vibration of the N−H amino group not involved in a hydrogen bond. It is red shifted by only 8 cm^{-1} relative to the ν_3 vibration of 2AP·Ar. Its frequency is nearly

TABLE 2: Observed Vibrational Bands in the IR/R2PI Spectra and Calculated Values by B3LYP Method (All Values in cm^{-1})

	2AP·NH$_3$ (isomer I)			2AP·NH$_3$ (isomer II)		
		calculated			calculated	
	observed	6-311G (d, p)	cc-aug-pVDZ	observed	6-311G (d, p)	cc-aug-pVDZ
bonded NH (−NH$_2$ group)	3329	3245(394)[a]	3296(635)	3373	3297(569)	3328(471)
free NH (−NH$_2$ group)	3538	3551(47)	3557(63)	3517	3524(61)	3535(86)
ν_1(NH$_3$)	3268	3294(288)	3273(4)	3322	3349(2.2)	3336(66)
ν_3(NH$_3$)	3406	3423(40)	3419(56)		3460(4)	3455(8)
	3438	3468(1)	3463(4)		3463(4)	3455(7)

[a] The values given in bracket are the calculated IR intensities.

TABLE 3: Energy of the Stretching Vibrations of 2AP·NH$_3$ and of Some Related Molecules and Clusters (All Values in cm^{-1})

molecule or cluster	bonded NH (−NH$_2$ group)	free NH (−NH$_2$ group)	ν_1(NH$_3$)	ν_3(NH$_3$)
2AP·Ar	3439	3546		
2AP·NH$_3$ (isomer I)	3329	3538	3268	3406, 3438
2AP·NH$_3$ (isomer II)	3373	3517	3322	
ammonia[a]			3337	3444
2AP·H$_2$O[b]	3315	3548		
2AP·(H$_2$O)$_2$[b]	3343	3536		
aniline[c]	3422	3508		
4-aminopyridine(4AP)[d]	3437	3536		
4AP·H$_2$O(>N···H−O−H)(isomer I)[d]	3442	3543		
4AP·H$_2$O(>N−H···O−H)(isomer II)[d]	3402	3526		

[a] See ref 25. [b] See ref 16. [c] See ref 23. [d] In Ar matrixes, see ref 26.

the same as for the corresponding bands of 2AP·H$_2$O, 2AP·(H$_2$O)$_2$, and 4AP and its clusters with water, as listed in Table 3.

The stretching vibration of the H bonded N−H amino group appears at 3329 cm^{-1} as a strong band, red shifted by 110 cm^{-1} relative to the ν_1 of 2AP·Ar. The large red shift and the increased width of this band reveal that it corresponds to a more or less local vibration of an N−H group acting as donor in a relatively strong hydrogen bond with ammonia. The calculated global minimum energy structure of isomer I is shown in Figure 1a. It fully supports this interpretation. The calculated NH···N bond distance is 2.011 Å. The N−H bond length increases from 1.009 in the monomer to 1.022 Å in cluster. Thus, the H bond formation elongates the NH bond and decreases its stretching frequency. For comparison in the cluster with one and two water molecules, these bond lengths are 1.017 and 1.023 Å, respectively.

Free ammonia exhibits two stretching vibrations in the observed spectral region. They correspond to three modes: two degenerate asymmetric ν_3 at 3444 cm^{-1} and one symmetric ν_1 at 3337 cm^{-1}.[22] However, when ammonia is bonded as in isomer I, where a second H bond is formed to the aromatic nitrogen (Figure 1a), the symmetry is lifted and the degeneracy of the two asymmetric modes is removed. The two asymmetric modes split up, with energies of 3438 and 3406 cm^{-1}. The two H bonds are also reflected in the calculated bond lengths of ammonia. Whereas the N−H bond length in isolated ammonia is 1.016 Å, in bonded ammonia, the lengths are different with values of 1.022, 1.015 and 1.015 Å, respectively, with the most elongated N−H group being that closest to the aromatic nitrogen.

The band at 3268 cm^{-1}, which is red shifted by 69 cm^{-1} relative to the ν_1 of free ammonia, is assigned to the stretching vibration of the H bonded NH of ammonia forming the hydrogen bond with aromatic nitrogen. According to the calculation, this hydrogen bond is weak and its length is 2.257 Å. This differs remarkably from 2AP·H$_2$O where water forms a very strong hydrogen bond with the aromatic nitrogen, also reflected by a red shift of the OH vibrational band by 254 cm^{-1}, and a much shorter H bond (1.940 Å). [16]

The shoulder band at 3344 cm^{-1} also appears in the spectrum of 2AP with one water cluster. There we tentatively assigned it to overtones of the bending vibration of either water or of the amino group. In the case of 2AP with ammonia, it should be then the overtone of the bending vibration of the amino group enhanced by a Fermi resonance with the nearby bonded NH vibration.[8]

With the 6-311G(d,p) basis set, the calculated value of the bonded NH vibration in the amino group is 3245 cm^{-1} and thus lower than that of the bonded NH vibration in ammonia (3294 cm^{-1}). Using a more diffuse basis set (aug-cc-pVDZ), the corresponding values are 3296 and 3273 cm^{-1}. This reversed order is consistent with the experimental results. In addition, the calculated relative IR intensities agree better with the measured ones when the aug-cc-pVDZ basis set is used, as shown in the Table 2 and Figure 3b.

3.3.3. Isomer II of 2AP·NH$_3$. When we fixed the UV laser to the weak band at 32 504 cm^{-1}, assigned to the origin of isomer II, a new IR/R2PI spectrum shows up (Figure 3c), which is totally different from that measured for isomer I as evident from Figure 3. The position of its bands are listed in Table 2. A second isomer of the 1:1 was also found by the calculations, exhibiting the structure depicted in Figure 1b. As for isomer I, the ammonia molecule is the acceptor in a H bond with the amino group, but it is no longer involved in a H bond with the aromatic nitrogen. This calculated local minimum energy isomer II is also supported by the measured vibrational spectrum.

Similar to isomer I, the band at 3517 cm^{-1} may be assigned to the free stretching vibration of the amino group. Compared with its value in 2AP·Ar, it is red shifted by 29 cm^{-1}. This decrease is rationalized by the attractive interaction with the aromatic nitrogen. The calculations confirm this conclusion. The bond lengths of free NH in isomers I and II are 1.006 and 1.008 Å, respectively.

The intense band at 3373 cm^{-1} is assigned to the H bonded NH of the amino group. Relative to the corresponding band in isolated 2AP, it is red shifted by 66 cm^{-1}. From the reduced shift of this band in isomer II as compared to the corresponding band in isomer I (3329 cm^{-1}), one may deduce that the H bond is stronger in isomer I than in isomer II. On the other hand, in

isomer II, the calculated angle of the N−H···N bond is 178.5° with the bond thus closer to linearity than in isomer I where it is 155.8°. As a matter of fact, the H bond in isomer II is a little weaker than in isomer I, because in isomer I the weak hydrogen bond with the aromatic nitrogen atom also increases this H bond to the amino group. The calculated value of its length in isomer II is 2.066 Å, which compares with 2.011 Å found for isomer I.

The very weak band at 3322 cm^{-1} is assigned to the symmetrical stretching vibration of NH_3. It is red shifted by only 15 cm^{-1} relative to the ν_1 band of free ammonia (3337 cm^{-1}). For comparison in isomer I, the vibration band of the H bonded NH strech of ammonia appears at 3268 cm^{-1} and is hence red shifted by 69 cm^{-1}. This also indicates that ammonia in isomer II is a proton acceptor and 2AP has only a weak influence upon its vibrations.

The asymmetrical vibration of ammonia in isomer II should be close to the corresponding band of free ammonia. We could not find such a depletion band in Figure 3c probably for intensity reasons. First of all, the ion signal intensity of isomer II is weak because its overall population is very low. In addition, the IR intensity of this mode is also very weak. In the calculations, the degeneracy of the two asymmetrical modes is still preserved (shown in Table 2 and Figure 3). Especially in the results from calculations utilizing the aug-cc-pVDZ basis set, the two bands are nearly degenerate, since the local symmetry of ammonia is preserved, when acting as an acceptor. The calculated length of the three NH bonds of ammonia in isomer II are 1.0156, 1.0157, and 1.0158 Å, which is nearly same as those of isolated ammonia (1.0158 Å).

4. Conclusions

The R2PI spectra of two isomers of 2AP·NH_3 have been measured in the region of their vibrational origins of the $S_1 \leftarrow S_0$ transition. In discrepancy to an earlier assignment in the literature,[13] their origins are shifted by 1108 and 962 cm^{-1}, respectively, relative to that of 2AP.

For isomer I, which is the global minimum energy structure, ammonia forms a relatively strong H bond with the amino group and a weak H bond with the aromatic nitrogen. The corresponding vibrational bands appear at 3329 cm^{-1} for the donating amino N−H and at 3268 cm^{-1} for the donating ammonia N−H bond. Thus, they exhibit red shifts of 110 and 69 cm^{-1}, respectively, relative to the corresponding symmetrical modes. The degeneracy of the two asymmetrical vibrations of ammonia is removed in the double-H bonded isomer because of the loss of symmetry. The band splits up to two bands at 3438 and 3406 cm^{-1}.

In isomer II, the stretching vibration of the free NH in the amino group has a larger shift than that in isomer I, which indicates that there is an interaction between the free NH in the amino group and the aromatic nitrogen. Compared with that in isomer I, the hydrogen bond in isomer II between ammonia and the amino group is weaker, because in isomer I the weak hydrogen bond with the aromatic nitrogen enhances the strength of the H bond with the amino group. In isomer II, the stretching vibrations of ammonia are nearly the same as for isolated ammonia because ammonia is only a H bond acceptor.

A comparison of the binding of water and ammonia with 2AP indicates that ammonia prefers to be a H bond acceptor because of its high proton affinity, whereas water with its distinctly lower proton affinity is a donor in the H bond to the aromatic nitrogen. This difference in proton affinity is the underlying reason for a nearly isoenergetic second 1:1 isomer with ammonia, in which the interaction with the aromatic nitrogen no longer exists. The population ratio of the two isomers is estimated to about 6: 1 in the molecular beam.

Acknowledgment. R.W. gratefully acknowledges a stipend of the Alexander von Humboldt Foundation and P.N. a guest professorship of the Hertie-Foundation enabling their stay. P.N. thanks to the Czech Ministry of Education for support for the Center for Complex Molecular Systems and Biomolecules (Grant No. LN00A032). B.B. acknowledges the generous financial support of the Fonds der chemischen Industrie.

References and Notes

(1) Riehn, Ch; Lahmann, Ch.; Wassermann, B.; Brutschy, B. *Chem Phys. Lett*. **1992**, *197*, 443.
(2) Plutzer, C.; Hunig, I.; Kleinermanns, K. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1158.
(3) Florio, G. M.; Zwier, T. S. *J. Phys. Chem. A* **2003**, *107*, 974.
(4) Zwier, T. S. *J. Phys. Chem. A* **2001**, *105*, 8827.
(5) Ebata, T.; Iwasaki, A.; Mikami, N. *J. Phys. Chem. A* **2000**, *104*, 7974.
(6) Snoek, L. C.; Robertson, E. G.; Kroemer, R. T.; Simons, J. P. *Chem. Phys. Lett*. **2000**, *321*, 49.
(7) Reimann, B.; Buchhold, K.; Barth, H.-D.; Brutschy, B.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2002**, *117*, 8805.
(8) Brutschy, B. *Chem. Rev*. **2000**, *100*, 3891.
(9) Kydd, R. D. A.; Mills, I. M. *J. Mol. Spectrosc*. **1972**, *42*, 320.
(10) Kim, B.; Thantu, N.; Weber, P. M. *J. Phys. Chem*. **1992**, *97*, 5384.
(11) Lin, J. L.; Wu, R. H.; Tzeng, W. B. *Chem. Phys. Lett*. **2002**, *353*, 55.
(12) Borst, D. R.; RoscioliJ, R.; Pratt, D. W. *J. Phys. Chem. A* **2002**, *106*, 4002.
(13) Hager, J. W.; Wallace, S. C. *J. Phys. Chem*. **1985**, *89*, 3833 and references therein.
(14) Hager, J. W.; Leach, G. W. L.; Demmer, D. R.; Wallace, S. C. *J. Phys. Chem*. **1987**, *91*, 3750.
(15) Baek, S. J.; Choi, K. W.; Choi, Y. S.; Kim, S. K. *J. Phys. Chem. A* **2003**, *107*, 4826.
(16) Wu, R. H.; Nachtigall, P.; Brutschy, B. *Phys. Chem. Chem. Phys.* **2004**, *6*, 515.
(17) Lommatzsch, U.; Gerlach, A.; Lahmann, C.; Brutschy, B. *J. Phys. Chem. A* **1998**, *102*, 6421.
(18) Krauss, O.; Brutschy, B. *Chem. Phys. Lett*. **2001**, *350*, 427.
(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.
(20) Tarakeshwar, P.; Kim, K. S.; Brutschy, B. *J. Chem. Phys.* **2001**, *114*, 1295.
(21) Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.
(22) Fujii, A.; Sawamura, T.; Tanabe, S.; Ebata, T.; Mikami, N. *Chem. Phys. Lett.* **1994**, *225*, 104.
(23) Sugawara, K.; Miyawaki, J.; Nakanaga, T.; Takeo, H.; Lembach, G.; Djafari, S.; Barth, H. D.; Brutschy, B. *J. Phys. Chem.* **1996**, *100*, 17145.
(24) Hollas, J. M.; Musa, H.; Ridley, T. *J. Mol. Spectrosc*. **1984**, *104*, 107.
(25) Herzberg, G. *Molecular spectra and Molecular structure*; Krieger Publishing Company: Malabar, FL, 1991; Vol. 2, p 295.
(26) Smets, J.; Adamowicz, L.; Maes, G. *J. Phys. Chem*. **1995**, *99*, 6387.