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Infrared Depletion Spectroscopy and Structure of the 2-Aminopyridine Dimer†

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The electronic and vibrational spectra of the 2-aminopyridine (2AP) dimer have been measured using resonant two-photon ionization (R2PI) and IR ion depletion (IR/R2PI) spectroscopy. Only two vibrational bands in the N−H stretch region have been observed at 3319 and 3529 cm^{-1}, which are red-shifted by 120 and 17 cm^{-1}, respectively, relative to the symmetric and antisymmetric N−H vibrations of the monomer. This provides evidence of the cyclic structure of this dimer with two antiparallel N−H···N hydrogen bonds. In addition, ab initio calculations at the B3LYP/6-311++G(d,p) level have been carried out. The cyclic structure is also the calculated minimum energy conformation. Each NH_2 group forms a σ-hydrogen bond with the ring nitrogen of the partner. Compared to the dimers of 2-pyridone ($(2PY)_2$) and 2-hydroxypyridine ($(2HP)_2$) and to the mixed dimer ((2PY)·(2HP)), the hydrogen bonds in $(2AP)_2$ are weaker. This is confirmed by the differences in the vibrational spectra and by the computational results. The binding energy of the 2AP dimer is the lowest among these dimers, and its hydrogen bonds are the longest. The weaker hydrogen bonds in 2AP may be rationalized by the nonplanar structure of the molecule in the ground state. The theoretical results are in good agreement with the experimental data.

1. Introduction

2-aminopyridine (2AP) is a heterocyclic molecule containing two nitrogen atoms. It may be used as a model molecule for studying the photophysics of biomolecules containing heteroaromatic molecules such as purines and pyrimidines. Several studies on clusters of 2AP have been reported in the literature. Hager and Wallace[1,2] studied clusters of 2AP with H_2O, methanol, ethanol and NH_3, and the homodimer by multiphoton ionization and threshold photoionization spectroscopy. They reported the resonant two-photon ionization (R2PI) spectrum of the 2AP dimer in the vicinity of the electronic origin of the $S_1 \leftarrow S_0$ transition and rationalized the strong red shift by a considerable strengthening of the dimer bonds upon electronic excitation. Moreover, they calculated its structure by the semiempirical atom−atom pair potential method. The dimer was found to be stabilized by two N−H···N hydrogen bonds, resulting in a cyclic and planar structure for the electronic ground state with C_{2h} symmetry. However, the authors considered planarity as a simplification of the real ground state. The cluster of 2AP with Ar has been studied by mass-analyzed threshold ionization spectroscopy.[3] We recently investigated clusters of 2AP with one and two water molecules and with one ammonia molecule using R2PI and IR ion depletion (IR/R2PI) spectroscopy, supplemented by ab initio calculations.[4,5] For the cluster of 2AP with one or two water molecules, only one isomer exists under molecular beam conditions, while, for the cluster of 2AP with ammonia, two different 1:1 isomers exist.[5]

In nucleic acid base pairing, antiparallel hydrogen bonds are crucial for molecular recognition and selectivity. Recently, several groups[6−16] investigated the homodimer of 2-pyridone (2PY) and the heterodimers of 2PY with 2-hydroxypyridine (2HP)—the tautomer of 2PY—and the base pair analogue 2PY·2AP, all of which form cyclic hydrogen bonds. While $(2PY)_2$ is bound by two O···HN and 2HP·2PY by O···HO/N···HN cyclic hydrogen bonds, both dimers are more or less planar. The dimer 2PY·2AP on the other hand is the closest mimic to the Watson−Crick (W−C) base pairing, since the N−H group is from a nonplanar amino group. The structure of the 2AP dimer also includes such double, antiparallel hydrogen bonds. Although it does not include any O···HO hydrogen bonds, as does DNA, its two identical hydrogen bonds are similar to the N−H···N bonds in W−C base pairing. Hence, the 2AP dimer has been considered as a mimetic model for the study of photoinduced double proton transfer (DPT) along the hydrogen bonds in W−C DNA base pairs. In a computational investigation of the excited state coupled electron−proton transfer, Domcke and Sobolewski[17] studied the low-lying $^1\pi\pi^*$ excited states of the 2AP dimer with multireference ab initio methods and, in particular, the reaction path and the energy profile for single proton transfer in the lowest $^1\pi\pi^*$ intermonomer charge transfer state. The question was whether the DPT reaction occurs in a concerted manner or as a two-step reaction with single proton transfer (SPT) intermediates. These reactions are considered to be relevant for the photostability of the genetic code.

IR/R2PI vibrational spectroscopy, combining R2PI and IR-induced vibrational predissociation spectroscopy, provides a powerful method for investigating structure sensitive vibrations in molecular clusters of those molecular groups which form hydrogen bonds. This vibrational spectroscopy incorporates not only mass and isomer selectivity but also the ultrahigh sensitivity inherent in ion-based detection schemes. The structure of a cluster may be deduced by comparing the measured vibrational spectrum with the calculated spectrum utilizing ab initio methods. Most ambiguities which normally complicate R2PI

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spectra, 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 bands due to lifetime broadening or excited state dynamics, clear spectroscopic IR fingerprints are often obtained by this method, since it probes the vibrations of the molecule in the ground state.[18] Recently, this IR/UV double resonance technique was widely applied to study hydrogen-bonding interactions in clusters.[18−23] De Vries et al. reported exciting results on the UV and IR spectroscopy of nucleic bases and their dimers.[25,26]

In this work, we probe the structure of the 2AP dimer by using IR ion depletion spectroscopy in the region of the N−H stretches. Ab initio calculations have been performed in order to obtain the structure, binding energy, and harmonic vibrational frequencies of the dimer in the electronic ground state. The calculated structure is compared to those of the dimers of 2PY and 2HP and to that of the mixed dimer 2HP·2PY (the IR depletion spectrum of the 2HP dimer is not currently available, but the calculated structure and the strength of the hydrogen bonds were reported in ref 11). Due to the differences in the planarity of these dimers, there are great differences in the bond strengths. This is also reflected in the vibrational spectra.

2. Experimental Setup and Calculation

The experimental setup for obtaining the R2PI and IR/R2PI spectra has been described in more detail elsewhere.[27,28] Clusters are produced in a supersonic expansion utilizing a pulsed nozzle operating at a frequency of 10 Hz. The vapor of 2AP at ∼60 °C is mixed with the He seed gas. The total stagnation pressure is ∼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 molecules in the beam are 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 (the R2PI spectrum). Aromatic molecules are ionized using the frequency-doubled output of an optical parametric oscillator (OPO) working in the UV region (Continuum Sunlite-OPO). The amplified ion signals are collected and analyzed with 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 recording an IR/R2PI spectrum, the laser pulses of a continuously tunable IR-OPO precede the UV laser pulses by ∼100 ns. The two counterpropagating laser beams are focused and intersect the skimmed molecular beam at a right angle. The focal lengths of the focusing lenses are about 1 and 0.5 m, respectively, for the UV and IR lasers. At the point of intersection, the two beams have a size of about 2 and 1 mm^2, respectively. If a cluster absorbs mid-IR light by the excitation of a stretching vibration, it rapidly dissociates by IVR as long as the binding energy is smaller than the photon energy. Thus, the IR absorption is observed as a depletion of the R2PI ion signal. The IR/R2PI spectrum of an individual cluster is recorded by scanning the IR wavelength, with the wavelength of the R2PI probe laser fixed to a transition specific to the cluster of interest. The ion dip spectrum represents the vibrational spectrum of the neutral cluster in the electronic ground state. The signal intensities in the IR spectra have not been normalized to the IR intensity. Since the laser intensity is often adjusted to get acceptable signal intensity for weaker bands, stronger transitions are often partly or fully saturated. Normalization of the spectra to the laser intensity is then of no use. However, the positions of the measured bands are very accurate.

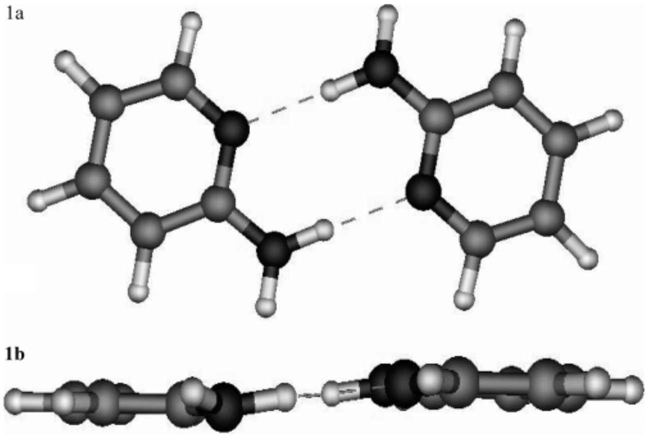

Figure 1. Structure of the 2AP dimer obtained at the B3LYP/6-311G++(d,p) level of theory, as viewed from above (1a) and along the ring plane (1b).

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 with a bandwidth of 0.2 cm^{-1}. The typical energy is ∼5 mJ/pulse. 2-Aminopyridine (2AP, 99+%) was purchased from Aldrich and used without further purification.

Ab initio calculations have been carried out with the Gaussian 03 program.[29] The energy of the cluster was optimized at the density functional theory level, employing the B3LYP exchange-correlation functional and the 6-311++G(d,p) basis set. The harmonic frequencies calculated at this level have been scaled by a factor of 0.965 for the monomer and by 0.98 for the dimer. The zero-point vibrational energies (ZPVEs) were calculated at the same theoretical level. The intermolecular interaction energy of the 2AP dimer was calculated and corrected for the basis set superposition error (BSSE) using the counterpoise correction method.[30]

3. Results and Discussion

3.1. Ab Initio Calculations. The minimum energy structure of the 2AP dimer as calculated at the B3LYP/6-311++G(d,p) level is shown in Figure 1. It was obtained after optimization from different starting configurations of the cluster. In all cases, a minimum energy structure, as given in Figure 1, was obtained, even when we started with a sandwichlike π-bound dimer like the aniline dimer. Being aware that the density functional theory (DFT) method gives only a poor description of π-hydrogen bonds, we abandoned calculations at the MP2 level for two additional reasons. First of all, we intended to compare the results with those of other clusters in the literature calculated at the same level of theory; second, we observed only one isomer, so that no indication of a second, possibly π-bound dimer was given by the experimental results.

To vizualize the nonplanarity of the dimer, views from above and parallel to the aromatic ring plane are given in Figure 1. The binding energies and some important structural parameters are listed in Table 1.

The binding energy calculated at the B3LYP/6-311++G(d,p) level is 9.29 kcal/mol. With the inclusion of the zero-point vibrational energies (ZPVEs), it is reduced to 8.48 kcal/mol. With the additional correction for the basis set superposition error (BSSE), it is further reduced to 7.93 kcal/mol. This value is considerably lower than those of the dimers of 2PY and 2HP

TABLE 1: Binding Energies and Some Structural Parameters Obtained at the B3LYP/6-311++G(d,p) Level of Theory for the 2AP Monomer and Dimer[a]

	2AP	2AP dimer
binding energy (kcal/mol)		9.29
binding energy with the ZPE included (kcal/mol)		8.48
binding energy with the ZPE and BSSE included (kcal/mol)		7.93
$R_{\mathrm{C-NH}}$	1.383	1.363
$R_{\mathrm{CN-H1}}$[b]	1.009	1.024
$R_{\mathrm{CN-H2}}$[c]	1.008	1.006
$R_{\mathrm{NH\cdots N}}$		2.020
Φ_{CNH1}	114.7	119.7
Φ_{CNH2}	117.9	118.5
$\Phi_{\mathrm{NH\cdots N}}$		177.2
Φ[d]	32.4	18.9
dipole moment (D)	2.03	0.02
rotational constant (GHZ)		
A	5.80	1.97
B	2.73	0.29
C	1.86	0.25

[a] All distances are in angstroms, and all angles are in degrees. [b] The bond length between nitrogen and the hydrogen in the NH_2 group which is close to the aromatic nitrogen. [c] The hydrogen pointing away from the aromatic nitrogen. [d] The angle between the amino group and the ring plane.

and that of 2PY•2HP. The corresponding binding energies, with the ZPVEs and BSSE included, are 13.62 kcal/mol for 2PY•2HP, 14.17 kcal/mol for $(2HP)_2$, and 17.61 kcal/mol for $(2PY)_2$ (calculated at the B3LYP/6-311++G(d,p) level).[11] Thus, the binding of $(2PY)_2$ is more than 2 times larger than that of $(2AP)_2$.

According to the calculations, the distance H···N of the two equivalent hydrogen bonds is 2.02 Å. The distance N−H···N is 3.04 Å, which is in good agreement with the experimental value (3.07 Å), as measured for the dimer in a crystal.[31] This distance is considerably larger than those in $(2PY)_2$ and 2PY•2HP. In the 2PY•2HP dimer, the distance is 2.65 Å for the OH···O hydrogen bond and 2.92 Å for the NH···N hydrogen bond. The corresponding NH···O separation in $(2PY)_2$ is 2.78 Å, which is also in very good agreement with the experimental value 2.77 ± 0.03 Å.[7] These calculated values were all obtained at the same theoretical level.[15] From the length of the hydrogen bonds, one also can conclude that the two hydrogen bonds in the 2AP dimer are weaker than those in the dimers of 2PY and 2HP and in the 2PY•2HP heterodimer. This is also consistent with the order of the binding energies.

The structure of the 2AP dimer is nonplanar. This is the major difference of the 2AP dimer compared to the dimers of 2PY and 2HP. The reason for the nonplanarity is the well-known pyramidality of the NH_2 group in the electronic ground state of the molecule (illustrated in Figure 1b). According to the calculation, in the monomer, the angle between the plane through the amino group and the ring plane is 32.4°. This is in good agreement with the 32° measured in the gas phase by Kydd and Mills.[32] In the crystal structure,[31] the same angle is reduced to 15°. Such a large difference in angle for the molecule in the gas and solid phases indicates that the geometry of the amino group strongly depends on its local environment. According to the calculations for the dimer, this angle is 18.9°, indicating that the amino nitrogen is close to a sp^2 configuration. The enhanced planarity is caused by the formation of the hydrogen bond in the cyclic dimer. It should be pointed out that this angle is close to the measured one for the molecule in a crystal, which is not that surprising. From the X-ray analysis,[31] a structure was deduced with parallel dimers stacked in infinite columns parallel to one of the symmetry axis.

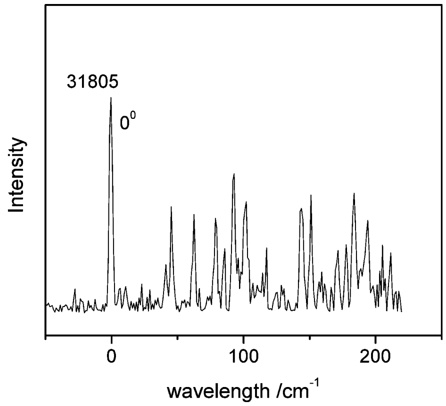

Figure 2. R2PI spectrum of the 2AP dimer in the vicinity of the vibrationless $S_1 \leftarrow S_0$ transition.

3.2. R2PI Spectra. The R2PI spectrum of the 2AP dimer is shown in Figure 2. The electronic origin (0_0^0) of the $S_1 \leftarrow S_0$ transition is assigned to the band located at 31 805 cm^{-1}. Compared to the origin of the monomer (33 466), it is red-shifted by 1661 cm^{-1}. This large red shift (1668 cm^{-1}) was already reported by Hager et al. in ref 2. The rationale for this change is a strong increase of the dipole moment of 2AP upon its electronic excitation, by which the dimer is stronger stabilized in the excited state as compared to the ground state.

The small bands near the strong origin band may be hot bands. When we compare our R2PI spectrum with that in ref 2, there is good agreement for most of the bands, although the signal-to-noise ratio in Figure 2 of this paper is lower. The main difference is the appearance of additional bands at 46, 62, 79, and 118 cm^{-1} in the spectrum in Figure 2, which do not appear in the R2PI spectrum of Hager et al. From identical IR depletion spectra for these bands and of the origin band, their assignment to larger fragmenting clusters may be excluded. The difference is hard to rationalize but could be caused by different experimental conditions. As the authors of ref 2 already asserted, the intensities of these bands were strongly temperature dependent. If the tiny bands at 5 and 10 cm^{-1} in Figure 2 are hot bands, it looks as if the temperature in the pulsed beam of this experiment is lower than that in the case of the continuous expansion of ref 2. The 50% decrease in bandwidth of the 0_0^0 band and the 20% higher intensity relative to the bands around 100 cm^{-1} in Figure 2 as compared to that in Figure 11 in ref 2 point to the same direction. A reason could be the striking difference in the experimental conditions of both studies: In our case, we used a skimmed pulsed beam. The pressure in the expansion chamber was $\sim 5 \times 10^{-6}$ mbar, and that in the ionization region was 2×10^{-7} mbar under operating conditions, thus ensuring collisionless conditions. In ref 2, the R2PI spectrum was measured for a free, unskimmed jet at background pressures below 10 mbar. Here, collisions cannot be excluded.

Large shifts of the origins have also been observed for 2AP with water and ammonia, respectively.[4,5] For 2AP with one and two water molecules, the origin is red-shifted by 919 and 1340 cm^{-1}, respectively. With ammonia, two isomers exist, with the origins red-shifted by 1108 and 962 cm^{-1}. For the 2PY dimer and the mixed dimer 2HP•2PY, the corresponding shifts are very different. $(2PY)_2$ exhibits a blue shift of 945 cm^{-1}, and 2PY•2HP has a blue shift of 825 cm^{-1} relative to the origin of 2PY. Müller et al.[12] suggested that the electronic excitation is localized on the 2PY moiety, which was later confirmed by high-resolution experiments.[15] For the mixed dimer of 2PY and

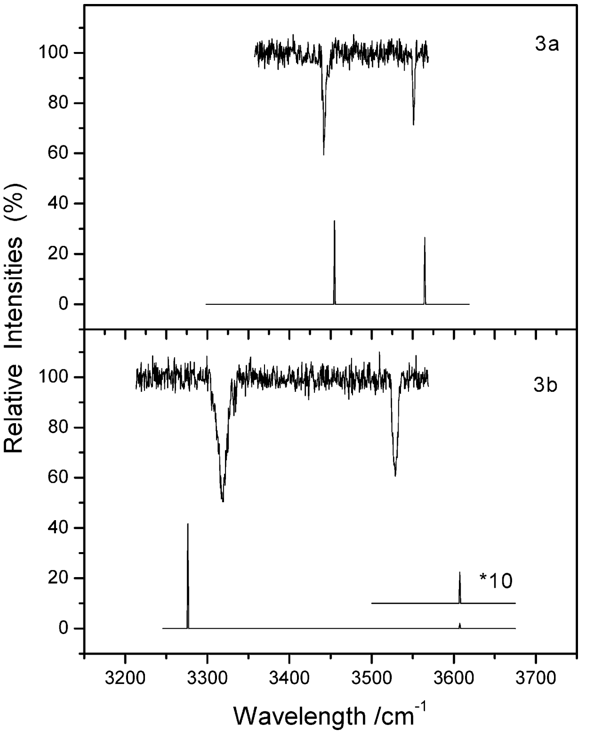

Figure 3. IR/R2PI spectra of 2AP·Ar (a) and the 2AP dimer (b). The spectra were recorded with the UV laser fixed to the 0_0^0 transitions of the clusters. The lower spectra in parts a and b were calculated at the B3LYP/6-311G++(d,p) level. The frequencies are scaled by the factor 0.965 for the monomer and 0.98 for the dimer.

TABLE 2: NH Stretching Vibrations (cm^{-1}) of the 2AP Dimer and of Some Related Molecules and Clusters

molecule or cluster	bonded NH	free NH
2AP·Ar	3439 (symm)	3546 (antisymm)
2AP dimer	3319 (−120)[d]	3529 (−17)
2AP·H_2O[a]	3315 (−124)	3548 (+2)
2AP·$(H_2O)_2$[a]	3343 (−96)	3536 (−10)
2AP·NH_3 (isomer I)[b]	3329 (−110)	3538 (−8)
2AP·NH_3 (isomer II)[b]	3373 (−66)	3517 (−29)
aniline[c]	3422 (symm)	3508 (antisymm)
aniline dimer[c]	3394 (−28)[e]	3467 (−41)[e]

[a] See ref 4. [b] See ref 5. [c] See ref 34. [d] The values in parentheses are the shifts relative to the modes in 2AP·Ar. [e] The values in parentheses are the shifts relative to the modes in aniline.

2AP, the electronic origin is observed at 30 266 cm^{-1}, corresponding to a blue shift of 435 cm^{-1} relative to 2PY.[13] As in the case of 2PY·2HP, the electronic excitation is also localized on 2PY. The blue shifts of the electronic origins in these dimers are caused by a weakening of the hydrogen bonds in the excited state, which is opposite to the strengthening of the bonds in the case of the 2AP dimer.

3.3. Infrared Ion Depletion Spectra. To observe the shifts in the vibrational modes of the amino group induced by the dimer formation, we first tried to determine these vibrations for the isolated monomer. Since predissociation is not possible for a monomer, an IR-induced depletion of the R2PI signal could be induced by depopulation of the ground state by optical pumping. However, in this case, IR/R2PI spectroscopy proved to be highly inefficient. One possible reason for this could be that the structure of the monomer does not differ that much between the ground and electronically excited states. Hence, the molecule may be resonantly ionized by R2PI even if it is vibrationally excited by the IR laser.

The chromophore shows depletion bands from the vibrations of the amino group if a noble gas atom is bound to the π-system. It acts as a scavenger or “spy” of the molecule’s IR absorption, if it does not change the intramolecular 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 vibrational frequencies represent those of the monomer.[33] In the R2PI spectrum of 2AP·Ar (not shown here), the origin is at 33 434 cm^{-1}. This value agrees with that reported in the literature for this complex.[3] It is red-shifted by 32 cm^{-1} relative to that of the monomer.

Figure 3a depicts the IR/R2PI vibrational spectrum recorded for 2AP·Ar with the wavelength of the UV laser fixed to the 0_0^0 transition of the cluster at 33 434 cm^{-1}. The symmetric (ν_1) and antisymmetric (ν_3) stretching vibrational bands of the amino group appear at 3439 and 3546 cm^{-1}. Compared with the corresponding vibrations in aniline (3422 and 3508 cm^{-1}),[34] they are blue-shifted by 17 and 38 cm^{-1}, respectively. This difference in frequency is induced by the ring nitrogen. Its lone pair electrons disturb the symmetry of the NH bonds.

Figure 3b shows the IR/R2PI spectrum of the 2AP dimer with the wavelength of the ionizing laser fixed to its 0_0^0 transition at 31 805 cm^{-1}. The same spectrum was observed for other strong bands in the R2PI spectrum in Figure 2, in particular the ones between 40 and 80 cm^{-1} which have not been observed by Hager et al. We found no indication of another isomer nor of any contribution of larger cluster sizes. The frequencies are listed in Table 2 together with the frequencies of the clusters of 2AP with water[4] and ammonia[5] and of aniline and its dimer.[34] Only two bands appear in the scanned frequency range (3200−3600 cm^{-1}). Since four bands are possible, the appearance of only two bands provides evidence that the NH_2 groups of both 2AP molecules have exactly the same molecular environment. This conclusion is consistent with the calculated structure in Figure 1. If this would not be the case, more bands would appear.

The band at 3529 cm^{-1} is red-shifted by 17 cm^{-1} relative to the antisymmetric stretching vibration of the NH_2 group. It is hence assigned to the stretching vibration of the free NH. The band at 3319 cm^{-1}, showing a large red shift of 120 cm^{-1} relative to the symmetric vibration of the NH_2 group, is assigned to the stretching vibration of the hydrogen-bonded NH. The large shift corresponds to a weakening of the NH bond, which is commonly rationalized by a transfer of partial charge from the acceptor highest occupied molecular orbital (HOMO) to the σ^* orbital of the hydrogen-bond donor. The magnitude of the frequency shift of the NH stretch is often used as a measure of the strength of the hydrogen bond. Thus, the large frequency shift indicates a strong hydrogen bond. This is consistent with the calculated bond lengths. After a dimer is formed, the length of the NH bond increases from 1.009 to 1.024 Å.

The large red shift in the vibrational frequency is similar to those in the 1:1 cluster with ammonia. In the two isomers, the hydrogen-bonded bands are red-shifted by 110 and 66 cm^{-1}, respectively.[5] Therefore, it is obvious that the NH_2 group forms a σ-hydrogen bond with the other 2AP. This result is in strong contrast with the N−H stretches in the aniline dimer. There, the two bands are red-shifted by only 28 and 41 cm^{-1} relative to the bands of the monomer. The structure of the aniline dimer is a head-to-tail, sandwichlike arrangement, stabilized by the two π-hydrogen bonds of the amino groups with the aromatic rings.[34] Because a typical σ-hydrogen bond is stronger than a π-hydrogen bond, the shift in $(2AP)_2$ is larger than that in the aniline dimer.

For the monomer, the calculated IR spectrum fits very well with the experimental one if a scaling factor of 0.965 is used, as shown in Figure 3a. For the dimer, however, the agreement between the calculated and measured frequencies is reduced. However, the accuracy in the theoretical description of chemical bonds is, in general, considerably higher than the relatively weak hydrogen bonds. This is also reported in the literature.[4,19,21] In addition, the calculated relative band intensity of the hydrogen-bonded NH stretch is larger than that of the free NH. This is in agreement with the experimental result. However, in comparing the relative intensities of calculated and measured vibrations, one has to take into account many sources of possible discrepancies, which were already discussed in section 2. Moreover, accurate intensities are difficult to calculate and depend on the level of theory, size of the basis set, anharmonicity, and vibrational coupling.

The bandwidth (full width at half-maximum (fwhm)) of the free NH vibrational band is <10 cm^{-1}, while that of the hydrogen-bonded one is $\sim$15 cm^{-1}. The bandwidths of hydrogen-bonded stretching vibrations are generally larger than that of free vibrations. Huang et al.[35] studied the lifetime and line width of the different OH stretching vibrational levels in the water dimer by high-resolution spectroscopy. The lifetime of the hydrogen-bonded OH stretch of the donor was considerably shorter than that of the free OH stretch of the acceptor molecule. The rationale for this difference is that the relaxation and predissociation rate depends strongly on the coupling of the intramolecular vibration to the intermolecular vibrational modes. The coupling of the hydrogen-bonded OH stretch to other lower frequency intermolecular vibrations is much stronger than that of the free OH stretch. This causes a decrease in the lifetime and, thus, an often observed increase of the line width.

When one compares the vibrational spectrum of the 2AP dimer with those of the $(2PY)_2$ and 2PY·2HP dimers, remarkable differences show up. For the last two dimers, the bands are extremely broad, that is, almost 500 cm^{-1}. Moreover, the position of the band maximum of $(2PY)_2$ occurs at $\sim$2800 cm^{-1}, corresponding to a red shift of as much as 650 cm^{-1}. For 2PY·2HP, the band appears at $\sim$2700 cm^{-1}, corresponding to a red shift of 750 cm^{-1} relative to the NH stretching vibration of 2PY (3448 cm^{-1}) and of 900 cm^{-1} relative to the OH stretch of 2HP (3598 cm^{-1}).[15] These extremely broad bands and the huge red shifts of the bands in $(2PY)_2$ and 2PY·2HP as compared with $(2AP)_2$ result from the formation of much stronger hydrogen bonds.

The large differences in the vibrational spectra of all three dimers reflect the differences in the strengths of their bonds. The hydrogen bonds in $(2PY)_2$ and 2PY·2HP are considerably stronger than those in the 2AP dimer. This is also consistent with the calculated bond lengths. In the 2AP dimer, the bond lengths are 2.02 Å, while, in the 2PY dimer, they are 1.8 Å.[7] In 2PY·2HP, they are 1.88 and 1.65 Å.[11] These data were obtained at the same theoretical level (B3LYP/6-311++G(d,p)). In addition, as already discussed in section 3.1, the binding energies of the 2PY dimer and of 2PY·2HP are much larger than that of the 2AP dimer.

The dimers of 2PY and 2HP have a planar structure in the ground state, enabling the aromatic rings to possibly participate in forming the hydrogen bonds by superconjugation. The reason that the hydrogen bonds are weaker in the 2AP dimer is hence due to its nonplanar structure in the ground state. For 2AP, in the excited state, the amino group is in-plane.[36] Thus, the interaction in the excited state of $(2AP)_2$ is stronger than that in its ground state. This view was already put forward by Hager et al. in ref 2. It is also supported by the large red shift of the transition to the vibrationless origin observed in the R2PI spectra.

4. Conclusions

The R2PI spectrum of the 2AP dimer has been recorded in the region of the origin band of the $S_1 \leftarrow S_0$ transition. The origin is red-shifted by 1661 cm^{-1} relative to that of isolated 2AP. In the IR/R2PI vibrational spectrum, only two bands appear at 3319 and 3529 cm^{-1}. They are red-shifted by 120 and 17 cm^{-1}, respectively, relative to the symmetric and antisymmetric N−H stretching modes of the amino group of the monomer. This gives evidence of a "shifted head to tail" structure of two 2AP molecules bound by the antiparallel N−H···N hydrogen bonds of the amino group with the ring nitrogen. Compared to the dimers of 2PY and 2HP and their mixed dimer, the interaction in the 2AP dimer is considerably weaker. This is confirmed both by the vibrational spectra and by the results from DFT calculations. The binding energy of the 2AP dimer is lowest, and the hydrogen-bond lengths are correspondingly the largest among these dimers. The weaker hydrogen bonds in the 2AP dimer are rationalized by the nonplanar structure of the molecule in the ground state.

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