

# First Excited and Cationic Ground States of Jet-Cooled 2-Aminopyridine•Ar<sub>n</sub> (n = 1, 2) Clusters: Energetics and Structures

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Resonant-enhanced multiphoton ionization (REMPI) and mass-analyzed threshold ionization (MATI) spectra of 2-aminopyridine (2AP–NH<sub>2</sub>)•Ar<sub>n</sub> clusters are reported to give the S<sub>1</sub>–S<sub>0</sub> spectral origins of 33 439 and 33 411 cm<sup>–1</sup> for the 2AP–NH<sub>2</sub>•Ar and 2AP–NH<sub>2</sub>•Ar<sub>2</sub> clusters, respectively, and also their respective adiabatic ionization energies of 8.0881 ± 0.0021 and 8.0676 ± 0.0020 eV. The upper bound for the van der Waals binding energy of 2AP–NH<sub>2</sub> (S<sub>1</sub>) and Ar is estimated to be ~525 cm<sup>–1</sup>. Blue-shifts of the 10b<sup>2</sup> out-of-plane vibrational mode by clustering provide the evidence of one atom-caging effect in the vibrational motion. Van der Waals modes at internal energies of 21 and 13 cm<sup>–1</sup> are weakly observed in MATI spectra of 2AP–NH<sub>2</sub><sup>+</sup>•Ar and 2AP–NH<sub>2</sub><sup>+</sup>•Ar<sub>2</sub> clusters, respectively, indicating that the cluster ionization is accompanied by the minimum structural change. Ab initio calculated cluster structures are also reported.

## I. Introduction

Resonant-enhanced multiphoton ionization (REMPI) and zero-electron kinetic energy (ZEKE)/mass-analyzed threshold ionization (MATI) spectroscopic methods are quite popular nowadays for the spectroscopic study of jet-cooled molecules in the excited and/or cationic ground/excited states. Using the ZEKE/MATI spectroscopic tool, vibrational structures of ions, seldom resolved in conventional photoelectron spectroscopy, are now available for a variety of chemical systems.<sup>1–4</sup> The vacuum-UV ZEKE/MATI spectroscopy is an universal technique,<sup>5</sup> while two-photon (1+1') ZEKE/MATI spectroscopy using intermediate electronic states has been quite useful for accurate mode assignments of ionic vibrational levels.<sup>6–11</sup> Spectroscopy of relatively large chemical substances becomes more and more important, especially since detailed knowledge of ionization and charge-transfers occurring in such large chemical systems is essential for understanding the mechanisms involved in many organic syntheses and important biological processes. The title molecule here, 2-aminopyridine (2AP–NH<sub>2</sub>), is a good model compound to be studied in that sense, because its electronic structure is quite similar to that of one of the DNA bases which is used in nature as biological building blocks.

Ionization dynamics of 2-aminopyridine have been quite recently investigated by Tzeng<sup>12</sup> and our groups<sup>13</sup> independently. Our group has explored various 2AP–NH<sub>2</sub> isotope analogues not only to separate two different geometrical isomers of mono-deuterated 2-aminopyridines, 2AP–NHD and 2AP–NDH, but also to observe intriguing mode-coupling dynamics associated with the amino-group H/D inversion mode.<sup>13</sup> The other interesting aspect of the 2-aminopyridine molecule is the fact that it

readily forms clusters with other rare-gas atoms or molecules in the supersonic jet. Clustering dynamics studies are crucial for understanding the nature of intermolecular forces, and MATI is an extremely useful tool for the cluster ionization study since masses responsible for ionic vibrational thresholds are clearly identified in MATI spectra. Accordingly, excitation and ionization dynamics of the 2-aminopyridine•Ar<sub>n</sub> (n = 1, 2) clusters are investigated here using REMPI and MATI techniques. This work would be quite helpful in investigating the difference between aniline and 2-aminopyridine in intermolecular interaction.

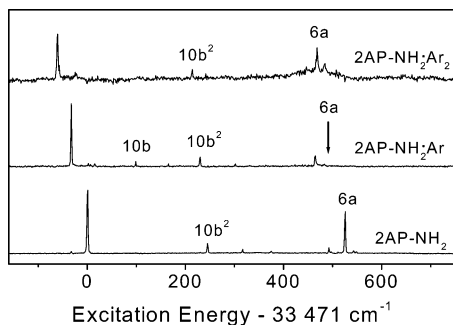
## II. Experimental Section

Experimental conditions have been described in detail in ref 13. Briefly, 2-aminopyridine (Aldrich) was heated to 80 °C, mixed with argon, and expanded into vacuum through a nozzle orifice (General Valve,  $\phi = 0.5$  mm) with a typical backing pressure of ~2 atm and a repetition rate of 10 Hz. Two independently tunable laser pulses in the 285–295 and 285–320 nm ranges were generated and overlapped with the molecular beam. Molecules excited to MATI states via two laser pulses at resonance wavelengths were allowed to stay for a few microseconds in the presence of a spoil field of ~2 V/cm, and ionized by applying a pulsed electric field of 20 ~ 120 V/cm. MATI ions were then accelerated, drifted along the field-free region, detected by dual microchannel plates (MCP, Jordan), digitized by an oscilloscope (LeCroy 9361), and stored in a personal computer which also controls two dye lasers and auto-trackers.

## III. Results and Discussion

The S<sub>1</sub>–S<sub>0</sub> origins of 2AP–NH<sub>2</sub>•Ar and 2AP–NH<sub>2</sub>•Ar<sub>2</sub> are determined to be 33 439 and 33 411 cm<sup>–1</sup>, respectively, in the

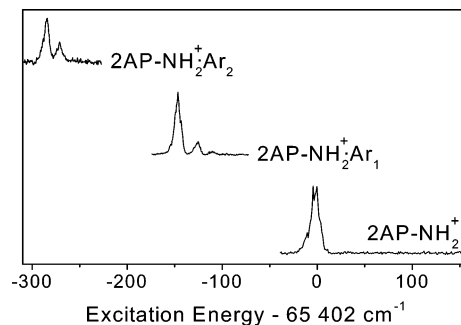
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**Figure 1.** REMPI spectra of 2AP-NH<sub>2</sub>, 2AP-NH<sub>2</sub>•Ar, and 2AP-NH<sub>2</sub>•Ar<sub>2</sub> in the region of origins showing relative shifts of the spectral origins and low-frequency vibrational bands.

REMPI spectra in Figure 1. These are slightly lower than the S<sub>1</sub>-S<sub>0</sub> origin of 33 472 cm<sup>-1</sup> determined for the bare molecule.<sup>13</sup> The red-shift of the S<sub>1</sub>-S<sub>0</sub> spectral origin induced by clustering has been commonly observed for many aromatic-rare gas van der Waals complexes.<sup>14</sup> Energetics involved in electronic excitations are closely related to the stabilization energies due to clustering. It is found that the 2AP-NH<sub>2</sub>•Ar or 2AP-NH<sub>2</sub>•Ar<sub>2</sub> cluster in the S<sub>1</sub> state, respectively, is ~33 or ~61 cm<sup>-1</sup> more stable than each in the S<sub>0</sub> state. The S<sub>1</sub>-S<sub>0</sub> excitation of 2-aminopyridine should be accompanied by the charge-rearrangement, which is followed by the change of dispersion force between 2AP-NH<sub>2</sub> and Ar. However, practically no low-frequency van der Waals modes are found to be optically active in the S<sub>1</sub>-S<sub>0</sub> excitation spectra of both clusters, indicating that there is little geometrical change upon the electronic excitation. One interesting spectral feature is that relatively strong bands due to 10b<sup>2</sup> modes are observed at internal energies of 262 and 274 cm<sup>-1</sup> of 2AP-NH<sub>2</sub>•Ar and 2AP-NH<sub>2</sub>•Ar<sub>2</sub>, respectively, while the corresponding frequency of the bare molecule in the S<sub>1</sub> state is 244 cm<sup>-1</sup>.<sup>13</sup> Blue-shifts of the 10b<sup>2</sup> frequency in clusters indicate that the out-of-plane motion of nuclei associated with the 10b mode may be restricted by the presence of argon atom(s), giving the steeper potential along the 10b normal coordinate for the molecule in the clusters. An important point to be made here is that the blue-shift of the 10b<sup>2</sup> mode frequency increases gradually with the number of Ar atom being clustered. Thus, it could be an interesting and important experimental evidence of one atom-caging effect for the vibrational motion. It is also intriguing to note that the fundamental of the 10b mode, which is not symmetry-allowed in the 2AP-NH<sub>2</sub> spectrum, is weakly observed at the internal energy of 131 cm<sup>-1</sup> in the 2AP-NH<sub>2</sub>•Ar spectrum. This experimental finding strongly suggests that the Ar atom is not in the molecular plane. Rather, it should be weakly bound to the top of the aromatic ring, leading to the breakage of the plane symmetry, and this is consistent with ab initio calculation (vide infra).

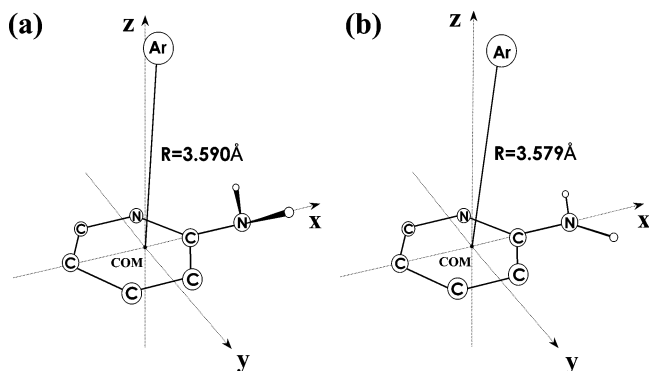
A band at 497 cm<sup>-1</sup> in the 2AP-NH<sub>2</sub>•Ar spectrum corresponds to the 492 cm<sup>-1</sup> band in the 2AP-NH<sub>2</sub> spectrum. The other vibrational mode observed at the internal energy of 525 cm<sup>-1</sup> in the 2AP-NH<sub>2</sub> spectrum corresponds to the 6a mode. Since this mode belongs to the in-plane ring skeletal mode of the molecule, the large shift of the vibrational frequency induced by clustering is not expected. However, the 6a band which is expected to be at the internal energy of ~525 cm<sup>-1</sup> is practically absent in the 2AP-NH<sub>2</sub>•Ar spectrum, as shown in Figure 1. This indicates that the dissociation energy of 2AP-NH<sub>2</sub>•Ar into 2AP-NH<sub>2</sub> and Ar might be less than 525 cm<sup>-1</sup>, which is not so unreasonable considering the fact that the upper bound of ~494 cm<sup>-1</sup> had been experimentally determined for the binding energy of aniline (S<sub>1</sub>) and Ar.<sup>15</sup> This sudden decrease of the 6a



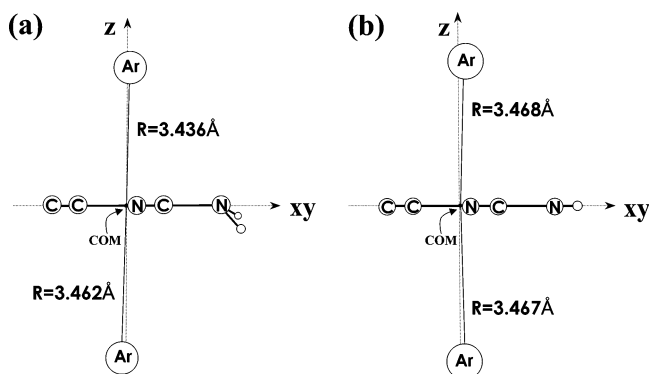
**Figure 2.** MATI spectra of 2AP-NH<sub>2</sub>, 2AP-NH<sub>2</sub>•Ar, and 2AP-NH<sub>2</sub>•Ar<sub>2</sub> taken via their spectral origins as intermediate states. Note the red-shifts of ionization energies induced by being clustered and van der Waals vibrational bands in the cluster MATI spectra.

band intensity in the excitation spectrum of 2AP-NH<sub>2</sub>•Ar suggests that the corresponding motion of nuclei could be strongly coupled to the van der Waals bond dissociating coordinate via effective intramolecular vibrational redistribution (IVR). Considering the spectral shift due to clustering (vide supra), the upper bound for the binding energy of 2AP-NH<sub>2</sub> (S<sub>0</sub>) and Ar is thus estimated to be ~492 cm<sup>-1</sup>. The 6a band in the 2AP-NH<sub>2</sub>•Ar<sub>2</sub> spectrum is relatively strongly observed at the internal energy of 528 cm<sup>-1</sup>, though line-broadening probably due to IVR is clearly observed in the same energy region, Figure 1. Further detailed studies would be necessary, however, for better understanding of van der Waals binding and dissociating mechanisms.

MATI spectra taken via S<sub>1</sub>-S<sub>0</sub> origins, Figure 2, provide accurate ionization energies of 8.0881 ± 0.0021 and 8.0676 ± 0.0020 eV for 2AP-NH<sub>2</sub>•Ar and 2AP-NH<sub>2</sub>•Ar<sub>2</sub>, respectively.<sup>16</sup> These ionization energies are certainly lower than the bare molecule ionization energy of 8.1098 ± 0.0012 eV.<sup>13,17</sup> As mentioned above, the difference between ionization energies of the bare molecule and clusters corresponds to the difference of the two species in their solvation energies. Accordingly, 2AP-NH<sub>2</sub>•Ar or 2AP-NH<sub>2</sub>•Ar<sub>2</sub> in the cationic ground D<sub>0</sub> state is ~180 or ~346 cm<sup>-1</sup> more stable than that in the S<sub>0</sub> state, respectively. If the above estimated upper bound of 525 cm<sup>-1</sup> for the binding energy of 2AP-NH<sub>2</sub> (S<sub>1</sub>) and Ar is provided, then the upper bound for the binding energy between 2AP-NH<sub>2</sub> cation (D<sub>0</sub>) and Ar should be around 672 cm<sup>-1</sup>. The larger stabilization energies induced by ionization could be explained by the additional binding energy due to the dipole-induced dipole interaction in the cationic clusters. It is very interesting to compare these energetics with those of aniline-Ar complexes. According to the Kimura group,<sup>18</sup> red-shifts in ionization energies of aniline-Ar and aniline-Ar<sub>2</sub> complexes compared to the aniline ionization energy are 111 and 219 cm<sup>-1</sup>, respectively, which are just twice as much as the red-shifts in S<sub>1</sub>-S<sub>0</sub> spectral origins of 54 and 109 cm<sup>-1</sup> for aniline-Ar and aniline-Ar<sub>2</sub>, respectively.<sup>15,18</sup> Therefore, an extra electron on the 2p orbital of the nitrogen atom on the aromatic ring should be responsible for the relatively stronger binding energy in cationic 2AP-NH<sub>2</sub>•Ar<sub>n</sub> clusters in terms of the dipole strength of the molecular ion. It is interesting to note that noncovalent binding energy of 2AP-NH<sub>2</sub> is higher than that of aniline, especially because the 2-aminopyridine molecule has a similarity in its electronic structure with the biological DNA building block. Differently from the S<sub>1</sub>-S<sub>0</sub> excitation spectra of Ar clusters, several van der Waals vibrational bands are observed in MATI spectra (Figure 2), indicating that the van der Waals bond length or angle between 2AP-NH<sub>2</sub> and Ar atom(s) should be changed in the cationic clusters. Van der Waals modes in



**Figure 3.** Ab initio [(U)MP2 with a 6-31+G(d) basis set] calculated geometry of (a) the 2AP-NH<sub>2</sub>·Ar in the ground state and (b) 2AP-NH<sub>2</sub><sup>+</sup>·Ar cluster in the ground cationic state.



**Figure 4.** Sideviews of ab initio [(U)MP2 with a 6-31+G(d) basis set] calculated geometry of (a) the 2AP-NH<sub>2</sub>·Ar<sub>2</sub> in the ground state and (b) the 2AP-NH<sub>2</sub><sup>+</sup>·Ar<sub>2</sub> cluster in the ground cationic state.

MATI spectra give associated vibrational frequencies of 21 and 13 cm<sup>-1</sup> for 2AP-NH<sub>2</sub><sup>+</sup>·Ar and 2AP-NH<sub>2</sub><sup>+</sup>·Ar<sub>2</sub> clusters, respectively. Similarly to the case of the aniline<sup>+</sup>·Ar<sub>n</sub> clusters study,<sup>18</sup> the former is assigned to the van der Waals symmetric bending in the 2AP-NH<sub>2</sub><sup>+</sup>·Ar cluster, while the latter is attributed to in-plane bending mode of the 2AP-NH<sub>2</sub><sup>+</sup>·Ar<sub>2</sub> cluster.

The ab initio calculation (MP2 or UMP2 with a 6-31+G(d) basis set)<sup>19</sup> suggests that that Ar is weakly bound to the top of the aromatic ring of 2AP-NH<sub>2</sub> in the ground state 2AP-NH<sub>2</sub>·Ar cluster, Figure 3. The distance of Ar from the center of mass of 2AP-NH<sub>2</sub> is calculated to be 3.590 Å in the ground state. In the 2AP-NH<sub>2</sub><sup>+</sup>·Ar cluster, the distance becomes slightly shortened to 3.579 Å, and Ar is tilted toward to the amino moiety as shown in Figure 3b. This ab initio calculation predicting little structural change of the cluster upon ionization is consistent with the experimental finding. That is, as mentioned earlier, from the spectra in Figure 1, it is expected that cluster structures in S<sub>1</sub> states are not much different from those in S<sub>0</sub> states. For the cationic clusters, large structural changes associated with cluster ionization are not expected either, judging from MATI spectra of 2AP-NH<sub>2</sub><sup>+</sup>·Ar and 2AP-NH<sub>2</sub><sup>+</sup>·Ar<sub>2</sub> in Figure 2 showing the most prominent D<sub>0</sub>-S<sub>1</sub> origin with weakly observed van der Waals bending modes. For 2AP-NH<sub>2</sub>·Ar<sub>2</sub>, several structural isomers are plausible to be populated. According to ab initio calculation, the most stable isomer is predicted to have the structure in which two Ar atoms are weakly bound to the aromatic ring from opposite directions with

distances of 3.436 and 3.462 Å from centers of mass of the ring, Figure 4. The symmetric structure of the 2AP-NH<sub>2</sub>·Ar<sub>2</sub> cluster is consistent with the experimental finding that the associated energy shifts of the S<sub>1</sub>-S<sub>0</sub> origin and ionization from those of the bare molecule are nearly twice as much as those found for the 2AP-NH<sub>2</sub>·Ar cluster. The geometrical change of the 2AP-NH<sub>2</sub>·Ar<sub>2</sub> cluster due to ionization is minimum as shown in Figure 4b, which is also consistent with the MATI spectrum in Figure 2.

#### IV. Summary

Here, energetics involved in the S<sub>1</sub>-S<sub>0</sub> excitation and ionization of 2-aminopyridine·Ar<sub>n</sub> (n = 1, 2) clusters are studied using REMPI and MATI spectroscopic methods. The spectral shift of the S<sub>1</sub>-S<sub>0</sub> origin is found to be ~33 or ~61 cm<sup>-1</sup> for 2AP-NH<sub>2</sub>·Ar or 2AP-NH<sub>2</sub>·Ar<sub>2</sub> clusters, respectively. The 10b<sup>2</sup> mode in the S<sub>1</sub> state shows the blue-shift in its vibrational frequency upon clustering, demonstrating the one-atom caging effect in the vibrational motion. The sudden decrease of the 6a band in the 2AP-NH<sub>2</sub>·Ar excitation spectrum provides the upper bound of ~525 cm<sup>-1</sup> for the van der Waals binding energy of 2AP-NH<sub>2</sub> (S<sub>1</sub>) and Ar. Ionization energies of 2AP-NH<sub>2</sub>·Ar or 2AP-NH<sub>2</sub>·Ar<sub>2</sub> are accurately determined to be 8.0881 ± 0.0020 and 8.0676 ± 0.0020 eV, respectively. Several van der Waals modes are active in MATI spectra of clusters, indicating that the cluster geometry changes upon molecular ionization.

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