

Resonant-enhanced two photon ionization and mass-analyzed threshold ionization spectroscopy of jet-cooled 2-aminopyridines (2AP-NH₂, -NHD, -NDH, -ND₂)

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Resonantly-enhanced two photon ionization and mass-analyzed threshold ionization (MATI) spectra of 2-aminopyridine (2AP-NH₂) and its deuterated analogs have been obtained using two-photon (1+1') excitation process via S_1 intermediate states for ionization. Ionization energies of 2AP-NH₂ and 2AP-ND₂ are both precisely and accurately determined to be 8.1086 ± 0.0005 and 8.1027 ± 0.0005 eV, respectively. Two geometrical isomers, 2AP-NHD or 2AP-NDH, of which H or D is hydrogen-bonded to the nitrogen atom on the pyridine ring, respectively, are spectroscopically well isolated using the hole-burning spectroscopy in the S_1 states. Corresponding ionization energies are thus separately determined to be 8.1067 ± 0.0005 or 8.1048 ± 0.0005 eV for 2AP-NHD or 2AP-NDH, respectively. Vibrational bands of 2-aminopyridine ions associated with various aromatic ring-skeletal modes are identified in the MATI spectra and appropriately assigned with the aid of *ab initio* calculation. All of the ring-skeletal vibrational frequencies observed in this work become slightly higher than those in the S_1 states when the molecules are ionized, consistent with the fact that the S_1-S_0 excitation is due to $\pi^*-\pi$ transition. According to *ab initio* calculation, the amino group is in the molecular plane both in the S_1 and D_0 states, while it is slightly distorted in the ground state of 2-aminopyridine. Inversion modes in 2AP-ND₂ and 2AP-NDH in S_1 states are split into two bands due to their strong coupling with the other mode, which is most probably due to torsional motion of the amino group. Strong mode couplings are clearly manifested in interferencelike patterns observed in vibrational band structures of MATI spectra taken via those two bands in S_1 states as intermediate states. A new spectroscopic scheme, in which MATI signals are used for obtaining mode-resolved spectra for the intermediate state is introduced. The vibrational band at 911 cm^{-1} from the S_1-S_0 origin that has been previously assigned as the inversion mode of 2AP-NH₂ is found to actually consist of two closely-spaced different modes giving two clearly-resolved different Franck-Condon active modes in corresponding MATI spectra. © 2002 American Institute of Physics. [DOI: 10.1063/1.1488922]

I. INTRODUCTION

Since the zero-electron kinetic energy (ZEKE) spectroscopic technique was developed, the energy resolution that could be achieved in photoelectron spectra has been enormously improved so that rovibrational structures of molecular ions are readily accessible nowadays.¹⁻⁴ Lifetimes of ZEKE states are quite long and it is easy to separate out ZEKE-electrons from directly-formed electrons by employing the pulsed-field ionization (PFI) technique. Rydberg electrons are located quite far from ionic cores, and excitation energies to ZEKE states are exactly correlated to internal energies of ions added to their adiabatic ionization energies. Thus rovibrational spectra of ions are obtained when the ZEKE signal is monitored as a function of the excitation energy. Identical spectroscopic information can also be obtained by mass-analyzed threshold ionization (MATI) spectroscopy in which ions, instead of electrons, are detected.^{5,6} In MATI spectroscopy, a spoil field of a few V/cm, which

may also eliminate ZEKE state, should be applied to differentiate the path of MATI ions from that of direct ions along the time-of-flight axis. ZEKE has been more popular than MATI since the former has some advantages in terms of the signal to noise (S/N) ratio and energy resolution. It should be noted, however, that mass identities responsible for ZEKE-electrons are not available in ZEKE spectroscopy, while they could be exactly measured in MATI spectroscopy. Therefore, MATI would be extremely valuable in studies of cluster ions and/or photodissociation dynamics of ions.⁶⁻⁸ Here, we have used the MATI spectroscopic tool to investigate ionization processes of not only 2-aminopyridine ions but also its clusters with argon.

Either one-photon or two-photon excitation schemes can be used to reach ZEKE-states for high-resolution photoelectron spectroscopy. One-photon ZEKE or MATI is universally applicable to various kinds of molecules since the two-photon excitation is sometimes not efficient especially for molecules having ultrashort lifetimes at their intermediate states.⁹ Meanwhile, two-photon ZEKE or MATI is quite useful in determining ionic vibrational frequencies and also in assigning those to appropriate vibrational modes, since vari-

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ous vibrational states in the first excitation process can be selected as intermediate states in the ionization process.^{1,2,10} In recent years, ZEKE or MATI spectroscopy has been both intensively and extensively carried out to provide high-resolved rovibrational spectra of ionic ground states for a number of organic molecules and clusters.^{1,2,10–16} Those spectral features are essential in investigating nuclear and electrical change upon ionizations of molecules, and eventually understanding the role of electrons in forming various kinds of chemical bonds.

Spectroscopy of 2-aminopyridine (2AP-NH₂) and its deuterated analogs such as 2AP-ND₂, 2AP-NHD, 2AP-NDH had been studied for *S*₀ and *S*₁ states by Hollas *et al.* using absorption and dispersed fluorescence spectroscopy taken at room temperature.^{17,18} Later, the Wallace group refined peak assignments for 2AP-NH₂ using jet-cooled fluorescence excitation spectroscopy.^{19,20} For monodeuterated 2-aminopyridine, Hollas *et al.* had observed spectral features due to two geometrical isomers, 2AP-NHD or 2AP-NDH, of which H or D is hydrogen-bonded to the nitrogen atom on the pyridine ring, respectively.¹⁶ However, band assignments for those could not be made unambiguously since spectral bands of two isomers were hardly separable in the absorption spectrum. For the 2-aminopyridine cation (2AP-NH₂⁺), the Weber group has used photoelectron spectroscopy to obtain its vibrational spectrum with a resolution of ~40 cm⁻¹ (5 meV).^{21,22} In this work, vibrational spectra are obtained with a resolution of ~1 cm⁻¹ using MATI spectroscopy for molecular ions of 2AP-NH₂⁺, 2AP-ND₂⁺, 2AP-NHD⁺, and 2AP-NDH⁺. Especially, spectral features due to two different isomers of monodeuterated 2-aminopyridines, 2AP-NHD⁺ and 2AP-NDH⁺, are clearly separated in both *S*₁ and *D*₀ states using a hole-burning spectroscopy. New spectral features of mode-couplings mainly related with inversion modes are investigated by employing a new spectroscopic technique using MATI signals to get mode-resolved *S*₁-state spectra. Density functional theory (DFT) calculation has been carried out for refining band assignments and also identifying nuclear motions involved in those modes.

II. EXPERIMENT

2-aminopyridine was purchased from Aldrich and used without further purification. For the preparation of deuterated compounds, 2-aminopyridine was mixed with CH₃OD and the solvent was evaporated completely. This procedure was carried out for several times before it was used. The sample 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. The nozzle was heated at 85 °C, which is slightly higher than the sample temperature to avoid sample condensation on the nozzle orifice. A supersonically cooled molecular beam was then skimmed through a 1 mm diam skimmer (Precision Instrument Services). Background pressures of source and ionization chambers were maintained at ~10⁻⁵ and 10⁻⁷ Torr, respectively, when the nozzle was on. The laser pulse of 2–3 mJ/pulse with a duration time of ~6 ns in the 285–295 nm range was generated by frequency-

doubling of the laser output from a dye laser (Lambda-Physik, ScanmateII) pumped by the second harmonic output of a Nd:YAG laser (Spectra-Physics GCR-150). The other laser pulse (3–4 mJ/pulse, 6 ns) was generated in the 285–320 nm region via doubling the laser output from the other dye laser (Lumonics, HD500) pumped by the 532 nm output of the other Nd:YAG laser (Continuum SureliteII). Frequency doubling was made by KD*P crystals placed on homemade autotracker to maintain both intensities and directions of laser beams while their wavelengths were scanning. Two independently tunable laser pulses were then spatially and temporally overlapped and crossed the molecular beam in a counterpropagating geometry.

Molecules excited to ZEKE states via two laser pulses at resonant wavelengths were allowed to stay for a few μ s 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 autotrackers. To enhance the MATI signal, a scrambling field was applied at the moment of laser excitation.^{7,8} For resonantly-enhanced two-photon ionization (R2PI) spectra, ionization occurred in the presence of the extracting electric field, and thus directly-formed ion signals were monitored as a function of excitation energy. Absolute frequencies of dye laser outputs were calibrated within the accuracy of ± 0.5 cm⁻¹ using the optogalvanic effect in an iron hollow-cathode lamp with Ne gas.

III. RESULTS AND DISCUSSION

R2PI and MATI spectra of 2-aminopyridines are presented in the order of (a) molecular structures and normal modes by *ab initio* calculation, (b) 2AP-NH₂⁺ (*D*₀), (c) 2AP-ND₂⁺ (*D*₀), and (d) 2AP-NHD⁺ and 2AP-NDH⁺ (*D*₀). The relatively high PFI field applied for ionization of ZEKE states often causes the underestimation of ionization energies compared to true values.^{1–4} The MATI peak shape is found to be typically unsymmetric showing a long tail in the red side of the peak. As the PFI field decreases, for example from 120 to 20 V/cm, it is found that the maximum peak positions remains constant within ± 1 cm⁻¹, while the peak width decreases. Ionization energies and ionic vibrational energies reported here are taken from MATI peak positions at their maximum intensities. It should be noted that the benzene-type numbering system according to Ref. 23 is adopted here for labeling normal modes of 2-aminopyridines.

A. Molecular structures and normal modes by *ab initio* calculation

According to our *ab initio* calculations using the GAUSSIAN 98 program,²⁴ the amino group of 2AP-NH₂ in both *S*₁ and *D*₀ states is in the molecular plane, while it is slightly bent in the *S*₀ state, which is consistent with spectroscopic evidence presented in previous other spectroscopic works.^{25,26} It has been estimated in previous other works that hydrogen atoms of the amino group are bent out of plane of

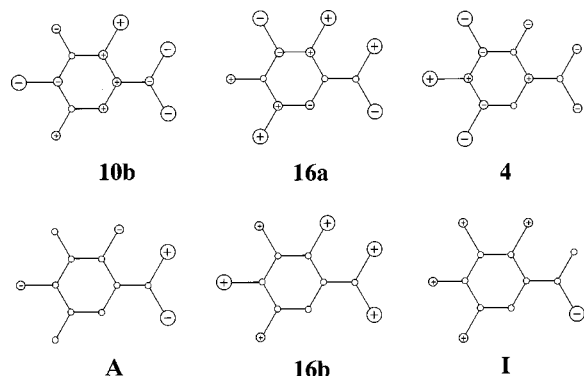


FIG. 1. Calculated normal mode descriptions for low-frequency out-of-plane vibrations of $2AP-NH_2^+(D_0)$. Labeling of normal modes is given according to Ref. 23.

the pyridine ring by 32° .^{25,26} It should be pointed out though that one of the hydrogen atoms is intramolecularly hydrogen-bonded to the nitrogen atom on the pyridine ring (N1). This intramolecular hydrogen bond results in asymmetric structure of two amino-group hydrogen atoms, giving calculated [DFT, RB3LYP, 6-31G(*d*)] bend angles of 17.4° and 29.1° for the hydrogen atom near to N1 and that of the other side, respectively. The existence of the intramolecular hydrogen-bond between one of the amino-group hydrogen atoms and N1 is definitely proven in distinct R2PI spectra of $2AP-NHD$ and $2AP-NDH$ (*vide infra*). The $C(2)-NH_2$ bond length of $2AP-NH_2^+$ is found to be dramatically shortened compared to that in the neutral state since a nonbonding electron on the amino N atom participates in the conjugation with the aromatic ring to give the double-bond character of the $C(2)-NH_2$ bond.²⁷⁻²⁹ This is the main reason why the amino group of $2AP-NH_2$ becomes planar in the cation state, which is similar to that for the conclusion that had been drawn for the aniline ionization by the Reilly group.²⁹ The shortening of the $C(2)-NH_2$ bond upon ionization should give the deeper potential wells along the normal coordinates associated with $C(2)-NH_2$ torsion, NH_2 wag, or the other out-of-plane NH_2 motions, resulting in the higher vibrational frequencies for cations.

For clear identification of normal modes being referred by labeling numbers, *ab initio* normal modes of $2AP-NH_2^+(D_0)$ with their calculated vibrational frequencies lower than 1600 cm^{-1} are shown in Figs. 1–3 along with corresponding benzene-type labels and representations of vectors for relative nuclear motions involved. The *ab initio* calculation is carried out by the GAUSSIAN 98 program using the DFT-UB3LYP method on the 6-31G+(*d*) basis set. Scaled *ab initio* values (scale factor=0.9613) for 15 normal modes of which vibrational frequencies are lower than 1600 cm^{-1} are also listed for $2AP-NH_2^+$, $2AP-ND_2^+$, $2AP-NHD^+$, and $2AP-NDH^+$ in Table I.

B. $2AP-NH_2^+(D_0)$

The S_1-S_0 excitation spectrum of $2AP-NH_2$ taken via the R2PI method is shown in Fig. 4. The origin band is found at $33\,472\text{ cm}^{-1}$. Since the S_1-S_0 excitation is a $\pi^*-\pi$ transition, the transition dipole moment is on the molecular

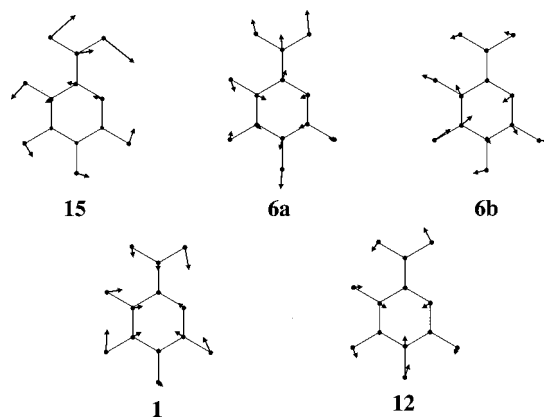


FIG. 2. Calculated normal modes for several in-plane vibrations of $2AP-NH_2^+(D_0)$ in the $300-950\text{ cm}^{-1}$ range.

plane. Only in-plane vibrational modes or even-quanta of out-of-plane modes are symmetry allowed. Relatively strong bands are observed at 525 , 823 , and 1049 cm^{-1} which are attributed to in-plane modes of $6a$, 1 , and $18b$ modes, respectively. These assignments are mostly consistent with those in previous works,^{19,20} though labeling for normal modes may cause some confusion; for example, the 823 cm^{-1} band is assigned here as 1 instead of 12 . Even quanta of out-of-plane modes mainly associated with the amino-group moiety motion are also strongly observed since the slightly bent $2AP-NH_2$ molecule in the ground electronic state becomes planar in the S_1 state. The 244 cm^{-1} band is assigned to the $10b^2$ mode, which is mostly associated with NH_2 wagging motion, while the I^2 (inversion) mode of NH_2 is apparently observed at 911 cm^{-1} , Fig. 4.

1. MATI spectra via the S_1-S_0 origin and $10b^2$ (S_1) bands

The MATI spectrum taken via the S_1-S_0 origin band shows the strongest peak at the second photon energy of $31\,928\text{ cm}^{-1}$, giving the adiabatic ionization energy of $65\,400 \pm 4\text{ cm}^{-1}$ ($8.1086 \pm 0.0005\text{ eV}$) for $2AP-NH_2$, Fig. 4. This ionization energy is $\sim 80\text{ cm}^{-1}$ higher than the previously reported value of $65\,320\text{ cm}^{-1}$ (8.099 eV).²¹ Addi-

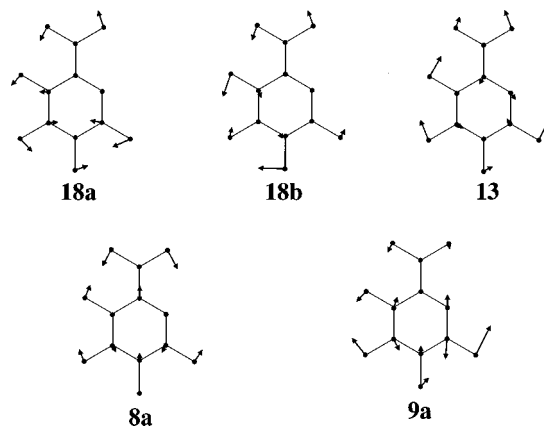


FIG. 3. Calculated normal modes for several in-plane vibrations of $2AP-NH_2^+(D_0)$ in the $950-1600\text{ cm}^{-1}$ range.

TABLE I. Scaled *ab initio* vibrational frequencies of 2AP-NH₂⁺, 2AP-ND₂⁺, 2AP-NHD⁺, and 2AP-NDH⁺ in *D*₀ states for low-frequency normal modes and some experimentally determined fundamental frequencies.

<i>D</i> ₀ state						
2AP-NH ₂ ⁺		2AP-ND ₂ ⁺		2AP-NHD ⁺ (NDH ⁺)		Assignment
Obs. (cm ⁻¹)	Calc. (cm ⁻¹)	Obs. (cm ⁻¹)	Calc. (cm ⁻¹)	Obs. (cm ⁻¹)	Calc. (cm ⁻¹)	
157	159		154		157 (157)	10b ⁺
	355		338		346 (349)	16a ⁺
355	383	346	339	352(351)	358 (358)	15 ⁺
	435		418		423 (422)	4 ⁺
542	535	533	522	534(539)	532 (525)	6a ⁺
	573		439		459 (498)	A ⁺
599	589	600	586	598(598)	587 (588)	6b ⁺
	640		661		627 (665)	16b ⁺
	680		519		682 (590)	I ⁺
836	822	813	793		816 (795)	1 ⁺
	943		945	(824)	945 (949)	12 ⁺
996	972	1007	985		985 (987)	18a ⁺
1086	1095	1067	1087		1088 (1092)	18b ⁺
1336	1370				1367 (1329)	13 ⁺
	1535		1539		1541 (1539)	9a ⁺

tional peaks are also weakly observed at 355, 599, and 712 cm⁻¹ higher than the ionization threshold, and these are assigned to be due to 15⁺, 6b⁺, and 15⁺² modes, respectively, as listed in Table II. Scaled *ab initio* values for 15⁺ and 6b⁺ modes are 383 and 589 cm⁻¹, as listed in Table I, are quite consistent with the experiment. In the MATI spectrum via 10b² modes (244 cm⁻¹), the 0⁺-10b² band is very weakly observed. Meanwhile, the stronger peaks are observed at 313 and 514 cm⁻¹. Considering the propensity rule of Δ*v*=0, the 313 cm⁻¹ peak is assigned to 10b⁺² mode. This is close to twice of the barely observable 157 cm⁻¹ band, which is most likely due to the symmetry-forbidden 10b⁺-10b² transition. The *ab initio* value of 159 cm⁻¹ for the 10b⁺ mode is in

excellent agreement with this assignment. The more strongly observed 514 cm⁻¹ band could be assigned to 10b⁺⁴ or the other mode such as 16a⁺². The assignment for this mode is not quite yet through, since the former requires the severe anharmonicity in the 10b⁺ mode while the latter assignment is not likely due to the lack of Franck-Condon overlap between the *S*₁ and *D*₀ states.

2. MATI spectra via the 6a, 1, and 18b (*S*₁) bands

The strongest peak is observed at the ionic vibrational energy of 542 cm⁻¹ in the MATI spectrum via the 6a mode, providing its obvious assignment to the 6a⁺ mode of the cation in Fig. 4. The origin band is only weakly observed, while the 6b⁺ band is relatively strongly observed at 599 cm⁻¹. It is interesting to note that the 6b⁺ mode is relatively strong as observed in the *D*₀-*S*₁ MATI spectra, while the 6b mode does not seem to be optically active in the *S*₁-*S*₀ spectrum, Fig. 4. This observation should be the consequence of the ring deformation occurring upon ionization due to the participation of an electron of N atom into the ring conjugation in the cation state. The combination band of 6a⁺ and 6b⁺ is observed at the vibrational energy of 1143 cm⁻¹, and the first overtone of 6b⁺ is quite weakly found at 1200 cm⁻¹. The 899 cm⁻¹ band is due to 6a⁺+15⁺, and the small peak at 1255 cm⁻¹ is ascribed to the 6a⁺+15⁺² mode. The 1⁺ mode is very weakly observed at 836 cm⁻¹, while the combination mode of the 1⁺+6a⁺ mode is more strongly observed at 1378 cm⁻¹. The 1501 cm⁻¹ band should be due to the 6a⁺+959 cm⁻¹, which will be discussed later in this section. The assignment is not quite certain for the 1658 cm⁻¹ band.

The MATI spectrum taken via the 1 mode of the *S*₁ state (823 cm⁻¹) clearly shows that the corresponding 1⁺ mode of 2AP-NH₂⁺ is located at 836 cm⁻¹, Fig. 4. Its first overtone 1⁺² band is found at 1672 cm⁻¹. The 959 cm⁻¹ band is also weakly observed, while the 1⁺+15⁺ and 1⁺+6b⁺ bands can be easily identified at 1194 and 1431 cm⁻¹, respectively.

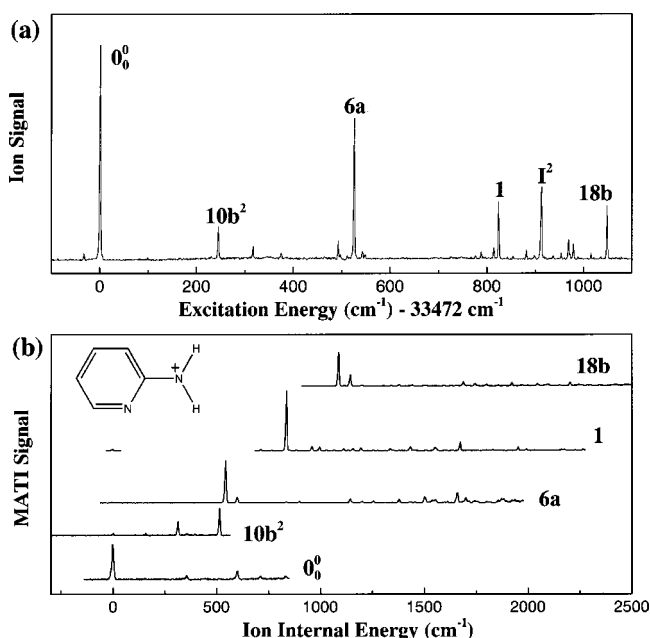


FIG. 4. (a) The *S*₁-*S*₀ excitation spectrum of 2AP-NH₂. (b) MATI spectra taken via the *S*₁-*S*₀ origin, 10b², 6a, 1, and 18b *S*₁-state modes of 2AP-NH₂.

TABLE II. Vibrational frequencies of $2AP-NH_2^+(D_0)$ and mode assignments from various MATI spectra.

2AP-NH ₂ ⁺ ; Δ, cm ^{-1a}						
Origin	10b ²	6a	1	911 cm ^{-1b}	18b	Assignment
0						Origin
	313					10b ⁺²
355		514				15 ⁺
						10b ⁺⁴ or 16a ⁺² ?
		542				6a ⁺
599		599				6b ⁺
712						15 ⁺²
		836	836			1 ⁺
		899				6a ⁺ + 15 ⁺
				937		I ⁺²
				959		12 ⁺
				996	992	18a ⁺
					1086	18b ⁺
					1142	6a ⁺ + 6b ⁺
			1194			1 ⁺ + 15 ⁺
			1200			6b ⁺²
			1255			6a ⁺ + 15 ⁺²
				1336	1339	13 ⁺
				1378	1377	1 ⁺ + 6a ⁺
				1431		1 ⁺ + 6b ⁺
				1501		6a ⁺ + 959 cm ⁻¹
					1538	I ⁺² + 6b ⁺
					1561	12 ⁺ + 6b ⁺
			1658			1 ⁺ + 2
				1672		18b ⁺ + 6b ⁺
					1687	I ⁺² + 1 ⁺
					1773	12 ⁺ + 1 ⁺
					1797	I ⁺² + 12 ⁺
					1895	12 ⁺² or 18b ⁺ + 1 ⁺
					1920	

^aShifts from the ionization threshold.

^bSee the text for the assignment.

The bands at 996 and 1336 cm⁻¹ are tentatively assigned to 18a⁺ and 13⁺ modes, respectively, from the comparison of the experimental and *ab initio* values.

The 18b⁺ mode is found to have the vibrational energy of 1086 cm⁻¹ as shown in the MATI spectrum via the S₁ 18b mode (1049 cm⁻¹) in Fig. 6, which is quite consistent with the corresponding *ab initio* value of 1095 cm⁻¹, Table I. The combination band of 6a⁺ and 6b⁺ modes is quite strongly observed at 1142 cm⁻¹. Other combination bands of 18b⁺ + 6b⁺ and 18b⁺ + 1⁺ are also observed at 1687 and 1920 cm⁻¹, respectively.

3. Mode-resolved spectra of the 911 cm⁻¹ (S₁) band and its MATI spectra

The most intriguing mode of 2AP-NH₂ is the inversion mode involving the out-of-plane motion of amino hydrogen atoms with respect to the molecular plane. According to the normal mode calculation as shown in Fig. 1, the inversion mode of 2AP-NH₂⁺ is mainly associated with the out-of-plane motion of the hydrogen atom which is hydrogen-bonded to N1 on the pyridine moiety. As mentioned earlier, and also reported in previous studies, the 911 cm⁻¹ band is assigned to I² modes in the S₁ state.¹⁷⁻²¹ However, two strong, well-separated MATI peaks located at 937 and 959 cm⁻¹ are found when the 911 cm⁻¹ band is used as an inter-

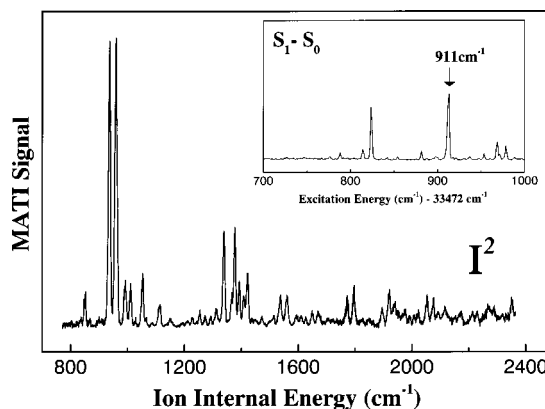


FIG. 5. The MATI spectrum taken via the 911 cm⁻¹ band of 2AP-NH₂ (S₁). The S₁-S₀ excitation spectrum is also shown in the inset for comparison.

mediate state for ionization, as clearly shown in Fig. 5. One is tempted to assign those striking spectral features as being due to inversion doubling caused by tunneling through an inversion barrier in the cation state. However, it is very unlikely since the structure of 2AP-NH₂⁺ in its ground ionic state is expected to be planar. The other possible explanation is that the 911 cm⁻¹ band in the S₁ state is not just due to the inversion mode only. For unraveling the mode-purity of the 911 cm⁻¹ band, we have used a novel experimental scheme in which the MATI signal is monitored while the first excitation energy to intermediate states is varied, as shown in Fig. 6. In this experimental scheme, the energy for the D₀-S₁ transition is fixed either at 31 954 = origin + 937 - 911 or 31 976 = origin + 959 - 911 cm⁻¹. Now, the laser wavelength for the S₁-S₀ transition is scanned to give two different mode-resolved spectra for the S₁ state. In this way, intermediate states of which modes having the largest Franck-Condon factors with either 937 or 959 cm⁻¹ MATI band can be separated out. When the D₀-S₁ energy is fixed at 31 954 cm⁻¹, the position and bandwidth of the 911 cm⁻¹ band is found to be almost the same as the one in the R2PI spectrum to give the A-band in Fig. 6. On the other hand, however, the

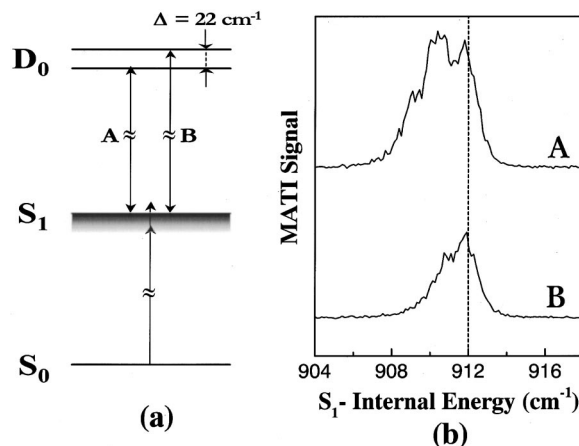


FIG. 6. (a) The excitation scheme for obtaining mode-resolved spectra. (b) Mode-resolved spectra taken by monitoring the MATI signal as a function of S₁-S₀ excitation energy at a fixed D₀-S₁ excitation energy of 31 954 or 31 976 cm⁻¹, giving the A and B bands, respectively.

bandwidth becomes much narrower and the maximum peak position is slightly shifted to the higher frequency of 911.5 cm^{-1} when the D_0-S_1 excitation energy is fixed at $31\,976\text{ cm}^{-1}$, giving the B -band in Fig. 6. Since A and B bands in the S_1 state are so closely spaced in their vibrational energy, it is not trivial to separate them out spectroscopically even with the higher spectral resolution. In this sense, the mode-resolved spectra first introduced in this work could be extremely useful in resolving overlapping bands without using ultrahigh resolution spectroscopic tool.

This experimental finding indicates that the 959 cm^{-1} MATI band has the mode character identical to that of the B -band, while the 937 cm^{-1} band in MATI should be correlated to the A -band in terms of its vibrational mode character. Assignments for those peaks in D_0 and S_1 states are not unambiguous at this time. However, the plausible assignment can be made based on the experimental fact that the 959 cm^{-1} and its combination bands are observed in MATI spectra taken via $6a$ and 1 (*vide supra*), which suggests that the 959 cm^{-1} mode may belong to one of in-plane ring skeletal modes. From the comparison with *ab initio* values, the most probable mode responsible to 959 cm^{-1} is 12^+ . This means that the 937 cm^{-1} mode is due to I^{+2} mode of $2AP-NH_2^+$. And also, it suggests that the A -band may be due to I^2 mode, while the B -band can be ascribed to 12 mode in the S_1 state. The A -band is certainly broader than the B -band, which might imply the existence of strong couplings to dark states in the S_1 state. Therefore, intensity borrowing of the 12 mode from Franck-Condon active I^2 mode might be also possible. High resolution spectroscopic works though would be desirable for further refinement of assignments.

According to the above assignment, many ionic vibrational bands in the MATI spectrum via 911 cm^{-1} are assigned, as listed in Table II. The 992 and 1339 cm^{-1} bands are due to $18a^+$ and 13^+ modes, respectively. The $6a^+$ + 1^+ mode is observed quite strongly at 1377 cm^{-1} . The 1538 , 1773 , 1895 cm^{-1} bands are ascribed to combination bands of the I^{+2} mode with $6b^+$, 1^+ , and 12^+ modes, respectively. Meanwhile, it is found that the 1561 and 1797 cm^{-1} bands are due to combination modes of 12^+ with $6b^+$ and 1^+ modes, respectively. The first overtone of the 12^+ mode is also observed at 1920 cm^{-1} in the MATI spectrum in Fig. 5.

C. $2AP-ND_2^+$ (D_0)

The R2PI (S_1-S_0) spectrum of $2AP-ND_2$ is shown in Fig. 7. The origin band is found to be located at $33\,465\text{ cm}^{-1}$. Relatively strong bands due to in-plane ring-skeletal modes of $6a$, 1 , and $18b$ modes are observed at 513 , 813 , and 1023 cm^{-1} , respectively. These vibrational frequencies are only slightly redshifted compared to those of $2AP-NH_2$, indicating that corresponding ring modes are hardly associated with the amino group motion. The 975 cm^{-1} band is also strongly observed and this is assigned to be due to the $18a$ (S_1) mode. The $10b^2$ mode of the S_1 state is found at 235 cm^{-1} . The most dramatic spectral change upon the NH_2/ND_2 substitution is found for the I^2 mode. The 911 cm^{-1} band that was strongly observed in the $2AP-NH_2$ spectrum completely disappeared in the $2AP-ND_2$ spectrum. In-

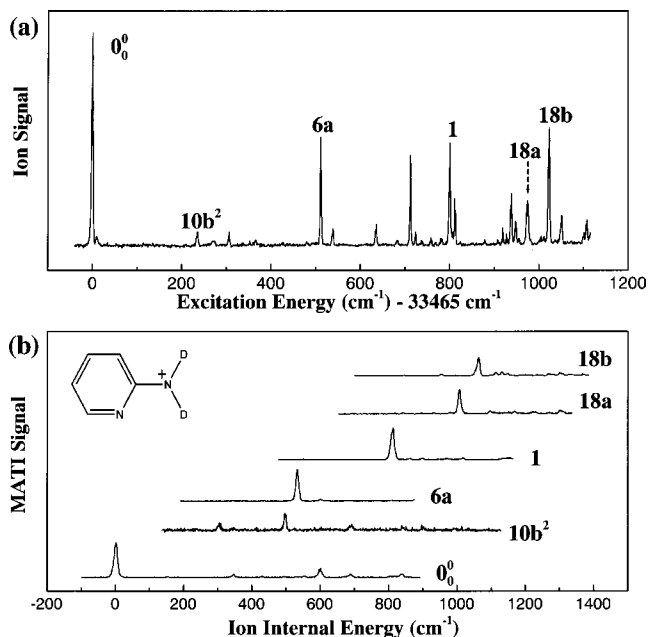


FIG. 7. (a) The S_1-S_0 excitation spectrum of $2AP-ND_2$. (b) MATI spectra taken via the S_1-S_0 origin, $10b^2$, $6a$, 1 , $18a$, and $18b$ S_1 -state modes of $2AP-ND_2$.

stead, two new bands located at 636 and 713 cm^{-1} appear relatively strong in the S_1 state spectrum, as shown in Fig. 7. One expects the large H/D isotopic shift for the inversion mode. Thus, it is most likely that one or both of these two bands should be responsible for the I^2 mode in the S_1 state. MATI spectra taken via 636 and 713 cm^{-1} S_1 bands show interesting spectral patterns indicating that these two bands are strongly mixed to each other.

1. MATI spectra via the S_1-S_0 origin and $10b^2$ (S_1) bands

The MATI spectrum of $2AP-ND_2$ taken via the S_1-S_0 origin band shows the strongest peak at the second ionization energy of $31\,888\text{ cm}^{-1}$, giving the adiabatic ionization energy of $65\,353 \pm 4\text{ cm}^{-1}$ for $2AP-ND_2$, Fig. 7. Low-frequency peaks are weakly observed at 346 , 600 , and 689 cm^{-1} , which correspond to 15^+ , $6b^+$, and 15^{+2} modes, respectively. Scaled *ab initio* frequencies for 15^+ and $6b^+$ modes of $2AP-ND_2^+$ are 339 and 586 cm^{-1} , respectively, which are quite consistent with the experiment. The MATI spectrum via the $10b^2$ mode shows the relatively strong band at 304 cm^{-1} due to the $10b^{+2}$ mode. Similar to the case of $2AP-NH_2^+$, the other strong band is also observed at 498 cm^{-1} (*vide supra*).

2. MATI spectra via the $6a$, 1 , $18a$, and $18b$ (S_1) bands

Since in-plane ring skeletal modes are not so sensitive to the NH_2/ND_2 isotopic substitution, MATI spectroscopic works on $2AP-ND_2^+$ are concentrated on identifying its fundamental vibrational bands rather than exploring many weakly-observed combination bands. In Fig. 7, MATI spectra taken via $6a$, 1 , $18a$, and $18b$ (S_1) bands are shown all together. As being expected, strongest peaks in MATI represent corresponding ionic vibrational modes. Accordingly, the

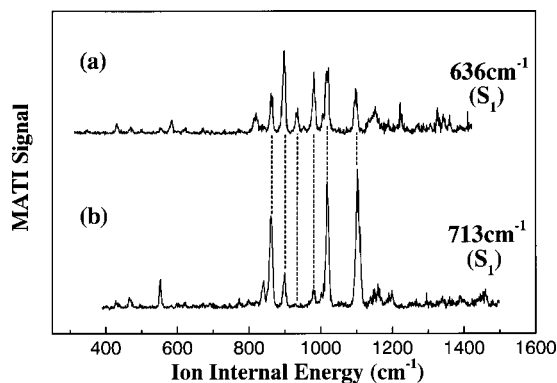


FIG. 8. MATI spectra taken via (a) 636 and (b) 713 cm^{-1} S_1 -state bands of 2AP-ND₂.

$6a^+$ mode is responsible for the strongly observed 533 cm^{-1} in the MATI spectrum taken via the $6a$ (S_1) band. Similarly, the 813, 1007, and 1067 cm^{-1} bands are found to be most strong in MATI spectra via 1, 18a, and 18b modes in the S_1 state, respectively, indicating that those bands are due to fundamentals of 1^+ , $18a^+$, and $18b^+$ modes of 2AP-ND₂⁺, Table I. The ND₂/NH₂ isotopic substitution effect for these in-plane ring modes is predicted by *ab initio* calculation to give approximately $\sim 97/100$ ratios for vibrational frequencies of 2AP-ND₂⁺ with respect to those of 2AP-NH₂⁺, Table I. This prediction is quite consistent with our experimental observations.

3. MATI spectra via the 636 and 713 cm^{-1} (S_1) bands

It is not unambiguous to assign not only the 636 and 713 cm^{-1} bands in the S_1 state but also many MATI bands associated with those bands. However, there are some interesting spectral features (Fig. 8) that can give some clues for band assignments. First, all of MATI peak positions associated with 636 cm^{-1} (S_1) are identical to those associated with 713 cm^{-1} (S_1). Second, however, intensity patterns of MATI peaks in the 636 cm^{-1} MATI spectrum are quite different from those in the 713 cm^{-1} MATI spectrum. That is, strong peaks in the MATI spectrum via 636 cm^{-1} are relatively weak in the MATI spectrum taken via 713 cm^{-1} , and vice versa. Third, most of strongly observed MATI peaks are quite blueshifted from the S_1 vibrational frequencies. The experimental fact that peaks positions are same in both MATI spectra in Fig. 8 suggests that the 636 and 713 cm^{-1} bands in the S_1 state may originate from the same mode. However, distinct intensity patterns in two different MATI spectra indicate that the 636 and 713 cm^{-1} bands may have characteristics of mixed modes. For instance, if j th and k th modes are mixed to give $a\Psi_j + b\Psi_k$ or $a\Psi_j - b\Psi_k$ states, corresponding Franck-Condon factors associated with upper states would result in interference spectral intensity patterns because of the quantum mechanical effect. That is, some MATI peaks via the $a\Psi_j + b\Psi_k$ intermediate state may be relatively strong where those via the $a\Psi_j - b\Psi_k$ state are weak, and vice versa. Though this is the simplest version of the plausible scenario, it explains the interference patterns of intensities observed in this work.

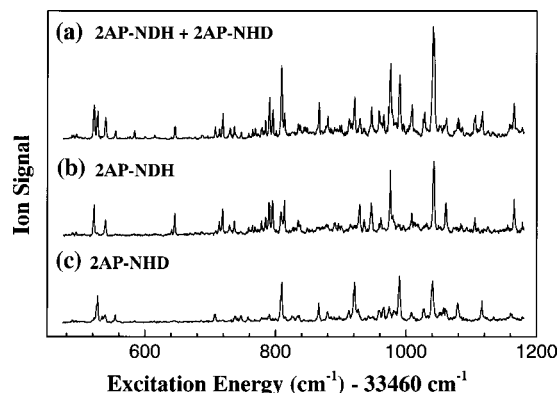


FIG. 9. (a) The R2PI spectrum of the mixture of 2AP-NHD and 2AP-NDH. Hole-burning spectra corresponding to S_1 - S_0 excitation spectra of (b) 2AP-NDH and (c) 2AP-NHD.

The most probable mode to be coupled with inversion mode is the ND₂ torsional mode. Both inversion and torsional modes are out-of-plane modes, and they are expected to be strongly coupled to each other especially since both modes are mainly associated with the amino group moiety motion.³⁰ According to *ab initio* calculation as above, the C(2)-ND₂ bond in the ionic state is expected to be shortened compared to that in the S_1 state, giving the higher potential barrier for ND₂ torsion in the ionic state compared to that in the S_1 state. Therefore, the torsional vibrational frequency is expected to be blueshifted in the ionic state compared to that in the S_1 state, which is consistent with the experimental observation. The strongest MATI peaks are observed at ionic vibrational energies of 897 and 981 cm^{-1} in the MATI spectrum taken via the 636 cm^{-1} (S_1) band, indicating that vibrational frequencies associated with the most similar modes to that of the 636 cm^{-1} band are quite blueshifted upon ionization. Similarly, the peaks at 861, 1019, and 1105 cm^{-1} are strongly observed in the MATI spectrum via the 713 cm^{-1} (S_1) band. Assignments for MATI peaks associated with 636 and 713 cm^{-1} bands are not quite certain at this time. However, it is most likely that those bands are associated with the mixed character of inversion and amino-group torsion modes. Theoretical calculation of the potential energy surfaces along these modes would be desirable to understand these interesting spectral features.

D. 2AP-NHD⁺ and 2AP-NDH⁺ (D_0)

The S_1 - S_0 excitation spectrum of the 2AP-NHD and 2AP-NDH mixture is shown in Fig. 9(a). Since masses of two isomers are identical, it is nontrivial to separate them out spectroscopically. Thus the hole-burning spectroscopic technique is employed to identify vibrational bands belonging to each isomer. Two distinct S_1 - S_0 origins located at 33474 and 33460 cm^{-1} are assigned to those of 2AP-NHD and 2AP-NDH, respectively. Though it seems to be nontrivial to determine which origins are exactly responsible for which isomers, there are several evidences that will be discussed later for the above assignment. It should be emphasized again that we refer to 2AP-NHD or 2AP-NDH as the isomer of which H or D is hydrogen-bonded to the N(1) atom of

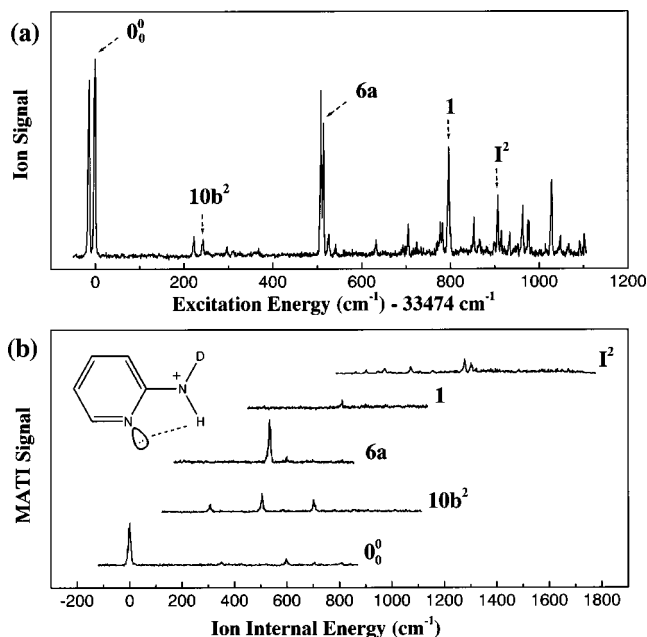


FIG. 10. (a) The R2PI spectrum of the 2AP-NHD and 2AP-NHD mixture, (b) MATI spectra of 2AP-NHD taken via the origin, 10b², 6a, 1, and I² (S₁) modes as intermediate states.

the pyridine ring, respectively. The pump laser fixed either at 33 474 or 33 460 cm⁻¹ depopulates 2AP-NHD or 2AP-NDH, respectively, to give hole-burning spectra representing S₁ vibrational spectra of 2AP-NDH or 2AP-NHD in Figs. 9(b) or 9(c), respectively. Vibrational energies associated with ring-skeletal modes are almost the same for two isomers. The 10b² modes of the S₁ state are found at 243 and 237 cm⁻¹ for 2AP-NHD and 2AP-NDH, respectively. Interesting spectral features are found for bands due to inversion modes of two isomers. Similar to the case of 2AP-NH₂, the 921 cm⁻¹ band which is responsible for the inversion mode is found in the 2AP-NHD spectrum. Meanwhile, in the spectrum of 2AP-NDH, two bands associated with the inversion mode are found at 646 and 719 cm⁻¹, as similarly observed in the spectrum of 2AP-ND₂. These observations are quite consistent with the normal mode calculation for the inversion mode (*vide supra*). That is, since the inversion mode mainly involves the motion of H(D) which is hydrogen-bonded to N(1) of pyridine ring, corresponding inversion vibrational frequencies of 2AP-NHD and 2AP-NDH are almost identical to those of 2AP-NH₂ and 2AP-ND₂, respectively. This is one of the main reasons why the 33 474 or 33 460 cm⁻¹ bands are assigned to origins of 2AP-NHD or 2AP-NDH, respectively.

1. MATI spectra via the S₁-S₀ origin and 10b² (S₁) bands

MATI spectra of 2AP-NHD and 2AP-NDH taken via the S₁-S₀ origin bands show the strongest peaks at the second ionization energies of 31 911 and 31 910 cm⁻¹, respectively, giving adiabatic ionization energies of 65 385±4 and 65 370±4 cm⁻¹ for 2AP-NHD and 2AP-NDH, respectively, Figs. 10 and 11. This difference of ionization energies can be explained by the difference of zero-point vibrational

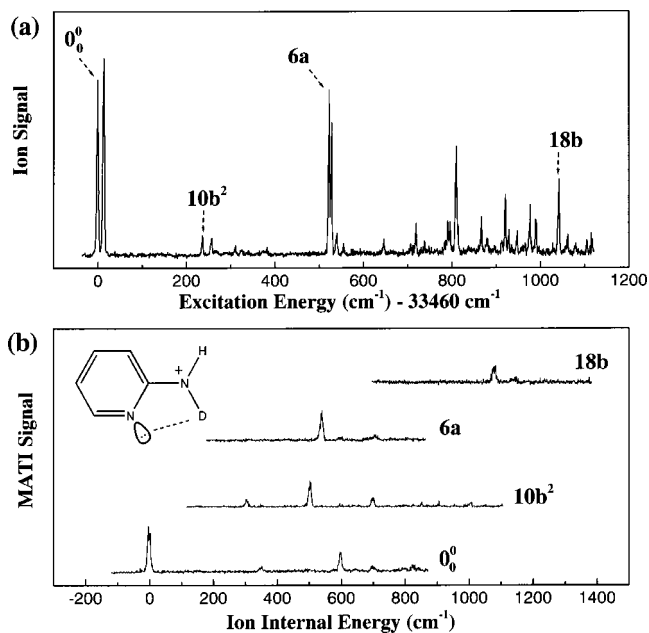


FIG. 11. (a) The R2PI spectrum of the 2AP-NHD and 2AP-NDH mixture, (b) MATI spectra of 2AP-NDH taken via the origin, 10b², 6a, 18b (S₁) modes as intermediate states.

energies of two isomers. Interestingly, the zero-point energy difference of two isomers in their cationic states is calculated to be ≤1 cm⁻¹, while that in the ground states of 2AP-NHD and 2AP-NDH is calculated to be 11 cm⁻¹.²⁴ The zero-point energy of 2AP-NHD is calculated to be less than that of 2AP-NDH, giving the higher ionization energy for 2AP-NHD. This is also consistent with the above isomeric assignment. Low-frequency MATI peaks are weakly observed at 352 (351), 598 (598), and 705 (702) cm⁻¹, corresponding to 15⁺, 6b⁺, and 15⁺ modes, respectively, of 2AP-NHD⁺ (2AP-NDH⁺). Scaled *ab initio* frequencies for 15⁺ and 6b⁺ modes of 2AP-NHD⁺ (2AP-NDH⁺) are 358 (358) and 587 (588) cm⁻¹, which are quite consistent with the experiment. In MATI spectra via 10b² modes, the relatively strong band is observed at 308 (304) cm⁻¹ due to the 10b⁺ mode of 2AP-NHD (2AP-NDH). Experimentally determined fundamental frequencies are compared with the *ab initio* calculation in Table I.

2. MATI spectra via the 6a, 1, and 18b (S₁) bands

In Fig. 10, MATI spectra taken via 6a and 1 (S₁) bands of 2AP-NHD are shown all together. The MATI band is strongly observed at the ionic vibrational energy of 534 cm⁻¹, which is ascribed to the 6a⁺ mode in the MATI spectrum via the 6a (S₁) band at 514 cm⁻¹. The 6b⁺ mode is also observed at 598 cm⁻¹ in the same spectrum. The 810 cm⁻¹ band is found to be most strong in the MATI spectrum taken via the 1 mode in the S₁ state, and ascribed to the fundamental of 1⁺ mode. Similarly, in Fig. 11, the 6a⁺ and 6b⁺ modes of 2AP-NDH⁺ are observed at 539 and 598 cm⁻¹, respectively, in the MATI spectrum taken via the 6a (S₁) mode at 523 cm⁻¹. The 18b⁺ mode of 2AP-NDH⁺ is found to have the vibrational energy of 1079 cm⁻¹ in the MATI spectrum taken via the 1041 cm⁻¹ S₁ band.

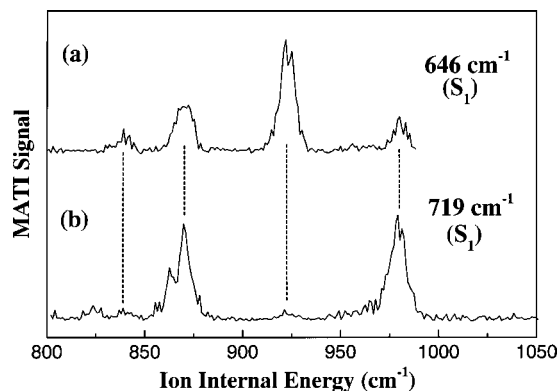


FIG. 12. MATI spectra of 2AP-NDH taken via the (a) 646 and (b) 719 cm^{-1} (S_1) bands.

3. MATI spectra via the 921 cm^{-1} (S_1) band for 2AP-NHD and those via the 646 and 719 cm^{-1} (S_1) bands for 2AP-NDH

The MATI spectrum taken by the 921 cm^{-1} band in the S_1 - S_0 spectrum of 2AP-NHD gives several bands, one of which may correspond to the inversion mode of 2AP-NHD⁺, Fig. 10. No doubletlike feature, which has been observed in the MATI spectrum of 2AP-NH₂ for the inversion mode, is observed in the MATI spectrum of 2AP-NHD. This indicates that the 921 cm^{-1} band of 2AP-NHD (S_1) is not associated with more than one vibrational mode, verifying again that the doubletlike feature observed in the 2AP-NH₂ MATI spectrum is not due to splitting caused by an inversion barrier (*vide supra*). It is not unambiguous at this time though to assign the inversion mode of 2AP-NHD⁺ just from the MATI spectrum in Fig. 10. That is, even though it is most plausible for the 1071 cm^{-1} band to be due to the I⁺2 mode, the strongest MATI peak is observed at the vibrational energy of 1277 cm^{-1} . The more detailed spectroscopic work would be desirable for the more reliable inversion mode assignment.

Similar to the case of 2AP-ND₂, MATI peaks associated with 646 and 719 cm^{-1} bands of 2AP-NDH are identical in terms of their spectral positions while showing interference patterns in their intensities. However, it is quite noteworthy that MATI spectral patterns of 2AP-NDH⁺ are so different from those of 2AP-ND₂⁺, even though the S_1 state vibrational spectra of those molecules are almost identical. Compared to the 2AP-ND₂⁺ spectra, MATI spectra via 646 and 719 cm^{-1} (S_1) bands of 2AP-NDH are found to be much simpler. The strongest peak is observed at the vibrational energy of 924 cm^{-1} in the MATI spectrum via the 646 cm^{-1} (S_1) band, while MATI peaks at 870 and 980 cm^{-1} show relatively weak intensities, as shown in Fig. 12. On the other hand, in the MATI spectrum taken via the 719 cm^{-1} (S_1) band, MATI peaks are most strongly found at 870 and 980 cm^{-1} . Meanwhile, the 924 cm^{-1} MATI band is only weakly observed in the 719 cm^{-1} (S_1) MATI spectrum. Since the inversion mode of 2AP-NDH is mainly associated in the out-of-plane motion of the amino D atom, the inversion frequency of 2AP-NDH⁺ is not expected to be largely shifted from that of 2AP-ND₂⁺. Therefore, the main reason why MATI spectra of 2AP-NDH⁺ and 2AP-ND₂⁺ are so differ-

ent to each other would be due to the frequency difference of the amino-group torsional modes of two ions, which are coupled to their own inversion modes. Actually, it is true that the amino-group torsional frequency of 2AP-NDH⁺ should be blueshifted from that of 2AP-ND₂⁺. Detailed and more reliable assignments for MATI peaks associated with 646 and 719 cm^{-1} bands of 2AP-NDH⁺ should wait accurate theoretical calculation of the multidimensional potential energy surfaces along inversion and torsional motion of the amino group moiety of the title molecule.

IV. SUMMARY AND CONCLUSIONS

In this work, the R2PI and MATI spectra of jet-cooled 2-aminopyridines (2AP-NH₂, 2AP-ND₂, 2AP-NHD, and 2AP-NDH) are reported. The S_1 - S_0 excitation spectra provide accurate S_1 state vibrational frequencies of these molecules for optically active modes including ring-skeletal and amino-group inversion modes. Two structural isomers, 2AP-NHD and 2AP-NDH, are spectrally well separated in their S_1 states using the hole-burning spectroscopy, giving accurate excited state vibrational frequencies belonging to each isomer. Ionization energies, from MATI spectra, are precisely determined to be 8.1086, 8.1027, 8.1067, and 8.1048 eV for 2AP-NH₂, 2AP-ND₂, 2AP-NHD, and 2AP-NDH, respectively. Many ionic vibrational bands of those compounds are investigated by MATI spectra taken via various vibrational modes in S_1 states. Mode assignments are appropriately done by the comparison of the experiment with the *ab initio* calculation. The amino-group inversion mode in the S_1 state is found to be responsible for the 911 or 921 cm^{-1} band for 2AP-NH₂ or 2AP-NHD, respectively. Meanwhile, it is found to be split into two bands at 636 (646) and 713 (719) cm^{-1} for 2AP-ND₂ (2AP-NDH). Interferencelike intensity patterns between MATI spectra taken via those two split bands are observed for both 2AP-ND₂ and 2AP-NDH, suggesting that the inversion mode is strongly coupled with the other mode, which is most probably the amino-group torsional mode. Accurate theoretical calculation of potential energy surfaces along inversion and torsional modes of the amino-group moiety would be necessary for the better understanding of mode couplings and associated intriguing MATI spectra. Mode-resolved spectra for the 911 cm^{-1} band of 2AP-NH₂ (S_1) are obtained by monitoring MATI signals as a function of the S_1 - S_0 excitation energy while the D_0 - S_1 second ionization energy is fixed. This new excitation scheme would be quite valuable for resolving the spectrum into different modes without using high-resolution lasers. Many biological molecules form inter- or intramolecular hydrogen bonds and undergo charge transfers. In such senses 2-aminopyridines could be important model compounds for studying structures and functions of biological systems. Understanding vibrational motions of these molecules in excited and cationic states, therefore, would eventually contribute to thorough understanding of biological systems in detail.

Note added in proof. After submission of this paper, it was noticed that the MATI spectrum for one of the four molecules studied in this work was independently reported

very recently.³¹ Energetics are consistent with those in this work.

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