Resonantly-enhanced Two-photon Ionization and Mass-Analyzed Threshold Ionization (MATI) Spectroscopy of 2-Hydroxypyridine

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Mass-analyzed threshold ionization (MATI) spectra of 2-hydroxypyridines existing as lactims (2-pyridinol) in a molecular beam are obtained *via* (1+1′) two-photon process to give accurate ionization energies of 8.9344 ± 0.0005 and 8.9284 ± 0.0005 eV for 2-pyridinol (2Py-OH) and its deuterated analogue (2Py-OD), respectively. Resonantly-enhanced two-photon ionization spectra of these compounds are also presented to give vibrational structures of their S_1 states. Vibrational frequencies of 2Py-OH and 2Py-OD in ionic ground states are accurately determined from MATI spectra taken *via* various S_1 intermediate states, and associated vibrational modes are assigned with the aid of *ab initio* calculations.

Keywords : 2-Hydroxypyridine, Mass-analyzed, Threshold, Ionization, Spectroscopy.

Introduction

Conventional photoelectron spectroscopy (PES) does not provide the spectral resolution high enough for the determination of rovibrational structures of ions, mainly due to the limitation of resolving power of electron kinetic energy analyzer. For those purposes, zero electron kinetic energy (ZEKE) or mass-analyzed threshold ionization (MATI) spectroscopy has been proven to be extremely useful.[1] Since ZEKE or MATI is usually carried out for supersonically cooled molecules in the beam, it is like carrying out conventional vibrational spectroscopy of ions with almost zero internal energies. Especially when certain vibrationl modes in the S_1 state are used as intermediate states for ionization, vibrational frequencies of ions associated with corresponding modes can be very precisely determined since the Franck-Condon overlap integral is usually maximized when $\Delta \upsilon = 0$.[1,2] For recent decades, ZEKE or MATI spectroscopy has been extensively carried out to provide highly-resolved rovibrational spectra of ionic ground states for a number of organic molecules.[1,2] Those spectral features are essential in investigating nuclear or electrical change upon ionizations of molecules, and eventually understading the role of electrons in forming chemical bonds.

The 2-Hydroxypyridine molecule may undergo intramolecular hydrogen atom transfer, thus it may exist as two forms, lactim (2-pyridinol) or lactam (2-pyridone) forms.[3-6] Because of interesting tautomerism of this molecule and the similarity of its hydrogen bonding to many biological compounds, numerous spectroscopic studies have been carried out for S_0 and S_1 states of both tautomers.[7-11] Thus spectral characteristics of two tautomeric forms of 2-hydroxypyridine are quite well known. For the ionic state, the Kimura group[12] has reported ZEKE spectra of 2-hydroxypyridine to give ionization energies of lactam and lactim. According to them,

the ZEKE spectrum of lactim does not show any vibrational bands other than the spectral origin. However, it is found in this work that many ring-skeletal vibrational modes are optically active in MATI spectra of lactim, providing not only the more accurately refined ionization energy but also many vibrational frequencies of 2-hydroxypyridine existing as a form of lactim.

Experimental Section

2-Hydroxypyridine (Py-OH) was purchased from Aldrich and used without further purification. For the preparation of Py-OD, 2-hydroxypyridine was mixed with CH_3OD for several times before the solvent was evaporated completely. The sample was heated to 80 °C, mixed with argon, and expanded into vacuum through a nozzle orifice (General Valve, $\phi = 0.8$ mm) with a typical backing pressure of ~2 atmosphere and a repetition rate of 10 Hz. The supersonically cooled molecular beam was then skimmed through a skimmer (~1 mm diameter). Background pressures of source and ionization chambers were maintained at ~10^{-5} and 10^{-7} Torr, respectively, when the nozzle was on. Two separately tunable laser outputs in the 260-280 nm range were generated by frequency-doubling of laser outputs from two different dye lasers (Lambda-Physik Scanmate2 & Lumonics HD-500) pumped by 355 nm outputs of two Nd:YAG lasers (Spectra-Physics GCR-150 & Continuum). Two final laser pulses (1-2 mJ/pulse, 6 ns duration) were both spatially and timely overlapped and crossed the molecular beam in a counter-propagation manner.

Given by two laser pulses, molecules were excited to ZEKE states, allowed to stay for a few μs in the spoil filed of ~2 V/cm which was originally given to remove directly-formed ions from the probing zone, and ionized by the pulsed electric field of ~120 V/cm. Pulsed-field ionized ions flew in the field-free region, detected by dual micro-channel plates (MCP, Jordan), digitized by an oscilloscope, and stored in a personal computer which also controls two dye

lasers and home-made auto-trackers for frequency doubling crystals. For resonantly-enhanced two-photon ionization (R2PI) spectra, ionization occurred in the presence of extracting electric field, and thus a directly-formed ion signal is monitored as a function of the excitation energy. Absolute frequencies of dye laser outputs were calibrated to the accuracy of ± 0.5 cm^{-1} using the optogalvanic effect in a hollow-cathode lamp (Ne gas).

Results and Discussion

As mentioned earlier, 2-hydroxypyridine may exist as two forms, the lactim (2-pyridinol) or lactam (2-pyridone), in the molecular beam. Spectral origins of those isomers are quite distinct and it has been reported that interconversion between lactim and lactam is not allowed in the energy range employed in this work.[12] Therefore, spectroscopic information here is exclusively about 2-hydroxypyridine existing as a form of lactim. R2PI and MATI spectra of 2-pyridinol (2Py-OH) and its deuterated analogue (2Py-OD) are reported. It should be noted that spectral bandwidths of MATI bands are relatively broad mainly due to pulsed-field ionization,[1] and peak positions in MATI spectra reported in this work have uncertainties of ± 4 cm^{-1}.

A. 2-Pyridinol (2PY-OH). R2PI spectrum of 2Py-OH provides an accurate value for the origin of the S_1-S_0 transition and absolute frequencies associated with vibrational modes of the molecule in the S_1 state, Figure 1. The spectral origin is found to be 36119 cm^{-1}, which is ~16 cm^{-1} lower than the previously reported value of 36135 cm^{-1}.[12] Rotational contour analysis for the origin band indicates that the S_1-S_0 transition is AB-hybrid type, suggesting that the transition dipole moment is parallel to the molecular plane. The S_1 vibrational frequencies are listed in Table 1 with partial assignments using the benzene-type Wilson numbering system.[13] Vector models of nuclear motions for some of in-plane normal modes of 2Py-OH are represented in Figure 2. The **6a**, **6b**, **1**, and **12** modes, which are all in-plane
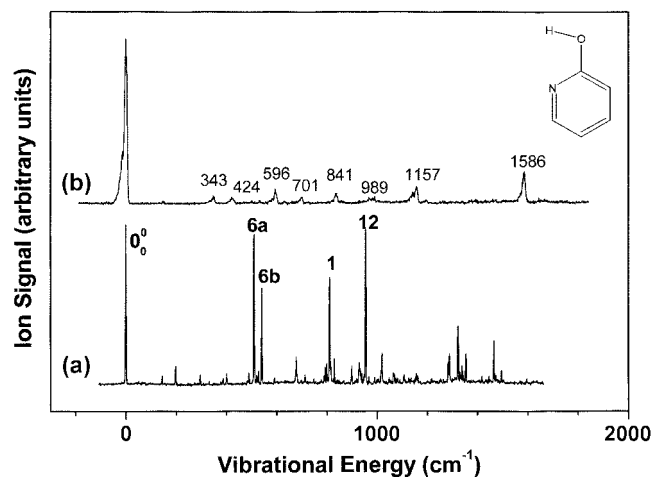

Figure 1. (a) R2PI spectrum of 2Py-OH and (b) MATI spectrum taken via the 0-0 band.

Table 1. Vibrational frequencies (cm^{-1}) and assignment of 2Py-OH and 2Py-OD ions

2Py-OH			2Py-OD			Assignment
S_1	D_0	Cal.^{a}	S_1	D_0	Cal.^{a}	
0 (+36119)	0 (+35941)		0 (+36124)	0 (+35888)		origin
	343			341		
	424	424		392	399	**15$^+$**
	596	608		594	606	**6b$^+$**
	701			693		
	841	849		815	848	**1$^+$**
				921		
	1157	1173		1105	1127	**18b$^+$**
	1586	1615		1575	1610	**9a$^+$**
511	534	547	499	524	537	**6a$^+$**
	596	608		594	606	**6b$^+$**
	1370					
				1477	1458	**921+6a$^+$**
	1691	1720		1624	1664	**6a$^+$+18b$^+$**
	2113	2163		2098	2147	**6a$^+$+9a$^+$**
541	596	608	541	594	606	**6b$^+$**
	1196	1216		1187	1212	**6b$^+$(v$^+$=2)**
				1513	1527	**921+6b$^+$**
	1754	1781				**6b$^+$+18b$^+$**
	2111					
	2177	2223		2170	2216	**6b$^+$+9a$^+$**
810	841	855				**1$^+$**
	1154					
	1669	1710				**1$^+$(v$^+$=2)**
	1991	2028				**1$^+$+18b$^+$**
	2417	2470				**1$^+$+9a$^+$**
954	989	985				**12$^+$**
	1082					
	2139	2158				**12$^+$+18b$^+$**
	2560	2600				**12$^+$+9a$^+$**
	2654					

^{a}Calculated frequencies for the combination bands are without consideration of anharmonicities.

modes, are found to be optically active at 511, 541, 810, and 954 cm^{-1}, respectively. The MATI spectrum, obtained by scanning the ionizing laser wavelength while the first excitation energy is fixed at the S_1-S_0 origin band, shows the strongest signal at the D_0-S_1 origin band at 35941 $\pm$ 4 cm^{-1}, giving the ionization energy of 72060 $\pm$ 4 cm^{-1} (8.9344 $\pm$ 0.0005 eV), Figure 1. This ionization energy is ~33 cm^{-1} lower than the previously reported value.[12] The experimental observation that the **0-0$^+$** band is most intense in the MATI spectrum indicates that the molecular geometry changes little upon ionization from the S_1 state. The pulsed-field ionization makes it difficult to determine the more precise value for the ionization threshold energy.[1] Other than the origin band, many different bands associated with ionic vibrational modes are also observed, and their frequencies corresponding to shifts from the MATI origin are listed in Table 1. It is interesting to note that the **6b$^+$** band found at
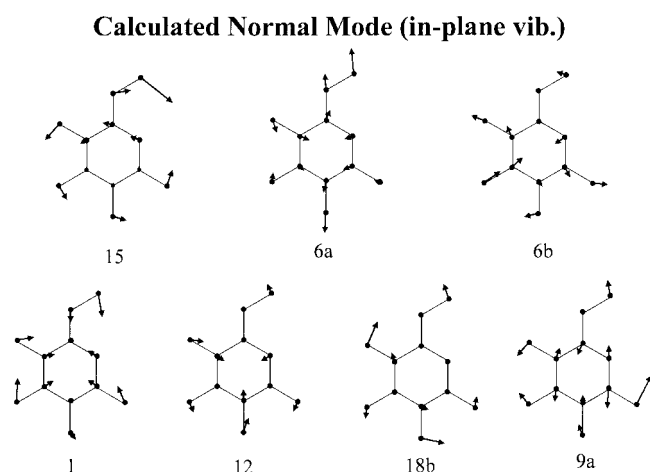
Calculated Normal Mode (in-plane vib.)

Figure 2. Vector description of several in-plane normal modes of the 2Py-OH ion classified according to the benzene-type Wilson numbering system.

596 cm^{-1} is relatively strong, while the **6a**$^+$ band is absent. The **1**$^+$ and **12**$^+$ bands are observed at 841 and 989 cm^{-1}, respectively. These assignments are firmly established in MATI spectra taken *via* S$_1$ intermediate states associated with those vibrational modes (*vide infra*). *Ab initio* calculation (DFT) using the UB3LYP level with a 6-31G+(d) basis set[14] has been carried out for ions, and calculated vibrational frequencies are compared with the experimental values, Table 1. *Ab initio* vibrational frequencies are 608, 855, and 985 cm^{-1} for **6b**$^+$, **1**$^+$, and **12**$^+$ modes, respectively, which are in good agreement with the experiment. The bands observed at 1157 and 1568 cm^{-1} are tentatively assigned to **18b**$^+$ and **9a**$^+$ modes, respectively. A relatively weak band at 424 cm^{-1} is most likely to the **15**$^+$ mode, as predicted by *ab initio* calculation.

MATI spectra taken *via* the **6a** and **6b** bands of S$_1$ state as intermediate states are shown in Figure 3. The most intense peaks are found at 534 and 596 cm^{-1} above the adiabatic
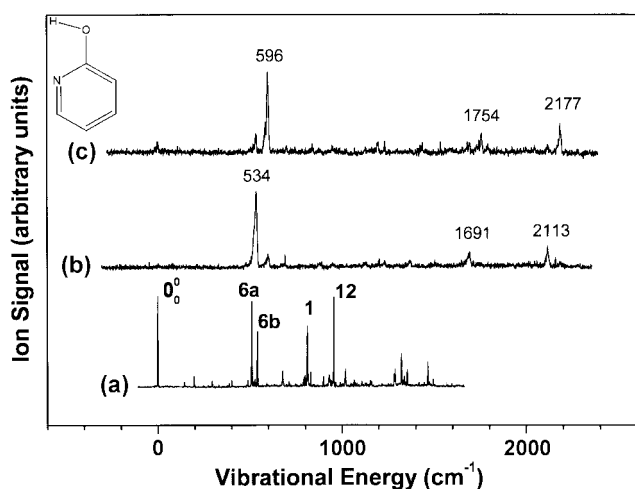

Figure 3. (a) R2PI spectrum of 2Py-OH, (b) MATI spectrum taken *via* the **6a** band, and (c) MATI spectrum taken *via* the **6b** band of the S$_1$ state of 2Py-OH.
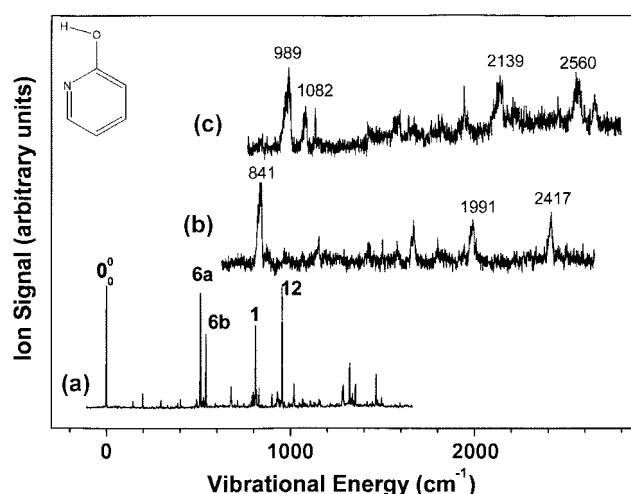

Figure 4. (a) R2PI spectrum of 2Py-OH, (b) the MATI spectrum taken *via* the **1** band, and (c) MATI spectrum taken *via* the **12** band of the S$_1$ state of 2Py-OH.

ionization energy in MATI spectra taken *via* **6a** and **6b** bands, respectively, indicating that the 534 and 596 cm^{-1} bands are associated with **6a**$^+$ and **6b**$^+$ modes of the 2Py-OH ion, respectively. It is interesting to note that most other weakly observed bands in the MATI spectrum *via* **6b** are ~62 cm^{-1} blue-shifted compared to those in the MATI spectrum taken *via* the **6a** band. This indicates that those bands in MATI *via* **6a** (or **6b**) are combined with **6a**$^+$ (or **6b**$^+$). Accordingly, the 1691 and 2113 cm^{-1} bands in MATI *via* **6a** are assigned to be **6a**$^+$ + **18b**$^+$ and **6a**$^+$ + **9a**$^+$ modes, respectively. Meanwhile, the bands at 1754 and 2177 cm^{-1} observed in MATI *via* **6b** are ascribed to **6b**$^+$ + **18b**$^+$ and **6b**$^+$ + **9a**$^+$ modes, respectively. MATI spectra were also taken *via* **1**^{1} and **12**^{1} of the S$_1$ state as intermediate states, Figure 4. Vibrational bands at 841 and 989 cm^{-1}, whose intensities are strongest in MATI *via* **1** and **12**, respectively, are associated with **1**$^+$ and **12**$^+$ modes of 2Py-OH ion, respectively. Other weakly observed bands at 1669, 1991, and 2417 cm^{-1} bands in MATI *via* **1** are most likely due to **1**$^+$(v$^+$=2), **1**$^+$ + **18b**$^+$ and **1**$^+$ + **9a**$^+$ modes, respectively. In MATI *via* **12**, the 2139 and 2560 cm^{-1} bands are ascribed to **12**$^+$ + **18b**$^+$ and **12**$^+$ + **9a**$^+$ modes, respectively.

B. Deuterated 2-Pyridinol (2PY-OD). R2PI and MATI spectra of 2Py-OD are obtained to give an accurate value of 36124 cm^{-1} for the 0-0 band of the S$_1$-S$_0$ transition and the ionization energy of 72012 ± 4 cm^{-1} (8.9284 ± 0.0005 eV), Figure 5. Similar to the case of 2Py-OH, the **6a**, **6b**, **1**, and **12** modes are found to be optically active in the R2PI spectrum, giving corresponding vibrational frequencies of 499, 541, 801, and 952 cm^{-1}, respectively. Shifts from the 0-0$^+$ origin in MATI represent various vibrational bands of the 2Py-OD ion. The **6b**$^+$ band is found at 594 cm^{-1}, whilst assignments for other modes are not quite certain. The **15**$^+$ mode seems to be responsible for the 392 cm^{-1} band, which shows a large isotopic shift from 424 in 2Py-OH, as predicted by *ab initio* calculation, Table 1. It is most likely that the 1105 and 1575 cm^{-1} bands are due to **18b**$^+$ and **9a**$^+$
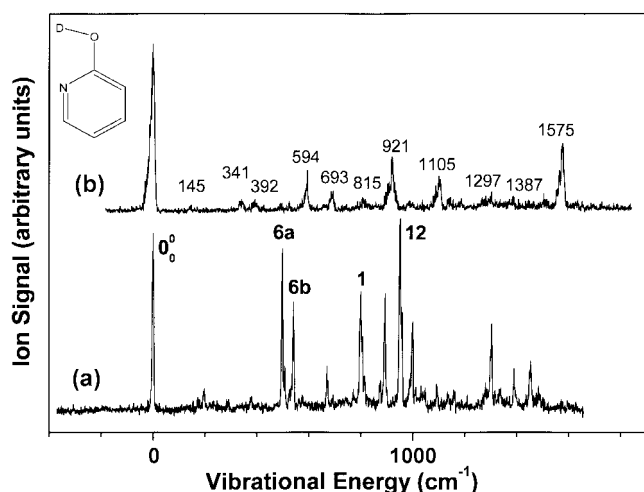
Figure 5. (a) The R2PI spectrum of 2Py-OD and (b) MATI spectrum taken *via* the 0-0 band of 2Py-OD.

modes of 2Py-OD, respectively. These assignments are quite consistent with *ab initio* values of 1127 and 1610 cm^{-1} for those modes. A relatively strong band observed at 921 cm^{-1} in MATI of 2Py-OD, which is absent in MATI spectrum of 2Py-OH, might be associated with a mode involving the out-of-plane motion of D atom, even though further experimental evidence is necessary for confirmation.

MATI spectra of 2Py-OD are also taken *via* the **6a** and **6b** bands of S$_1$ state as intermediate states, Figure 6. The bands located at 524 and 594 cm^{-1} above the adiabatic ionization energy are found to be most intense in MATI spectra taken *via* **6a** and **6b** bands, respectively. Therefore, the 524 and 594 cm^{-1} bands should be due to **6a**$^+$ and **6b**$^+$ modes of the 2Py-OD ion, respectively. The 1447, 1624, and 2098 cm^{-1} bands in MATI *via* **6a** can be ascribed to the **6a**$^+$ + 921, **6a**$^+$

+**18b**$^+$ and **6a**$^+$ + **9a**$^+$ modes, respectively. In MATI spectrum of 2Py-OD *via* **6b** gives bands at 1187, 1513, and 2170 cm^{-1}, which are most likely to be associated with **6b**$^+$(v$^+$=2), **6b**$^+$ + 921, and **6b**$^+$ + **9a**$^+$ modes, respectively.

Overall, most of vibrational frequencies of ion are found to be slightly higher compared to those of the neutral compound in the S$_1$ state, indicating that the removal of a π-electron results in a slight increase of force constants involved in optically active normal modes. According to *ab initio* calculation, the molecular structure of 2Py-OH changes little upon ionization, which can also be predictable from experimental MATI spectra in Figures 1 and 5. However, it is interesting to note that bond lengths of C(2)-O, C(2)-N, C(2)-C(3), C(5)-C(6), and N-C(6) bonds are calculated to be slightly modified upon ionization, and this may be the reason why ring skeletal in-plane normal modes are optically active in MATI spectra.

In summary, the ionization energy of 2-hydroxypyridine existing as a form of lactim in the gas phase is accurately determined to be 72060 ± 4 cm^{-1} (8.9344 ± 0.0005 eV). The ionization energy of its deuterated analogue, 2Py-OD, is 72012 ± 4 cm^{-1} (8.9284 ± 0.0005 eV). Many in-plane normal modes of 2-hydroxypyridine ions are identified in MATI spectra taken *via* various vibrational modes of S$_1$ state as intermediate states. *Ab initio* calculation is found to be quite consistent with the experiment.

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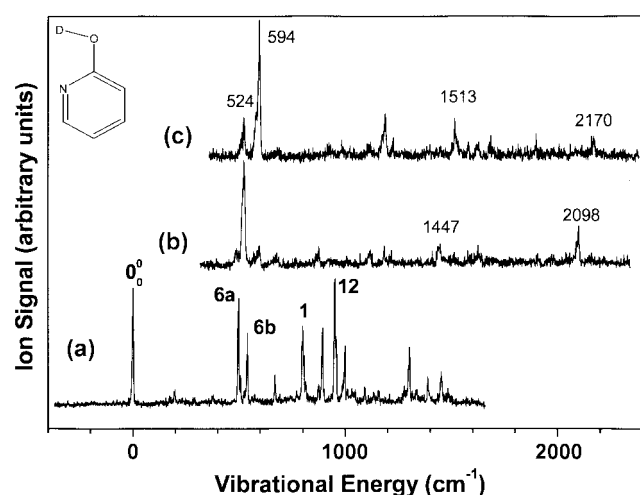

Figure 6. (a) R2PI spectrum of 2Py-OD, (b) the MATI spectrum taken *via* the **6a** band, and (c) MATI spectrum taken *via* the **6b** band of the S$_1$ state of 2Py-OD.