

SCIENTIFIC PAPERS

Multiphoton ionization of pyrrole-water mixed clusters*

HU Yongjun (胡勇军), CAI Yong (蔡永), LÜ Richang (吕日昌)

and WANG Xiuyan (王秀岩)**

State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, Dalian 116023, China

Received October 13, 2000; revised December 11, 2000

Abstract Multiphoton ionization of the hydrogen-bonded pyrrole-water clusters $(C_4H_5N)_n(H_2O)_m$ is studied with a reflectron-time of flight mass spectrometer at 355 nm. With increasing partial concentration of pyrrole in a gas mixture source, a series of poly-pyrrole-water binary-mixed cluster ions can be observed, including unprotonated cluster ions $[(C_4H_5N)_x(H_2O)_y]^+$, protonated cluster ions $[(C_4H_5N)_x(H_2O)_yH]^+$ and dehydrogenated cluster ions $[(C_4H_4N)(C_4H_5N)_x(H_2O)_y]^+$. *Ab initio* calculations of their structures, bond strengths, charge distributions and reaction energies are carried out. Stable structures of these clusters are obtained from the calculations. A probable formation mechanism of the cluster ions $[(C_4H_5N)_x(H_2O)_y]^+$, $[(C_4H_5N)_x(H_2O)_yH]^+$ and $[(C_4H_4N)(C_4H_5N)_x(H_2O)_y]^+$ is supposed to be the ionization of clusters followed by dissociation.

Keywords: multiphoton ionization, time of flight, *ab initio*, pyrrole, proton transfer.

Proton transfer process in hydrogen-bonded clusters has attracted great interest of many chemists in the fields of physical chemistry and biochemistry. It has been found that in the ionization processes of many hydrogen-bonded clusters, such as the binary-mixed clusters $C_4H_5N-H_2O$, $C_4H_5N-NH_3$ and NH_3-CH_3OH , the dominant products were the protonated ions^[1-5]. These protonated cluster ions were supposed to come from an intracuster proton transfer reaction accompanied by dissociation processes^[5-8]. Proton transfer is a fundamental process in life phenomena, and pyrrole is one of the building blocks of some important biomolecules^[9]. The investigation of this kind of cluster systems may provide a relatively simple prototype to help understand the proton transfer process in biochemical systems.

Pyrrole (C_4H_5N) is a compound of five-membered hetero-cyclic aromatic ring, in which a lone pair of electrons offered by the N atom and the two double bonds forms a delocalized big π bond. We have carried out a study on the multiphoton ionization of the clusters $C_4H_5N-(H_2O)_n$ ^[5], and made it clear that the protonated cluster ions are produced via intracuster proton transfer reactions.

In the present work the measurements were performed using a modified apparatus. Because of a new reflectron the resolution of mass spectra was improved by an order of magnitude. It is possible

* Project supported by the National Natural Science Foundation of China (Grant No. 29833080).

** Corresponding author, E-mail: wangxy@ms.dicp.ac.cn

to detect the dissociation processes of the cluster ions in metastable states and investigate the larger size clusters. To produce larger size clusters containing more than one pyrrole molecule, the relative concentration of pyrrole in the beam source was increased. In this paper some new results of the formation mechanism and structures of the clusters will be presented.

1 Experimental and computation

All the experiments were performed on a homemade time of flight (TOF) mass spectrometer which has been described in detail in Ref. [5]. And the incorporation of the reflectron has improved the resolution of the mass spectrometer. The reflectron consists of 30 stainless steel circular plates. The diameter and thickness of these plates are 100 and 2 mm, respectively. There is a hole 30 mm in diameter at the center of each plate. The plates are assembled parallelly and coaxially, at equal intervals of 8mm. The 30 plates are electrically divided into two groups in order to build two electric fields with different intensities. The resistance values of the resistors that are used to connect the plates are equal in each group, but are different between the two groups. The voltage across the 30 plates is 1010V, which builds a two-stage electric field in the reflectron space.

The stagnation pressure of the gas mixture in the beam source was 1.5×10^5 Pa in the present experiments. The output of the Nd:YAG laser was 355 nm, 10 ns pulse width and 13mJ/pulse. The pyrrole (95%, from British Drug Houses Ltd.), water (deionized) and helium (99.999%, from Dalian Chemical Industry Ltd.) were used without further purification.

The computation methods were the same as in our previous paper^[5]. The B3LYP/6-31G* // HF/6-31G* + 0.893 × (ZVPE) (HF/6-31G*) method was used to calculate the energies of all species. All the calculations were performed using a Gaussian-94W program package^[10].

2 Results and discussion

2.1 Mass spectra

The typical mass spectra obtained are shown in Fig. 1. The application of the reflectron has provided the possibility to distinguish the daughter ions after they are produced from dissociation of their parent ions on the way to the detector^[7]. The fact that no daughter ion is observed in the mass spectra implies that the probability of dissociation of the cluster ions during the free flight is minor.

As is clear in Fig. 1(b), two sequences of pyrrole-water cluster ions are produced in the ionization process. They are assigned as the binary-mixed cluster ions $[(C_4H_5N)_x(H_2O)_y]^+$ and $[(C_4H_5N)_x(H_2O)_yH]^+$ ($x \geq 2$), respectively. Compared with the previous results^[5], the yield increase of the cluster ions containing more than one pyrrole molecule is attributed to the increase of the partial concentration of pyrrole in the molecular beam. The mass spectra also show that a sequence of dehydrogenated cluster ions $[(C_4H_4N)_x(H_2O)_y]^+$ is produced in the ionization process, which implies that decomposition of pyrrole in the cluster ions occurs.

2.2 Poly-pyrrole-water clusters

As shown in Fig. 1, the predominant products are the cluster ions of $[(C_4H_5N)-(H_2O)_n]^+$. Meanwhile, a sequence of cluster ions $(C_4H_5N)_n^+$ with the number of pyrrole molecules as many as 5

can be identified. In Fig. 1(b), the sequences of binary cluster ions $[(C_4H_5N)_x(H_2O)_y]^+$ ($x \geq 1$, $y \geq 0$), $[(C_4H_5N)_x(H_2O)_yH]^+$ ($x \geq 2$, $y \geq 0$) and $[(C_4H_4N)(C_4H_5N)_x(H_2O)_y]^+$ ($x \geq 1$, $y \geq 0$) can be observed. Though these poly-pyrrole cluster ions ($x \geq 2$) are observable, their low intensities imply that the poly-pyrrole clusters $(C_4H_5N)_n(H_2O)_m$ are not as stable as $C_4H_5N-(H_2O)_n$. The structures of the clusters $(C_4H_5N)_2$ and $(C_4H_5N)_2(H_2O)$ and their relevant ions obtained from an *ab initio* calculation are shown in Fig. 2.

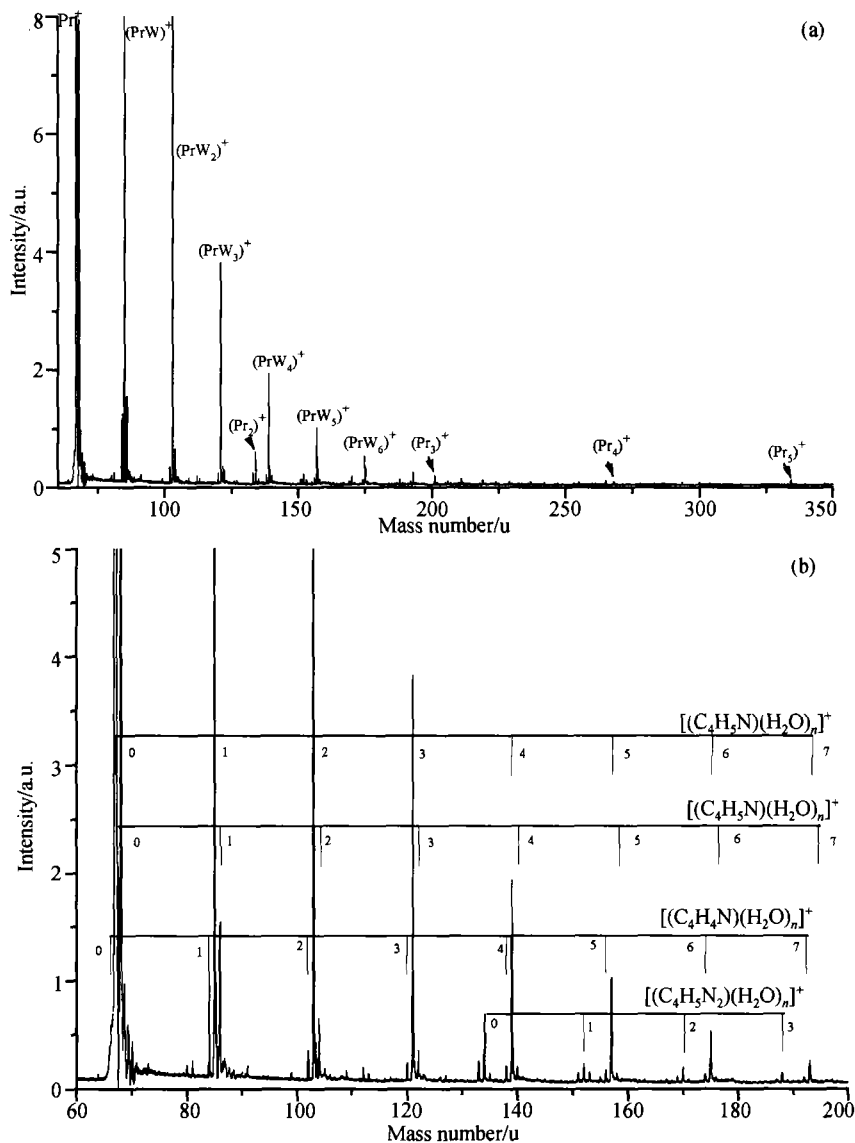


Fig. 1 Mass spectra of pyrrole-water binary clusters obtained at 355nm with a reflectron TOF mass spectrometer (Pr: C_4H_5N ; W: H_2O).

Fig. 2(a) shows the stable structure of the neutral dimer $(C_4H_5N)_2$, in which the two pyrrole molecules are linked with a hydrogen bond $N-H \cdots \pi$. One of the pyrrole molecules donates a hydrogen

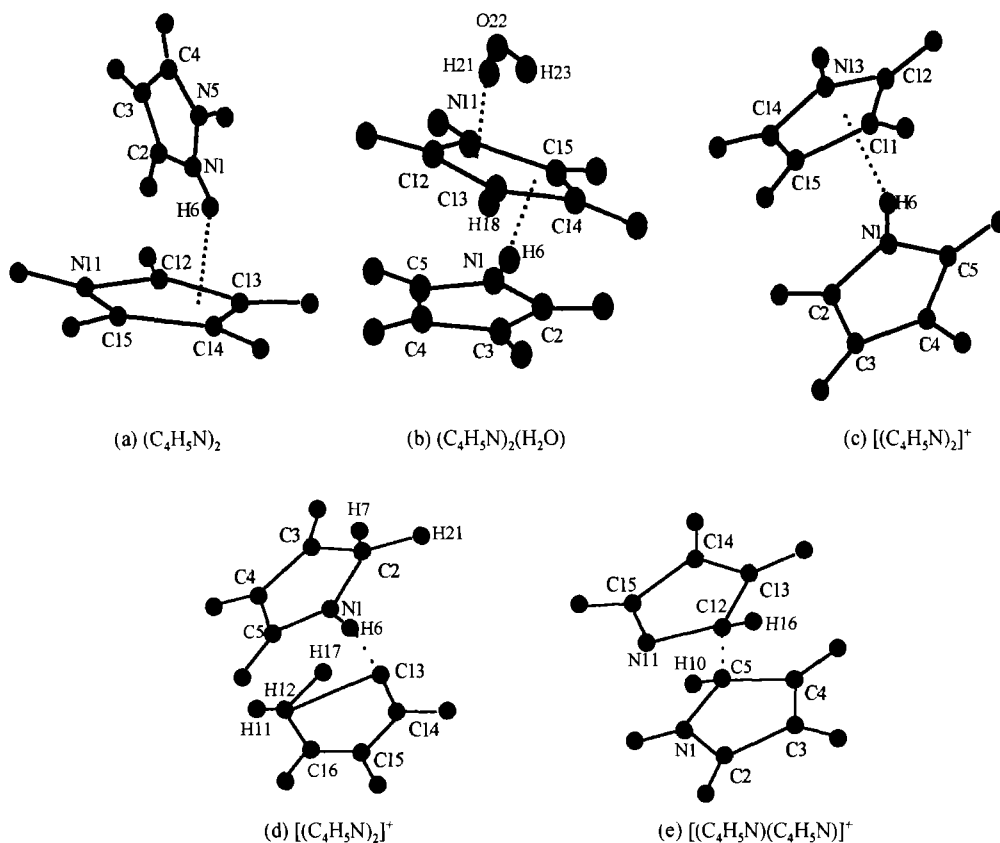


Fig. 2 Structures of pyrrole-water clusters calculated at HF/6-31G* level.

atom (H6 from N1), which is coupled with the π electrons of the other pyrrole molecule. Fig. 2(b) shows the stable structure of the neutral binary cluster $(C_4H_5N)_2-H_2O$. The structure of $(C_4H_5N)_2-H_2O$ is different from the structure of $C_4H_5N-H_2O$ shown in Ref. [5]. In Ref. [5], the water molecule is the proton acceptor, forming a hydrogen bond $N\cdots H-O$, while the cluster $(C_4H_5N)_2-H_2O$ is constructed with two hydrogen bonds: $N-H\cdots\pi$ and $O-H\cdots\pi$, where the water molecule is the proton donor. The difference in bond energy between the two types of bonds is about 6.69 kJ/mol^[11]. The hydrogen bond $N-H\cdots O$ is obviously stronger than the bond of $N-H\cdots\pi$ or $O-H\cdots\pi$. The structure of the cluster ions $(C_4H_5N)_2^+$ is similar to the neutral dimer $(C_4H_5N)_2$. In the structures of the protonated cluster ions $[(C_4H_5N)_2H]^+$, the two pyrrole rings are linked by the bond $N1-H6\cdots C13$, combined by hydrogen atoms transfer: one (H21) is transferred to the α -C (C2), and the other (H11) to the nitrogen atom (N12) (Fig. 2(d)). The structure of the dehydrogenated cluster ion $[(C_4H_4N)(C_4H_5N)]^+$ is shown in Fig. 2(e), in which one of the pyrrole molecules loses an H atom bound with the N atom. The two pyrrole rings are bridged by a C-C bond between the α -carbon atoms of the two pyrrole molecules.

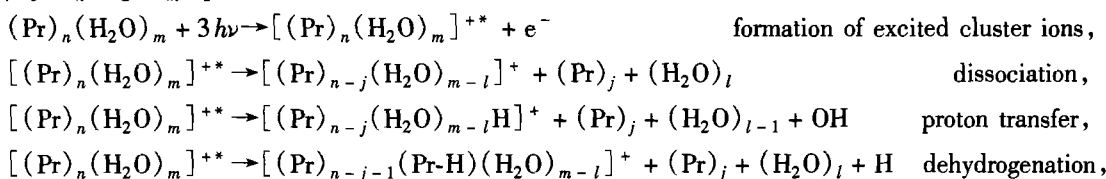
From the discussion on the structures, it is understandable why the yields of the clusters of $(C_4H_5N)_2$ and $(C_4H_5N)_2-H_2O$ are much smaller than that of $C_4H_5N-(H_2O)_n$.

2.3 Ionization and fragmentation of $(C_4H_5N)_n(H_2O)_m$

The ionization and fragmentation of $C_4H_5N-(H_2O)_n$ have been investigated and discussed in Ref. [5] which suggested that the formation of the protonated cluster ions were through the ionization of pyrrole molecules in the cluster, followed by intracuster proton transfer reactions, and the dehydrogenated cluster ions $[(C_4H_4N)-(H_2O)_n]^+$ were produced from the decomposition of pyrroles, in which the bond of N-H was broken. In the present experiments, all the above cluster ions can be observed in the mass spectra. We are interested in the poly-pyrrole-water cluster ions, including $[(C_4H_5N)_x(H_2O)_y]^+$ ($x \geq 2; y \geq 0$), $[(C_4H_5N)_x(C_4H_4N)(H_2O)_y]^+$ ($x \geq 0; y \geq 0$) and $[(C_4H_5N)_x(H_2O)_yH]^+$ ($x \geq 2; y \geq 0$). By checking the mass spectra obtained at 355 nm in Fig. 2 of our previous paper^[5], there are small shoulders on the left side of each peak of $[C_4H_5N-(H_2O)_n]^+$, which represent the fragment ions of $[C_4H_4N-(H_2O)_n]^+$. Since the concentration of the pyrrole is increased, the laser power used in this experiment is higher and the resolution of the mass spectrometer has been improved, so these small signals can be better resolved in this work.

The energy of a photon at 355 nm is 3.49 eV, which is enough to excite a pyrrole molecule up to the 4^1A_1 state (6.78 eV)^[12] through near-two-photon resonance excitation. The ionization potential (IP) of pyrrole is 8.21 eV. Although the formation of the clusters can make the pyrrole's IP red-shift a little^[13], at least three photons at 355 nm are needed for the ionization. As a result, there is an excess energy of about 2.26 eV kept in the cluster ion after ionization. These nascent cluster ions with excess energy are unstable, leading to the fragmentation of them. The species containing C_4H_4N are produced and stabilized in the decomposition after the excess energy is released.

With this consideration, the ionization and decomposition processes of the binary clusters $(C_4H_5N)_n(H_2O)_m$ upon laser excitation at 355 nm can be described as follows:



where (Pr) stands for C_4H_5N , and (Pr-H) for C_4H_4N .

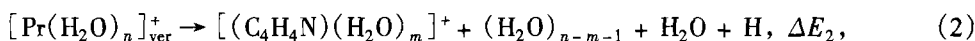
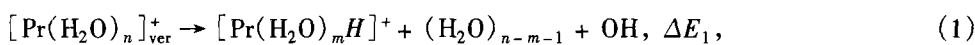
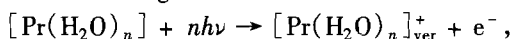
There are three reaction channels for the decay of the excited cluster ions of $[(\text{Pr})_n(\text{H}_2\text{O})_m]^{**}$. In the first channel, the detected species are the decayed binary mixed cluster ions $[(C_4H_5N)_x(H_2O)_y]^+$; in the second channel, proton transfer occurs and protonated cluster ions are produced. The dehydrogenation occurs in the third channel, where the bond N-H of the pyrrole molecule is broken. It is obvious that these three channels are competitive. From the viewpoint of energy, it seems that the breakup of hydrogen bonds should be the dominant channel. The experimental results show that the cluster ions $[(\text{Pr})_x(\text{H}_2\text{O})_y]^+$ are the dominant products. However, we do see a pretty amount of the decomposition products $[(\text{Pr-H})(\text{Pr})_x(\text{H}_2\text{O})_y]^+$. Stace et al.^[14] investigated the unimolecular decomposition of van der Waals cluster ions such as ArCH_xO^+ , and found that the intramolecular relaxation or the intramolecular energy flow played an important role in the dissociation processes. In other words, the speeds of energy flow are not equal for different vibration modes in a

polyatomic cluster and the time for predissociation in different vibration modes is different also. Because of this difference, the predissociation in the N-H vibration mode still may probably occur, forming the dehydrogenated fragment ions $[(\text{Pr-H})(\text{Pr})_x(\text{H}_2\text{O})_y]^+$.

2.4 Protonated cluster ions and dehydrogenated cluster ions

Fig. 1(b) clearly shows that there is a small peak on both sides of every big peak of $[\text{C}_4\text{H}_5\text{N} - (\text{H}_2\text{O})_n]^+$ at unit mass intervals. They are the protonated and dehydrogenated cluster ions produced through the second and the third reaction channels respectively. As discussed above, the protonated ions are produced through proton transfer and the dehydrogenated ions are generated from the breakup of the N-H bond. The signal intensities of both sequences of products decrease with the increase in the number (n) of the water molecules in the cluster ions.

As shown in the mass spectra in Fig. 1, the yields of these two sequences of cluster ions are almost in the same order of magnitude, but the decreasing slopes of their signal intensities are different. The decrease of signals of $[\text{C}_4\text{H}_4\text{N} - (\text{H}_2\text{O})_n]^+$ is slower than that of $[\text{C}_4\text{H}_5\text{N} - (\text{H}_2\text{O})_n\text{H}]^+$. The signals of the dehydrogenated ions are smaller than that of the protonated ions when $n < 4$, while the situation is reversed when $n > 4$. What is the reason? It can be understood if we simplify the whole reactions into the following reactions:



$$\Delta E_1 = E([\text{PrW}_{n-1}\text{H}]^+) + E(\text{OH}) - E([\text{PrW}_n]_{\text{ver}}^+),$$

$$\Delta E_2 = E([\text{(Pr-H)W}_{n-1}]^+) + E(\text{H}_2\text{O}) + E(\text{H}) - E([\text{PrW}_n]_{\text{ver}}^+),$$

here ΔE_1 and ΔE_2 stand for the reactive endothermic values of reactions (1) and (2), respectively.

The calculated reactive endotherms (ΔE_1 , ΔE_2) of the two reactions versus n are shown in Fig. 3, Tables 1 and 2. The endothermic values of the two reactions decrease with the increase in n .

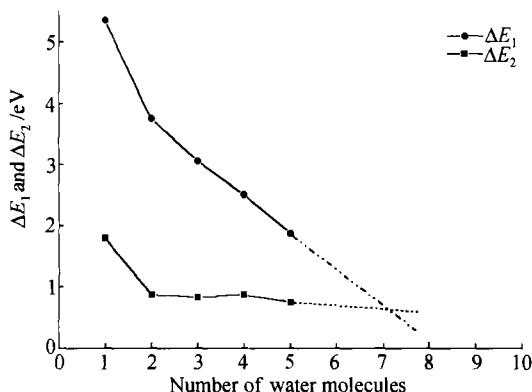


Fig. 3 Values of (ΔE_1) and (ΔE_2) vs. different number of water molecules included in the cluster (Pr: $\text{C}_4\text{H}_5\text{N}$; W: H_2O). ●, ΔE_1 ; ■, ΔE_2 .

But their decreasing slopes are different. The endothermic value of reaction (1) decreases faster than that of reaction (2). Contrary to the experimental results, we cannot find the reverse phenomenon in the calculation of energy when $n = 4$. It implies the endotherm in the reaction is not the only factor that affects our experimental result. However, both the experimental and the calculated results show that the dehydrogenation tends to occur more easily than the protonation does while the value of n is raised.

The reaction energies are correlated with the geometrical structures of the products. The calculated structures are shown in Fig 4. For $n = 1$, the stable structure of the dehydrogenated ion, the O atom of the water molecule, is connected to the α -C atom of the pyrrole molecule. For $n = 2$, the second water molecule is linked to the first water molecule via a hydrogen bond. When $n = 3$, the hydrogen atom (H17) of the third water molecule is connected to the nitrogen atom (N1) of the pyrrole molecule, forming a ring structure by hydrogen bond (O16-H17 \cdots N1) in the dehydrogenated cluster ion. Our calculated results show that the ring structure exists for $n \geq 4$. The formation of ring structure stabilizes these cluster ions. In other words, the products with ring structures are at lower energy levels, and the exotherm of the reaction should be larger. Accordingly, similar structure does not occur for the protonated ions. This difference results in the change of ΔE_1 , ΔE_2 with the number n .

Table 1 Calculated energies (E) and zero-point energies (ZPE) of the cluster ions (Hartree)

n	$E_{(\text{Pr-H})}$	$ZPE_{(\text{Pr-H})}$	$E_{(\text{PrH})}$	$ZPE_{(\text{PrH})}$	$E_{\text{Pr Ver}}$	$ZPE_{\text{Pr Ver}}$
1	-285.7516	0.1065	-287.0633	0.1282	-286.4097	0.1135
2	-362.2538	0.1327	-363.5416	0.1545	-362.8623	0.1415
3	-438.7524	0.1606	-440.0167	0.1808	-439.3402	0.1690
4	-515.2446	0.1868	-516.4906	0.2072	-515.8182	0.1965
5	-591.7225	0.2137	-592.9660	0.2348	-592.2885	0.2241

E stands for the energies calculated at B3LYP/6-31G**//HF/6-31G** level; Pr-H stands for the dehydrogenated cluster ions $[(\text{C}_4\text{H}_4\text{N})(\text{H}_2\text{O})_n]^+$; ZPE stands for the zero point energies calculated at HF/6-31G**//HF/6-31G** level; PrH stands for the protonated cluster ions $[(\text{C}_4\text{H}_5\text{N})(\text{H}_2\text{O})_n\text{H}]^+$; $E_{\text{Pr Ver}}$ stands for the energy of the cluster $[(\text{C}_4\text{H}_4\text{N})(\text{H}_2\text{O})_n]$ after vertical ionization.

Table 2 The endothermic energies of the protonation and the dehydrogenation reactions containing n water molecules in the cluster

n	$\Delta E_1/\text{eV}$	$\Delta E_2/\text{eV}$
1	1.794	5.357
2	0.877	3.754
3	0.835	3.059
4	0.88	2.509
5	0.747	1.872

n stands for the number of the water molecule contained in the cluster; $\Delta E_1 = E([\text{PrW}_{n-1}\text{H}]^+) + E(\text{OH}) - E([\text{PrW}_n]_{\text{ver}}^+)$; $\Delta E_2 = E([\text{Pr-HW}_{n-1}]^+) + E(\text{H}_2\text{O}) + E(\text{H}) - E([\text{PrW}_n]_{\text{ver}}^+)$.

3 Summary

Multiphoton ionization of the hydrogen-bonded clusters $(\text{C}_4\text{H}_5\text{N})_n(\text{H}_2\text{O})_m$ is studied with a relectron—time of flight mass spectrometer at a laser wavelength of 355 nm. As the mass spectrum resolution is improved and the pyrrole concentration is increased in the molecular beam, a series of new binary cluster ions with more than one pyrrole molecule is observed. The *ab initio* calculations show that the two pyrrole molecules in a cluster are linked by hydrogen bond N-H \cdots π , which is not as

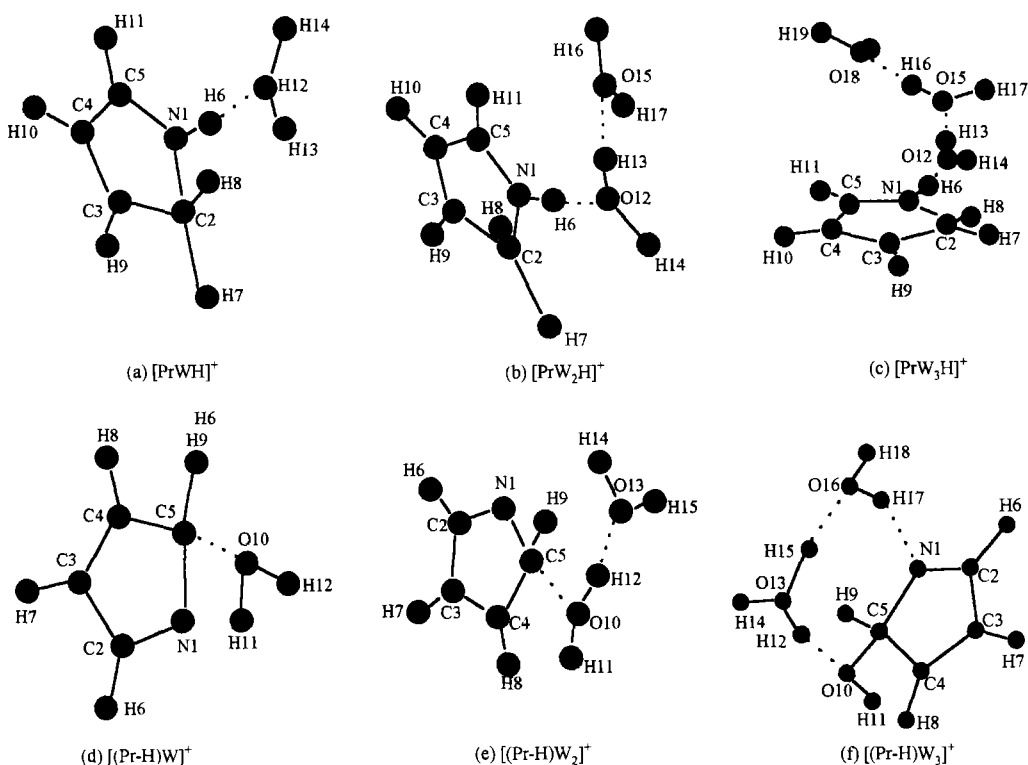


Fig. 4 Structures of protonated and dehydrogenated pyrrole-water cluster ions calculated at HF/6-31G* level. $[(\text{Pr-H})\text{W}_n]^+$: dehydrogenated cluster ion; $[\text{PrW}_n\text{H}]^+$: protonated cluster ion.

strong as the hydrogen bond $\text{N-H}\cdots\text{O}$ in the binary clusters $\text{C}_4\text{H}_5\text{N} - (\text{H}_2\text{O})_n$. This is the reason why the yield of poly-pyrrole-water cluster ions is so small that they are difficult to be detected. A most probable mechanism for the formation of the cluster ions $[(\text{C}_4\text{H}_5\text{N})_x(\text{H}_2\text{O})_y]^+$, $[(\text{C}_4\text{H}_5\text{N})_x(\text{H}_2\text{O})_y\text{H}]^+$ and $[(\text{C}_4\text{H}_4\text{N})(\text{C}_4\text{H}_5\text{N})_x(\text{H}_2\text{O})_y]^+$ is proposed. The ionization processes are accompanied by cluster dissociation, proton transfer reaction and dehydrogenation, which are three competitive reaction channels. The dissociation is the main reaction channel, while the proton transfer reaction and the dehydrogenation is also probable. The energy released in the reactions and the stability of the cluster ions both play an important role in the reaction dynamics.

References

- 1 Choo, K. Y. et al. Molecular beam multiphoton-ionization studies on ammonia-water clusters. *Chem. Phys. Lett.*, 1983, 95: 102.
- 2 Shinohara, H. et al. Mass spectroscopic observation of an enhanced structural stability of water-ammonia binary clusters at $n = 20$ in the series $(\text{H}_2\text{O})_n(\text{NH}_3)_m\text{H}^+$ ($0 < n + m < 32$). *Chem. Phys. Lett.*, 1984, 111: 511.
- 3 Xia, P. et al. Metastable decomposition of $(\text{ROH})_n(\text{NH}_3)_m\text{H}^+$ heterocluster ions. *J. Phys. Chem.*, 1995, 99: 3448.
- 4 Lee, S. Y. et al. Proton-transfer reactions within ionized methanol clusters; mass spectrometric and molecular orbital studies. *J. Mass Spectrom.*, 1995, 30: 969.
- 5 Li, Y. et al. Multiphoton ionization and *ab initio* calculation studies of the hydrogen-bonded clusters $\text{C}_4\text{H}_5\text{N} - (\text{H}_2\text{O})_n$. *J. Chem. Phys.*, 1999, 103: 2572.
- 6 Hineman, M. F. et al. Excited-state proton transfer in 1-naphthol/ammonia clusters. *J. Phys. Chem.*, 1992, 97: 3341.

- 7 Castleman, A. W. Jr. Cluster reactions *Annu. Rev. Phys. Chem.*, 1994, 45: 685.
- 8 Bernstein, E. R. Dynamics and photochemistry of neutral vdW clusters. *Annu. Rev. Phys. Chem.*, 1995, 46: 197.
- 9 Tubergen, M. J. et al. Microwave spectrum and structure of a hydrogen-bonded pyrrole-water complex. *J. Phys. Chem.*, 1993, 97: 7451.
- 10 Frisch, M. J. et al. *Gaussian 94W (revision A)*. Pittsburgh: Gaussian Inc., 1995.
- 11 Nagy, P. I. et al. Theoretical studies on hydration of pyrrole, imidazole, and protonated imidazole in the gas phase and aqueous solution. *J. Am. Chem. Soc.*, 1993, 115: 2912.
- 12 Andres, L. S. et al. Theoretical study of the electronic spectra of cyclopentadiene, pyrrole, and furan. *J. Am. Chem. Soc.*, 1993, 115: 6184.
- 13 Li, Y. et al. Proton transfer reactions within the $\text{NH}_3\text{-CH}_3\text{OH}^+$ cluster. *Chem. Phys. Lett.*, 1997, 276: 339.
- 14 Bernard, D. M. et al. Unimolecular fragmentation of the methyl formate ion in association with large inert gas clusters. *Int. J. Mass Spectrom Ion Processes*, 1990, 95: 327.