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Original article

Structure of Pro_4H^+ investigated by infrared photodissociation (IRPD) spectroscopy and theoretical calculations

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ABSTRACT

Combining with electrospray ionization (ESI) mass spectrometry, infrared photodissociation (IRPD) spectroscopy is a powerful method to study structures of cluster ions in the gas phase. In this paper, infrared photodissociation spectrum of Pro_4H^+ in the range of 2700–3600 cm^{-1} was obtained experimentally. Both theoretically predicted spectra of the two most stable isomers of Pro4-1 and Pro4-2 obtained at the level of M062X/6-31 + G(d, p) are in good consistent with the experimental results. The two isomers have similar structures and close energies. Both of them only consist of zwitterionic units, indicating the strong salt-bridged interactions inside the clusters. And the calculated collision cross section (ccs) of Pro4-1 is found to be very close to the experimental result previously reported.

1. Introduction

Infrared photodissociation (IRPD) spectroscopy can provide a wealth of structural information of gas-phase ions [1–4]. For example, amino acids are known to be in their zwitterionic forms in solution and in their non-zwitterionic forms in isolated states. So interactions with other molecules or ions can greatly stabilize the zwitterionic structures of amino acids. In order to accurately deduce their gas-phase structures, a lot of amino acid relative complex ions were studied by combining the method of IRPD spectroscopy and theoretical calculations [1–16]. Typically, these complex ions were generated by electrospray ionization (ESI) method, trapped in the cell of a Fourier transform ion cyclotron (FT ICR) mass spectrometer, and irradiated by a trunable IR laser. Then the spectral intensity of the selected ions at each wavelength can be calculated as:

$$I = -\ln\left(\frac{I_p}{(\sum I_f + I_p)}\right) \quad (1)$$

in which the I_p and I_f represent intensities of precursor and fragment ions observed in the mass spectra, respectively.

Besides metal ions, amino acids themselves can greatly affect the structure of its partner in the corresponding cluster ions. For example, structures of several protonated homodimers of amino acids, including Gly_2H^+ [1,5], Ser_2H^+ [1,6], Thr_2H^+ [1,16], Pro_2H^+ [5] and Lys_2H^+ [9,15], have been studied by experimental IRPD method and theoretical calculations. IRPD spectrometry has been also applied for hetrodimers of amino acids and some magic clusters with larger size [6,10,13]. On the other hand, the chiral composition of amino acid clusters is also a very interesting and important topic, due to the basic question about the origins of chirality in biological systems. For example, the magic cluster of serine octamer is strongly characterized by its preference for homochirality [17–20]. Research also showed that this cluster could be generated under simulated prebiotic conditions, indicating that its possible role in the chemistry of homochirogenesis [19]. Proline cluster is another interesting example [21–24]. It could form a remarkably stable cluster ion of $Pro_{12}H^+$, which underwent spontaneous chiral resolution in the gas phase [22]. An oscillation between strong preferences for homochiral and heterochiral structures as a function of cluster size was also discovered [23]. A better understanding of the structures of these clusters and their relatives is very important. As a complementary method to ion mobility (IMS) mass spectrometry [24], IRPD spectroscopy can be applied in these clusters to help to identify their structural characterizes, such as the location of the proton and the hydrogen bonding interactions.

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In the present work, IRPD method has been applied for the cluster ions of L-Pro_4H^+. And its experimental result was compared with the theoretical predicted spectra of the suggested isomers.

2. Experimental

All experiments were performed on a 7.0 T FT ICR mass spectrometer (IonSpec, Varian Inc., Lake Forest, CA, USA) in the positive ion mode. A solution of L-Pro (1 mmol/L in 49:49:2 H_2O:MeOH:AcOH) was sprayed at an infusion rate of 240 μL/h. A Zspray ESI source was used here. And the probe was set to 3.6 kV. After their generation, all ions were injected into an open-ended cylindrical Penning trap *via* an rf-only quadrupole ion guide. Then the precursor ions of Pro_4H^+ were further selected by the method of stored waveform inverse Fourier transform [25]. IRPD spectrum was obtained using the same experimental setup described previously [14–16]. The infrared OPO laser (Firefly-IR, M Squared, UK) was operated in the normal mode, with an output irradiation tunable from 2700 cm^{-1} to 4000 cm^{-1} and a line width of 7 cm^{-1}. The average IR power was 400 mW. The irradiation time (with a typical value of 4 s) was controlled using a mechanical shutter (Sigma-Koki, Japan). The spectral intensity at each wavelength was calculated using (1).

For theoretical calculation, about 40 isomers of Pro_4H^+ were suggested based on the experimental IRPD spectra and previous studies [5,24]. At the first step, these structures were optimized using the semi-empirical AM1 method. Then, 10 structures were selected, optimized, and verified by the DFT method of M062X/6-31G(d) [26]. The four most stable isomers were further selected and optimized at the levels of M062X/6-31 + G(d, p). All frequencies obtained at the level of M062X/6-31 + G(d, p) were scaled with a factor of 0.948. The electronic energy was calculated at 0 K with zero-point energy corrections and free energies were calculated at 298 K. All calculations were carried out with the Gaussian 09 program [27]. The theoretical collision cross sections (ccs's) of corresponding isomers were calculated with the MOBCAL program developed by Jarrold and coworkers [28,29].

3. Results and discussion

Fig. 1a shows a typical ESI mass spectrum of proline. The cluster ions of Pro_4H^+ and Pro_3H^+ can be identified clearly. Weak signal of Pro_3H^+ can be observed too. For our purpose here, the ions of Pro_4H^+ were selected and isolated (Fig. 1b) and then irradiated by the IR laser. Under suitable wavelength, the absorbed IR photons can cause the dissociation of the cluster ions. Fig. 1c shows one example, at the wavenumbers of 2930 cm^{-1}, the irradiation caused the parent ions dissociated to be cluster ions with smaller sizes (Pro_3H^+ and Pro_2H^+ observed here). By turning the wavelength of the IR laser and recording corresponding mass spectra, the IRPD spectrum can be calculated according to (1). Fig. 2a shows the IRPD spectrum of Pro_4H^+ in the range 2700–3600 cm^{-1}. A broad peak

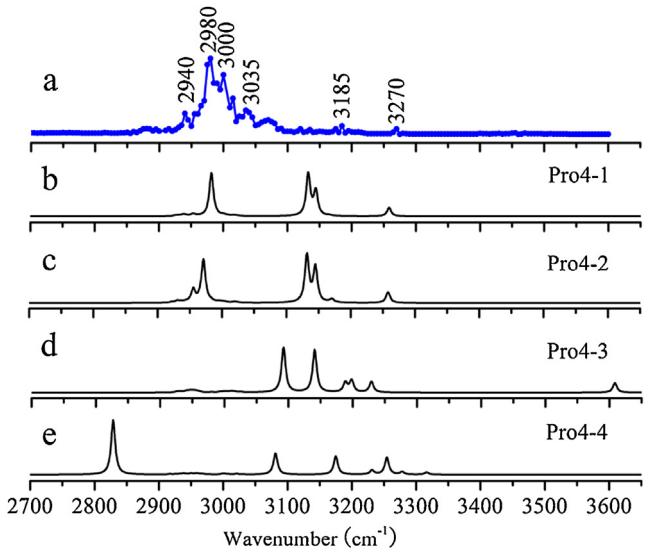

Fig. 2. Comparison of (a) the experimental IRPD spectrum of Pro_4H^+ and predicted IR spectra of isomers of (b) Pro4-1, (c) Pro4-2, (d) Pro4-3, (e) Pro4-4. The calculations were performed at the M062X/6-31 + G(d, p) level and scaled with a single factor of 0.948. Structures of these isomers are shown in Fig. 3.

centered at 2980 cm^{-1} was observed. Some weak peaks at 2940 cm^{-1}, 3035 cm^{-1}, 3075 cm^{-1}, 3185 cm^{-1} and 3270 cm^{-1} were also observed.

The structures of Pro_4H^+ were investigated using the calculation strategy described above. The most stable six isomers, which were optimized at the level of M062X/6-31 + G(d, p), are shown in Fig. 3. Their relative energies and free energies are summarized in Table 1. According to their total energy (at 0 K), the most stable structure is the isomer Pro4-1, which has an energy 0.34 kcal/mol lower than that of Pro4-2, and about 9–15 kcal/mol lower than those of other structures. However, Pro4-2 has the lowest value of Gibbs free energy (at 298 K), which is 0.19 kcal/mol lower than that of Pro4-1. Interestingly, all the top five conformations are shown to be arranged into geometry of a tetrahedral type. These structures are also very close to the previously suggested structure of D-Pro_4H^+ by Clemmer *et al.* [24]. Those isomers with geometry of a ring type are found to be higher in their energies. It is also found that the three unprotonated proline units in the top 5 structures are all characterized by their zwitterionic forms. For the most stable isomer Pro4-1, it has six strong intermolecular H-bonds of NH···O and one of OH···O, whose distances are all less than 1.90 Å. These H-bonds are greatly enhanced by the Coulomb interaction. The structure of isomer Pro4-2 is very close to the Pro4-1. It also has totally seven intermolecular H-bonds.

Theoretically predicted IR spectra of the four most stable isomers at M062X/6-31 + G(d, p) level were compared with the experimental IRPD spectrum and shown in Fig. 2. The predicted spectra of Pro4-1 (Fig. 2b) and Pro4-2 (Fig. 2c) are both

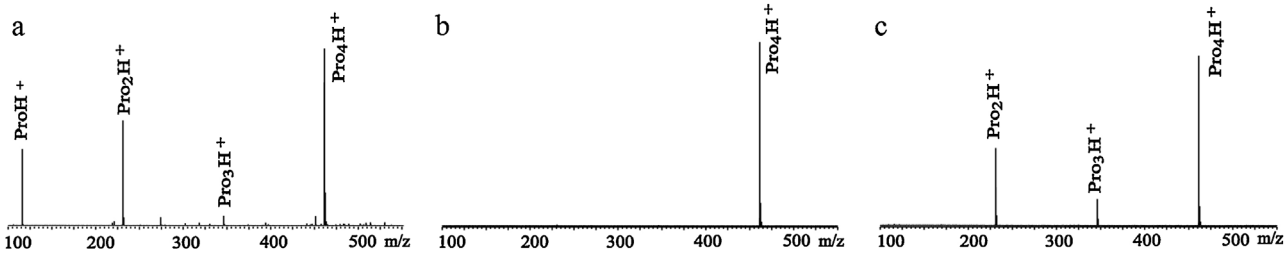

Fig. 1. (a) ESI mass spectrum of the solution of L-Pro, (b) the mass spectrum of the isolated ion of Pro_4H^+ and (c) the IRPD mass spectrum of Pro_4H^+ obtained by the irradiation of IR laser at 2930 cm^{-1} with a period of 4 s.