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Collision-induced dissociation mass spectrometry of phosphorus cluster anions P_{2m+1}^- $(3 \leq m \leq 20)$

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ABSTRACT

Phosphorus cluster anions were generated and investigated using collision-induced dissociation mass spectrometry. Results show that the primary dissociation channels of P_{2m+1}^- $(3 \leq m \leq 11)$ are generally characterized by the loss of a P_2 unit, which distinguishes them from their counterpart cations. However, P_{11}^- and P_{13}^- are two exceptions. The former is characterized by the loss of a P_4 unit, and the latter is characterized by two parallel dissociation channels, which lead to the loss of P_2 and P_6 units. The dissociation behaviors of larger cluster anions of P_{8k+1}^- $(k = 3–5)$ are more complex. The primary dissociation pathway of P_{25}^- is the loss of a P_8 unit, and those of P_{33}^- and P_{41}^- are the loss of P_{16} and P_2 units respectively. Theoretical calculations were performed for anions of P_{2m+1}^- $(3 \leq m \leq 9)$. Results show that their dissociation channels characterized by the loss of the P_2 unit are more thermodynamically favored, which is generally consistent with the experimental results.

1. Introduction

The variety of structural phases of phosphorus [1–4] has stimulated a flurry of research into the structures of phosphorus-related clusters [5–25]. Using laser ablation, gas-phase phosphorus clusters have been generated and studied by mass spectrometry [5–16]. Cationic phosphorus clusters of P_n^+ $(n < 25)$ were first investigated by Martin [5]. These clusters were generated by quenching the vapor of red phosphorus in a helium beam. The recorded mass spectra were clearly shown to alternate between odd and even signal intensity. Huang et al. reported mass spectra of cationic and anionic phosphorus clusters generated by direct laser vaporization of red phosphorus [6–9]. The maximum cluster sizes were extended to 89 and 49 atoms, respectively. For both large cluster ions of P_n^+ and P_n^- $(n \geq 25)$, those ions with $n = 8k + 1$ $(k \geq 3)$ showed greater intensity than their neighbors. Bulgakov et al. also studied different phosphorus clusters across a wide size range using mass spectra [10–12]. Large phosphorus cluster anions up to $n = 500$ were also recently observed by Kong using a Fourier transform ion cyclotron resonance (FT ICR) mass spectrometer [13].

Many studies have used theoretical calculations in order to better understand the structures of phosphorus clusters [17–25]. For example, Chen et al. investigated the ground-state structures of neutral, cationic, and anionic phosphorus clusters (with $n = 3–15$) based on the B3LYP/6-311+G* method [24]. Xue et al. systematically studied the global minimum structures of odd-sized cations of P_{2m+1}^+ $(m = 1–12)$ using first-principles simulated annealing [25]. Experimental scientists also studied phosphorus clusters with different methods, such as collision-induced dissociation (CID) mass spectrometry [15,16]. Using a home-made tandem time-of-flight mass spectrometer, Huang et al. studied P_n^+ $(n = 4–25)$ via collision-induced dissociation by crossing the mass-selected phosphorus cluster ion beam with a supersonic nitrogen beam [15]. Recently, medium-sized phosphorus cluster cations of P_{2m+1}^+ $(6 \leq m \leq 32)$ were also investigated with the method of CID in a FT ICR mass spectrometer [16]. Results showed the primary dissociation pathways of P_{2m+1}^+ $(6 \leq m \leq 11)$ to be all characterized by the loss of a P_4 unit. For those magic cluster ions of P_{8k+1}^+ $(3 \leq k \leq 8)$, the dissociation pathways progressively changed from the loss of P_4 to loss of P_8.

Compared to phosphorus cluster cations, their cluster anions are rarely studied by the CID mass spectrometry. Although the alternation between odd and even was observed for both cations and anions, theoretical calculations reflected that the most stable structures for P_n^+ and P_n^- $(n = 3–15)$ to be quite different [24]. In order to better understand these cluster anions, the CID mass spectra of

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some phosphorus cluster anions of P^-_{2m+1} ($3 \le m \le 20$) were investigated here with a FT ICR mass spectrometer. The results clearly reflect the difference between the dissociation behaviors of cluster anions and cations.

2. Experiments and calculations

Experiments were performed on a 7.0 T FT ICR mass spectrometer (Varian IonSpec, Lake Forest, CA, U.S.) equipped with a proMALDI source. A 355 nm Nd:YAG laser (Orion, New Wave) was used as the source of the laser for the experiments. Typically, laser energy was set to 55% relative to its maximum energy of 4 mJ/pulse. The sample of red phosphorus (RP) powder (100 mesh, 98%) was purchased from Alfa Aesar and used without any pretreatment. It was dispersed in acetonitrile at a concentration of 15 mg/ml. Then 1 μL of the suspension was deposited onto the metal target and dried in the air before it was sent into the source region of the mass spectrometer.

In the experiment, ions produced by eight laser pulses were injected into an open-ended cylindrical Penning trap via an rf-only quadrupole ion guide. After 1 ms accumulation of the ions in the hexapole, they were transferred into the FT ICR cell at last. All mass spectra reported here were measured in the negative ion mode. In CID experiments, the ions of interest were selected using the stored waveform inverse Fourier transform (SWIFT) method [26]. Both sustained off-resonance irradiation (SORI) and on-resonance irradiation excitation were tried to produce better tandem mass spectra [27,28]. Typically, the excitation was performed at amplitudes of 0.06–0.6 V ($V_{p\text{-}p}$) with a frequency offset of 100 Hz relative to the precursor ion cyclotron frequency. During each excitation event of 10 ms, the pressure in the ICR cell was raised to approximately 10^{-7} Torr by a brief pulse of nitrogen gas.

Theoretical calculations were performed using Gaussian 09 [29]. Considering that B3LYP has been widely used for phosphorus clusters and their relatives, geometric optimization and vibrational calculation of all phosphorus clusters were conducted on the level of B3LYP/6-311+G(d) in the final stage [21–24,30–32]. Among them, the structures of P^-_{2m+1} ($3 \le m \le 7$) were taken from previous structures suggested by Chen et al., while those of P^-_{2m+1} ($m = 8$, 9) were constructed here for the first time [24]. All structures were verified by vibrational analysis and electronic energies were calculated at 0 K with zero-point energy (ZPE) corrected.

3. Results and discussion

As shown in the previously reported laser ablation mass spectra, phosphorus cluster anions in a wide range of sizes were observed [13]. Among them, the odd-numbered ones dominated over the signal. Like the results of phosphorus cluster cations, those cluster anions satisfied $n = 8k + 1$ ($k = 3$–11) exhibited greater intensity than their neighbors. In this paper, some anions of P^-_{2m+1} ($m = 3$–20) were selected and studied with CID.

The CID mass spectra of anionic clusters P^-_{2m+1} ($m = 3$–5) under different collisional energies are shown in Fig. 1. As shown in Fig. 1a, P^-_5 was the only fragment ions from the precursor ions of P^-_7 detected at low-collisional energy. When the collisional energy increased (Fig. 1b), P^-_3 was also observed, which could be thought of as fragment ions from P^-_5 through the sequential loss of the P_2 unit. For anions of P^-_9, the results were quite similar (Fig. 1c and d). Its primary dissociation channel is also characterized by the neutral loss of a P_2 unit. High-collisional energy can cause sequential loss of the P_2 unit. However, for P^-_{11}, the CID mass spectra are different (Fig. 1e and f). Only fragment ions of P^-_7 could be detected under low-collisional energy conditions, and no anions of P^-_9 were

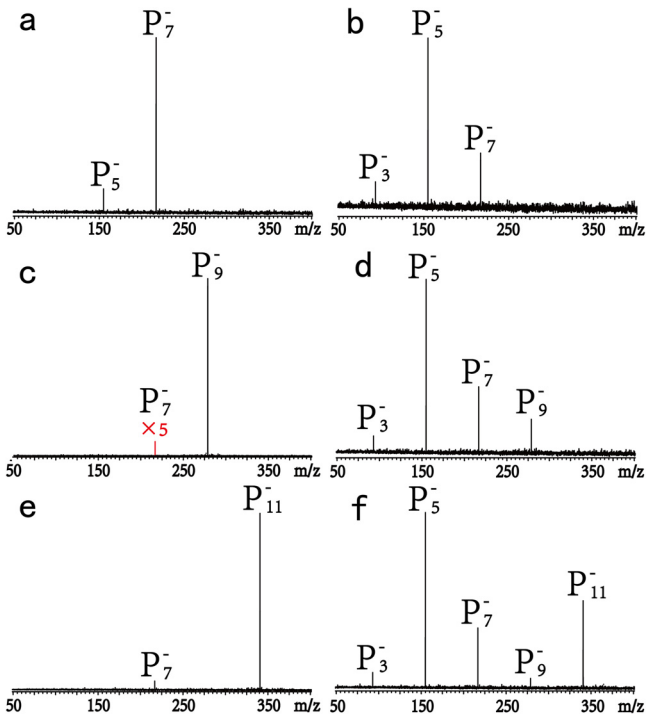

Fig. 1. CID mass spectra of some selected anions, which were obtained at different values of $V_{p\text{-}p}$'s: (a) P^-_7, $V_{p\text{-}p} = 0.02$ V; (b) P^-_7, $V_{p\text{-}p} = 0.045$ V; (c) P^-_9, $V_{p\text{-}p} = 0.025$ V; (d) P^-_9, $V_{p\text{-}p} = 0.239$ V; (e) P^-_{11}, $V_{p\text{-}p} = 0.025$ V; and (f) P^-_{11}, $V_{p\text{-}p} = 0.4$ V; The frequency offset is set to 100 Hz relative to cyclotron frequencies of corresponding precursor ions. Peak intensities of some fragment ions have been amplified by a factor of 5.

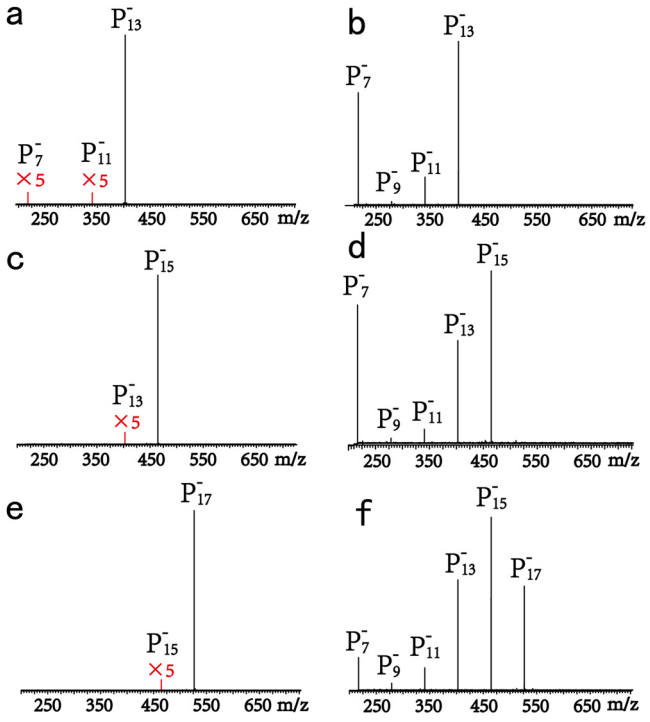

Fig. 2. CID mass spectra of some selected anions, which were obtained at different values of $V_{p\text{-}p}$'s: (a) P^-_{13}, $V_{p\text{-}p} = 0.07$ V; (b) P^-_{13}, $V_{p\text{-}p} = 0.14$ V; (c) P^-_{15}, $V_{p\text{-}p} = 0.09$ V; (d) P^-_{15}, $V_{p\text{-}p} = 0.18$ V; (e) P^-_{17}, $V_{p\text{-}p} = 0.09$ V; and (f) P^-_{17}, $V_{p\text{-}p} = 0.11$ V; The frequency offset is set to be 100 Hz relative to cyclotron frequencies of corresponding precursor ions. Peak intensities of some fragment ions have been amplified by a factor of 5.