

Vibrationally resolved photoelectron spectroscopy of PO_3^- and the electronic structure of PO_3

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Abstract

A vibrationally resolved photoelectron spectrum has been obtained for PO_3^- at 193 nm in the gas phase. Transitions to the ground (X^2A_2) and first excited state (A^2E'') of PO_3 were observed. The current spectrum represents the first observation of the $^2E''$ state, which splits into two states, 2B_1 and 2A_2 , due to the Jahn–Teller effect. The 2A_2 ground state shows a vibrational progression in the ν_1 symmetric stretching mode with a frequency of 1000 (100) cm^{-1} . The adiabatic electron affinity of PO_3 was measured to be very high, 4.95 (0.06) eV. The 2B_1 and 2A_2 states of PO_3 show very broad features due to the large geometry changes between these states and the anion ground state. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The monomeric metaphosphate anion (PO_3^-) is believed to be a key intermediate in many phosphoryl transfer reactions occurring in biological systems [1–4]. PO_3^- and the neutral PO_3 radical are also related to phosphorus impurities in coal-fired magnetohydrodynamic electric generators [5–7]. Although there is some controversy of the existence of PO_3^- in protic solution, PO_3^- has been shown to occur in aprotic solvents [8–10] and is very stable and unreactive in the gas phase [11–14]. The hydration of PO_3^- has been extensively studied experimentally [15,16] and theoretically [17–19]. PO_3^- has also been the

subject of several quantum mechanical calculations [7,20–24].

PO_3^- is expected to have a D_{3h} equilibrium geometry [7,20–24] with a molecular orbital configuration, ... $(e')^4(e'')^4(a_2')^2$, in the $^1A_1'$ ground state, same as NO_3^- [25–27]. The ground ($^2A_2'$) and first two low-lying electronic excited states ($^2E''$, $^2E'$) of the neutral PO_3 radical have the configurations, ... $(e')^4(e'')^4(a_2')^1$, ... $(e')^4(e'')^3(a_2')^2$, and ... $(e')^3(e'')^4(a_2')^2$, respectively. They are accessible via one-electron photodetachment transitions from the ground state of PO_3^- . However, unlike the analogous NO_3 radical, considerably less is known about the ground and excited states of PO_3 . There have been only two studies reported by Andrews et al. using IR and UV absorption in solid argon matrix [28,29]. They observed the antisymmetric stretching and in-plane bending modes of PO_3 and the $^2E' \leftarrow ^2$

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A'_2 transition with its origin at 696 nm (1.78 eV above the ground state). The first excited state (${}^2E''$) has not been observed because the ${}^2E'' \leftarrow {}^2A'_2$ transition is electric-dipole forbidden. This ‘dark’ ${}^2E''$ state has only been calculated by Lohr and Boehm [7], who also obtained a very high electron affinity (EA) for PO_3 , consistent with an experimental estimate (4.9 ± 1.3 eV) by Viggiano and co-workers [11].

In this letter, we report the first examination of the ground (${}^2A'_2$) and low-lying excited states (${}^2E''$) of PO_3 by photoelectron spectroscopy (PES) of the PO_3^- anion at 193 nm (6.424 eV). The EA of PO_3 was measured more accurately to be 4.95 ± 0.06 eV. The ${}^2E''$ state and its Jahn–Teller splittings were observed for the first time. In particular, we found that the theoretical results by Lohr and Boehm [7] are generally in good agreement with our experimental measurements.

2. Experiment

Our experiment was performed with a magnetic-bottle photoelectron spectrometer coupled with an electro-spray ionization source. The details of this apparatus have been described elsewhere [30], only a brief description is given here. A 10^{-4} M $\text{Na}_5\text{P}_3\text{O}_{10}$ (Aldrich, Milwaukee, WI, USA) solution in a water/methanol (2/98 ratio) mixed solvent was sprayed through a ~ 10 micrometer inner diameter fused quartz syringe needle, which was biased at -2.2 kV at ambient atmosphere. The resulting negatively charged droplets were fed into a 20 cm long, 0.8 mm inner diameter desolvation capillary, which was heated to $\sim 70^\circ\text{C}$. Anionic species emerged from the desolvation capillary were collimated by a 1.5 mm diameter skimmer to a radio-frequency quadrupole ion-guide. The anions then entered a quadrupole ion-trap and were accumulated for 0.1 second before being pushed into the extraction zone of a TOF mass spectrometer. $\text{P}_3\text{O}_{10}^{5-}$ was not observed and the major ion signals were protonated species and PO_3^- . The latter was formed due to fragmentation of $\text{P}_3\text{O}_{10}^{5-}$ in the desolvation capillary. After mass-selection and deceleration, the PO_3^- anions were intercepted by a 193-nm laser beam from an ArF excimer laser in the detachment zone of the magnetic-bottle photoelectron analyzer. Photoelec-

trons were collected at nearly 100% efficiency by the magnetic-bottle and analyzed in a 4-meter long TOF tube. The experiment was done at 20 Hz repetition rate with the ion beam off at alternating laser shots for background subtraction. The photoelectron TOF spectra were converted to kinetic energy spectra calibrated by the known spectra of I^- and O^- . The electron binding energy spectra presented were obtained by subtracting the kinetic energy spectra from the detachment photon energy. The energy resolution of the apparatus was about 11 meV at 0.4 eV kinetic energy [30]. However, the resolution deteriorated at 193 nm due to both the laser bandwidth and the strong background at low kinetic energies.

3. Results and discussion

The PES spectrum of PO_3^- at 193 nm is shown in Fig. 1 at two photon fluxes. We found that at higher photon fluxes a broad feature at lower binding energy appeared, as shown in Fig. 1a. It disappeared at lower photon fluxes, as shown in Fig. 1b, whereas the other PES features remained the same. This broad feature was found to be due to PO_2^- as a result of a two-photon process: photodissociation of PO_3^- ($\text{PO}_3^- \rightarrow \text{PO}_2^- + \text{O}$) and subsequent photodetachment of ($\text{PO}_2^- \rightarrow \text{PO}_2 + e$) at 193 nm. The binding energy of this feature is consistent with the vibrationally resolved PES spectrum of PO_2^- measured by Neumark et al. [31]. However, we did not observe signals due to O^- , probably due to the much smaller EA of O atom compared to that of PO_2 .

Two major PES bands were observed for PO_3^- , an intense and partially vibrationally resolved band around 5 eV, and a second broad and weaker band around 6 eV. The spacings among the vibrational features in the first band is about 0.12 eV. However, the intensities of the higher vibrational levels seemed to be too strong considering the Franck–Condon envelope of a single vibrational progression. Thus, we suspected that there was another weaker band overlapping with the intense ground state band at about the $\nu = 3$ peak (5.35 eV) and that this weaker band has a similar vibrational spacing as the ground state (~ 1000 cm^{-1}). Partial vibrational structures were also discernible in the weaker 6 eV band (Fig. 1a) with a spacing of ~ 500 cm^{-1} , although they

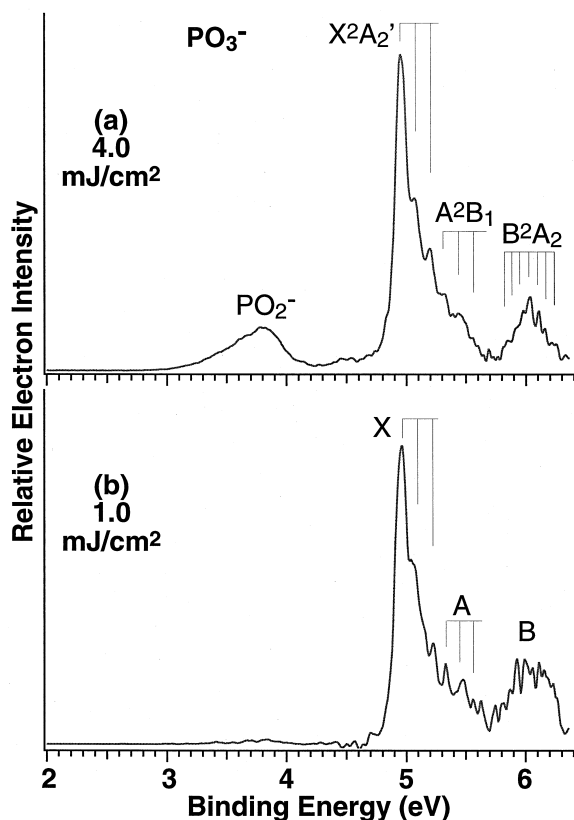


Fig. 1. Photoelectron spectrum of PO_3^- at 193 nm and two different laser fluxes: (a) 4.0 mJ/cm^2 and (b) 1.0 mJ/cm^2 . The PO_2^- feature was due to photofragmentation of PO_3^- at the higher detachment laser flux (see text).

could not be identified in Fig. 1b due to the poor signal-to-noise ratio.

The PES spectra represent transitions from the ground state of the anion ($^1A_1'$) to the ground and two excited states of PO_3 . The 0–0 transition of the X band defines the adiabatic EA of PO_3 . The instrumental resolution at this peak was about 50 meV. The measured peak width was about 120 meV, suggesting that there were other broadening factors, probably due to rotational and thermal effects. The temperatures of the ions in the ion-trap should be slightly above room temperature [30] and a hot band feature to the left of the 0–0 peak was clearly visible in Fig. 1a. The vertical peak position could be measured rather accurately and reproducibly. We determined the EA for PO_3 to be 4.95 (0.06) eV, where a large uncertainty was assigned considering

the thermal effects. This EA value compares well to the 4.9 (1.3) eV number, previously estimated by Viggiano et al. [11] using a thermodynamic cycle.

The ground state of PO_3 ($^2A_2', D_{3h}$) is due to removal of one electron from the a_2' orbital of PO_3^- . In Fig. 2, we show the structural parameters of the ground state of PO_3^- (Fig. 2a) and PO_3 (Fig. 2b) from the previous calculations [7]. The P–O bonds are slightly shorter in the ground state of PO_3 compared to that in PO_3^- , consistent with our observation of a short vibrational progression in the ν_1 mode. Our obtained vibrational frequency is slightly low compared to the value of 1151 cm^{-1} calculated for the ν_1 mode of PO_3 .

The first excited state of PO_3 should be the ‘dark’ state, $^2E''$, due to detaching an electron from the e'' orbital of PO_3^- . The $^2E''$ state is not stable under D_{3h} symmetry because of the Jahn–Teller effect and will split to 2B_1 and 2A_2 with C_{2v} symmetry [7]. These states have been calculated by Lohr and Boehm [7] and the structural parameters are shown in Fig. 2c and 2d. The large geometry changes of the 2B_1 and 2A_2 states compared to the anion ground states are consistent with the broad spectral features shown in Fig. 1.

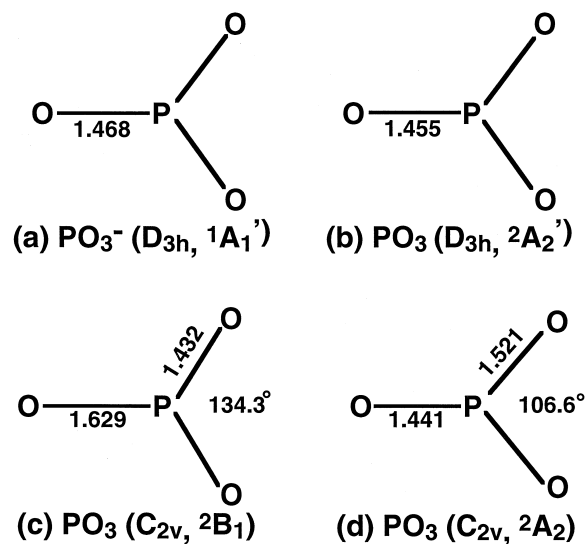


Fig. 2. Structural parameters of PO_3^- and PO_3 from Ref. [7]. (a) ground state of PO_3^- , $^1A_1'$; (b) ground state of PO_3 , $^2A_2'$; (c) the first excited state of PO_3 , 2B_1 ; (d) the second excited state of PO_3 , 2A_2 . Bond lengths are in Å.

The excitation energies of the two states were also calculated. The calculated excitation energy for the 2B_1 state was only 0.37 eV above the 2A_2 ground state, consistent with the position of the A band in our PES spectra of Fig. 1. The weak and overlapping nature of this state with the ground state vibrational levels made it difficult to determine the origin of this state. Based on the Franck–Condon envelope of the B band, we estimated a vertical binding energy of ~ 5.3 eV for the A band.

The B feature of the PES spectrum of PO_3^- was then assigned to the 2A_2 state of PO_3 . As seen from Fig. 2d, there is a large bond angle change in the 2A_2 state. Thus, a broad vibrational progression in the bending mode was expected. This was clearly born out from the spectra shown in Fig. 1. The small vibrational frequency estimated from the vibrational progression of the B feature was $\sim 500\text{ cm}^{-1}$, in good agreement with the frequency of the in-plane deformation vibrational mode from the previous calculation, which obtained a value of 462 cm^{-1} [7]. Because of the weak signal-to-noise ratio and the broad Franck–Condon envelope, it was also difficult to determine the 0–0 transition of the B band. Our measured vertical binding energy for the B^2A_2 state is 6.04 (0.06) eV. The obtained spectroscopic parameters from the present work are summarized in Table 1.

It is interesting to compare PO_3 with the isoelectronic NO_3 . The Jahn–Teller splitting in the ${}^2E''$ state was calculated to be much smaller in NO_3 [32,33]. The separation between the 2B_1 and 2A_2 states in NO_3 were calculated to be 700 cm^{-1} by Schaefer et al. [32] and 2300 cm^{-1} by Boehm and Lohr [33]. Indeed, in the previous PES study of NO_3^- , Neumark et al. [25] obtained a complicated vibrationally resolved band for the ${}^2E''$ state and were not able to distinguish the two Jahn–Teller

states. The essential difference of chemical bonding between PO_3 and NO_3 is that there exists a large contribution from the P 3d π orbitals in the P–O bonding, compared to the N–O bonding in NO_3 [20]. The contribution of the 3d π orbitals seemingly induces a large Jahn–Teller splitting in the ${}^2E''$ state in PO_3 , as observed both from the current PES experiment and the previous theoretical calculations [7].

4. Conclusions

We report a vibrationally resolved photoelectron spectrum of PO_3^- in the gas phase at 193 nm. Photofragmentation of PO_3^- to PO_2^- and O was observed at high detachment laser fluxes. The electron affinity of PO_3 was measured more accurately and found to be very high (4.95 ± 0.06 eV). The low-lying excited state, ${}^2E''$, of PO_3 was observed and found to split to two states due to the Jahn–Teller effect. The Jahn–Teller splitting in PO_3 was found to be much larger than that in NO_3 .

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Table 1
Observed adiabatic (ADE) and vertical (VDE) binding energies and vibrational frequencies for PO_3

	ADE (eV)	VDE (eV)	Vib. freq. (cm^{-1})
X^2A_2	4.95 (0.06) ^a	4.95 (0.06)	1000 (100)
A^2B_1		~ 5.3	
B^2A_2		6.04 (0.06)	500 (80)

^a Adiabatic electron affinity of PO_3 .

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