Photoelectron spectroscopy of PO_2^-

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In this Note, we report the photoelectron spectrum of PO_2^- anion. The electron affinity of PO_2 is determined from the spectrum. The anion geometry is obtained by Franck–Condon simulations of the photoelectron spectrum and is compared with *ab initio* calculations and previous experimental work.

The oxidation reactions of phosphorus and phosphine have been studied for centuries. However, the mechanisms for these reactions were poorly understood until recently, when PO_2 was strongly suggested to play a key role.[1] Unlike the isovalent NO_2 molecule, which has been investigated extensively, only a few spectroscopic studies have been performed on PO_2. The UV absorption spectrum of PO_2 was first observed by Verma and McCarthy[2] using a flash photolysis technique. More recently, Kawaguchi *et al.*[3] obtained an accurate ground state geometry and estimates of the lowest vibrational frequencies from far-infrared laser magnetic resonance (FIR LMR) and microwave spectroscopy. Laser-induced fluorescence (LIF) and infrared absorption spectra observed by Hamilton and co-workers[1] also give similar ground state vibrational frequencies. Knight *et al.*[4] have investigated PO_2 in a Ne matrix using electron spin resonance. Several *ab initio* calculations[5–7] of geometries and frequencies show reasonable agreement with experiment.

Considerably less information is available on the PO_2^- anion. Spectroscopic studies of PO_2^- have been limited to the solid phase: Geometries and vibrational frequencies of PO_2^- in a potassium chloride crystal have been obtained from spectroscopic and optically detected magnetic resonance studies by Francis and co-workers.[8] *Ab initio* calculations carried out by Lohr[6] give ground state constants and vibrational frequencies. They also predict PO_2 has a very large electron affinity (3.6±0.2 eV). The work presented here represents the first experimental characterization of PO_2^- in the gas phase.

The apparatus used in the present work is a fixed-frequency negative ion photoelectron spectrometer that has been described in detail elsewhere.[9] PO_2^- is a byproduct of our previous study of indium phosphide clusters[10] and was generated in a pulsed beam valve/laser vaporization source. A second harmonic (532 nm) of a YAG laser is focused onto a rotating and translating indium phosphide rod. The resulting plasma is entrained in a supersonic pulse of helium gas. Anions in the beam are injected into a time-of-flight mass spectrometer. After being accelerated by 1 keV energy, ions separate according to mass and are detected by a microchannel plate detector. The resulting ion beam is crossed by a second pulsed laser, the fourth harmonic (266 nm, 4.657 eV) of a YAG laser beam. By controlling the laser firing time, PO_2^- is selectively photodetached. The kinetic energy of the photoelectrons is determined via their time-of-flight. The instrumental resolution is 8–10 meV for an electron kinetic energy (eKE) of 0.65 eV and degrades as $(\mathrm{eKE})^{3/2}$.

Figure 1(a) shows the 266 nm photoelectron spectrum of PO_2^- at laser polarization angle $\theta = 90°$ with respect to the detection angle. The electron kinetic energy (eKE) is given by

$$\mathrm{eKE} = h\nu - \mathrm{EA}(\mathrm{PO}_2) - E^{(0)} + E^{(-)},$$

where $h\nu$ is the laser photon energy (4.657 eV) and EA (PO_2) is the electron affinity of PO_2. $E^{(0)}$ and $E^{(-)}$ are the internal energies of PO_2 and PO_2^-, respectively. The spectrum corresponds to the transition between the ground elec-

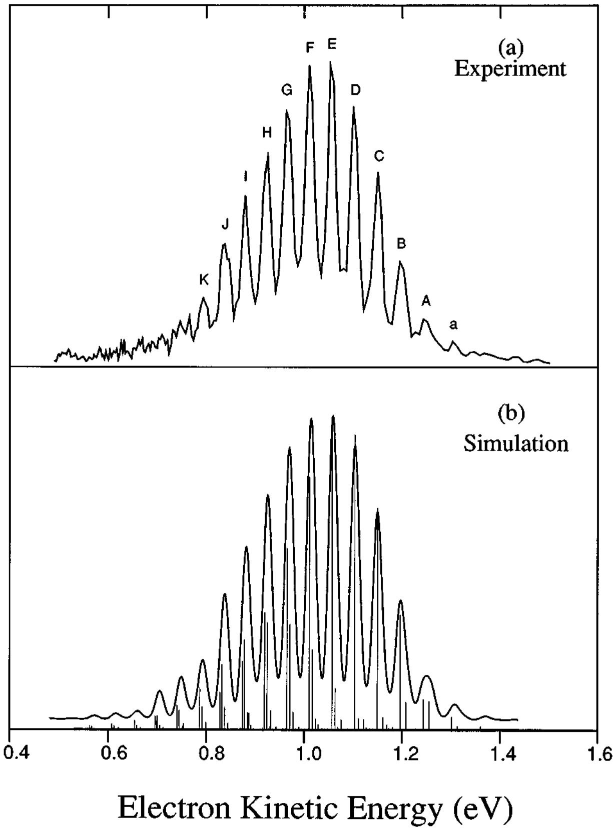

FIG. 1. (a) Photoelectron spectrum of PO_2^- measured using a photodetachment energy of 4.657 eV at laser polarization angle $\theta = 90°$, (b) Frank–Condon simulation with 2 active modes ν_1 and ν_2, convoluted with the experimenmtal resolution (curve line) and the corresponding stick spectrum.

TABLE I. Molecular parameters for the ground $^2A_1$ state of PO_2.

Method/Basis set	$r_{\rm PO}$ (Å)	$\theta_{\rm OPO}$	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})
SCF/6-31G* [a]	1.446	134.4	1048	396	1260
HF/6-31G* [b]	1.440	135.8	1126.5	445.6	⋯
SCF[c] (valence electrons)	1.454	135.6	1210	460	1540
SCF+CORR[c] (valence electrons)	1.496	134.3	1060	380	1340
SCF[c] (all electrons)	1.439	135.4	1256	463	1564
HF/6-31+G* [d]	1.446	134.86	1201	451	1451
MP2/6-31+G* [d]	1.496	136.83	1075	396	1585
MP2/6-311+G* [d]	1.480	136.65	1091	398	1570
CISD/6-31G* [d]	1.471	134.7	1136	425	1421
FILMR, microwave[e]	1.4665	135°17′	1090	377	1278
LIF, IR absorption[f]	⋯	⋯	1117	387	1300/1345

[a] Reference 6.

[c] Reference 5.

[b] Reference 7.

[d] This work.

[e] Reference 3.

[f] Reference 1.

tronic states of the anion and neutral, with an extended vibrational progression over the kinetic energy range from 0.7 to 1.4 eV. The spacing between adjacent peaks is about 400 cm^{-1} except for peaks G and H, which are separated by only 330 cm^{-1}. This indicates that there might be more than one active vibrational mode. Peak A is assigned to the 0–0 transition. It has a kinetic energy of 1.24 eV, yielding an electron affinity of 3.42 eV for PO_2. The smaller peak "a" occurs at 520 cm^{-1} higher kinetic energy than the origin. It has been assigned as a hot band transition, which indicates that the vibrational frequency of the main active mode is higher in the anion than in the neutral.

We have also performed *ab initio* calculations on PO_2 and PO_2^-. The calculations are aimed at determining the geometries, force constants, and vibrational frequencies of the ground electronic states. The results are summarized in Tables I and II. The geometries are optimized at the MP2 and CISD levels of theory, and harmonic vibrational frequencies are obtained at both levels of theory.

Tables I and II also show the geometry and vibrational frequencies of PO_2 ground state ($^2A_1$) and PO_2^- ground state ($^1A_1$) obtained from previous work. Compared with the FIR LMR and microwave study of PO_2 by Kawaguchi *et al.*,[3] our MP2 level calculations give good agreement with frequencies and geometries. The CISD level calculation with a small basis set gives better results on geometry, but not on frequencies. There are no gas phase experiments for PO_2^- to compare with the calculations. Based on the calculations, PO_2^- has a longer bond length and smaller bond angle in the solid phase than in the gas phase.

Ab initio calculations predict that the PO_2 and PO_2^- ground electronic states have C_{2v} symmetry. PO_2^- has a $^1A_1$ ground state with a $...(3b_2)^2(1a_2)^2(4a_1)^2$ valence electron configuration. Photodetachment from the $4a_1$ orbital will form the PO_2 $^2A_1$ ground state. *Ab initio* calculations also show that the $4a_1$ orbital is O–O bonding and P–O antibonding, so photodetachment should result in a O–P–O bond angle increase and a P–O bond length decrease, in agreement with the calculated geometries.

The isovalent species NO_2 also has a $^2A_1$ ground electronic state with the same electron configuration as PO_2. However, the composition of the molecular orbitals differs in the two molecules. The $4a_1$ orbital in PO_2 is formed by mixing of $3s$(P) and $2p\sigma$(O) orbitals; whereas in NO_2, the $2p$(N) and $2p$(O) orbitals are close in energy, and the $4a_1$ orbital is primarily a linear combination of these orbitals.

PO_2 and PO_2^- each have three vibrational modes: the symmetric stretch (ν_1), bend (ν_2) and asymmetric stretch (ν_3). The ν_1 and ν_2 modes are totally symmetric and can therefore be active in the photoelectron spectrum. Calculations show ν_1 is around 1100 cm^{-1} for both PO_2 and PO_2^-; ν_2 is around 400 cm^{-1} for PO_2 and 500 cm^{-1} for PO_2^-. Recall

TABLE II. Spectral constants of the ground $^1A_1$ state of PO_2^-.

Method/Basis set	$r_{\rm PO}$ (Å)	$\theta_{\rm OPO}$	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})
SCF/6-31G* [a]	1.483	118.9	1051	465	1192
HF/6-31G* [b]	1.483	119	1097	501	⋯
HF/6-31+G* [c]	1.4867	118.7			
MP2/6-31+G* [c]	1.5381	119.483	999.03	436.0	1151.7
MP2/6-311+G* [c]	1.5194	119.177	1046.0	465.0	1207.8
CISD/6-31G* [c]	1.5048	119.381	1135.1	497.5	1303.0
PO_2^- in KCl[d]	1.65	110	1097	501	1207

[a] Reference 6.

[c] This work.

[b] Reference 7.

[d] Reference 8.

the peak spacing of the spectrum is around 400 cm^{-1}, so the ν_2 mode appears to be the main activated mode. The assignment of peak "*a*" as a hot band transition is also supported. Since the ratio between ν_1 and ν_2 is about 3:1, overlap between the combination bands is expected, making it difficult to ascertain the contribution of the ν_1 mode by inspection alone.

To be more quantitative, we perform a Franck–Condon analysis to determine the normal coordinate displacements between PO_2 and PO_2^-. The normal coordinate displacements in the ν_1 and ν_2 modes are varied to obtain the best fit with the experimental spectrum. While the spectrum is reasonably well fit assuming only the ν_2 mode is active, the fit is improved with a small normal coordinate displacement in the ν_1 mode. The computer code we used has been discussed elsewhere.[11] Figure 1(b) shows the simulated spectrum from Franck–Condon analysis. The fitting yields electron affinity $\mathrm{EA}=3.42\pm0.01$ eV. Due to the $1_0^0 2_0^{n+3}/1_0^1 2_0^n$ overlapping and sequence bands, the observed width of the peaks is around 25 meV. From the intensity of peak "*a*", assigned as the $1_0^0 2_1^0$ hot band transition, we estimate the anion temperature $T=300$ K. Other fitting parameters are $\nu_1' = 1070\ \mathrm{cm}^{-1}$, $\nu_2' = 380\ \mathrm{cm}^{-1}$, $x_2' = 0.8 \pm 0.2\ \mathrm{cm}^{-1}$ for PO_2 and $\nu_1'' = 1000\ \mathrm{cm}^{-1}$, $\nu_2'' = 470\ \mathrm{cm}^{-1}$ for PO_2^-. The normal coordinate displacements from the anion to the neutral are $\Delta Q_1=-0.16$, $\Delta Q_2=0.79$, which correspond to a bond angle increase and a bond length decrease.

From the normal coordinate displacements, one can obtain geometry changes between the anion and neutral given the force constants. The force constants can be determined from either experimental vibrational frequencies or *ab initio* calculations.

We first construct the force constant matrix in internal coordinates, based on the vibrational frequencies and geometry obtained by Kawaguchi *et al.*[3] We use the *FG* matrix method,[12] assume that the bend–stretch force constant (h) equals half of the bend force constant (H). The F matrix in the units of mdyne/Å is calculated to be

$$F=\begin{pmatrix} K & k & h \\ k & K & h \\ h & h & H \end{pmatrix} = \begin{pmatrix} 9.077 & 0.9105 & 0.4109 \\ 0.9105 & 9.077 & 0.4109 \\ 0.4109 & 0.4109 & 0.8217 \end{pmatrix}, \quad (1)$$

where K and k are the stretch and the stretch–stretch force constants, respectively. Since the neutral geometry is known from microwave experiments, we use the normal coordinate displacements ($\Delta Q_1=-0.16$, $\Delta Q_2=0.79$) to find the PO_2^- geometry: $r_{\mathrm{PO}}=1.504$ Å and $\theta_{\mathrm{OPO}}=120.0°$. Changing the approximation condition for the bend–stretch force constant to $h=0$ and $h=H$ gives similar results which are shown in Table III. We use averages as the reported values.

TABLE III. Anion geometry comparison from FG matrix method calculation.

Assumptions	r_{PO} (Å)	θ_{OPO}
$h=0$	1.492	120.1
$h=H/2$	1.504	120.0
$h=H$	1.519	120.1
Average	1.50±0.01	120.0±0.1

As a comparison, we can use the force constant matrix from our MP2/6−311+G* level calculation on PO_2. This yields the following anion geometry: $r_{\mathrm{PO}}=1.523$ Å, $\theta_{\mathrm{OPO}}=120.4°$. These values are in reasonable agreement with those from *FG* matrix method but are very different from solid-state geometry, indicating strong perturbations in the potassium chloride crystal. The *FG* results are slightly preferred as they are from force constants determined from experimental frequencies.

This work represents the first spectral observation of gas phase PO_2^-. PO_2^- is found out to be a very stable gas phase anion having a large electron affinity, 3.42±0.01 eV. The anion geometry is determined to be: $r_{\mathrm{PO}}=1.50\pm0.01$ Å, $\theta_{\mathrm{OPO}}=120.0\pm0.1°$. MP2 level *ab initio* calculations on PO_2 and PO_2^- based on different basis sets have been performed as comparisons. They are consistent with previous experimental work done by other groups and the one reported in this Note.

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