NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF P_2^-

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We have recorded the photoelectron spectrum of P_2^- using a Penning ion source and a negative ion photoelectron spectrometer. The adiabatic electron affinity of P_2 is determined to be 0.589 ± 0.025 eV. The negative ion parameters determined in this work are: $\omega_e''(P_2^-) = 640 \pm 50$ cm^{-1}, $R_e''(P_2^-) = 1.979 \pm 0.010$ Å, and $D_0(P_2^-) = 4.88 \pm 0.06$ eV.

1. Introduction

Extensive spectroscopic data is available about the P_2 molecule [1]. By contrast relatively little information is available about its negative ion, P_2^-. This ion appears to have first been observed mass spectrometrically by Dukel'skii and Zanberg [2] in 1952. Carette and Kerwin [3] generated P_2^- by dissociative electron attachment to P_4 in 1961. From their work they were able to give an estimate of 0.3 ± 0.5 eV for the electron affinity of P_2. Later, the appearance potential and ion translational energy measurements of Bennett, Margrave and Franklin [4] gave an electron affinity for P_2 of 0.24 ± 0.23 eV. A low-resolution, tunable-frequency threshold photodetachment experiment on P_2^- was conducted by Feldmann, Rackwitz, Kaiser and Heinicke [5] using a Penning source to generate P_2^-. They observed a broad rise in the photodetachment cross section with little discernible structure. Upon assuming that vibrationally excited P_2^- ions were not present, they were able to provide an upper limit to the electron affinity of P_2 of 0.65 eV from the extrapolated threshold behavior of their spectrum. Here, we report the recording of the photodetachment spectrum of P_2^- by negative ion photoelectron spectroscopy. We obtain a highly structured photoelectron spectrum for P_2^- from which the adiabatic electron affinity of P_2 and the spectroscopic constants B_e'' and ω_e'' for the P_2^- ion are determined. Using these data, we also calculate R_e'' and D_0 for P_2^-.

2. Experimental

In negative ion photoelectron spectroscopy a mass-selected negative ion beam is crossed with a fixed-frequency laser beam, and the resulting photodetached electrons are subjected to energy analysis. Our apparatus, which has been described previously [6], employs a Wien velocity filter for mass selection, an argon ion laser operated intra-cavity in the ion–photon interaction region, and a magnetically shielded, hemispherical electron energy analyzer. The ion source used in this work was a cold-cathode Penning discharge source of the type originally developed by Heinicke et al. [7]. This source consists of a cylindrical anode, two disc cathodes located near opposite ends of the anode, an oven for supplying vapors to the anode, and an electromagnet for generating a magnetic field along the axis of the anode cylinder. Negative ions were extracted radially through an aperture in the side of the anode into the photoelectron spectrometer.

To generate P_2^- and other phosphorus-containing negative ions, red phosphorus was heated in the oven to ≈325°C to supply phosphorus vapor to the anode, and argon was added as the discharge support gas (nominal pressure ≈0.3 Torr). Mass spectra of the negative ions produced in this fashion showed the presence of $P_{n=1-9}^-$, PO^-, PO_2^-, PO_3^-, PH^-, and PH_2^-. Several of these species are shown in the negative ion mass spectrum presented in fig. 1.

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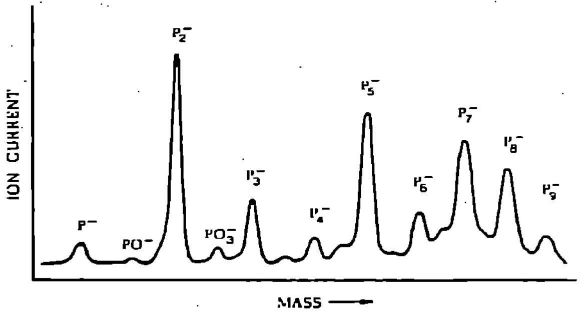

Fig. 1. A negative ion mass spectrum showing some of the phosphorus-containing species generated by the Penning ion source during these experiments.

3. Results and discussion

3.1. Data for P_2^-

Our photoelectron spectrum of P_2^-, which was recorded with 2.540 eV photons, is presented in fig. 2. The well-known atomic photodetachment transitions [8] of P− were used to calibrate our P_2^- spectra and to provide an energy scale compression factor. In order to obtain peak centers and peak heights of optimal accuracy, the raw data peaks were fit to an asymmetric Gaussian function prior to analysis.

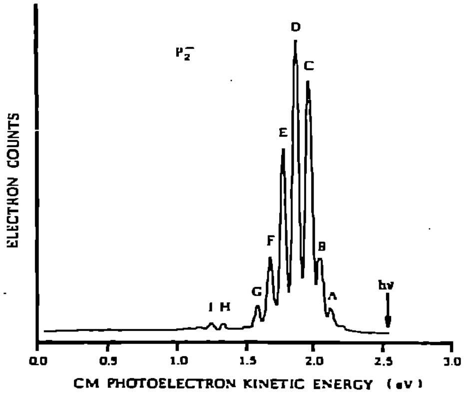

Fig. 2. The photoelectron spectrum of P_2^- presented in terms of center-of-mass electron kinetic energies. This spectrum was recorded over about 1/2 h with 0.8 × 10^{-9} A of P_2^- ion current and 150 W of 2.540 eV photons.

Table 1
Peak locations, spacing, and assignments of the P_2^- photoelectron spectrum

Peak	C.m. electron kinetic energy (eV)	Adjacent spacing (cm^{-1})	Assignment (v', v'') P_2, $^1\Sigma_g^+ \leftarrow P_2^-$, $^2\Pi_g$
A	2.110		(0,2)
		630	
B	2.032		(0,1)
		630	
C	1.954		(0,0)
		790	
D	1.856		(1,0)
		790	
E	1.758		(2,0)
		790	
F	1.660		(3,0)
		770	
G	1.564		(4,0)

3.2. Spectral assignment

Table 1 presents the center-of-mass electron kinetic energies of the peak centers for peaks A through G as well as the adjacent peak spacings and our assignments. The spacing between peak couples C/D, D/E, E/F and F/G are all approximately equal to the vibrational level spacing in the X $^1\Sigma_g^+$ state of P_2 ($\Delta G_{1/2}$ = 775 cm^{-1}). The spacings between peak couples A/B and B/C, however, are smaller and are equal to 630 cm^{-1}. We assign peaks, C, D, E, F and G, respectively, as transitions from the v'' = 0, X $^2\Pi_g$ state of P_2^- to the v' = 0, 1, 2, 3 and 4 vibrational levels in the X $^1\Sigma_g^+$ state of P_2. We assign peaks A and B, respectively, to transitions from the v'' = 2 and the v'' = 1 vibrational levels of the X $^2\Pi_g$ state of P_2^- to the v' = 0, X $^1\Sigma_g^+$ state of P_2. This assignment of peaks C through G to transitions originating in the vibrational ground state of P_2^-, and of peaks A and B to transitions originating in vibrationally excited states of P_2^- is supported by the observation that while the relative intensities of peaks C through G are invariant with ion source conditions, the intensities of peaks A and B relative to peaks C through G change considerably with ion source conditions.

In order to confirm these assignments and to obtain spectroscopic parameters for P_2^-, a Franck–Condon analysis and a comparative modeling of the photoelectron spectrum was performed. When the spectrum was modeled on the assumption that peak C is the ($v' = 1, v'' = 0$) transition, the peak predicted to occur in the vicinity of peak B is found to be taller and at higher electron kinetic energy than it is actually observed to be. When, however, the spectrum is modeled on the assumption that peak C is the (0,0) transition, good agreement is obtained with the observed spectrum. Negative ion potential parameters for P_2^- obtained from the spectrum and the modeling process are $\omega_e'' = 640 \pm 50$ cm^{-1}, $B_e'' = 0.2776 \pm 0.0028$ cm^{-1}, and therefore $R_e'' = 1.979 \pm 0.010$ Å. The longer R_e and the lower ω_e which we find for P_2^- as compared to P_2 are expected because of the antibonding character of the excess electron in P_2^-.

The relatively small peaks, H and I, as well as other low signal peaks which we occasionally observe at still lower electron kinetic energies, do not appear to be P_2^- transitions. P_2 does not possess low-lying electronic states that could account for any of these peaks [1]. These features are probably due to the photodetachment of "impurity" ions with masses close to that of P_2^- which have "leaked" into the ion–photon interaction region at our available mass resolution. The PO_2^- ion seems an unlikely possibility as an interferent ion because the electron affinity of PO_2 is known to be greater than 3 eV [9,10]. The P_2H^-, $P_2H_2^-$ and $P_2H_3^-$ ions, on the other hand, have been observed previously in Penning sources [11] and are probably more reasonable candidates.

3.3. Ion vibrational temperatures

In an effort to investigate the vibrational temperature of molecular negative ions produced in Penning sources, we recorded photoelectron spectra of P_2^- and O_2^- under a variety of Penning source operating conditions. (The photoelectron spectrum of O_2^-, generated in a hot-cathode ion (Branscomb) source, is well understood [12].) Rough temperatures for the various hot-band peaks were calculated from the Boltzmann distribution law by comparing the intensities of individual hot-band peaks with the intensity of their corresponding (0,0) peak and scaling appropriately for Franck–Condon factors. From such arrays of P_2^- and O_2^- "temperatures", we found that the population distributions were decidedly non-Boltzmann with the higher vibrational states of the ions exhibiting the higher "temperatures". We also found that the vibrational "temperatures" of these ions were strongly dependent on source conditions with higher relative source pressures correlating to lower vibrational "temperatures". Using "temperatures" calculated from the ratios of (0,1) to (0,0) peak intensities, we obtained vibrational "temperatures" for O_2^- ions ranging from ≈900 to 1600 K as source pressure was varied and those for P_2^- ions ranging with source pressure from ≈600 to 1400 K. Even though absolute source pressures were difficult to measure, these "temperatures" continued to increase as the source pressure was lowered still further. The "temperature", calculated by this procedure, for the P_2^- spectrum presented in fig. 2 was ≈700 K. Its best fit "temperature" was nearer 600 K.

3.4. Electron affinity of P_2

The adiabatic electron affinity of P_2 was calculated from

$$\mathrm{EA}(P_2) = \mathrm{EA}(P) + \gamma[\Omega(P^-) - \Omega(P_2^-)] + mW[1/M(P) - 1/M(P_2)], \qquad (1)$$

where EA(P) is the electron affinity of phosphorus, γ is the energy scale compression factor, $\Omega(P^-)$ is the laboratory electron kinetic energy position for the P, $^4S_{3/2} \leftarrow P^-$, $^3P_2$ transition, $\Omega(P_2^-)$ is the laboratory electron energy for the (0,0) transition in the P_2^- spectrum (peak C), m is the mass of an electron, W is the beam energy, and $M(P)$ and $M(P_2)$ are the respective masses of P and P_2. Making these determinations in this manner relative to a calibrant ion with a known electron affinity compensates for any contact potential corrections, and the last term in this equation provides a kinematic correction from laboratory electron energies to center-of-mass electron kinetic energies. The value of $\mathrm{EA}(P_2)$ determined from this equation was 0.586 ± 0.009 eV where the uncertainty is the experimental uncertainty. This value was then corrected for the effects of hot-band pulling, rotational-state populations, and spin–orbit splitting in the $^2\Pi_g$ state of P_2^-. Transitions from excited vibrational states of P_2^-, which add asymmetrically to the height of peak C, shift its location by 3 meV, thus adding a correction of −3 meV to the electron affinity. To make a rotational correction we supposed that the rotational state distribution in the negative ion is at least somewhat approximated by a Boltzmann distribution, and that the rotational temperature of the ion is roughly equal to the vibrational temperature of 700 K mentioned earlier. For this rotational temperature the most prevalent rotational state in the negative ion should be $J''(\max) = 29.1$. An approximate rotational energy correction is then given by [12]:

$$(B_e'' - B_e')J''(\max)[J''(\max) + 1], \qquad (2)$$

where B_e'' and B_e' are the rotational constants of the ground electronic states of P_2^- and P_2, respectively. This correction is −3 meV. The spin–orbit splitting correction for P_2^- is more difficult to estimate. Modeling peak C in our spectrum with several different magnitudes of this splitting showed that a spin–orbit splitting of ≈300 cm^{-1} would cause a visible peak asymmetry that we do not observe. Since the maximum shift in the peak location due to a spin–orbit splitting of between 100 and 300 cm^{-1} occurs in the middle of this range and is ≈9 meV, we have chosen to employ a spin–orbit correction of +9 meV. The combination of all these corrections and uncertainties gives a final value for the adiabatic electron affinity of P_2 of 0.589 ± 0.025 eV. The positive electron affinities of P and P_2 compared with the non-positive electron affinities of N and N_2 emphasizes the often noted electronic differences between phosphorus and nitrogen [13].

3.5. Bond dissociation energy of P_2^-

Given the electron affinities of P and P_2 and the dissociation energy of P_2, the dissociation energy of P_2^- can be calculated from a thermochemical cycle. Using EA(P) = 0.7464 eV [8,14] and $D_0(P_2)$= 5.033 eV [1,15] we obtain 4.88 ± 0.06 eV for the dissociation energy of P_2^- into the ground state of P and P^-.

4. Summary

By applying negative ion photoelectron spectroscopy to the study of P_2^-, we have determined the electron affinity of P_2 and the spectroscopic constants for P_2^-. We find EA(P_2) = 0.589 ± 0.025 eV, $D_0(P_2^-)$ = 4.88 ± 0.06 eV, $\omega_e''(P_2^-)$ = 640 ± 50 cm^{-1}, $B_e''(P_2^-)$ = 0.2776 ± 0.0028 cm^{-1} and $R_e''(P_2^-)$ = 1.979 ± 0.010 Å.

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