

Laser photoelectron spectrometry of PO^- , PH^- , and PH_2^- *

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Fixed-frequency laser photoelectron spectrometry has been used to study the ions PO^- , PH^- , and PH_2^- . The electron affinities of PO , PH , and PH_2 were determined to be (1.092 ± 0.010) , (1.028 ± 0.010) , and (1.271 ± 0.010) eV, respectively. A bound excited state ($\bar{a}^1\Delta$) of PO^- was observed with a term energy of (0.556 ± 0.010) eV. The vibrational frequencies of $\bar{X}^3\Sigma^- \text{PO}^-$, $\bar{a}^1\Delta \text{PO}^-$, $\bar{X}^2\Pi \text{PH}^-$, and $^2B_1 \text{PH}_2^-$ were found to be (1000 ± 70) , (1020 ± 80) , (2230 ± 100) , and (2270 ± 80) cm^{-1} , respectively. A Franck-Condon factor analysis of the PO^- and PH^- spectra gave the equilibrium internuclear separations $r_e(\bar{X}^3\Sigma^- \text{PO}^-) = (1.540 \pm 0.010)$ Å and $1.414 \geq r_e(\bar{X}^2\Pi \text{PH}^-) \geq 1.400$ Å. The geometries of $^1A_1 \text{PH}_2^-$ and $^2B_1 \text{PH}_2^-$ were found to be nearly the same. The PH^- photoelectron spectrum includes transitions to the $\text{PH} \bar{X}^3\Sigma^-$ and $\bar{a}^1\Delta$ states, allowing determination of the intercombination separation of (0.950 ± 0.010) eV.

I. INTRODUCTION

Fixed-frequency laser photoelectron spectrometry of negative ions¹⁻⁶ has proved to be a valuable technique for determining electron affinities (EA), term energies, and vibrational energies of molecular neutrals and negative ions. This paper reports the application of this technique to PO^- , PH^- , and PH_2^- .

The $\dots \pi^2$ ground electronic configuration of PO^- gives rise to low-lying $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ electronic states. By analogy with the isoelectronic molecules SO^2 ,⁷ and PF ,⁷ the energy ordering is undoubtedly $\bar{X}^3\Sigma^- < \bar{a}^1\Delta < \bar{b}^1\Sigma^+$. Removal of a π electron leaves PO in the $^2\Pi_r$ ground state, which has been studied spectroscopically in great detail.⁸ The electron affinity of PO , as well as the term energies, vibrational frequencies, and equilibrium internuclear separations of the low-lying PO^- states, have not previously been studied experimentally. Our experiment describes the $\bar{X}^3\Sigma^-$ and $\bar{a}^1\Delta$ states of PO^- , but does not provide a definitive detection of the $\bar{b}^1\Sigma^+$ state.

By analogy to NH , which has the same $\dots \sigma^2\pi^2$ ground configuration of valence electrons, PH is expected to have low-lying $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ electronic states. The $\bar{X}^3\Sigma^-$ ground state of PH has been studied spectroscopically.⁹ Theoretical calculations have determined the energy ordering $\bar{X}^3\Sigma^- < \bar{a}^1\Delta < \bar{b}^1\Sigma^+$ (like NH), predicting an $(\bar{X}^3\Sigma^- - \bar{a}^1\Delta)$ intercombination energy splitting¹⁰ of ~ 0.95 eV, as well as an electron affinity¹¹ of ~ 0.93 eV. The spectra shown here determine $\text{EA}(\text{PH})$ and the $(\bar{X}^3\Sigma^- - \bar{a}^1\Delta)$ splitting, as well as the vibrational frequency and internuclear separation for the $\bar{X}^2\Pi \text{PH}^-$ ion.

Previous photodetachment experiments¹² have determined the electron affinity of PH_2 to be 1.25 ± 0.03 eV. Our results, $\text{EA}(\text{PH}_2) = 1.271 \pm 0.010$ eV, agrees well with the previous value. In addition, the ν_1 symmetric stretching frequency of PH_2 is measured, and the geometry of the 1A_1 ground state of PH_2^- is shown to be very similar to the geometry of the 2B_1 ground state of the neutral.

II. EXPERIMENTAL

The photodetachment apparatus used in this work has been described previously.¹ Phosphine (PH_3) is burned with N_2O in a low pressure discharge source to produce beams of PO^- , PH^- , and PH_2^- ions. In some runs, PO^- ions have been produced by burning phosphorous and N_2O in a higher pressure, higher temperature Colutron ion source. The ions are accelerated to 680 V and mass analyzed by a Wein filter. Currents of mass selected ions range from 0.5–2.0 nA. The ion beam is crossed in the interaction region by the intracavity beam of a 4880 Å (2.540 eV) cw argon-ion laser beam, and electrons ejected into the acceptance angle of a hemispherical electrostatic monochromator are energy analyzed. The energy resolution of the monochromator (~ 60 mV FWHM) is not sufficient to resolve individual rotational transitions, and the many rotational components of a particular vibronic transition are smoothed into a very nearly Gaussian-shaped peak 90–110 mV in width. Peaks in the PO^- , PH^- , and PH_2^- spectra are fit with Gaussians to determine peak centers to ~ 3 mV and relative integrated intensities to $\sim 5\%$.

It is well known^{1,3} that the intensity of photodetached electrons at a given electron energy depends on the angle (θ) between the direction of the laser polarization and the direction of electron ejection in the following way for electric dipole transitions and linearly polarized light:

$$I(\theta) = (\sigma/4\pi)[1 + \beta P_2(\cos\theta)],$$

where σ is the average detachment cross section, β is the anisotropy parameter, and $P_2(X)$ is the second Legendre polynomial. For the spectra reported here, the polarization of the argon-ion laser is oriented with respect to the direction of electrons entering the energy analyzer such that $P_2(\cos\theta) \equiv 0$. The peak intensities in our spectra are thus proportional to the average detachment cross section.

The detachment energies of peaks in the spectra have been determined using simultaneously produced O^- as a calibration ion and the expression^{1,3}

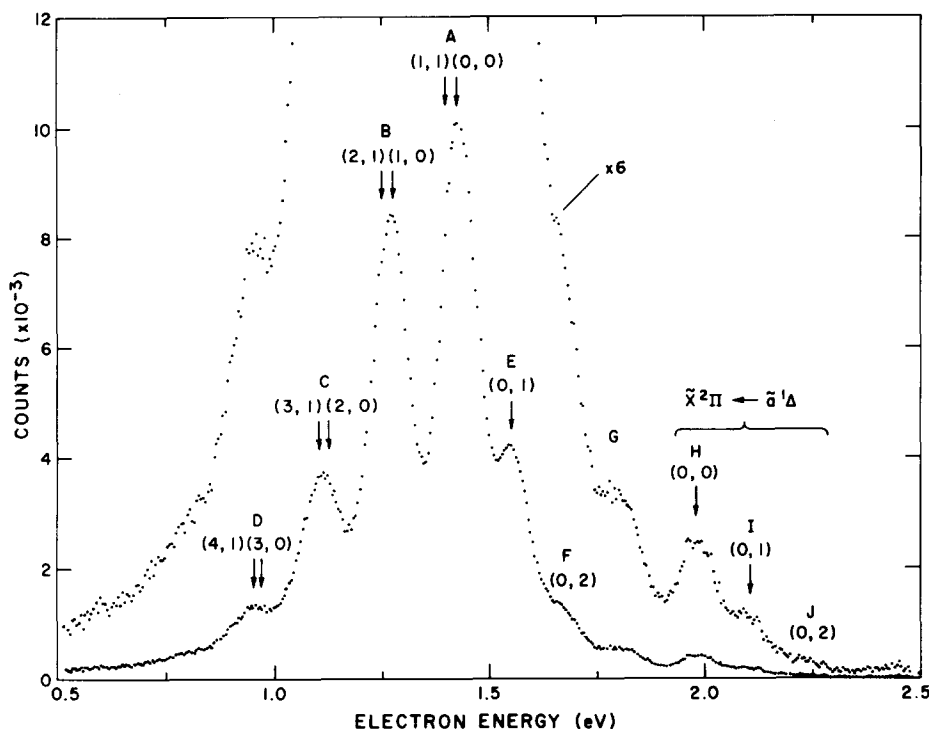


FIG. 1. Photoelectron spectrum of PO⁻. Detachment peaks H-J are assigned to the $\bar{X}^2\Pi$ PO⁻ ← $\bar{a}^1\Delta$ PO⁻ system. The other peaks are associated with the $\bar{X}^2\Pi$ PO⁻ ← $\bar{X}^3\Sigma^-$ PO⁻ system. Vibrational states are denoted by (v' , v''), where v' and v'' are the vibrational quantum numbers for PO and PO⁻, respectively.

$$E_x = EA(O) + 1.022(\Omega_{O^-} - \Omega_{X^-}) + mW(1/M_O - 1/M_X); \quad (1)$$

$EA(O) = 1.465$ eV is the "effective"¹³ electron affinity of the oxygen atom, determined from the center of the O⁻ photodetachment peak; $(\Omega_{O^-} - \Omega_{X^-})$ is the laboratory energy difference between the O⁻ peak center and a particular X⁻ peak center (where X⁻ is PO⁻, PH⁻, or PH₂⁻). The factor 1.022 is an energy scale compression factor described previously^{3,14} and is determined in our work by calibrating an NO⁻ photodetachment spectrum against the known values for NO vibrational splittings.¹ The final term in Eq. (1) accounts for the fact that the electrons we detect must be backscattered (in the c.m. frame) into the energy analyzer and thus have a c.m. component of energy perpendicular to the analyzer axis¹; W is the kinetic energy of the ion beam (680 eV), and m , M_O , and M_X are the masses of electron, oxygen atom, and molecule X, respectively.

III. PO⁻

A. Spectrum

Figure 1 shows the photodetachment spectrum of PO⁻. Peaks A-D are primarily due to transitions from the ($\bar{X}^3\Sigma^-$, $v'' = 0$) ground state of PO⁻ to the ($\bar{X}^2\Pi$, $v' = 0-3$) levels of PO. The strong off-diagonal peaks B-D reflect a significant change in equilibrium internuclear separation between PO⁻ and PO and are analyzed below to obtain a value for $r_e''(\bar{X}^3\Sigma^- \text{ PO}^-)$. The measured energy differences between adjacent peaks are slightly larger than predicted from the well-known⁹ values of $\bar{\omega}_e$ and $\bar{\omega}_e x_e$ for $\bar{X}^2\Pi$ PO. This is because transitions beginning from the $v'' = 1$ level of PO⁻ contribute significantly to peaks B-D, broadening them and shifting the peak centers to slightly lower electron energies. For example, peak B is the unresolved combination of the

(1, 0) and (2, 1) transitions. (The numbers in parentheses refer to the vibrational quantum numbers of neutral and ion, respectively.) Because of the (2, 1) component peak B is slightly broader than peak A, which is almost entirely (> 94%) due to the (0, 0) transition, and the peak center occurs at an electron energy slightly lower than expected for a purely (1, 0) transition. The calculated positions of relevant transitions beginning from PO⁻ ($v'' = 0$ and 1) are indicated by vertical arrows in Fig. 1, assuming the center of peak A is the center of the PO($\bar{X}^2\Pi$, $v' = 0$) ← PO⁻($\bar{X}^3\Sigma^-$, $v'' = 0$) transition, and utilizing the PO⁻ vibrational frequency determined below. The assumption that peak A is almost entirely (> 94%) due to the (0, 0) transition is justified in Sec. IIIB on the basis of a very small Franck-Condon factor for the (1, 1) transition.

Peaks E and F are primarily due to the transitions (0, 1) and (0, 2), arising from vibrationally excited levels of PO⁻, which are produced by the hot ion source. These peaks change in intensity relative to the (0, 0) peak from run to run and are clearly hot bands. The energy separation between A and E gives a value for $\bar{\nu}_{10}(\bar{X}^3\Sigma^- \text{ PO}^-) = 1000 \pm 70 \text{ cm}^{-1}$.

Peaks H-J, also hot bands, do not fit the smooth progression in $v''(\bar{X}^3\Sigma^- \text{ PO}^-)$ either in energy spacing or relative intensity. They originate from a bound, electronically excited state of PO⁻, undoubtedly the $\bar{a}^1\Delta$ state. The measured energy difference between peaks A and H is ~ 0.55 eV, somewhat smaller than the ($\bar{X}^3\Sigma^- - \bar{a}^1\Delta$) splittings in the isoelectronic molecules SO ($T_e = 0.734$ eV)² and PF ($T_e = 0.879$ eV),⁷ but still quite reasonable. Peaks I and J are vibrational hot bands, originating from the $v'' = 1$ and 2 levels of $\bar{a}^1\Delta$ PO⁻. The H-I spacing gives a value for $\bar{\nu}_{10}(\bar{a}^1\Delta \text{ PO}^-) = 1020 \pm 80 \text{ cm}^{-1}$. The similar values for $\bar{\nu}_{10}(\bar{X}^3\Sigma^- \text{ PO}^-)$

and $\bar{\nu}_{10}(\bar{a}^1\Delta \text{PO}^-)$ are quite reasonable, considering that both states, as well as a possible $\bar{b}^1\Sigma^+$ state, arise from the same $\dots(\pi)^4(\sigma)^2(\pi)^2$ ground electronic configuration. In the isoelectronic molecules $\text{SO}^{2,7}$ and PF^7 , the vibrational frequencies, as well as the equilibrium internuclear distances, are virtually identical ($\pm 20 \text{ cm}^{-1}$, $\pm 0.01 \text{ \AA}$) for the $\bar{X}^3\Sigma^-$, $\bar{a}^1\Delta$, and $\bar{b}^1\Sigma^+$ states of a particular molecule.

Peak G is considerably broader than the two adjacent peaks and is in fact an unresolved combination of the (0,3) hot band in the $\bar{X}^2\Pi - \bar{X}^3\Sigma^-$ system and the (1,0) transition in the $\bar{X}^2\Pi - \bar{a}^1\Delta$ system. One can subtract from peak G a computer-simulated ($\bar{X}^2\Pi$, $v' = 1 - \bar{a}^1\Delta$, $v'' = 0$) peak with the same width as peak H, spaced from peak H by $\bar{\nu}_{10}(\bar{X}^2\Pi \text{PO})$, and with an intensity in the same ratio to the intensity of peak H as peak B is to peak A. The remaining peak has an energy spacing, width, and intensity which fit very well as the (0,3) member of the $\bar{X}^2\Pi - \bar{X}^3\Sigma^-$ hot band sequence. This procedure for estimating the intensity of the ($\bar{X}^2\Pi$, $v' = 1 - \bar{a}^1\Delta$, $v'' = 0$) transition was adopted because the equilibrium internuclear separations for the $\bar{X}^3\Sigma^-$ and $\bar{a}^1\Delta \text{PO}^-$ states, and thus the Franck-Condon factors for transitions to $\bar{X}^2\Pi \text{PO}$, should be nearly identical.

No strong evidence exists for transitions originating from a $\bar{b}^1\Sigma^+$ PO^- state, although the state is bound and low lying in SO^2 [$T_e(\bar{b}^1\Sigma^+) = 1.303 \text{ eV}$] and PF^7 [$T_e(\bar{b}^1\Sigma^+) = 1.656 \text{ eV}$]. The $\bar{b}^1\Sigma^+$ state may be bound in PO^- , but may not be produced in significant amounts in the ion source. There is some evidence of a very small peak in the detachment spectrum at an electron energy of 2.40–2.45 eV, but there was not sufficient signal to identify the transition conclusively.

No features in the PO^- spectrum involve transitions to electronically excited states of PO. The $\bar{A}^2\Sigma^+$ state of PO lies 3.81 eV⁷ above the ground state, and quartet states, although unknown, must be even more energetic; these states are thus not accessible with our present 2.54 eV photon energy.

B. Determination of $r_e(\bar{X}^3\Sigma^- \text{PO}^-)$

The relative intensities of the (v' , v'') transition can be utilized, via a harmonic-oscillator Franck-Condon factor analysis, to determine the negative ion r_e'' , in the following manner: The experimentally determined intensity of a particular (v' , v'') transition relative to another transition is given by the product of an electron transition matrix element, a Franck-Condon factor, and the (possibly) energy-dependent transmission function of the electron energy analyzer. The first and last terms are not precisely known, but can usually be shown to be small over the relevant energy range, generally less than 0.5 eV. The ratios of Franck-Condon factors depend strongly on $|r_e' - r_e''|$ and less strongly on ω_e'' and ω_e' . Normally we know ω_e'' , and ω_e' sufficiently well that calculated relative transition intensities are not affected by possible uncertainties in these quantities. One can then vary $|r_e' - r_e''|$ in a harmonic oscillator Franck-Condon factor calculation until a best fit to the experimental intensities is obtained. Such a

fit is sensitive to $|r_e' - r_e''|$ changes of 0.001 \AA , but the major uncertainty in the $|r_e' - r_e''|$ determination lies not in the fitting procedure, but in the fact that one has to allow for possible variations of electron analyzer transmission and electronic matrix elements over the energy range of the analysis. For this reason it is generally sufficient to use simple harmonic oscillator vibrational wavefunctions in the analysis. Once $|r_e' - r_e''|$ has been determined in this fashion, knowledge of r_e' leads to two possible values for r_e'' . Independent arguments must be utilized to decide which value is proper. This procedure, which has been described in more detail previously,¹ is employed in the following analysis.

The intensities of the off-diagonal peaks B–D in Fig. 1 show that $r_e''(\bar{X}^3\Sigma^- \text{PO}^-)$ is substantially different from $r_e'(\bar{X}^2\Pi \text{PO})$. Approximating $\omega_e(\bar{X}^3\Sigma^- \text{PO}^-)$ by the experimentally determined value of $\bar{\nu}_{10} = 1000 \text{ cm}^{-1}$ and utilizing the known values of r_e and PF , or for PO , one predicts from Badger's Rule^{15,16} that $r_e''(\text{PO}^-) \approx 1.545 \text{ \AA}$. The result, $r_e''(\text{PO}^-) > r_e'(\text{PO})$, as well as $\omega_e''(\text{PO}^-) < \omega_e'(\text{PO})$, is consistent with the picture of the extra PO^- electron being in an essentially antibonding π molecular orbital. The analogous orbitals in O_2 and S_2 (both isoelectronic with PO^- in valence electrons) are $p\pi_g$ antibonding orbitals.

With the knowledge that $r_e''(\text{PO}^-) > r_e'(\text{PO})$ and the known values⁸ $\bar{\nu}_{10}(\bar{X}^2\Pi \text{PO}) = 1220.1 \text{ cm}^{-1}$, $r_e'(\bar{X}^2\Pi \text{PO}) = 1.476 \text{ \AA}$, and $\bar{\nu}_{10}'(\bar{X}^3\Sigma^- \text{PO}^-) = 1000 \pm 70 \text{ cm}^{-1}$, a precise value for $r_e''(\bar{X}^3\Sigma^- \text{PO}^-)$ can be determined by calculating Franck-Condon factors to fit the observed spectrum. Since the vibrational levels of PO, and presumably PO^- by analogy with SO and PF, are very harmonic ($\omega_e x_e = 4.5\text{--}6.5 \text{ cm}^{-1}$),^{7,8} harmonic oscillator wavefunctions were used for PO and PO^- vibrational levels. Franck-Condon factors were calculated for the (v' , 0) and (v' , 1) transitions for $v' = 0\text{--}4$. The intensity of each of the peaks A–D was assumed to be the sum of intensities contributed by two unresolvable transitions, (v' , 0) and ($v' + 1$, 1), with $v' = 0\text{--}3$ for peaks A–D, respectively. Peak E was initially assumed to be entirely due to the (0,1) hot band. The relative intensities of peaks A and E and the calculated Franck-Condon factors for the (0,0), (1,0), and (0,1) transitions allow one to determine the relative populations of $\text{PO}^-(v'' = 0, 1)$. The intensities of peaks B–D are then calculated using these relative populations and the relevant Franck-Condon factors.

The calculated Franck-Condon factors, calculated peak intensities, and experimental peak intensities for several values of $r_e''(\bar{X}^3\Sigma^- \text{PO}^-)$ appear in Table I. The value of r_e'' which best reproduces the experimental spectrum is $r_e'' = 1.538 \pm 0.010 \text{ \AA}$. As one sees in Table I, the intensity of peak A is essentially (>94%) due to the (0,0) transition because the (1,1) Franck-Condon factor is very small. The same is presumably true for peak H, the (0,0) transition of the $\bar{X}^2\Pi - \bar{a}^1\Delta$ system, because $r_e''(\bar{a}^1\Delta \text{PO}^-)$ should be nearly identical to $r_e''(\bar{X}^3\Sigma^- \text{PO}^-)$. This makes the determination of EA, $T_0(\bar{a}^1\Delta)$, and subsequent rotational corrections to peaks A and H less complicated.

TABLE I. Experimental and calculated intensities for PO⁻ photodetachment transitions.

Transition (<i>v'</i> , <i>v''</i>)	Calculated Franck-Condon factor ^a <i>r''_e</i> ($\tilde{X}^3\Sigma^-$ PO ⁻)			Experimental peak intensity
	1.530 Å	1.538 Å	1.550 Å	
(0, 0)	1.000	1.000	1.000	1.00
(1, 0)	0.462	0.609	0.867	0.84 ± 0.05
(2, 0)	0.153	0.244	0.459	0.40 ± 0.03
(3, 0)	0.041	0.079	0.187	0.16 ^{+0.04} -0.02
(0, 1)	0.553	0.728	1.037	0.39 ± 0.03
(1, 1)	0.242	0.110	0.002	
(2, 1)	0.446	0.461	0.388	
(3, 1)	0.273	0.378	0.530	
(4, 1)	0.109	0.186	0.364	

P. E. S. peak	Calculated peak intensity ^b			Experimental peak intensity
A	1.00	1.00	1.00	1.00
B	0.70	0.82	1.01	0.84 ± 0.05
C	0.32	0.43	0.66	0.40 ± 0.03
D	0.11	0.17	0.32	0.16 ^{+0.04} -0.02
E	0.39	0.39	0.39	0.39 ± 0.03

^aRelative to (0, 0). Calculated with harmonic oscillator wavefunctions and $\bar{\nu}(\tilde{X}^2\Pi$ PO⁻) = 2276 cm⁻¹, $\bar{\nu}(\tilde{X}^3\Sigma^-$ PO⁻) = 2230 cm⁻¹, $r''_e(\tilde{X}^2\Pi$ PO⁻) = 1.422 Å. Results are relatively insensitive to changes of ± 50 cm⁻¹ in $\bar{\nu}$.

^bThis calculation assumes that only the *v''* = 0, 1 levels of $\tilde{X}^3\Sigma^-$ PO⁻ are significantly populated.

A second fit to the observed spectrum includes contributions to peaks A–E from hot bands originating at the *v''* = 2 level of PO⁻. The assumption [*v''* = 2]/[*v''* = 1] = [*v''* = 1]/[*v''* = 0] is made, the relative populations of *v''* = 0, 1, 2 are determined, and intensities for peaks A–E are calculated. Corrections to the previous fit are small, and the resulting value of $r''_e(\tilde{X}^3\Sigma^-$ PO⁻) is 1.540 ± 0.010 Å. The error bars include possible effects of a 50% change in the electronic transition moment or the electron energy analyzer transmission function over the 1–1.5 eV electron energy range covered by peaks A–D.

C. Rotational corrections

The PO($\tilde{X}^2\Pi$, *v'* = 0) – PO⁻($\tilde{X}^3\Sigma^-$, *v''* = 0) detachment peak in Fig. 1 is the unresolved composite of many individual transitions between specific rotational levels. The EA, however, is defined as the energy difference between the lowest rotational levels of ion and neutral. Since the center of the (0, 0) peak does not necessarily correspond to the transition between lowest rotational levels, a small correction must be made to the EA, as measured from the center of the (0, 0) peak.

Kasdan, Herbst, and Lineberger⁵ have described the rotational correction for the analogous case $\tilde{X}^2\Pi$ SiH – $\tilde{X}^3\Sigma^-$ SiH⁻, and this procedure is followed here for PO. Neglecting spin–spin and spin–rotation effects, the rotational levels of PO⁻($\tilde{X}^3\Sigma^-$, *v''* = 0) are given by¹⁶

$$F''(N) = B'_0 N(N+1); \quad N \geq 0, \quad (2)$$

where B'_0 is the rotational constant for PO⁻. The value $B'_0 = 0.6710$ cm⁻¹ is determined from r'_e , r''_e , and $B'_0(\tilde{X}^2\Pi$ PO⁻)⁸ = 0.7039 cm⁻¹, assuming $B'_0/B_0 = B'_e/B_e$. The rotational levels of PO($\tilde{X}^2\Pi$, *v'* = 0) are described by Hund's case (b)¹⁶ with $B'_0 = 0.7309$ cm⁻¹ and the coupling constant⁸ $A_0 = 223.92$ cm⁻¹

$$F'_2(N) = B'_0 \left\{ N^2 - 1 + \frac{1}{2} \left[4N^2 + \frac{A_0}{B'_0} (A_0 - 4) \right]^{1/2} \right\}, \quad (3)$$

$$F'_1(N) = B'_0 \left\{ (N+1)^2 - 1 - \frac{1}{2} \left[4(N+1)^2 + \frac{A_0}{B'_0} (A_0 - 4) \right]^{1/2} \right\}$$

for $N \geq 1$, where, for PO, $F'_2(N) > F'_1(N)$ for all N . The detachment energy E_c determined from the centroid of the observed photodetachment peak is assumed to be equal to the ensemble average of the energies of all $\Delta N = 0$ transitions from rotational levels of $\tilde{X}^2\Sigma^-$ PO⁻ to the centers of gravity of the spin–orbit–split rotational levels of $\tilde{X}^2\Pi$ PO. The expression relating E_c and EA is⁵

$$E_c = EA(\text{PO}) + \sum_{N=1}^{\infty} p(N) \frac{[g_1 F'_1(N) + g_2 F'_2(N)]}{g_1 + g_2} - \left[\sum_{N=1}^{\infty} p(N) F''(N) \right] - F'_1(N=1), \quad (4)$$

where $g_1 = 2N+2$ and $g_2 = 2N$ are the statistical weights of F'_1 and F'_2 , and $p(N)$ is the simple diatomic rotational partition function for PO⁻ at temperature T_R . The rotational temperature T_R is assumed to be 1000 ± 500 °K.¹⁷ The result of evaluating Eq. (4) is

$$EA(\text{PO}) = E_c - (20.8 \pm 4) \text{ meV}.$$

The final value for EA(PO), including all sources of error, is

$$EA(\text{PO}) = 1.092 \pm 0.010 \text{ eV}.$$

A similar correction can be made to the $\tilde{X}^2\Pi$ PO – $\tilde{a}^1\Delta$ PO⁻ detachment energy. By analogy with the iso-electronic molecules SO and PF, the internuclear separation should be nearly identical (± 0.005 Å) in the $\tilde{X}^3\Sigma^-$ and $\tilde{a}^1\Delta$ states of PO⁻. We therefore assume $B'_0(\tilde{a}^1\Delta$ PO⁻) = $B'_0(\tilde{X}^3\Sigma^-$ PO⁻). The rotational levels of $\tilde{a}^1\Delta$ PO⁻ are described by Hund's case (a)¹⁶

$$F''(N) = B'_0 [N(N+1) - 4]; \quad N \geq 2. \quad (5)$$

The correction to the $\tilde{X}^2\Pi$ – $\tilde{a}^1\Delta$ detachment energy may be evaluated using Eq. (4) with the following changes: The sums begin with $N=2$, and an additional term + $F''(N=2)$ must be added to the right side of the equation, reflecting the fact that the rotational energy of the lowest PO⁻ level is no longer zero. If the rotational temperature of $\tilde{a}^1\Delta$ PO⁻ is assumed equal to the rotational temperature of $\tilde{X}^3\Sigma^-$ PO⁻, the correction to the $\tilde{X}^2\Pi$ – $\tilde{a}^1\Delta$ detachment energy differs from the correction to the $\tilde{X}^2\Pi$ – $\tilde{X}^3\Sigma^-$ detachment energy by the nearly constant amount $-6B'_0 = -0.54$ mV. Thus, the energy difference between the lowest rotational levels of the $\tilde{X}^3\Sigma^-$ PO⁻ and $\tilde{a}^1\Delta$ PO⁻ states is

$$\Delta E(\tilde{X}^3\Sigma^- - \tilde{a}^1\Delta) = \Delta E_c + 0.00054 \text{ eV} = 0.556 \pm 0.010 \text{ eV},$$

where ΔE_c is the measured energy difference between the peak centers of the (0, 0) transitions for the $\tilde{X}^2\Pi$

TABLE II. Constants determined for PO, PO⁻, PH, PH⁻, and PH₂.

	EA (eV)	T ₀ ($\tilde{a}^1\Delta$) (eV)	$\bar{\nu}_{10}^a$ (cm ⁻¹)	r _e ^a (Å)
PO	1.092 ± 0.010	...	1220 ^b	1.476 ^b
PO ⁻	...	0.556 ± 0.010	1000 ± 70 1020 ± 80 ($\tilde{a}^1\Delta$)	1.540 ± 0.010
PH	1.028 ± 0.010	0.950 ± 0.010	2276 ^c	1.422 ^c
PH ⁻	2230 ± 100	1.414 ≥ r _e ≥ 1.400
PH ₂	1.271 ± 0.010	...	2270 ± 80 ($\bar{\nu}_1$)	...

^aFor ground electronic state, unless otherwise noted.

^bReference 8.

^cReference 9.

$-\tilde{X}^3\Sigma^-$ and $\tilde{X}^2\Pi - a^1\Delta$ systems. Corrections to $\Delta E(\tilde{X}^3\Sigma^- - \tilde{a}^1\Delta)$ due to differences in T_R , or B_0'' , for the $\tilde{X}^3\Sigma^-$ PO⁻ and $\tilde{a}^1\Delta$ PO⁻ states are expected to lie within the quoted error limits.

A summary of the experimentally determined constants for PO and PO⁻ appears in Table II. We are aware of only one *ab initio* calculation¹⁸ on PO and PO⁻. The result of the molecular SCF calculation $r_e(\tilde{X}^3\Sigma^- \text{ PO}^-) = 1.513 \text{ \AA}$ compares with our experimental value $r_e = 1.540 \pm 0.010 \text{ \AA}$. The calculated energy of $\tilde{X}^3\Sigma^- \text{ PO}^-$ relative to $\tilde{X}^2\Pi \text{ PO}$, is $\sim 1.67 \text{ eV}$ too high, as one might expect from a simple SCF calculation.

IV. PH⁻

A. Spectrum

Figure 2 shows the photodetachment spectrum of PH⁻. Two strong detachment peaks are apparent with an energy separation of $\sim 0.95 \text{ eV}$. They are assigned to the transitions $\text{PH}(\tilde{X}^3\Sigma^-, v' = 0)$, $\text{PH}(\tilde{a}^1\Delta, v' = 0) \rightarrow \text{PH}^-(\tilde{X}^2\Pi, v'' = 0)$. The energy separation compares well with cal-

culated values¹⁰ for the $\text{PH}(\tilde{X}^3\Sigma^- - \tilde{a}^1\Delta)$ splitting of $0.95 \pm 0.10 \text{ eV}$. Transitions to the $\tilde{A}^3\Pi$ state of PH ($T_0 = 3.66 \text{ eV}$)⁹ are not energetically possible, and transitions to a $\tilde{b}^1\Sigma^+$ state are either not energetically possible with 2.54 eV photons or produce electrons below the analyzer cutoff energy ($\sim 0.3 \text{ eV}$). The two strong peaks do not change in relative intensity as ion source conditions change and do not originate from electronically excited states of PH⁻, which by analogy with isoelectronic SH⁻ must lie several eV above the ground state.

A (0, 1) hot band at electron energy $\sim 1.80 \text{ eV}$, associated with the $\tilde{X}^3\Sigma^- \rightarrow \tilde{X}^2\Pi$ system, gives $\bar{\nu}_{10}(\tilde{X}^2\Pi \text{ PH}^-) = 2230 \pm 100 \text{ cm}^{-1}$. This compares with the spectroscopically observed value⁹ for neutral PH, $\bar{\nu}_{10}(\tilde{X}^3\Sigma^- \text{ PH}) = 2276 \text{ cm}^{-1}$. A second small peak at an electron energy of $1.260 \pm 0.015 \text{ eV}$ may be due partly to the (1, 0) transition of the $\tilde{X}^3\Sigma^- \rightarrow \tilde{X}^2\Pi$ system; however, a strong PH₂⁻ photodetachment peak falls at nearly the same electron energy (see Fig. 3). The electron energy of the peak center is intermediate between the energy expected for the PH transition (1.244 eV) and that expected for the PH₂ peak (1.273 eV). The possibility of a very small fraction of PH₂⁻ in the PH⁻ ion beam precludes assigning the 1.260 eV peak entirely to the PH⁻(1, 0) transition.

B. Determination of $r_e(\tilde{X}^2\Pi \text{ PH}^-)$

The nearly diagonal nature of the $\tilde{X}^3\Sigma^- \rightarrow \tilde{X}^2\Pi$ detachment spectrum and the similarity of $\bar{\nu}_{10}(\tilde{X}^2\Pi \text{ PH}^-)$ and $\bar{\nu}_{10}(\tilde{X}^3\Sigma^- \text{ PH})$ imply that $r_e''(\tilde{X}^2\Pi \text{ PH}^-)$ and $r_e'(\tilde{X}^3\Sigma^- \text{ PH})$ are nearly the same. The intensities of the (0, 1) transition and of the peak due partially to the (1, 0) transition of the $\tilde{X}^3\Sigma^- \rightarrow \tilde{X}^2\Pi$ system allow limits to be placed on the value of $r_e''(\tilde{X}^2\Pi \text{ PH}^-)$. Harmonic oscillator

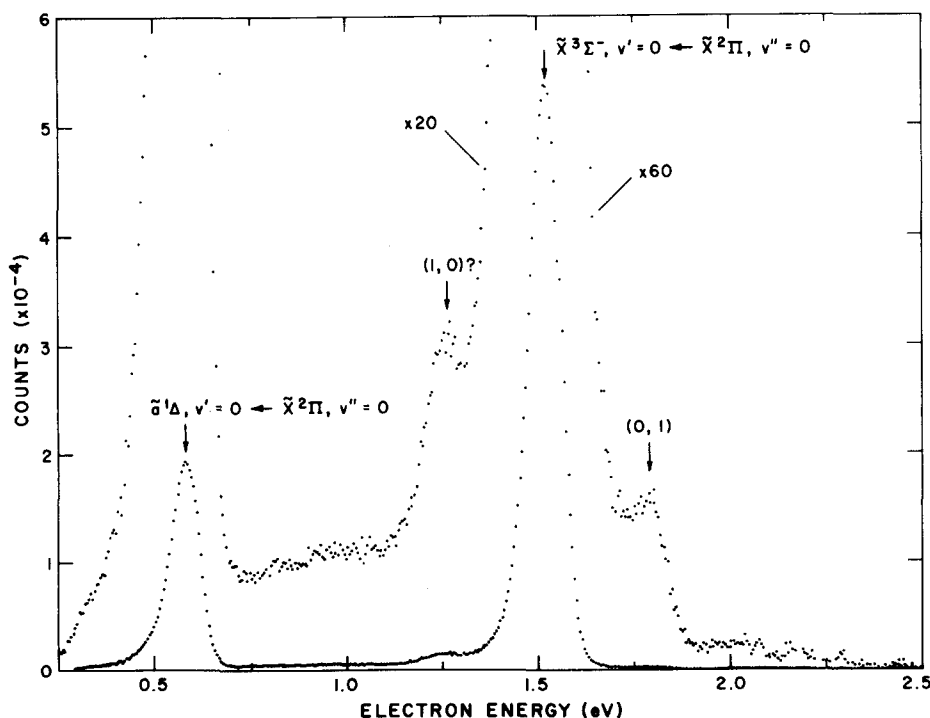


FIG. 2. Photoelectron spectrum of PH⁻. Nondiagonal transitions associated with the $\tilde{X}^3\Sigma^- \rightarrow \tilde{X}^2\Pi$ system are labeled (v', v''), where v' and v'' are the vibrational quantum numbers of PH and PH⁻, respectively. The peak labeled (1, 0) may be due partially to a PH₂⁻ photodetachment transition.

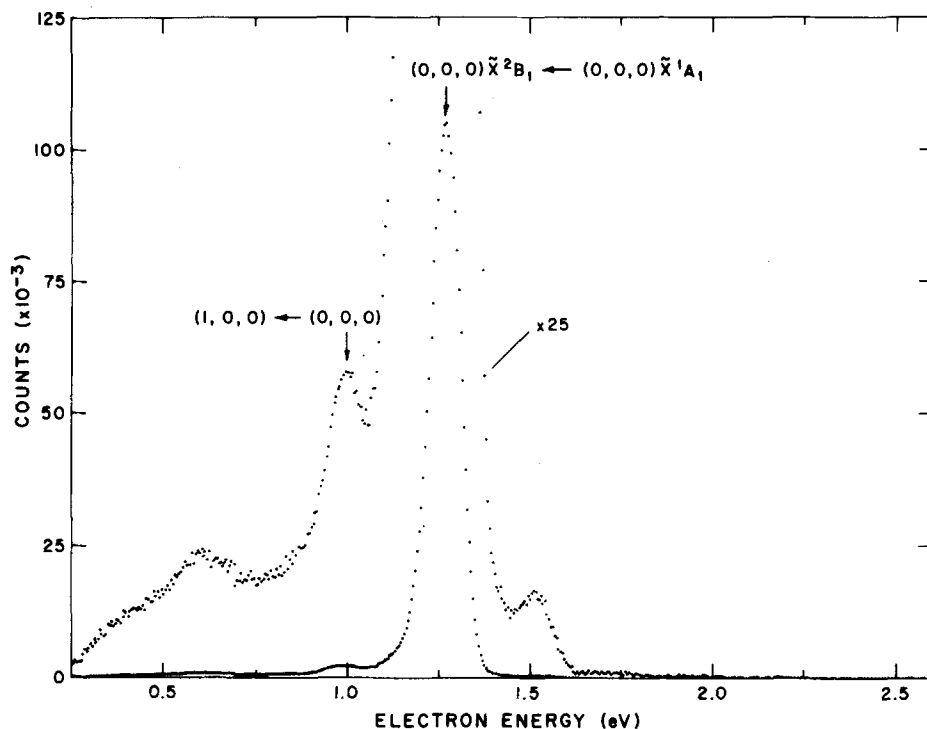


FIG. 3. Photoelectron spectrum of PH_2^- . The numbers in parentheses refer to the vibrational quantum numbers ν_1, ν_2, ν_3 . Unlabeled features may be due in part to PH^- photodetachment transitions. The dropoff at ~ 0.3 eV is due to the electron energy analyzer cutoff and has no significance.

wavefunctions are used to calculate relative Franck-Condon factors for the (1, 0), (0, 0), and (0, 1) transitions, utilizing the known parameters⁹ $r_e'(\tilde{X}^3\Sigma^- \text{PH}) = 1.422 \text{ \AA}$, $\bar{\nu}_{10}'(\tilde{X}^3\Sigma^- \text{PH}) = 2276 \text{ cm}^{-1}$, and $\bar{\nu}_{10}'(\tilde{X}^2\Pi \text{PH}^-) = 2230 \pm 100 \text{ cm}^{-1}$, and allowing r_e'' to vary. With the assumption $[\text{PH}^-, v'' = 1] \ll [\text{PH}^-, v'' = 0]$ the experimental relative intensities of the (0, 1) and (0, 0) peaks determine the limit $|r_e'' - 1.422 \text{ \AA}| \geq 0.008 \text{ \AA}$. With the assumption that the contribution of the (1, 0) transition to the 1.260 eV peak is $\leq 100\%$, the relative intensities of this peak and the (0, 0) peak place the limit $|r_e'' - 1.422 \text{ \AA}| \leq 0.022 \text{ \AA}$. The final conclusion is

$$0.022 \geq |r_e''(\tilde{X}^2\Pi \text{PH}^-) - 1.422 \text{ \AA}| \geq 0.008 \text{ \AA}.$$

The sign of Δr_e is not determined by the Franck-Condon factor analysis. For the molecules SH^+ (isoelectronic with PH) and SH (isoelectronic with PH^-) one finds⁷ $r_e(\tilde{X}^3\Sigma^- \text{SH}^+) = 1.369 \text{ \AA} \geq r_e(\tilde{X}^2\Pi \text{SH}) = 1.345 \text{ \AA}$. For the other⁷ first and second row diatomic hydrides with the $\dots(\sigma)^2(\pi)^x$ ground electronic configuration, addition of a π electron to the positive ion (CH^+ , NH^+ , PH^+ , OH^+ , SH^+ , HF^+ , HCl^+) or to the neutral (CH , SiH , OH) decreases the equilibrium internuclear separation. It seems reasonable to assume $r_e'(\text{PH}) > r_e''(\text{PH}^-)$ and therefore

$$1.414 \geq r_e(\tilde{X}^2\Pi \text{PH}^-) \geq 1.400 \text{ \AA}.$$

A recent determination¹⁹ of the hyperfine coupling constants for the $\tilde{a}^1\Delta$ state of PH has led to the conclusion that the partly filled $3p$ π orbital is essentially a phosphorous $3p$ atomic orbital. The relatively small change in r_e (and ω_e) on adding an electron to PH agrees with the conclusion that the electron enters an essentially nonbonding π orbital, which is primarily a phosphorus $3p$ atomic orbital.

C. Rotational corrections

The electron affinity and ($\tilde{X}^3\Sigma^- - \tilde{a}^1\Delta$) splitting of PH, as measured from experimental peak centers, require a rotational correction similar to the correction applied to PO. The rotational states of $\tilde{X}^2\Pi \text{PH}^-$, $F''(N)$, are described by Eq. (3). The value of $B_0''(\tilde{X}^2\Pi \text{PH}^-)$ is calculated from the expression $B_0''(\tilde{X}^2\Pi)/B_0'(\tilde{X}^3\Sigma^-) = [r_e'(\tilde{X}^3\Sigma^-)/r_e''(\tilde{X}^2\Pi)]^2$, where r_e'' is determined in Sec. IVB. The uncertainty introduced into the final correction by the uncertainty in r_e'' is small. The value of the PH^- spin-orbit coupling constant has been calculated theoretically²⁰ ($A_0 = -212 \text{ cm}^{-1}$) and is probably accurate to $\pm 15\%$. The rotational levels of $\tilde{X}^3\Sigma^- \text{PH}$, $F'(N)$ are given⁹ by Eq. (2) with $B_0'(\tilde{X}^3\Sigma^- \text{PH}) = 8.4114 \text{ cm}^{-1}$.

The expression relating E_c , the $\tilde{X}^3\Sigma^- \text{PH} - \tilde{X}^2\Pi \text{PH}^-$ detachment energy measured from the center of the experimental detachment peak, and $\text{EA}(\text{PH})$ is

$$E_c = \text{EA}(\text{PH}) + \sum_{N=1}^{\infty} [p_1(N) + p_2(N)] F'(N) - \left\{ \sum_{N=1}^{\infty} [p_1(N) F_1''(N) + p_2(N) F_2''(N)] \right\} + F_1''(N=1); \quad (6)$$

$p_1(N)$ and $p_2(N)$ are the rotational distribution functions for the spin-orbit-split rotational levels of $\tilde{X}^2\Pi \text{PH}^-$. Assuming a rotational temperature of $1000 \pm 500 \text{ K}$ and evaluating Eq. (6), one obtains

$$\text{EA}(\text{PH}) = E_c + (0.010 \pm 0.006) \text{ eV}.$$

The error limits in the correction term include all uncertainties in T_R , B_0'' , and A_0 . The final value for the electron affinity, including experimental errors, is

$$\text{EA}(\text{PH}) = 1.028 \pm 0.010 \text{ eV}.$$

The correction to the $\tilde{a}^1\Delta \text{PH} - \tilde{X}^2\Pi \text{PH}^-$ detachment

energy is made utilizing Eq. (6) with the following modifications: The rotational levels of $\tilde{a}^1\Delta \text{PH}^-$, $F'(N)$ are defined by Eq. (5) with $B'_0(\tilde{a}^1\Delta \text{PH}^-)^{19,21} = 8.443 \text{ cm}^{-1}$; the sums begin with $N=2$; and the equation has the extra term $-F'(N=2)$. The correction to the $\tilde{a}^1\Delta - \tilde{X}^2\Pi$ detachment energy differs from the $\tilde{X}^3\Sigma^- - \tilde{X}^2\Pi$ correction by the nearly constant amount $6 B'_0 = 5.9 \text{ meV}$, regardless of the chosen values of A_0 , B'_0 , and T_R . The rotational correction to the $\text{PH}(\tilde{X}^3\Sigma^- - \tilde{a}^1\Delta)$ splitting is therefore

$$\Delta E(\tilde{X}^3\Sigma^- - \tilde{a}^1\Delta) = \Delta E_c + 0.0059 \text{ eV},$$

where ΔE_c is the experimentally measured energy separation between the $(\tilde{X}^3\Sigma^-, v'=0 - \tilde{X}^2\Pi, v'=0)$ and $(\tilde{a}^1\Delta, v'=0 - \tilde{X}^2\Pi, v''=0)$ peak centers. The final result for the energy separation between the lowest rotational levels of the $\tilde{X}^3\Sigma^-$ and $\tilde{a}^1\Delta$ PH states, including experimental uncertainties in determining the peak centers, is

$$\Delta E(\tilde{X}^3\Sigma^- - \tilde{a}^1\Delta) = 0.950 \pm 0.010 \text{ eV}.$$

This result compares well with the theoretical calculations¹⁰ of $T_e(\tilde{a}^1\Delta \text{PH}) = 0.95 \pm 0.10 \text{ eV}$, and may also be compared to the splitting⁷ in SH^+ (isoelectronic with PH) $T_e(\tilde{a}^1\Delta \text{SH}^+) = 1.161 \text{ eV}$.

V. PH_2^-

The PH_2^- ground state is assumed to have the same 1A_1 symmetry and $\dots (a_1)^2(b_2)^2(a_1)^2(b_1)^2$ molecular orbital configuration as the isoelectronic molecule H_2S .²² Photodetachment of a b_1 electron gives the spectroscopically characterized^{23,24} 2B_1 ground state of PH_2 . Detachment of an a_1 electron would result in $^2A_1 \text{PH}_2$, which lies 2.27 eV above the 2B_1 ground state.²³ The strong photodetachment peak in Fig. 3 at an electron energy of $\sim 1.27 \text{ eV}$ must be assigned to the $(0, 0, 0)^2B_1 \text{PH}_2 - (0, 0, 0)^1A_1 \text{PH}_2^-$ transition. (The numbers in parentheses refer to the vibrational quantum numbers ν_1, ν_2, ν_3 .) Detachment to the 1A_1 state of PH_2 is not energetically accessible with 2.54 eV photons.

The absence of significant off-diagonal transitions in the $^2B_1 - ^1A_1$ spectrum implies that the geometries of ion and neutral are very similar. Presumably, the detached b_1 electron is essentially a phosphorous $3p$ non-bonding electron,²⁴ and removal from a doubly occupied b_1 orbital does not affect the geometry or vibrational frequency of the molecule significantly. A similar case arises for detachment of an electron from a b_1 orbital in the $^1A_1 - ^2B_1$ photodetachment transitions^{5,6} of SiH_2^- and CH_2^- , where geometries of the ion and neutral species are known to be very similar. In addition, SH_2 ($\theta_0 = 92.2^\circ$, $r_0 = 1.328 \text{ \AA}$),²² which is isoelectronic with PH_2^- , and PH_2 ($\theta_0 = 91.7^\circ$, $r_0 = 1.429 \text{ \AA}$)²³ are seen to have nearly identical bond angles and only slightly different bond lengths.

The electron affinity of PH_2 , determined from the major peak in Fig. 3, is

$$\text{EA}(\text{PH}_2) = 1.271 \pm 0.010 \text{ eV}.$$

Because the rotational constants of ion and neutral are very similar, we believe rotational corrections to $\text{EA}(\text{PH}_2)$ will fall within the quoted error limits. Our

result agrees well with Smyth and Brauman's¹² value of $\text{EA}(\text{PH}_2) = 1.25 \pm 0.03 \text{ eV}$.

A small detachment peak at an electron energy of $\sim 0.99 \text{ eV}$ is assigned to the $[(1, 0, 0) - (0, 0, 0)]$ transition of the $^2B_1 - ^1A_1$ spectrum, giving the vibrational energy $\bar{\nu}_1(^2B_1 \text{PH}_2) = 2270 \pm 80 \text{ cm}^{-1}$. This vibrational energy is similar to twice the PH_2 bending energy^{23,25} ($2\bar{\nu}_2 \approx 2200 \text{ cm}^{-1}$), but since no peak corresponding to the $[(0, 1, 0) - (0, 0, 0)]$ transition is seen, the assignment of the 0.99 eV peak to the symmetric stretch ν_1 is most reasonable.

Additional small peaks in the spectrum may be due partly to PH_2^- photodetachment transitions, but also coincide with strong PH^- detachment peaks and cannot be unambiguously assigned.

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