High-resolution photodetachment studies of $P^-$ and $Te^-$

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The photodetachment spectra of $P^-$ and $Te^-$ are measured in the wavelength region where excitation of the first excited state of $P$ and the ground state of $Te$ becomes energetically possible. A crossed ion-laser beam apparatus is used to measure relative total cross sections from the production of neutral atoms, while the $P^-\rightarrow P$ ground- and excited-state partial cross sections are separately determined by means of kinetic energy analysis of the photoelectrons. The spectra allow determination of the $P$ and $Te$ electron affinities (EA), which are found to be 0.746(4) and 1.970(3) eV, respectively. The fine-structure intervals of the negative ions are found to be $\Delta E_{\text{S}}(P^-) = 181(3)$ cm$^{-1}$, $\Delta E_{\text{D}}(P^-) = 263(3)$ cm$^{-1}$, and $\Delta E_{\text{X}}(Te^-) = 5008(5)$ cm$^{-1}$. Comparison is made with previous measurements and values which are predicted from extrapolations. A comparison of the $P^-$ multichannel measurements is made with equivalent measurements involving alkali negative ions on the basis of channel coupling. In addition, the relative strengths of the various fine-structure level transitions in $P^-\rightarrow P$ are determined; the observed strengths agree much better with the predictions of a geometrical model, than with those made by a statistical-weight argument.

I. INTRODUCTION

Measurements of the threshold energy dependence of the photodetachment cross section have been made for a number of atomic negative ions. The process is defined by the reaction

$$A^- + h\nu \rightarrow A + e^-,$$

where $A^-$ is an atomic negative ion, $h\nu$ is the photon frequency, and $e^-$ is the photoelectron. For most measurements thus far, the resulting neutral atom $A$ is in the ground state. Measurements involving production of excited states of the neutral atom have been made for alkali negative ions. In this paper are reported the first multichannel photodetachment measurements for the $P^-$ negative ion in the reaction

$$h\nu + P^+(P_{2s1,0}) \rightarrow \{P^+(S)+e^- \} + \{P^+(D_{3/2,5/2})+q \},$$

Also reported are single-channel measurements of $Te^-$ photodetachment, $Te^-(P_{1/2,3/2}) + h\nu \rightarrow Te^+(P_{2s1,0}) + e^-.$

The cross sections for these processes are measured by means of a crossed ion-laser beam apparatus utilizing a tunable dye laser. The total photodetachment cross section is determined from a measurement of the cross section for production of neutral atoms as a function of photon energy. For $Te^-$, photodetachment cross sections were obtained in the photon-energy region corresponding to the threshold for detachment to the $Te$ ground state. For $P^-$, however, the ~2 eV photons can access both the ground state and the first-excited $^2D$ state of $P$; measurements were made in the vicinity of the $^2D$ state channel opening. Under these conditions the large energy separation of the ground and first excited state of the neutral, 1.4 eV, gives rise to photoelectrons of widely different kinetic energies, depending on which channel of Eq. (2) is realized. Accordingly, the $P^-$ partial cross sections for ground- and excited-state detachment channels are found by means of low-resolution kinetic-energy analysis of the photoelectrons.

The energy-level diagram for $P$ and $P^+$ is depicted in Fig. 1, and the equivalent diagram for $Te$ is in Fig. 2. One would expect the photodetachment spectra for both ions to be characterized by several onset transitions to a given fine-structure level of the negative ion to a given fine-structure level of the neutral. The energy dependence of the individual onsets is expected to be given by the Wigner threshold law

$$\sigma = k^2l^4,$$

where $k$ is the magnitude of the momentum of the detached electron and $l$ is its orbital angular momentum with respect to the neutral atom. At threshold, the lowest value of $l$ in accordance with electric-dipole selection rules dominates the cross section. In $P^-$ and $Te^-$ a bound $np$ electron is detached into an $s$-wave continuum with the threshold
energy dependence $\sigma \sim E^{1/2}$, where $E$ is the electron kinetic energy in the detachment channel of interest. Identification of the observed thresholds provides direct determination of the electron affinity (EA) and the spin-orbit splitting in the negative ion.

Recent multichannel photodetachment measurements\(^6\) with K\(^+\) and Cs\(^+\), detached to the first excited $^2P$ state of the neutral atom, have shown that, under conditions of strong channel coupling, the energy range of validity of the threshold law is less than 0.1 meV. In that work, the major perturbation of the ground-state partial cross section, which resulted when the $^2P_{1/2}$, $^2P_{3/2}$ channels opened, was interpreted to be a result of mixing between $^2S$ and $^2P$ states in the neutral atom due to the perturbation of the nearby detached electron. It was assumed that much of this coupling was the result of second-order Stark mixing of $^2S$ and $^2P$ states in the electric field of the detached electron.

The $P^-$ data presented here provide an interesting contrast to the alkali spectra, since the $^4S$ and $^4D$ states of the neutral are of the same parity, and experience no mixing through the Stark mechanism. As will be seen, the $P^- \rightarrow P$ detachment channels show no obvious coupling, a result consistent with the interpretation of the alkali spectra. Although we have measured no partial cross sections for Te\(^-\) detachment, the channel onsets are consistent with the Wigner threshold law for at least several meV and we can assume that only weak-channel coupling exists.

II. EXPERIMENTAL APPARATUS

The crossed ion-laser beam apparatus used for these measurements has been described elsewhere\(^4,5\) and is discussed only briefly here. The $P^-$ and Te\(^-\) relative total photodetachment cross sections are determined as a function of photon energy from the detection of neutral atoms produced. With $P^-$, the partial cross section for the excited-state detachment channel is found by means of kinetic-energy analysis of the photoelectrons.

The negative ions are generated in a hot-cathode discharge, in PH\(_3\) for P\(^-\) and in As\(_2\)Te\(_3\) with a CO buffer gas for Te\(^-\). Negatively charged particles are extracted electrostatically from the source, accelerated to 2.0 keV and mass analyzed to provide a pure beam of the species of interest. The ions are then intersected with the output beam of a tunable flashlamp-pumped dye laser. The laser pulses typically have an energy content of several mJ in a 0.3-μsec pulse duration with a linewidth of 1–5 cm\(^{-1}\); the laser is operated at a repetition rate of 5 sec\(^{-1}\). Following the beam intersection, the remaining negative ions are separated from the neutral atoms by deflecting electric field and the high-energy neutral atoms are detected by means of secondary emission on the front surface of a Channeltron continuous dynode multiplier. The negative ions are collected in a Faraday cup. The relative total photodetachment cross section is then determined from the relative number of neu-

![Te, Te\(^-\) Energy Levels](image1)

![P, P\(^-\) Energy Levels](image2)
neutral atoms produced as a function of laser wavelength, using the known photon flux and negative ion-beam current. Typically 500 laser shots suffice for a single data point.

Since the lifetime of the P $^2D$ metastable state is much longer than the 4-$\mu$sec flight time from the interaction region to the neutral detector, P atoms produced in this state will strike the neutral detector with ~1.5-eV internal energy. There is a possibility that the secondary electron yields for 2.0-keV P $^4S$ and P $^2D$ are different, resulting in a distortion of the measured total cross section, as the $^2D$ channels open. However, we assume that at the 2-keV beam energies the $^4S$ and $^2D$ detection efficiencies are identical, based on earlier measurements involving O $^3P$ and O $^1D$. For 1800-eV neutrals impacting on a BeCu detector surface, the ratio of O($^1D$) to O($^3P$) secondary electron yields was unity; as the energy was decreased below 1 keV, the ratio increased until at 200 eV energy, the ratio became six.

The P($^2D$) state partial cross section is determined by measuring the production of $^2D$-channel photoelectrons. In the spectral region studied the $^2D$-channel photoelectrons have a maximum kinetic energy (in the laboratory frame) of 0.16 eV while the $^4S$-channel photoelectrons have kinetic energies of 1.4 eV. The discrimination between these two groups of photoelectrons is provided by a low-pass kinetic energy filter which utilizes a weak electric field (~1 V/m) to trap the low-energy $^2D$-channel electrons and accelerate them onto a Channeltron electron multiplier. The $^4S$-channel electrons are essentially undeflected by the weak field and are collected with a much smaller efficiency. An important feature of this device is that it allows collection over the entire 4T photoelectron ejection solid angle, thus allowing meaningful measurements with signal levels on the order of one $^2D$ channel detachment per laser pulse. Based on extensive measurements with alkali negative ions, the collection efficiency of $^4S$-channel electrons is estimated to be 2% that of the $^2D$-channel photoelectrons.

III. EXPERIMENTAL RESULTS

The P$^+$ photodetachment spectrum near the threshold for production of the $^2D$ state of the neutral is shown in Fig. 3. The upper data are the total cross section and the lower data are the $^2D$ partial cross section. Five fine-structure onsets are seen in the partial cross section, as would be expected from the energy level diagram of Fig. 1, with the $^3P_0-^2D_{5/2}$ channel forbidden by the angular-momentum considerations in the threshold area.

Within the precision of the data, the channel onsets are consistent with the Wigner threshold law for $s$-wave detachment, $\sigma_i \propto E_i^{1/2}$, where $\sigma_i$ is the photodetachment cross section for fine-structure onset $i$ and $E_i$ is the corresponding electron kinetic energy. The data are qualitatively consistent with the threshold law for ~100 cm$^{-1}$, much greater than the $^2D$ fine-structure interval 15 cm$^{-1}$. Accordingly, it is a reasonable assumption that the coupling among detachment channels is small, and that the total cross section may be straightforwardly interpreted as a simple noninterfering sum of partial cross sections. On this basis the $^2D$ partial and the total cross section of Fig. 3 have normalized so that their difference, the $^4S$ partial cross section, is a relatively smooth curve through the $^2D$ state threshold region. The data points of the partial and total cross sections in Fig. 3 do not lie in vertical alignment and the difference curve, the $^4S$ partial shown in Fig. 3 as a solid line, is generated by means of a linear interpolation. The relatively weak energy dependence of this cross section is consistent with the interpretation of small channel coupling. On the basis of this interpretation the normalization of Fig. 3 is considered to be accurate to within 20%.

The phosphorus electron affinity (EA) can be determined from the position of the strongest channel onset, $^3P_{3/2}-^2D_{5/2}$, using the known energy levels of the neutral. The result is EA(P) = 0.7464(4) eV. The fine-structure intervals of the negative ion are also found from the data of Fig. 3. The

![Fig. 3. Photodetachment total and $^2D$ partial cross sections for P$^+$ at photon energies near the $^2D$-channel threshold. Channel openings can be determined to ~2 cm$^{-1}$ accuracy, and are indicated by arrows. The solid line is the P $^4S$ partial cross section, obtained by taking the difference between the total and $^2D$ partial cross sections.](image-url)
lution of the electron spectrometer. A high-resolution crossed-beam apparatus similar to that of the present paper has been used by Feldmann. However, the light source of this apparatus was the infrared output of a laser-pumped optical parametric oscillator, and the P electron affinity was determined from the position of the 4S ground-state channel threshold. The result was EA(P) = 0.74676(20) eV, in agreement with the present work. Feldmann also measured the J(2−1) and J(2−0) fine-structure intervals in the negative ion to be 181(4) and 263(4) cm⁻¹, respectively, again in agreement with the present work. A complete discussion of calculations of EA(P) appears elsewhere.

There has been only one other measurement of the Te electron affinity, that by Feldmann et al. with crossed-beam techniques but a nonlaser light source. A xenon-arc lamp and prism monochromator were used to determine EA(Te) = 1.90(15) eV, less accurate but in agreement with the present results.

No other measurements of the Te(4P₂/₃₋³P₁/₂) spin-orbit interval have been made and we compare our measured value to that predicted by Hotop et al. using an isoelectronic extrapolation technique. Ratios of fine-structure intervals are extrapolated along the isoelectronic sequence. The sequence which includes the Te spin-orbit interval is

\[ \frac{\Delta E_{J=3/2-1/2}(Te^-)}{\Delta E_{R_{3-0}}(Te)} , \frac{\Delta E_{J=(3/2-1/2)}}{\Delta E_{R_{3-0}}(P^\circ)} , \frac{\Delta E_{J=(3/2-1/2)}}{\Delta E_{R_{3-0}}(Xe^\circ)} . \]

Ratios such as these are found to vary slowly with atomic number and are considered to provide reliable spin-orbit estimates. Treating the Te interval as an unknown, Hotop et al. predicted \(\Delta E_{J=(3/2-1/2)}(Te^-) = 5000 \) (150 cm⁻¹), in fortuitously good agreement with the measured value of 5008(5) cm⁻¹. An equivalent extrapolation was made for the P* series, previous to any measurements. The result for the J = 2−1 and J = 2−0 intervals was 190(20) and 280(30) cm⁻¹, which again is very close to the measured values of 181(3) and 263(3) cm⁻¹.

B. Comparison of channel onset strengths with predicted values

As discussed in Sec. III, the P* data of Fig. 3 seem to result from a sum of noninterfering partial cross sections, an assumption reinforced by the weak energy dependence of the 5S partial cross section near the 3D channel threshold. Accordingly, the various fine-structure onset strengths can be determined and compared with simple statis-
TABLE I. Phosphorus transition strengths.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Transition</th>
<th>Statistical weight</th>
<th>Geometrical factor</th>
<th>Measured strength $S_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3P_2 \rightarrow ^1D_{2/2}$</td>
<td>6 (4.7)</td>
<td>10 (7.8)</td>
<td>$7.8 \pm 1.5$</td>
</tr>
<tr>
<td>$^3P_2 \rightarrow ^1D_{3/2}$</td>
<td>9 (7.0)</td>
<td>0 (0)</td>
<td>0</td>
</tr>
<tr>
<td>$^3P_1 \rightarrow ^1D_{2/2}$</td>
<td>18 (15.1)</td>
<td>21 (17.6)</td>
<td>$19.5 \pm 3$</td>
</tr>
<tr>
<td>$^3P_1 \rightarrow ^1D_{3/2}$</td>
<td>27 (22.7)</td>
<td>11 (7.6)</td>
<td>$10.5 \pm 4.5$</td>
</tr>
<tr>
<td>$^3P_2 \rightarrow ^1D_{3/2}$</td>
<td>30 (30)</td>
<td>5 (5)</td>
<td>$7.5 \pm 3$</td>
</tr>
<tr>
<td>$^3P_2 \rightarrow ^1D_{5/2}$</td>
<td>45 (45)</td>
<td>45 (45)</td>
<td>$50.0 \pm 5$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Transition strengths for various fine-structure onsets in $P^+$ photodetachment. Numbers in parentheses are Boltzmann factors corrected for an ion source temperature of 1500 K, and are the quantities which are to be compared with the measured strengths.

The effective-ion source "effective temperature" to be sufficiently high that $kT$ is much larger than the spin-orbit splitting in the negative ion, all relative strengths $S_j$ can be estimated for a first approximation as the relative statistical weights of the transitions. Such a simple model does not produce good agreement with experimental results, and Rau and Pano\textsuperscript{4} have shown that these strengths obey a more complicated angular momentum algebra than simple statistical weights, and find transition strengths in terms of dynamics-independent geometrical factors. Rau\textsuperscript{15} has extended this treatment to obtain a general expression for these geometrical factors, which has been evaluated for the $^3P - ^1D$ case, appropriate to $P^+$ detachment, by Rackwitz.\textsuperscript{16} The measured strengths $S_j$, along with the statistical weights and geometrical factors, are presented in Table I.

The corrected numbers appear in parentheses in Table I and are those values which should be compared with the experimental results. The agreement between the measured strengths and the geometrical factors is fairly good.

From each negative ion fine-structure level, the detachment strength is divided among the two $^2D$ states of the neutral. According to the geometrical factors, this branching ratio is not the same as the ratio of the statistical weights of the two $^2D$ states. However, it should be noted that if the $^2D$ states are unresolved, so that the $^2D$ states strengths are added, the geometrical factors and statistical weights are identical. While this is generally true, in this case the disallowed $^3P_0 \rightarrow ^2D_{5/2}$ transition complicates the matter, since not all fine-structure levels of the negative ion detach to final states of the same statistical weight. The strengths from Table I can be added as they would be if the $^2D$ states were unresolved, and the result shown in Table II, with the difference in geometrical factor and statistical weights for the $^3P_0 \rightarrow ^2D$ transition being a result of the disallowed transition. In Table II the statistical weights have been renormalized and the Boltzmann-factor-corrected numbers are again in parentheses. In this table the corrected geometrical factors and experiment results agree within the experimental uncertainty.

Equivalent considerations hold for the fine-structure onsets of the $Te^-$ detachment spectrum of Fig. 4. In this case there is no direct verification of weak-channel coupling, since no partial cross sections are determined, but the $E^{3/2}$ nature of the onsets for several meV is consistent with a weak coupling condition. Due to the inaccurately known ratio of $^3P_{5/2}$ to $^3P_{1/2}$ ions in the beam, the only ratio of interest which can be determined from Fig. 4 is that of the $^3P_{1/2} \rightarrow ^3P_1$ to $^3P_{1/2} \rightarrow ^3P_0$ onsets. The statistical weight ratio is 3 and the

TABLE II. Phosphorous transition strengths.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Transition</th>
<th>Statistical weight</th>
<th>Geometrical factor</th>
<th>Measured strength $S_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3P_0 \rightarrow ^1D$</td>
<td>4 (3.1)</td>
<td>10 (7.8)</td>
<td>$7.8 \pm 1.5$</td>
</tr>
<tr>
<td>$^3P_1 \rightarrow ^1D$</td>
<td>30 (25.2)</td>
<td>30 (25.2)</td>
<td>$30.0 \pm 7.5$</td>
</tr>
<tr>
<td>$^3P_1 \rightarrow ^1D$</td>
<td>50 (50)</td>
<td>50 (50)</td>
<td>$50.0 \pm 7.5$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Transition strengths for various fine-structure onsets in $P^+$ photodetachment. The numbers are obtained from Table I, assuming unresolved $^1D$-state fine structure. Numbers in parentheses are Boltzmann factors corrected for an ion source temperature source of 1500 K and are the quantities which are to be compared with the measured strengths.
theory of Rau and Fano predicts 2.25. The measured value of 2.9(4) is uncertain because the baseline below the \(^2P_{1/2} \rightarrow \ ^2P_0\) threshold, due to the \(^2P_{1/2} \rightarrow \ ^2P_{3/2}\) channel, is not well determined. Unfortunately this large uncertainty makes the result somewhat uninteresting. The \(^2P_{3/2} \rightarrow \ ^2P_{1/2}\) thresholds, which occur around 4700 Å, are within the dye laser range and could be measured to check another ratio from Rau's theory. In this case the statistical weight ratio is again 3, but Rau's geometrical factor is 4.5.

It is interesting to note the model of Rau and Fano assumes that immediately after the absorption of the photon, the neutral atom and nearby electron form an \(LS\)-coupled complex. The Te ground state has inverted \(J = 1, 0\) levels, a clear indication of the near breakdown of \(LS\) coupling. Any deviation of fine-structure onset strengths in a high-precision measurement might be related to this coupling problem.

V. CONCLUSIONS

The relative photodetachment cross sections of \(P^-\) and \(Te^-\) have been measured using crossed ion-laser beam techniques. The \(P^-\) measurements were made in the vicinity of the threshold for detachment to the first-excited state of the neutral and the \(Te^-\) measurements are in the vicinity of the threshold for detachment to the ground state of the neutral.

The spectra provide determinations of the electron affinities of the neutral atoms and the spin-orbit intervals of the negative ion

\[
\begin{align*}
EA(P) &= 0.746(4) \text{ eV}, \\
\Delta E_{T(2s)}(P^-) &= 181(3) \text{ cm}^{-1}, \\
\Delta E_{T(2p)}(P^-) &= 263(3) \text{ cm}^{-1}, \\
EA(\text{Te}) &= 1.9708(3) \text{ eV}, \\
\Delta E_{T(3p/2,4s)}(\text{Te}^-) &= 5008(5) \text{ cm}^{-1}.
\end{align*}
\]

Direct measurements show that the \(P^-\) \(4S\) and \(^3D\) detachment channels are weakly coupled and the energy dependence of the \(^2D\) channel is consistent with the assumption that the \(^2D\) fine-structure channels are not strongly coupled to one another. Under these circumstances the strengths of individual fine-structure onsets can easily be measured. The onset strengths obtained are found to be in good agreement with the theory of Rau and Fano. Equivalent considerations hold for \(\text{Te}^-\), but in this case the measured spectral range of the photodetachment cross section was insufficient to provide a meaningful comparison with the theory.

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\*E. P. Wigner, Phys. Rev. 73, 1002 (1948).