Inner-Shell Photodetachment Thresholds: Unexpected Long-Range Validity of the Wigner Law

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Threshold behavior in inner-shell photodetachment is studied for the first time, specifically with 2-, 3-, or 4-electron emission from He^- and S^-. The threshold shapes are surprisingly consistent with the Wigner threshold law in all cases, despite large PCI effects observed in He^-. In S^-, the *s*-wave law is observed to agree with the data over an unprecedented range, more than an order of magnitude greater than predictions, and allows for the observation of the *d*-wave component. The measurements also demonstrate a means for obtaining precise core-excitation energies of free atoms.

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Descriptions of the energy dependence of a reaction yield near a threshold (or "threshold laws"), are of general interest in many areas of physics. Such threshold laws are independent of the specifics of the reaction or reaction products [1,2], and can therefore be equally applicable to, for example, fragmentation at the molecular, atomic, or even subatomic level. In addition, observed agreement or departure from accepted threshold laws can yield insight into the dynamics of the process under study, be a sensitive probe of the effects of external electric [3,4] and/or magnetic fields [5], reveal details of the binding potential [6], or yield insight into the classical-quantum mechanical correspondence of physical processes [7].

Threshold behaviors for the dissociation of a target into a pair of particles were first derived by Wigner in 1948 [1]. Wigner's results underline that threshold behaviors are governed by the longest-range interaction between the products. The potential formed by the relative angular momenta (l) of the products [the "centrifugal potential," $l(l+1)/2r^2$] is generally used to demarcate the distinction between long- and short-range potentials. In the absence of longer-range potentials (e.g., Coulombic, $\propto r^{-1}$), the threshold behavior depends only on the angular momenta of the products and is independent of the nature of shorter-range potentials. For example, photodetachment threshold laws in negative ions (governed by the short-range induced-dipole potential, $\propto r^{-4}$) differ substantially from photoionization of neutral atoms or positive ions (governed by the long-range Coulomb interaction). In fact negative ions have long been recognized as convenient test systems for short-ranged interactions [8]. In negative ion photodetachment we can write the near-threshold cross section as $\sigma = \sigma_0 \epsilon_e^{l+1/2}$, where σ_0 is the amplitude, $\epsilon_e = h\nu - \epsilon_t$ the photoelectron energy, ϵ_t the threshold energy, and $l = |l_0 \pm 1|$ the photoelectron angular momentum, with l_0 the angular momentum of the bound electron being detached. This threshold law has been verified in numerous cases for both single-photon [9,10] and multiphoton [4] processes and is central to high-precision measurements of binding energies of *valence* electrons using laser photodetachment threshold spectroscopy [10].

The recently developed experimental realm of inner-shell photodetachment from negative ions leading to positive ion formation [11,12] provides a new opportunity to explore threshold behaviors at the boundary between short-ranged and long-ranged interactions. It is commonly accepted that the formation of singly charged positive ions from inner-shell detachment of a negative ion is a two step process: detachment of the inner-shell electron, to form a core-excited neutral atom, followed by the emission of an Auger electron. However, due to the typical short decay lifetimes of core holes, there is a significant probability of the Auger electron being ejected before the slow photoelectron escapes, causing the latter to be recaptured and suppressing positive ion production. This post-collision interaction (PCI) effect, leads to significant reduction of positive ion signal, especially for small photoelectron energies [13], and can therefore alter the behavior of the near-threshold cross section.

In this Letter we report the first investigations of the threshold behavior in inner-shell photodetachment of atomic negative ions. The $1s$ photodetachment of He^- is found to give rise to a Wigner *p*-wave threshold law, despite strong PCI effects. Up to four electrons are released following the $2p$ photodetachment of S^-. The near-threshold cross sections for all three detected positive ionic products are consistent with a Wigner *s*-wave threshold law up to $\epsilon_e \approx 3$ eV, after which inclusion of the *d*-wave channel gives better agreement. This unprecedented range of validity for the Wigner law is over an order of magnitude larger than seen in valence photodetachment studies, and is inconsistent with standard threshold law corrections [14,15].

The experiments were performed using the ion-photon beam line [16] at the Advanced Light Source (ALS). A 9.96 keV, ≈ 60 nA He^- or 7.48 keV, ≈ 280 nA S^- ion beam [17] was merged with a counter-propagating photon beam from beam line 10.0.1. Photon-ion interaction in the merged region induced photodetachment followed by autoionization (Auger decay). The resulting positive ions were deflected by a demerging magnetic field and counted using a multichannel plate-based detector. Background from ion collisions with vacuum gas ($\approx 5 \times 10^{-10}$ Torr) was removed by chopping the photon beam at 6 Hz.

The photon energy was calibrated against accurately known absorption lines [18] of Ne and Ar between 26.5 and 48 eV for the He^- experiments, and lines in Ar [19] and SF_6 [20] between 120 and 250 eV for the experiments in S^-. The total uncertainty for energy calibration, including Doppler correction, for the He^- and S^- experiments is estimated to be 7 and 30 meV, respectively [uncertainties are quoted to 1 standard deviation (SD) throughout].

The He^+ yield resulting from $1s$ photodetachment of He^- $1s2s2p\ ^4P^o$ observed near the $2s2p\ ^3P^o$ threshold is shown in Fig. 1. Removal of the $1s$ electron forms the hollow He $2s2p$ state which quickly autoionizes to form the He^+ signal. For a purely sequential process, the He^+ production rate would follow the He^- $1s$ photodetachment cross section. However, due to the short decay lifetime of this state (width of $\Gamma = 8.14$ meV, i.e., $\approx$40 fs [21]), there is a significant probability for the photoelectron to be recaptured through PCI effects and thus suppress He^+ production. This was recently used to explain the discrepancy between observed [12] and calculated [22] $1s$ photodetachment cross sections of He^-. The photoelectron escape probability within the semiclassical approximation was modeled with $P_{esc} = e^{-\Gamma T_c}$, where $T_c = 1/\sqrt{2\epsilon_e^3}$ (in a.u.).

Although P_{esc} varies (nonlinearly) from 0 to ≈ 0.4 in the scanned region, there is surprisingly little effect on the shape of a Wigner-law threshold, other than predicting an

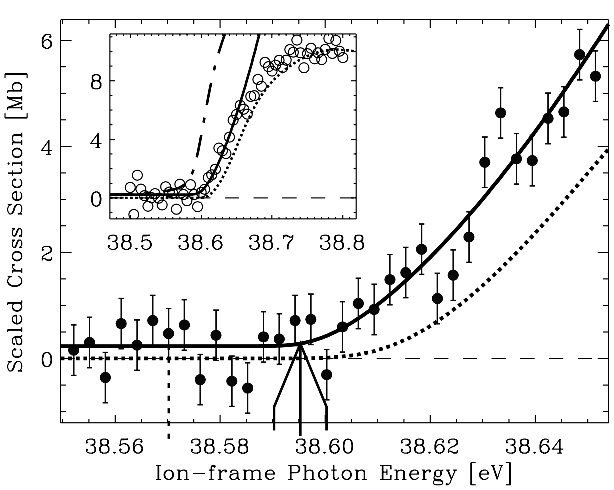

FIG. 1. Observed He^+ signal following $1s$ photodetachment of He^- (10 meV nominal resolution; inset: 15 meV). The data are scaled to the PCI-corrected theory by Sanz-Vicario *et al.* [22] (dotted curve) at 38.8 eV. Curves are theory without PCI corrections (dot-dashed line) and fit Wigner law (solid line). The "arrow" indicates the fit threshold position, the width of which is the statistical error. The dashed vertical line at 38.5702 eV marks the predicted He $2s2p\ ^3P^o$ position.

energy shift of about +43 meV. A power-law fit [$\sigma = \sigma_0(h\nu - \epsilon_t)^p$] to the data of Fig. 1 yields an exponent $p = 1.47(7)$, in excellent agreement with the Wigner threshold law for photodetachment of an s electron ($p = 1.5$). The resulting threshold energy from the Wigner-law fit is $\epsilon_t = 38.595(9)$ eV (including calibration error).

We obtain a theoretical He^- $1s2s2p\ ^4P^o \rightarrow$ He $2s2p\ ^3P^o$ threshold energy of 38.5702 eV, from the He $1s^2$ energy of $-79.00\,353$ eV [23,24], He $2s2p\ ^3P^o$ energy of $-20.69\,120$ eV [21,24], He $1s2s\ ^3S$ excitation energy of 19.81 963 eV [25], and He^- $1s2s2p\ ^4P^o$ binding energy to He $1s2s\ ^3S$ of 0.07 752 eV [26]. The dotted curve in Fig. 1 shows photodetachment calculations by Sanz-Vicario *et al.* [22] corrected for semiclassical PCI effects, with the above threshold energy and $\Gamma = 8.14$ meV [21]. (Note: the experimental cross section has been scaled to the PCI-corrected theory at 38.8 eV.) While the general shape of the signal up to 38.8 eV is well reproduced (see inset), there is a clear energy shift. A photon energy shift of 15 meV is required to bring the curves into agreement. Given the calibration uncertainty (7 meV), this seems unlikely. Other possibilities are an error in the calculated $2s2p\ ^3P^o$ energy (58.31 232 eV) of -19 meV, and/or an overestimation of the autoionization width ($\Gamma \approx 5$ meV is required for good agreement). Being the lowest triplet doubly-excited state, the energy of $2s2p\ ^3P^o$ is not obtainable from high-precision x-ray emission experiments, however this state has been measured to a precision of 30 meV in electron impact experiments: excitation energy = 58.29(3) and width ≈ 0.01 eV [27]. Assuming the theoretical width, we obtain an improved excitation energy of 58.294(9) eV. A final possibility is the failure of the semiclassical PCI correction itself at this level of analysis. We note that some differences have been observed between semiclassical and recent quantum mechanical formulations [13], but dismissed as probable artifacts of incorrect boundary conditions.

To verify the effect of angular momentum on the threshold behavior of the cross section, we investigated the photodetachment of a $2p$ electron from S^-. In this case the photoelectron can leave with $l = |1 \pm 1| = 0$ or 2, i.e., an s or d wave. In valence studies, the d wave is always seen to be suppressed by the centrifugal barrier and the Wigner s-wave law dominates the photodetachment cross section: $\sigma = \sigma_0(h\nu - \epsilon_t)^{1/2}$.

At photon energies in excess of 117.79 eV it is energetically possible to remove up to 5 valence electrons from S^-, to form charge states up to S^{4+} [25]. Different final charge states are easily identified and separated experimentally with the magnetic and electric fields in the detection stage of the apparatus. S^{2+} (Fig. 2), S^+, and S^{3+} (Fig. 3) signals were sufficiently strong to be detected in the current experiment, while S^{4+} was not observed. In the present experiments we observed average photoion rates (at $\approx$165 eV) of about 190, 40, and 4.5 Hz for S^+, S^{2+}, and S^{3+} respectively, while background from collisional strip-

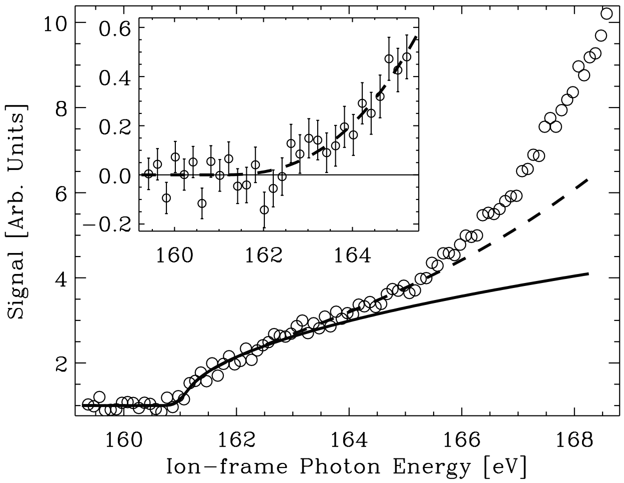

FIG. 2. S^{2+} signal near the $2p$ threshold of S^- (0.3 eV nominal resolution). Curves are the best-fit s wave (solid line) and s- plus d-wave (dashed line) laws, and agree well with the data near the threshold, but diverge significantly above $\approx$165.5 eV. This trend is also seen for S^+ and S^{3+}. Inset: Data with s-wave component subtracted. Dashed curve is a power-law fit to the data [best fit $p = 2.5(7)$]. (For display of inset, 2 data points were binned together; fit was performed on nonbinned data.)

ping with residual gas produced rates of nearly 40 kHz for S^+, but only $\approx$10 Hz for S^{2+} and S^{3+}. As a result, signal to background levels were vastly superior for S^{2+} and allowed for more detailed examination of the near-threshold cross section for that product.

A fit of a Wigner s wave to the near-threshold S^{2+} signal (solid curve in Fig. 2) shows excellent agreement up to $\approx$164 eV, fully 2.5 eV above threshold. Optimizing the Wigner-law exponent for fits including energies up to about 163 eV yields $p = 0.53(12)$, but including higher energies results in a slightly larger exponent (up to $p \approx 0.65$ at 165.5 eV). Such an apparent monotonic change in the exponent with increasing energy range of the fit is not uncommon and can often be ascribed to a breakdown of the Wigner law for larger photoelectron energies. The Wigner law is essentially the first term in a series expansion about small photoelectron energies. Two main approaches have been explored in order to extend the range of validity of the Wigner law. Farley [14] obtained the leading term correction under the zero core contribution approximation, which assumes that the atomic core does not interact with the ejected electron. On the other hand, O'Malley [15,28] obtained a correction term estimating the effect of the polarizability of the atomic core on the outgoing electron. Both models predict a lowering of the cross section for larger photon energies, contrary to what is observed here. We also note that preliminary calculations by Gorczyca [29] give an Auger decay width for $2p$ excited S of $\approx$ 0.001 a.u. (27.2 meV), thus making PCI effects insignificant beyond $\approx$ 0.5 eV above threshold.

Another possibility for the increase in cross section is the contribution of the d-wave channel, which produces a $p = 2.5$ threshold behavior. Including this additional power law yields excellent agreement with the data up to $\approx$ 165.5 eV. To further verify the contribution of the d wave to the cross section, the s-wave fit to the data below 163 eV is subtracted from the data (see Fig. 2 inset). A power-law fit to this difference, with the threshold fixed to 161.04 eV (see below), yields $p = 2.5(7)$, in excellent agreement with the expected $p = 2.5$.

Higher angular momentum channels are generally suppressed in valence electron detachment, and a d-wave Wigner-law component has not been observed previously in single-photon detachment (although it has in 2-photon detachment [4], where the channels can be selected with appropriate photon polarization). The much higher photoelectron energy range considered here may explain why the d-wave component is observed, even though it remains relatively weak ($\approx$1% of the s-wave component at $\epsilon_e =$ 1 eV). In fact, the S^- threshold remains faithful to the Wigner law for a surprisingly large range, at least up to $\epsilon_e \approx 3$ eV. To our knowledge, this is unprecedented in negative ion photodetachment, where deviations are easily observable for $\epsilon_e = 0.01$ to 0.1 eV [9,30]. Although the polarizability of the core-excited S atomic core is likely small, due to the nearly filled $3p$ orbital, a polarizability as small as 10 a.u. should lead to 10% deviation from the Wigner law even only 25 meV above threshold, according to O'Malley's theory [15]. The large range over which the Wigner law applies here is therefore difficult to explain.

The substantial increase in the cross section observed beyond 165.5 eV in all three detected channels is most likely due to an excited state of S near 165.5 eV that may facilitate Auger decay following the photodetachment step. We note that the negative ion ground state fine structure splitting of 59.95 meV [10] and the expected (based on S [31]) $2p_{3/2} - 2p_{1/2}$ splitting of $\approx$ 220 meV are too small to be involved in the structure. Further theoretical investigations of the inner-shell excited S states and decay mechanisms are required to shed light on the odd behavior.

The signal observed for S^+ and S^{3+} production shows little qualitative difference from that of S^{2+}, and is evidence that all charge states near the threshold are sampling the same process—i.e., the initial $2p$ photodetachment. Fits to the S^+ and S^{3+} threshold data shown in Fig. 3 yield power-law exponents of 0.50(18) and 0.62(25), respectively, again consistent with a Wigner s-wave threshold law. Wigner-law fits yield threshold energies of 161.57(30), 161.024(50), and 161.26(41) eV (statistical errors only) for S^+, S^{2+}, and S^{3+} respectively (note the much higher precision for S^{2+}, due to the superior statistics), and yield a weighted mean of 161.042(49) eV, for a final S^- $2p$ threshold energy of 161.04(6) eV (including calibration uncertainty). This is about 2.7 eV smaller than the atomic S edge ($2p_{1/2} = 163.60(30)$ eV, $2p_{3/2} =$ 163.820(61) eV [31]). While PCI effects do not alter the shape of the threshold detectably, including PCI effects in the fit yields a threshold 204 meV lower. With this, and the

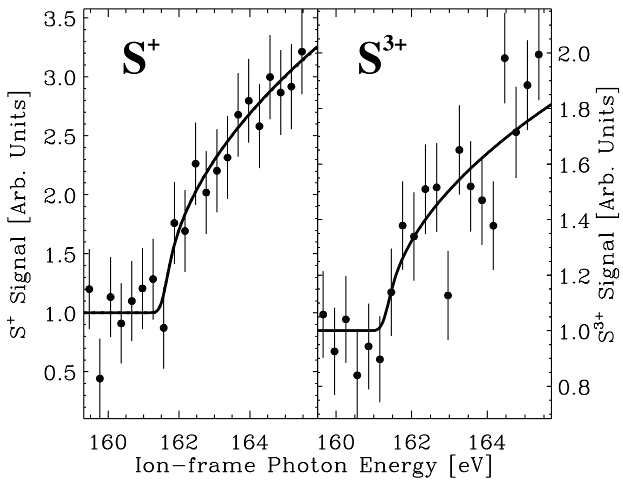

FIG. 3. S^+ (left panel) and S^{3+} (right panel) signal near the $2p$ threshold of S^- (0.3 eV nominal resolution). Curves are fit Wigner s-wave threshold laws. (For display, 3 data points were binned together; fits were performed on nonbinned data.)

binding of S^- $3s^2 3p^5\ {}^2P_{3/2}$ (2.077 102 9(10) eV [10]), we obtain a S $2p \rightarrow 3p$ excitation energy of 158.76(6) eV. This result demonstrates that inner-shell threshold spectroscopy is uniquely suited as a precise method for determining core-excited states of free atoms generally not measurable with conventional techniques.

In summary, we have studied the threshold regions in inner-shell negative ion photodetachment for the first time. The cross section behavior for both s and p inner-shell electron detachment was found to be consistent with Wigner's threshold law, indicating that PCI effects in these systems do not significantly alter the shape of the threshold cross section, only effectively shift the spectrum to higher energies. In addition, for s-wave detachment, the range of validity of the Wigner law is found to exceed by more than an order of magnitude the range found in valence photodetachment. Further theoretical studies explaining the differences between valence and inner-shell photodetachment processes could shed light on the long-standing questions of the range of validity of these threshold laws and into photodetachment physics in general. The present study clearly demonstrates that threshold spectroscopy can be valuable for determining binding energies of inner-shell electrons in free atoms, be a sensitive probe of PCI effects, and yield insight into the decay pathways of these complex systems.

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