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Promoting a core electron to fill a *d* shell: A threshold law and shape and Feshbach resonances

R. C. Bilodeau* and I. Dumitriu
Physics Department, Western Michigan University, Kalamazoo, Michigan 49008-5151, USA and Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

N. D. Gibson and C. W. Walter
Department of Physics and Astronomy, Denison University, Granville, Ohio 43023, USA

N. Berrah
Physics Department, Western Michigan University, Kalamazoo, Michigan 49008-5151, USA

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Absolute cross sections for the formation of Pt^+, Pt^{2+}, and Pt^{3+} following $4f$ and $5p$ inner-shell photoexcitation and detachment of Pt^- $4f^{14}5d^96s^2\ ^2D$ are measured. Signal in the Pt^{3+} production channel is dominated by $4f$ detachment and allows for the observation of a *d*-wave Wigner threshold law following single-photon absorption. Promoting a $5p$ electron into the $5d$ orbital produces a shape resonance while promoting a $4f$ electron produces Feshbach resonances, demonstrating the importance of core-valence interactions.

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Negative ions (NIs) are important in many physical processes (e.g., stellar atmospheres, molecular clouds, atomic mass spectrometry, and plasma physics [1]). They have also attracted much interest due to the qualitatively different features deriving from the short-ranged potential that binds them. Prior to 2001, photodetachment experiments on NIs employed laser-based techniques and were thus limited to studies of valence electrons (for recent reviews see [2]). The advent of high-intensity synchrotron sources enabled inner-shell photodetachment studies and attracted considerable recent experimental [2–9] and theoretical [10] interest.

This Rapid Communication presents two results emerging from inner-shell photodetachment of atomic NIs. First, the *d*-wave form of the Wigner threshold law [11] is observed in single-photon measurements [12]. Second, single-vacancy valence shells are filled with a core electron in order to test the proposition that this process should lead to stabilization of the state. This stabilization is characterized by the state being bound below the atomic core-excited parent state, producing a long-lived state seen as a narrow Feshbach resonance [4,6,8]. Contrary to conventional expectations, we find that such stabilization does not always occur and a shape resonance, having an energy above that of the parent state, is observed with $5p \rightarrow 5d$ excitation.

Sixty years have passed since Wigner [11] first obtained general expressions to describe the cross section near a threshold for dissociation of a target into a pair of particles. These threshold laws are general and do not depend on the nature of the particles themselves nor the mechanism for their dissociation. As a result, the laws have far-reaching applications including in nuclear physics [13], positron scattering [14], electron attachment [15], dissociative recombination [16], ultracold atomic collisions [17] and molecular reactions [18], and high-precision measurements of atomic NI states [19].

One common form of Wigner's laws arises in the case where the centrifugal potential is the longest interaction present between particles, such as in photodetachment from NIs. For a NI with a binding energy of ε_t, the photodetachment cross section is $\sigma \propto \varepsilon_e^{\ell+1/2}$, where $\varepsilon_e = h\nu - \varepsilon_t$ is the energy and ℓ is the angular momentum of the photoelectron. An electron bound with angular momentum $\ell_\circ$ and absorbing a single photon is ejected into at most two angular momentum channels: $\ell = |\ell_\circ \pm 1|$. The centrifugal barrier suppresses the higher angular momentum channel at sufficiently low photoelectron energies, and the lower partial wave dominates the cross section. Photodetachment of a valence f ($\ell_\circ = 3$) or larger angular momentum electron has never been observed, and only $s-(\ell=0)$ and $p-(\ell=1)$ wave threshold laws have been observed in single-photon detachment [12]. Recent work in He^- $(1s)$ and S^- $(2p)$ [3] has shown that the threshold law is valid for inner-shell detachment in *p*- and *s*-wave detachment. Pt^- presents a case where *f*-electron detachment dominates the spectrum, and a single-photon *d*-wave continuum is observed.

The addition of an electron to all atomic species with a singly-vacant valence shell or subshell stabilizes the shell (e.g., filling *p* or *d* shells resulting in strongly bound NIs [19]). It is natural to expect such stabilization to also occur in core-excited atomic states with a singly-vacant valence shell or subshell. Previous studies on S^- [4] and Te^- [6], each having a single-vacancy valence *p*-shell, showed that filling the vacancy with a core electron of the ion (equivalent to attaching an electron to a core-excited neutral atom) resulted in strong stabilization of the valence shell. Stabilization of the valence shell for *d*-shells (e.g., in transition metals) has not previously been explored. The presence of *f* electrons makes Pt^- $6s^24f^{14}5d^9$ of particular interest as this allows access to the $5d$-shell with both *p* and *f* electrons. In this Rapid Communication, we present the results of inner-shell photodetachment in a transition metal, Pt^-. Clear Feshbach resonances corresponding to the excitation of $4f$ electrons into the $5d$ orbital are observed, but similar stabilization is not observed for $5p$ excitation, which appears as a shape reso-

*rcbilodeau@lbl.gov

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TABLE I. Measured absolute cross sections (total 1 SD instrumental error of +16/−12%.)

Photon energy (eV)	Cross section (Mb)[a]		
	Pt^+	Pt^{2+}	Pt^{3+}
41.01	$2.6(^{+4}_{-3})$	$0.123(^{+19}_{-15})$	
52.52	$4.5(^{+7}_{-5})$	$0.32(^{+5}_{-4})$	
63.52	$5.1(^{+8}_{-6})$	$0.56(^{+9}_{-7})$	
74.52	$4.1(^{+6}_{-5})$	$1.06(^{+17}_{-13})$	0.006(4)
87.03	$2.8(^{+6}_{-5})$	$1.10(^{+24}_{-18})$	0.032(10)

[a]The reported Pt^{3+} cross sections have been adjusted for the estimated 8.8(13) kb background signal.

nance above the $5p$ threshold. Pt^- thus offers a case where valence-shell stabilization does not occur. Since the valence shell is identical in both excitations, the difference observed between these two excitations gives an example for the importance of core-valence interactions in such systems and offers a sensitive probe into these difficult to calculate interactions [2,20].

The experiments were performed using the ion-photon beamline [21] at the Advanced Light Source (ALS). A 7.45 keV, ≈100 nA beam of Pt^- was extracted from a NEC SNICS II cesium sputter source and merged with a counterpropagating photon beam from ALS beamline 10.0.1. Pt^{n+} ions formed by photon-ion interactions in the merged region are deflected by a magnetic field and counted using a channeltron-based detector.

Given the Pt^- binding energy of 2.125 10(5) eV [19,22] [uncertainties quoted to 1 standard deviation (SD)] and ionization potentials (IPs) $(Pt)_{IP}=8.9588$ [23,24], $(Pt)^+_{IP}=18.563$ eV [23,25], $(Pt)^{2+}_{IP}=35.3(28)$, and $(Pt)^{3+}_{IP}=51(3)$ eV [26], it is energetically possible to remove up to four valence electrons from Pt^-, to form charge states up to Pt^{3+}, at photon energies exceeding 65(3) eV. All energetically allowed ionic products were detected. Neutral products cannot be detected with this apparatus. Careful tests were conducted to determine that isobaric contaminations were insignificant. Also, repeating the Pt^{3+} measurements using the weaker ^{198}Pt isotope showed no difference in structure, ruling out isobaric interferences. Formation of charge states higher than +1 has been observed previously in a limited number of detachment studies; namely, in S^- [4], Te^- [6], and I^- [7] where up to 5, 3, and 4 electrons were emitted, respectively.

The plots have been scaled to the measured absolute cross sections (Table I) as in previous experiments [5,4,21]. Absolute cross sections for Pt^+ production were obtained at five energies and those for Pt^{2+} and Pt^{3+} were scaled from Pt^+ using measured cross-section ratios following the procedure developed in Ref. [4].

Figure 1 shows the signal observed in the Pt^+, Pt^{2+}, and Pt^{3+} product channels following $5p$ and $4f$ photoexcitations and detachment of Pt^-. While stepwise ionization may be possible following $4f$ photodetachment, core-excited Pt formed by $5p$ detachment cannot decay to Pt^{2+} through sequential Auger decay and must be formed by auto doubleionization. Production of Pt^{3+} is possible only above the four-electron threshold at 65(3) eV and must necessarily involve highly correlated many-electron processes over the range detected here .

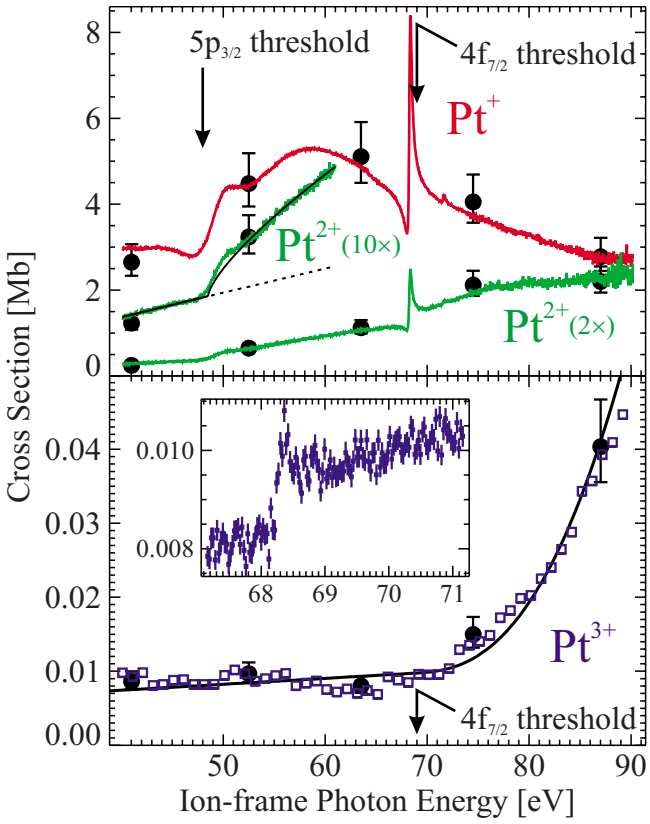

FIG. 1. (Color online) Observed Pt^+, Pt^{2+} [top panel], and Pt^{3+} [bottom panel] production following photoabsorption in Pt^- scaled to measured absolute cross sections (filled circles, see Table I). For presentation purposes, the Pt^{2+} signal has been multiplied by the factors shown. The solid curve in the lower panel is the best-fit d-wave curve to the Pt^{3+} data. The inset shows higher statistics data of the region near the $4f$ threshold in Pt^{3+}.

The excitation of a $4f$ electron into the $5d$ orbital, producing a NI resonant state below the neutral atom parent state, results in strong Feshbach resonances dominating the spectrum around 68 eV. Figure 2 shows this region with better statistics. Two Feshbach resonances can be clearly seen in both Pt^+ and Pt^{2+}. The Fano profile [28] fits to the resonances (solid curves) reproduce the shape very well. While ΔJ selection rules allow three resonant transitions for a $^2D \rightarrow {}^2F$ transition, the large fine structure splitting [1.207 72(6) eV [29]] in Pt^- precludes populating the $^2D_{3/2}$ state to any significant amount [about 10^{-3} of the ground-state (GS) population [22]]. Since the $4f^{13}5p^65d^{10}6s^2\ {}^2F$ state has a more than half-filled orbital, Hund's rule suggests the highest J state likely lies lowest in energy. The first (large) resonance is therefore likely the $^2D_{5/2} \rightarrow {}^2F_{7/2}$ excitation. The fits yield a line center $\varepsilon_r=68.286(17)$ eV, natural line width $\Gamma=0.243(2)$ eV, and shape parameter $q=2.07(3)$. [Spectral bandwidth of 95(5) meV and photon energy calibration accuracy of 17 meV are assumed.] The $4f$ to $5d$ excitation in Pt

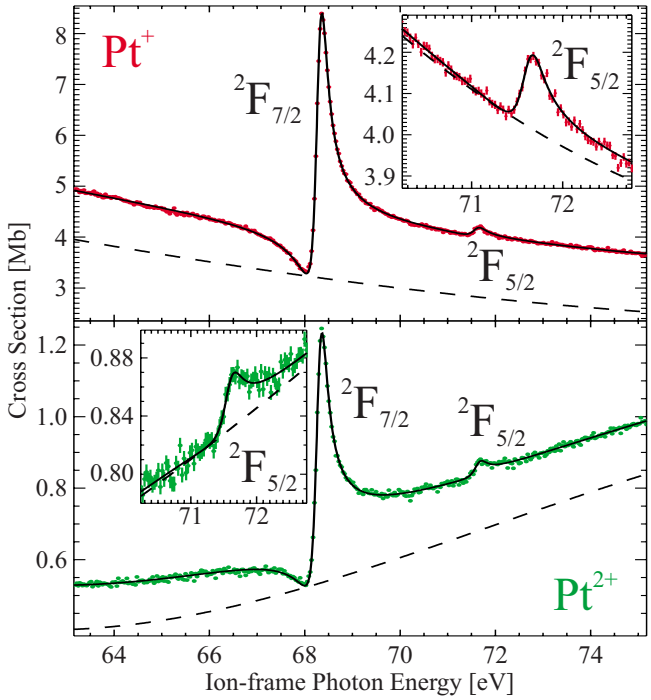

FIG. 2. (Color online) Signal observed from Pt^+ (top) and Pt^{2+} (bottom) near the $4f$ threshold with fit Fano profiles (solid curves). Dashed curves are the estimated noninterfering continua. The insets show higher-statistics results of the $J=5/2$ fine structure resonance.

has been measured to be 68.5 eV [30], locating the Pt^- $4f$ threshold at 70.6 eV. The $^2F_{7/2}$ state is therefore bound by about 2.3 eV. Fits to the second resonance ($^2D_{5/2} \rightarrow {}^2F_{5/2}$) yield $\varepsilon_r = 71.62(3)$, $\Gamma = 0.30(4)$ eV, and $q = 2.60(7)$. (Consistent parameters were obtained between fits to the Pt^+ and Pt^{2+} data, confirming that the initial detachment process is the same, with the products subsequently formed via different Auger decay channels from the same intermediate Pt state.) The $J=5/2-J=7/2$ splitting [3.334(24) eV] is similar to the splitting of the $4f$ core hole in Pt (3.3 eV [31]), as well as the calculated splitting in isoelectronic Au (3.7 eV [32]). Finally, the decay of the large resonance is $\sim 7\times$ more likely into Pt^+ than into Pt^{2+}, in contrast to Te^- ($4d \rightarrow 5p$), where the Te^{2+} state was too weak to detect ($\lesssim 10\%$ Te^+), and S^- ($2s \rightarrow 3p$), where approximately the same strength was observed in the two channels. The ratio of the two resonance strengths, $\sigma(J=7/2)/\sigma(J=5/2)$, is 28.7(15) for Pt^+, while it is considerably less, 18.6(15), for Pt^{2+}, indicating a greater relative preference for the $J=5/2$ state to decay to Pt^{2+}. The variation in these decay branchings is likely a result of the dependence on the details of intermediately lying states and Auger rates.

Three excitation transitions are also allowed for $5p \rightarrow 5d$ excitation. However, the small $^2D_{3/2}$ population allows only one resonance ($4f^{14}5d^96s^2\ {}^2D_{5/2} \rightarrow 4f^{14}5p^55d^{10}6s^2\ {}^2P_{3/2}$) to be visible. This corresponds to the small feature just above 50 eV. The dip seen around 48 eV in the Pt^+ spectrum does not appear in Pt^{2+}, which is an indication that it is likely due to variations in the underlying valence two-electron photodetachment background. The resonance is more conspicuous in the better-behaved Pt^{2+} spectrum. A power-law fit to the data, with the data near the resonance excluded, is plotted over the expanded Pt^{2+} data region. The fit yields a threshold energy around 48 eV, close to the 49.4 eV expected from calculations by Sladeczek *et al.* [33] (after correction for a systematic shift in their calculations [34]), and an exponent $=0.67(21)$ similar to the expected 0.5 for a Wigner *s* wave. However, it is unlikely that the Wigner law is reliable over this very large range, especially since the very short lifetime of this state could produce significant postcollision interaction (PCI) effects over several eV above the threshold, and the curve serves mainly to guide the eye. Based on the theoretical threshold value, the $5p$ to $5d$ resonance center is about 1 eV above, although likely overlapping, the $5p$ detachment threshold, in contrast to the 2.3 eV binding for the $4f$ excitation. Since the valence shell is the same in both resonances, this difference in binding energy is attributed to the very different core-valence interactions from the different core holes. This can be understood on the basis of the mean radii of the orbitals. Using Pt as a benchmark, the mean radii are approximately $0.05a_0$, $1.11a_0$, and $1.63a_0$ for the $4f$-, $5p$-, and $5d$-shell electrons, respectively [35]. The much closer proximity of the $5p$ to the $5d$ electrons leads to a stronger interaction, destabilizing the orbital. Finally, we note that $4f^{14}5p^55d^{10}6s^2\ {}^2P$ is not a pure state and interacts strongly with $5p^65d^8nf$ ($n=5,6,7,\ldots$). It can therefore reach a multitude of excited states with slightly different energies, hence forming a broad resonance. In contrast, the $4f^{13}5p^65d^{10}6s^2\ {}^2F$ hole state is almost pure, forming the strong narrow Feshbach resonances observed here.

Detachment of a $5p$ electron leaves the system with an energy below the Pt^{3+} GS [65(3) eV], and so no $5p$ detachment is observed in the Pt^{3+} signal. Furthermore, the $4f^{13}5p^65d^{10}6s^2\ {}^2F$ resonances have a very small branching fraction to Pt^{3+} (nearly 2000 times weaker than Pt^+), as can be seen in the inset of Fig. 1. As a result, the spectrum is dominated by the direct $4f$-electron detachment. However, a small, nearly constant background signal is present even below the threshold for Pt^{3+} production indicating some form of contamination. Isobaric contaminants were ruled out, as noted above. A more likely source of the signal is higher-order light contamination, known to exist in the beamline. Although this is a small percentage of the first order light and thus unlikely to affect the Pt^+ and Pt^{2+} signal, the Pt^{3+} cross section increases greatly with photon energy and thus is likely much larger at the second- and third-order photon energies. Given the very small cross sections observed over this region, the small contribution of the higher-order light could account for the background signal.

As previously noted, the threshold for simultaneous detachment of 4 valence electrons is 65(3) eV. While the cross section for this process is not known for Pt, based on measurements in other systems it should be <1 kb even 20 eV above threshold [36] and is therefore insignificant over the scanned range. The rise in the signal beyond ≈ 70 eV must therefore be due to the *d*- and *g*-wave continuum from the *f*-electron detachment. As previously observed [22], the gradual zero-slope onset of *p*-wave laws makes extracting reliable threshold energies notoriously difficult if any background is present. A *d*-wave law is even more sensitive to background variations. Although the quality of the data is not

sufficient to extract a reliable threshold energy, given the $4f_{7/2}$ binding energy in Pt (71.2 eV [31]) and given that a binding of ~1 eV or less may be expected for the $4f$ excitation resonances, we estimate a threshold position of around 68–70 eV. Except for small oscillations produced by the background, a power law with the threshold fixed to 69 eV fits the data well over a range of 20 eV and returns an exponent of 2.4(2), consistent with the expected Wigner d-wave law exponent of 2.5. It is important to note that very near the threshold, an Auger electron may be ejected before the photoelectron has time to leave the influence of the atomic core. The resulting PCI effect on the threshold has been studied experimentally in previous work [3] and may lead to a modification of the threshold law at small photoelectron energies. Assuming a short Auger lifetime of ≈3 fs (≈100 meV width), PCI is significant only up to ≈1.4 eV [10(c)] above threshold and thus not observable for the range studied here.

In summary, the inner-shell photodetachment spectrum of transition-metal NIs is observed to be rich in structure due to the presence of the $5p$ and $4f$ electrons and the mostly filled d orbital. The absence of any significant underlying photodetachment structure in Pt^{3+} allowed for the observation of a d-wave detachment threshold law in a single-photon process. A shape resonance around 50 eV can be assigned to a $5p \rightarrow 5d$ excitation, lying just above the $5p$ threshold. Finally, high-precision measurements of two Feshbach resonances from $4f \rightarrow 5d$ excitations are observed in Pt^+ and Pt^{2+} channels but are nearly completely absent in Pt^{3+}. These observations coupled with previous studies show that orbital stabilization is generally, but not always, observed when a single-vacancy orbital is filled.

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