Measurement of the electron affinity of atomic Ce

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Photoelectron spectra of Ce^- obtained using both 2.33- and 3.49-eV photon energies resolve numerous transitions between the $^4H_{7/2}$ ($\cdots 4f\ 5d^2\ 6s^2$) anion ground state and excited neutral states, in addition to transitions from excited anion states to the ground and excited neutral states. Building on the theoretical work of O'Malley and Beck [S. M. OMalley and D. R. Beck, Phys. Rev. A **74**, 042509 (2006)] and the known term energies of Ce excited states, we determined the adiabatic electron affinity of Ce to be 0.570(20) eV, which is lower than previously reported experimental values. The term energy of the lowest-energy excited anion state arising from the $\cdots 4f\ 5d\ 6s^2\ 6p$ configuration was also determined to be 0.210(20) eV.

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I. INTRODUCTION

The cerium atomic anion is remarkable in that there are numerous bound excited states that are optically accessible from the ground state [1–3]. Determining the adiabatic electron affinity (EA) of the neutral atom via the $Ce^- + h\nu \rightarrow Ce + e^-$ photodetachment transition is a challenge, however. Based on the leading L-S characters of the ground electronic states of the anion ([Xe] $4f\ 5d^2\ 6s^2\ ^4H_{7/2}$ [4]) and the neutral ([Xe] $4f\ 5d\ 6s^2\ ^1G_4$ [5]), the direct detachment transition is spin forbidden.

Observation of the Ce^- atomic anion was first reported in 1993 [6]. Several years later, a threshold photodetachment spectrum of Ce^- was reported by Berkovits *et al.* [7], who observed detachment thresholds attributed to transitions to neutral excited states, from which they determined an adiabatic electron affinity EA of 0.70(1) eV. Davis and Thompson subsequently measured the fixed-frequency photoelectron (PE) spectrum of Ce^-, and observed several broad spectroscopic features attributed to overlapping electronic transitions [8] in the 0.9–2.1-eV range. They reported an EA of 0.955(26) eV. O'Malley and Beck, using relativistic configuration interaction photodetachment calculations suggested that the 0.955 eV transition in Davis and Thompson's spectrum involved excited neutral states, and presented a 0.660-eV EA. Walter and coworkers measured total photodetachment cross-section measurements over a range near the predicted electron affinity in 2007 [9] and later recalibrated their light source and extended the range in 2011 in a collaboration with Beck and co-workers. Based on the positions of two resonances calculated to straddle the detachment threshold, they recommended an EA value of 0.628 eV [1]. Cao and Dolg previously presented similar theoretical results, and based on several approximate error corrections, estimated an EA of 0.58(1) eV [10]. Felfli *et al.* calculated the EA to be 0.61 eV [11]. Overall, the theoretically determined values have generally been in agreement, while the experimentally determined values have not.

While the total photodetachment cross-section measurements on Ce^- exhibited numerous excited-state anion resonances both above and below the predicted Ce^- ($^4H_{7/2}$) + $h\nu \rightarrow$ Ce ($^1G_4$) + e^- threshold energy [1], two features of the detachment process prevent the observation of threshold electrons that would unambiguously establish the EA, the first of which is the nominally spin-forbidden nature of the transition mentioned above. Secondly, assuming that strong j-j coupling overrides the spin change, the transition would still have zero cross section at threshold. Given the difference in electron configurations of the anion and neutral ground states, the photoelectron generated in direct detachment would be p wave ($l = 1$), which, given the Wigner threshold law [12], would have zero cross section at threshold.

We have measured a higher-resolution PE spectrum of Ce^- in which the positions and angular dependences of transitions from the ground and excited Ce^- states can be reconciled with theoretical studies by O'Malley and Beck [2]. We are able to establish a more definitive EA value for Ce, 0.570(20) eV, and determine the term energy for the lowest-lying electronic state with the even [Xe] $4f\ 5d\ 6s^2\ 6p$ configuration, $^2H_{9/2}$, to be 0.210(20) eV.

II. EXPERIMENTAL DETAILS

PE spectra of Ce^- were measured using an apparatus described in detail previously [13,14]. Ce^- was generated using a pulsed laser ablation–molecular beam source [15] in which a solid Ce target was ablated with approximately 3 mJ/pulse of the second-harmonic output of a Nd:YAG laser (532 nm, 2.33 eV) operated at 30 Hz repetition rate, and entrained in a pulse of ultrahigh-purity He carrier gas. The resulting atomic and molecular species in all charges states were swept through a 2.5-cm-long, 0.3-cm-diameter channel and expanded into a vacuum chamber. Anionic species that passed through a 3-mm skimmer were accelerated to 1.00 keV into a 1.2-m time-of-flight mass spectrometer, and detected using a dual multichannel plate detector. The mass resolution ($m/\Delta m$) in the region of the Ce atom is 300, which is more than sufficient for separating the two primary isotopes at 140 and 142 amu.

Prior to colliding with the ion detector, $^{140}Ce^-$ was photodetached at the intersection of the ion drift tube and a 1-m field-free drift tube situated perpendicular to the ion drift path with the second- and third-harmonic outputs of a second Nd:YAG laser (532.10 nm, 2.330 eV and 354.7 nm, 3.495 eV, respectively), timed to intersect only the $^{140}Ce^-$ ion. A second dual microchannel plate detector assembly situated at the end of the field-free drift detected photoelectrons over a 0.0016-sr

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solid angle. The drift times of the small fraction of the detached electrons that traveled the length of the drift tube were recorded using a digitizing oscilloscope. The drift times were converted to electron binding energy (e^-E_B) by identifying common transitions observed in the spectra collected using both photon energies, and setting the difference in the electron kinetic energies (e^-E_K) to the fundamental energy (the difference between the energies of the second and third harmonics), which is specified as 1.1650(1) eV for the laser system used in this study, because of the relationships

$$e^-E_K = h\nu - EA - T_e^{\text{neutral}} + T_e^{\text{anion}},$$

and

$$e^-E_B = h\nu - e^-E_K.$$

The calibration turned out to be nonlinear over the broad range of electron kinetic energies measured, and we have consequently appointed an uncertainty in the absolute binding energy values that conservatively reflect the range of calibrated values that resulted from this approach applied to different sets of common transitions. The e^-E_B values reflect the energy difference between the final neutral state and the initial anion state, and are independent of the photon energy used. The linewidth of the laser system used is 1 cm^{-1}, which is small relative to the typical bandwidth of the photoelectron kinetic energy analyzer (*vide infra*).

Spectra were collected with the laser polarization both perpendicular to ($\theta = 90° \pm 10°$) and parallel to ($\theta = 0° \pm 10°$) the electron drift direction. In atomic systems, the angular distribution of photoelectrons follows the expression [16]

$$\frac{\partial\sigma}{\partial\Omega} = \frac{\sigma_{\text{total}}}{4\pi}\left[1 + \beta(E)\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)\right].$$

The asymmetry parameter $\beta(E)$ varies from -1 to 2, depending on the symmetry of the orbital associated with the detachment. Spectra were collected, alternating laser polarization every 80 000 laser shots on a single day to minimize the effects of drift in the ion source conditions, for a total of 320 000 laser shots at each polarization for both 2.330- and 3.495-eV detachment energies. Because the overall electron count rate was higher with $\theta = 0°$ polarization, the spectra were further signal averaged for a total of 1 000 000 laser shots for 2.330 eV and 3.495 eV ($\theta = 0°$) and 680 000 laser shots for 3.49 eV ($\theta = 0°$).

The energy bandwidth ΔE of the electron kinetic energy analyzer decays with $e^-E_K^{3/2}$ following

$$\Delta E = 0.004\ \text{eV} + 0.0078\ \text{eV}\left(\frac{e^-E_K}{\text{eV}}\right)^{3/2}.$$

Transitions observed in the spectrum obtained with 2.330-eV photon energy were therefore narrower than the same transitions observed in the spectrum obtained with 3.495 eV. The bandwidth is affected by stray magnetic and electric fields, which are minimized by a double-layered magnetic shield internally coated by graphite. Because a Bakker-style time-of-flight mass spectrometer [17] has been incorporated into the experiment, Doppler broadening is minimized, as well.

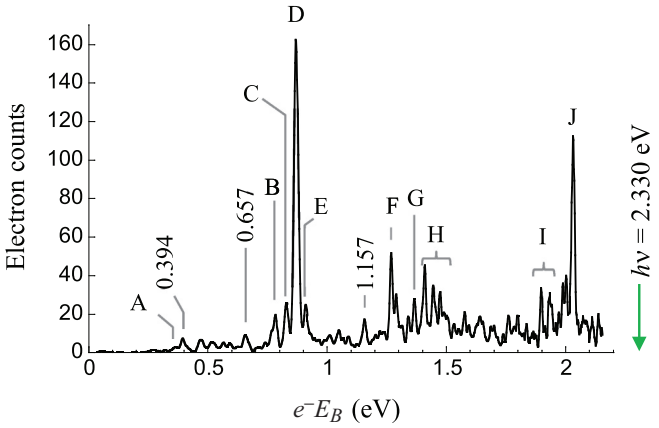

FIG. 1. (Color online) Photoelectron spectrum of Ce^- obtained using 2.33-eV photon energy, in which electrons are binned into 0.002-eV energy intervals. Peak positions and assignments for peaks labeled with letters are included in Table I. Several unassigned peaks are labeled by their position (eV) for reference.

III. RESULTS AND DATA ANALYSIS

Figure 1 shows the PE spectrum of Ce^- obtained with 2.330-eV photon energy, $\theta = 0°$ polarization. Numerous transitions are observed in the 0.3–2.2-eV e^-E_B range. A number, but not all, of the transitions are labeled by their e^-E_B/eV values. Because of uncertainty in the calibration, the absolute e^-E_B values have an uncertainty of 20 meV, though the energy intervals between the peaks have an uncertainty of 7–10 meV. While we generally present PE spectra as electron counts as a function of e^-E_B, in which the data points appear at ever decreasing energy increments with higher e^-E_B (electron counts are measured in equal time increments), the electron counts shown for this particular spectrum were binned over time intervals corresponding to 2-meV increments [18] to facilitate comparison with the PE spectrum reported previously [8] using a continuous wave apparatus with a spherical-sector energy analyzer. The spectra presented here and obtained previously are consistent, though we are able to resolve more transitions, and are able to distinguish low-intensity transitions at e^-E_B values below 0.8 eV.

Figure 2 shows PE spectra obtained with both 2.330 eV (top panel) and 3.49 eV (bottom panel) photon energies, and with laser polarizations both perpendicular and parallel to the direction of electron collection, using the equation

$$\beta(E) = \frac{I_0 - I_{90}}{\frac{1}{2}I_0 + I_{90}}.$$

The $\beta(E)$ parameters determined for the 2.330 eV PE spectrum, plotted just above the spectrum, range from $-0.2(3)$ for features below $e^-E_B = 0.7$ eV and around 2.0 eV, to $\sim$1.5 for the more intense features in the central portion of the e^-E_B range. Based on the theoretical work of Beck *et al.* [2], transitions involving detachment of a 6*s* electron are predicted to have much higher cross sections than transitions involving 5*d* electron detachment. The more intense features therefore likely indicate transitions to the excited $4f\ 5d^2\ 6s$ occupancy. The $\beta(E)$ parameters found for the more intense transitions are consistent with detachment from an atomic *s* orbital, which

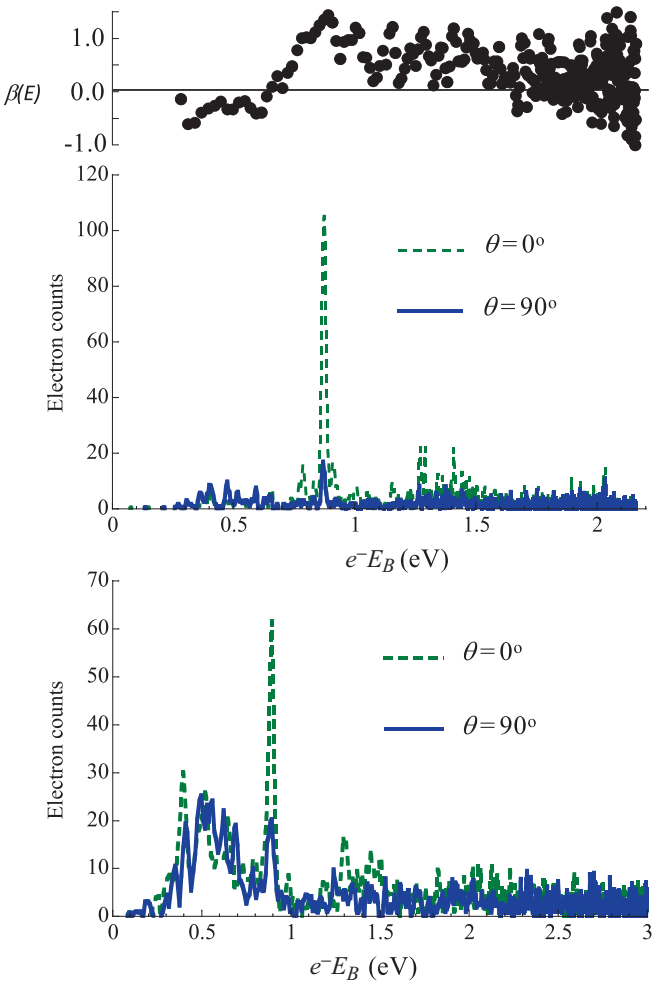

FIG. 2. (Color online) Photoelectron spectra of Ce^- obtained with the detachment laser electric field parallel to ($\theta = 0°$, dashed green traces) and perpendicular to ($\theta = 90°$, solid blue traces) the detected electron trajectory. Top panel spectra were collected with 2.33-eV photon energy, bottom panel spectra were collected with 3.49-eV photon energy. The asymmetry parameter determined for the 2.33-eV spectrum is shown just above the 2.33-eV spectrum.

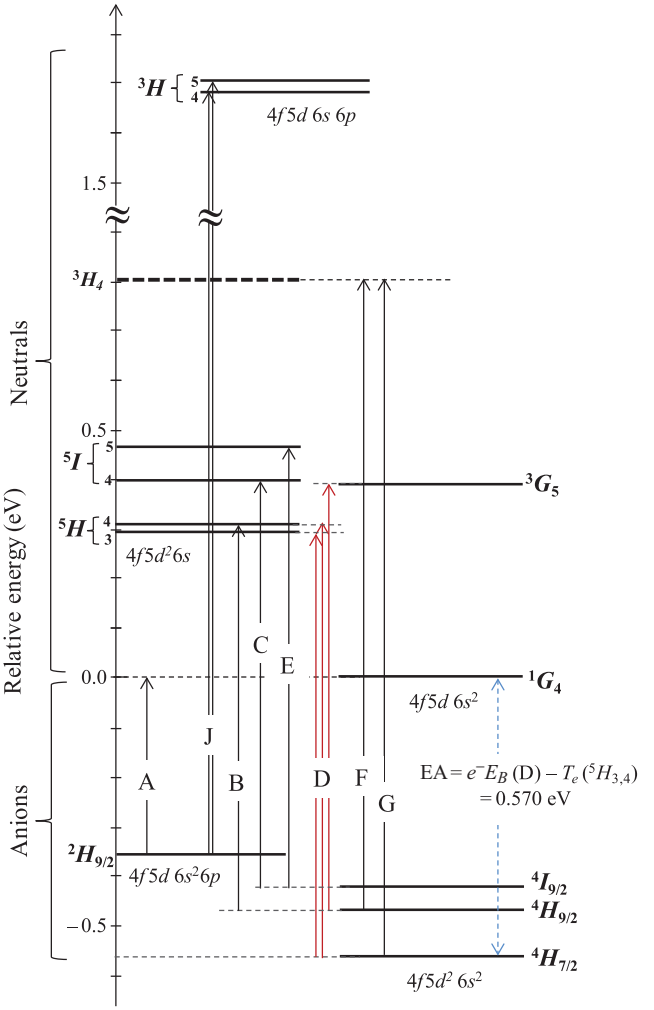

FIG. 3. (Color online) Simplified energy level diagram summarizing the relative energies of the various anion(Refs. [1,2], and this work) and neutral states (Ref. [5]) associated with the detachment transitions labeled in Fig. 1. Leading electronic configurations and LS terms are included, but note that most states are heavily mixed. The groups of transitions labeled H and I in Fig. 1 involve heavily mixed groups of final states.

would result in p-wave ($l = 1$) photoelectrons. The less intense features may be due to either transitions involving d-orbital detachment, or transitions from excited anion states with lower population in the ion beam.

Detachment of the 6s electron restricts transitions to a $\Delta J = \pm\frac{1}{2}$ selection rule and a $\Delta L = 0$ propensity rule. Because of the multiconfigurational nature of all the atomic anion and neutral states (for example, the $4f\ 5d^2\ 6s^2\ ^4H_{7/2}$ ground electronic state of the Ce^- was calculated to have 26% $^2G_{7/2}$ character, with a larger contribution from the ^2G state in the spin-orbit-excited $^4H_{9/2}$ state [1]), other $\Delta J = \pm\frac{1}{2}$, $\Delta L \neq 0$ transitions may be observed with lower intensity.

Overall, the spectrum is qualitatively very similar to the theory-based simulation generated by O'Malley and Beck [2]. There are three groupings of comparably intense features, which, according to the previous analysis, originate from numerous anion states. With this in mind, we assign the dominant peak "D" [$e^-E_B = 0.869(20)$ eV] to three overlapping transitions, $^5H_3 \leftarrow {}^4H_{7/2}$, $^5H_4 \leftarrow {}^4H_{7/2}$, and $^3G_5 \leftarrow {}^4H_{9/2}$. The term energies of the $J = 3$ and 4 levels of the ^5H neutral state, 2369 and 2438 cm^{-1} (separated by 8.5 meV; they are not resolved), the 3211 cm^{-1} term energy of the $^3G_5$ state, and the term energy of the $^4H_{9/2}$ excited anion state, 790 cm^{-1}, result in an overlap of these transitions, resulting in the most intense peak in the spectrum. Figure 3 shows a diagram that summarizes the relative energies of the various neutral and anion states to illustrate how these three transitions are expected to overlap, and Table I summarizes the various overlapping transitions, the transition energies observed in the spectrum, and hypothetical transition energies determined assuming the EA value determined in our study.

Based on the energy of peak "D" and the known term energies of the final neutral states [5], the EA of Ce is determined to be 0.570(20) eV. While it is significantly lower than earlier experimental values [7,8], it is in better agreement

TABLE I. Summary of several peak positions and assignments for the PE spectrum of Ce^- shown in Fig. 1. Note that not all peaks are assigned because the term energies for excited Ce^- states lying between the $^4I_{9/2}$ $(4f\ 5d^2\ 6s^2)$ and $^2H_{9/2}$ $(4f\ 5d\ 6s^2\ 6p)$ exited states have not been established.

Peak label	e^-E_B (eV)	Assignment *Neutral* + e^- ← *Anion*	T_e of neutral state from Ref. [5] and transition energy (e^-E_B) assuming EA = 0.570 eV
A	0.360	$^1G_4\ (4f\ 5d\ 6s^2) + e^-\ (l=0,2) \leftarrow {}^2H_{9/2}\ (4f\ 5d\ 6s^2 6p)$	0; 0.360 eV[a]
B	0.776	$^5H_4\ (4f\ 5d^2\ 6s) + e^-\ (l=1) \leftarrow {}^4H_{9/2}\ (4f\ 5d^2\ 6s^2)$	0.3023 eV; 0.774 eV[b]
C	0.829	$^5I_4\ (4f\ 5d^2\ 6s) + e^-\ (l=1) \leftarrow {}^4I_{9/2}\ (4f\ 5d^2\ 6s^2)$	0.3964 eV; 0.824 eV[c]
		$^5H_3\ (4f\ 5d^2\ 6s) + e^-\ (l=1) \leftarrow {}^4H_{7/2}\ (4f\ 5d^2\ 6s^2)$	0.2937 eV; 0.864 eV
D	0.869	$^5H_4(4f\ 5d^2\ 6s) + e^-\ (l=1) \leftarrow {}^4H_{7/2}\ (4f\ 5d^2\ 6s^2)$	0.3023 eV; 0.873 eV
		$^3G_5\ (4f\ 5d^2\ 6s) + e^-\ (l=1) \leftarrow {}^4H_{9/2}\ (4f\ 5d^2\ 6s^2)$	0.3981; 0.870 eV[b]
E	0.909	$^5I_5\ (4f\ 5d^2\ 6s) + e^-\ (l=1) \leftarrow {}^4I_{9/2}\ (4f\ 5d^2\ 6s^2)$	0.4667 eV; 0.895 eV[c]
F	1.268	$^3H_4\ (4f\ 5d^2\ 6s) + e^-\ (l=1) \leftarrow {}^4H_{9/2}\ (4f\ 5d^2\ 6s^2)$	0.8030 eV; 1.275 eV[b]
G	1.365	$^3H_4\ (4f\ 5d^2\ 6s) + e^-\ (l=1) \leftarrow {}^4H_{7/2}\ (4f\ 5d^2\ 6s^2)$	0.8030 eV; 1.373 eV
	1.409		
H	1.445	*Mixed neutral states* ← $^4H_{9/2}\ (4f\ 5d\ 6s^2)$	Based on simulations from Ref. [2]
	1.474		
I	1.897	*Mixed neutral states* ← $^4H_{9/2}\ (4f\ 5d\ 6s^2 6p)$	Based on simulations from Ref. [2]
	1.932		
J	2.031	$^3H_4\ (4f\ 5d\ 6s^2) + e^-\ (l=0,2) \leftarrow {}^2H_{9/2}(4f\ 5d\ 6s^2 6p)$	1.676 eV; 2.036 eV[d]
		$^3H_5\ (4f\ 5d\ 6s^2) + e^-\ (l=0,2) \leftarrow {}^2H_{9/2}(4f\ 5d\ 6s^2 6p)$	1.709 eV; 2.069 eV[d]

[a]This assignment sets T_e $(^2H_{9/2}) = 0.210(20)$ eV.
[b]T_e for the $^4H_{9/2}$ state is 0.098 eV based on Ref. [1].
[c]T_e for the $^4I_{7/2}$ state is 0.142 eV based on Ref. [1]
[d]Based on the T_e $(^2H_{9/2})$ value determined from (a).

with the more recently recommended value of 0.628 eV [1], and is generally in satisfactory agreement with theoretical values [1–3,10,11]. The recommended value from Ref. [1] was based on the energies of two excited anion states (one bound, one quasibound) between which the neutral ground state was theoretically predicted to lie. The excited anion state energies were determined from resonant detachment experiments, but the technique used was unable to definitively determine whether the observed anion resonances were associated with bound or quasibound states. Our value relies on the correct identification of the anion ground state as the $^4H_{7/2}$ state (as did Ref. [1]), the prediction that detachment of electrons from *s* orbitals will have the highest cross section, and the reliability of the neutral excited-state term energies [5]. Since the anion ground-state identity is not in dispute, the current determination of the *EA* of Ce is the most direct.

Again, from known neutral electronic structure [5] and the work of O'Malley and Beck [2], the peak "F" at 1.268(20) eV is reconciled with the $^3H_4 \leftarrow {}^4H_{9/2}$ transition, which would be found 0.405 eV higher in energy than the $^3G_5 \leftarrow {}^4H_{9/2}$ transition, indicating a significant population of electronically excited anions in the beam. Indeed, having established EA = 0.570(20) eV, all features observed at binding energies below 0.570 eV must be due to transitions from additional electronically excited anion states other than the $^4H_{9/2}$ and $^4I_{9/2}$ states, with excitation energies of up to 0.21 eV, based on the position of peak "A."

If indeed there are transitions due to detachment of excited anions, a variation in ion source conditions should affect the relative intensities of the peaks. Figure 4 shows the variation of intensity of features in the spectrum relative to peak "D" with source conditions. While it is difficult to correlate changes in source conditions with definitive temperature of the atomic anion beam, particularly since the atomic species can only be made under "hot" source conditions (clusters ions dominate under "colder" conditions), an increase in the number of observed transitions is definitively correlated with populating more excited states (by which more detachment channels become available), so the red trace represents hotter ions, and the blue trace is associated with relatively cold ions. Note that in addition to peaks below 0.570 eV, peaks at and above 1.3 eV also show an increase in relative signal.

The angular distribution of electrons associated with the electronic hot band transitions below 0.7 eV is consistent with *s* wave or *s-d* mixed wave electrons. That is, the asymmetry parameter is close to zero, if not slightly negative. Beck and co-workers [1,2] predicted several excited anions within

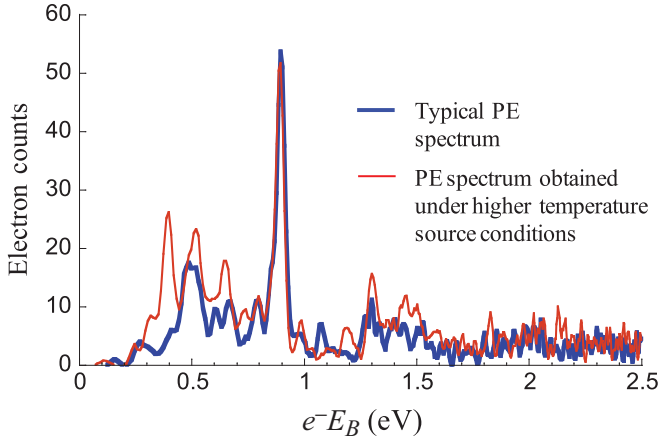

FIG. 4. (Color online) PE spectra of Ce^- obtained under different source conditions. 3.49-eV photon energy was used to collect the data.

0.21 eV of the calculated ground state. However, only anion states that derived from the even symmetry [Xe] $4f\ 5d\ 6s^2\ 6p$ occupancy were predicted to have large cross-section transitions that appear in the range of the hot transitions that are observed. The lowest-energy even electronic state, $^2H_{9/2}$, was predicted to lie 0.36 eV above the $^4H_{7/2}$ ground state, and also to have a lifetime of over 300 μs, well within the time scale of the experiment. The $^2H_{9/2}$ (even) state was additionally predicted to exhibit intense photodetachment transitions at e^-E_B values of 0.31 eV ($^1G_4 + e^- \leftarrow {}^2H_{9/2}$) and 2.01 eV (three overlapping transitions dominated by $^3H_5 + e^- \leftarrow {}^2H_{9/2}$) [2]. The striking similarity between peak "J" observed at 2.031(20) eV and Beck's simulated spectrum leads to assigning peak J to the $^3H_5 + e^- \leftarrow {}^2H_{9/2}$ transition, which would place the $^1G_4 + e^- \leftarrow {}^2H_{9/2}$ transition at 0.360(20) eV. This value coincides with the lowest-energy transition, peak "A," observed in the spectrum (Fig. 1). The term energy of $^2H_{9/2}$ (even) is then determined to be 0.210 (20) eV. Again, a summary of these assignments can be found in Table I and Fig. 3. The binding energy of the $^2H_{9/2}$ state can be read directly from the spectrum, since the detachment directly accesses the ground state: 0.360(20) eV.

There are several other features in the spectrum worth mentioning. The $^4H_{7/2} - {}^4H_{9/2}$ splitting was previously determined experimentally to be 0.097 75(4) eV [1]. This interval is consistent with the splitting observed between peaks "B" [0.776(20) eV] and "D" [0.869(20) eV]. Further, the group of peaks labeled "G" and "H" observed in the 1.32–1.53-eV range were predicted very nicely by O'Malley and Beck [2], and are primarily transitions to close-lying, heavily mixed states from the spin-orbit-excited $^4H_{9/2}$ anion state. These transitions are not indicated in Fig. 3 because of the heavily mixed nature of the final states.

In summary, we obtained PE spectra of Ce^- exhibit transitions that had not been resolved by Davis and Thompson [8]. The peak positions and angular distributions were reconciled with simulations generated by O'Malley and Beck [2], allowing a definitive determination of the EA of Ce to be 0.570(20) eV. The most intense signal observed in the spectra was associated with detachment of a $6s$ electron, which necessarily accesses excited neutral states. However, the neutral excited-state term energies are well established, allowing a straightforward determination of the neutral EA. Finally, we determined that the even configuration electronic state, $^2H_{9/2}$, has a term energy of 0.210(20) eV, which is slightly lower than what had been predicted [2].

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[18] As an example, the peak observed at 0.869 eV is 20 meV full width at half maximum (FWHM) in the electron counts versus e^-BE spectrum. In the raw data, the peak is 9 ns FWHM centered at 1380 ns. The peak at 2.031 eV is 12 meV FWHM. The raw signal is 66-ns-FWHM-wide peak centered at 3014 ns.