Electron Affinities of Atoms and Structures of Atomic Negative Ions

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🔟 Chuangang Ning and ២ Yuzhu Lu





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ABSTRACT

This Review presents electron affinities of atoms and structures of atomic negative ions. The negative ion properties of many elements in the main groups of the Periodic Table were well known in the late 20th century. However, our knowledge of the atomic negative ions of transitional elements, lanthanides, and actinides was completely lacking or largely rather qualitative at that time. Substantial progress both on experimental and theoretical sides in this subject has happened during the last two decades. New developments in the experimental methods that yield accurate electron affinities are described in this Review. Based on the previous reviews, a survey of the electron affinity toward the completion of the Periodic Table is presented. A set of atomic electron affinities and energy levels of atomic anions is recommended.

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Key words: actinides; atomic negative ions; cold ion trap; electron affinity; energy levels; lanthanides; laser cooling; laser photodetachment microscopy; laser photodetachment threshold; Periodic Table; photoelectron energy spectroscopy; slow-electron velocity-map imaging; transitional elements.

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1. Introduction

The ionization potential (IP) is the amount of energy required to remove an electron from a neutral atom. In contrast, the electron affinity (EA) is defined as the amount of energy released when an electron is added to a neutral atom. It measures the capability of an atom to form the corresponding negative ion. Both IP and EA are fundamental parameters for understanding chemical reactions and chemical properties. For example, the electronegativity of an atom (χ) is defined as $\chi = (IP + EA)/2$, and the hardness η = IP – EA. Efforts toward the completion of a periodic table for atomic negative ions for more than a half-century have established that most atomic elements can form stable negative ions, and their electron affinities have been accurately measured.¹⁻⁶ The progress in 1985-1999 on atomic electron affinities was reviewed by Andersen et al.3 in 1999 and was also covered in a later review on atomic and molecular electron affinities by Rienstra-Kiracofe et al.4 in 2002 and in a review about the structure, dynamics, and collisions of atomic negative ions by Andersen⁵ in 2004. The EA values of most main-group elements had an accuracy of ~0.1 meV or better. However, our knowledge of transitional, lanthanide, and actinide elements was rather limited at that time. The typical uncertainty of their EA values was 10 meV, or even no experimental data were available. The partially filled d orbital or f orbital makes the electronic structures of their negative ions and neutral atoms very complicated. The conventional experimental methods used 20 years ago could not well resolve the congested photodetachment channels.

The past 20 years have witnessed great progress from both theoretical and experimental sides in this field, especially for the transitional, lanthanide, and actinide elements. The high-level theoretical calculations of electronic structures of negative ions constitute a vast subject in their own right. This Review will focus on the experimental side. The field of atomic anions is an interdisciplinary subject between chemistry and physics, spanning decades of research, and the historical background was well summarized by the previous reviews. Therefore, we limit this Review to the recent developments. We begin with an introduction and basic concepts. Then, we present details of our method of measuring the electronic structures of atomic anions, which is in comparison with the other three experimental methods that are commonly used to measure EA values. The feature of our method is demonstrated with a specific example. Next, we give a brief survey of the negative ions of the main-group elements and then present more details of the recent experimental developments for transitional elements, lanthanides, and actinides, including the theoretic results in comparison. Finally, we summarize the EA values and energy levels of atomic anions toward the completion of the Periodic Table.

2. Definition of the Electron Affinity

The EA value of an atom A is the difference between the total energies (E_{tot}) of the ground states of A and its negative ion A⁻,³

$$EA(A) = E_{tot}(A) - E_{tot}(A^{-}).$$
(1)

The most effective method to measure EA values is via the photoelectric effect. The additional electron of A^- is photodetached by a laser beam of frequency v and monitors either the photodestruction of A^- or the appearance of the photoelectron e^- ,

$$A^{-} + h\nu \to A + e^{-}(E_k), \qquad (2)$$

where *h* is the Planck constant and E_k is the kinetic energy of the outgoing photoelectron. It should be pointed out that in a photode-tachment event, the initial state of the target A⁻ and the final state of the neutral atom A may not be their ground states. For example, A⁻ may be at its metastable state *i* with a long lifetime, and the final neutral atom A may be at an excited state *f*, which happens often after photodetachment. The difference between the photon energy hv and the kinetic energy E_k is called the binding energy (BE) of the specific photodetachment channel,

$$BE(A_f \leftarrow A_i) = hv - E_k. \tag{3}$$

Clearly, BE is not equal to EA, except if both the states i and f are their ground states. According to the definition in Eq. (1), an atom has only one EA value but may have many different BE values for different photodetachment channels. For example, the experimental EA(¹²C) = 1.262 122 6(11) eV is the energy difference between the ground state $2s^22p^2 {}^{3}P_0$ of C and the ground state $2s^22p^3 {}^{4}S_{3/2}$ of C^{-.7} C⁻ has a bound excited state $2s^22p^3 {}^{2}D_{j=5/2,3/2}$, and its BE relative to C ${}^{3}P_{0}$ is 0.033(1) eV, i.e., BE(C ${}^{3}P_{0} \leftarrow C^{-2}D_{j=5/2,3/2})$ = 0.033(1) eV.⁸ Note that the small fine-structure splitting between $^{2}D_{5/2}$ and $^{2}D_{3/2}$ was not resolved in the experiment. Helium cannot form a stable negative ion, and thus, EA(He) < 0, but He⁻ can form a metastable state 1s2s2p ${}^{4}P_{j=1/2,3/2,5/2}$. ^{9–19} The BE for the photodetachment channel He $1s2s^{3}S_{1} \leftarrow$ He⁻ $1s2s2p^{4}P_{5/2}$ was measured to be 77.516(6) meV.⁹ The final excited state $1s2s^{3}S_{1}$ is 19.819 615 eV above the neutral ground state $1s^{2} {}^{1}S_{0}$ of He.²⁰ Therefore, the metastable state $1s2s2p^{4}P$ of He⁻ is well above the photodetachment continuum limit. It can decay into He $({}^{1}S_{0}) + e^{-}$ via autodetachment through spin-orbital and spin-spin interaction. According to the EA definition in Eq. (1), one may obtain EA(He) = -19.742099(6) eV. However, this value is not very useful in the chemical physics field. It is enough to know EA(He) < 0 in most cases.

3. Experimental Methods

Although several methods have been employed to measure the EA of atoms historically, such as charge transfer reaction, collisional ionization, and plasma and optogalvanic spectroscopy,⁴ the powerful photoelectron spectroscopy is the dominant method used to produce the accurate experimental EA values. In a typical photodetachment experiment, a laser beam with a narrow linewidth crosses with the well-collimated anion beam. The extra electron of an anion

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is detached by absorbing one photon, and then the photoelectron or the neutral atom is detected. The negative ion beam can be produced using several types of ion sources. The atoms with a high EA value can form negative ions easily. A strong negative ion beam, such as H⁻, C⁻, O⁻, F⁻, Cl⁻, Br⁻, and I⁻, can be readily generated by using gas discharge or electrospray ionization.²¹ For the elements with a low EA value, roughly in the range from 0.1 to 1.0 eV, the negative ions can be generated via the laser ablation ion source or the cesium ion sputtering ion source.^{22,23} Atomic anions of most transitional metals can be generated using this method, such as Fe⁻, La⁻, and Th⁻. The generation of atomic anions of the elements with an extremely low EA value is a nontrivial task. Actually, it is the main practical obstacle that leads to the lack of experimental EA data of some elements. Some of them can be generated via the double charge exchange of the positive ion beam in an alkali vapor cell. For example, EA(Ca) = 24.55(10) meV was obtained by Petrunin *et al.*²⁴ They generated a ~3 nA beam of Ca⁻ via the double charge exchange of a 50 keV Ca⁺ beam in Na vapor.

According to Eq. (3), there are several ways to determine the EA value. One indirect way is to scan the photon energy hv and monitor either the appearance of the photoelectrons or the photodestruction of anions A^{-} .^{25,26} Near the photodetachment threshold, the Wigner threshold law predicts the behavior of the single-photon detachment cross section as²⁷

$$\sigma_{\text{tot}} = \begin{cases} a(hv - BE)^{l + \frac{1}{2}}, & hv > BE, \\ 0, & hv \le BE, \end{cases}$$
(4)

where $\sigma_{\rm tot}$ is the total photodetachment cross section, hv is the photon energy, BE is the BE and the photodetachment threshold, l is the angular momentum of outgoing photoelectrons, and *a* is a constant. For the single-photon detachment of an electron in the s subshell of an atom, the outgoing photoelectron is a p wave (l = 1) due to the conservation of the angular momentum. For a p electron, the outgoing photoelectron has two partial waves, s wave (l = 0) and d wave (l = 2), but the contribution of the d wave can be made negligible near the photodetachment threshold due to the Wigner threshold law. Therefore, only the s wave is observable for a p electron near the threshold. Similarly, only the *p* wave is observable for the photodetachment of a d electron near the threshold. Figure 1 compared the s-wave and p-wave photodetachment cross sections vs the kinetic energy near the threshold. It can be seen that the onset of σ_{tot} is quite sharp for the s wave. Therefore, the laser photodetachment threshold (LPT) method can provide a very accurate EA value if it is an s-wave photodetachment.³ For example, Neumark et al. obtained $EA(O) = 11784.645(6) \text{ cm}^{-1}$ via the LPT method in 1985.²⁸ Later, this value for ¹⁶O was updated as 11 784.676(7) cm⁻¹ by Chaibi et al.²⁹ However, this method becomes less precise for a p-wave photodetachment due to a zero-slope onset near the threshold. p-wave thresholds are very sensitive to baselines and slope changes near threshold. Although a few experiments with p-wave threshold measurements reported EA values with uncertainties ≈ 0.2 cm⁻¹, it may prove optimistic for the error bars if unknown systematic effects significantly influence the threshold behavior. It is the reason why the LPT method is dominantly used to measure the EA values of the main-group elements. For the transitional elements, only the *p* wave can be observed near the photodetachment threshold because their outer valence electrons occupy either d or s



FIG. 1. Simulated threshold behaviors of s-wave and p-wave photodetachment according to the Wigner threshold law. The arrows indicated three photodetachment channels with thresholds located at 10010, 10020, and 10050 cm⁻¹, respectively. Note that the intensity is on a relative scale for a better view. The cross section of a p-wave photodetachment is usually one order of magnitude lower than that of an s-wave at $E_k \sim 100$ cm⁻¹.

subshell. The poor ability to resolve the congested photodetachment channels and the rather low cross section near the threshold makes the LPT method not a right choice for measuring the EA values of the transitional elements.

The straightforward way to determine the EA value is to measure the kinetic energy of the photoelectron. A hemispherical energy analyzer is often used to measure the kinetic energy in the conventional photoelectron energy spectroscopy (PES).² Its typical energy resolution is a few meV. However, the photoelectron collection efficiency of this type of spectrometer is pretty low, typically less than 1%. Another common electron spectrometer is the time-of-flight (TOF) energy instrument. It has a similar problem of the low collection efficiency since only a very small fraction of electrons can arrive at the detector if in a field-free flight tube. This problem can be overcome by electrostatic refocusing or much more commonly by using magnetic fields. A divergent magnetic field in a magneticbottle electron spectrometer guides practically all electrons toward the detector, and thus, the collection efficiency is close to 100%. The magnetic-bottle spectrometer has a similar energy resolution to that of the hemispherical spectrometer for $E_k < 0.5$ eV but deteriorates as $E_{\rm k}$ increases.^{30,31} The energy resolution of the PES method, typically ~10 meV, is not good enough to resolve the congested photodetachment channels of negative ions of transitional, lanthanide, and actinide elements. The typical accuracy of the EA measurement via the PES method is ~10 meV. For example, the EA values of V, Nb, and Ta were 0.526(12), 0.894(25), and 0.323(12) eV, respectively, in the previous reviews, which were obtained by Feigerle et al. via this method in 1981.³

The velocity-map imaging (VMI) photoelectron apparatus is also a common type of electron spectrometer.³³ An electrostatic lens is used to accelerate photoelectrons toward a 2D position-sensitive detector with a collection efficiency of 100%. Photoelectrons with the same kinetic energy form a spherical shell, and it becomes a circle after being projected on the VMI screen. The radius of the circle is proportional to the velocity of the photoelectrons. The photoelectron energy spectrum and the angular distribution can be reconstructed from the projected photoelectron distribution since it has a cylindric symmetry when the laser is linearly polarized. The VMI spectrometer has an excellent energy resolution for the low-energy electrons because it is not sensitive to the environmental residual electromagnetic fields. The static electromagnetic stray fields only shift the position of the small spherical-photoelectron shell globally without distortion if the static residual field has no high gradient during the flight path.²⁹ A specially designed VMI for slow photoelectrons, named the slow-electron velocity-map imaging (SEVI) method,^{34–37} has taken this advantage. The basic idea of the SEVI method is very simple: if we can keep the relative energy resolution $\Delta E/E$ constant, it is obvious that the lower the kinetic energy *E*, the better is the absolute energy resolution ΔE . For example, if $\Delta E/E = 2\%$, which is a typical energy resolution of the VMI method, $\Delta E = 20$ meV for E = 1000 meV, but $\Delta E = 0.2$ meV for E = 10 meV. The idea is simple, but it works very well.^{34–37} An energy resolution of ~0.1 meV has been achieved. Recently, the author's group built a SEVI spectrometer to measure the EA values of transitional elements at Tsinghua University. The details of our instrument will be given in the following paragraph.

Another way to measure the kinetic energy of photoelectrons is the laser photodetachment microscopy (LPM) method.^{38–44} The kinetic energy of photoelectrons is measured through the interference patterns of low-energy photoelectrons flying in a uniform electric field. Since the interaction between the outgoing photoelectron and the residual atom is a short-range force, the trajectory of the photoelectron in a uniform electric field is a parabola, in analogy to a free fall. Every point within reach on the detector is hit by two parabolic trajectories, and the variations of the phase difference between the two ways give rise to an interference pattern, which is a series of concentric bright and dark rings. The LPM method is able to obtain the most accurate EA values so far, usually with a 1- μ eV uncertainty. For example, EA(¹²C) = 1.2621226(11) eV.⁷ However, to observe a clear interference pattern, the typical E_k is about 0.1 meV. Only the s-wave photodetachment has a large enough cross section at such low kinetic energy due to the Wigner threshold law. Because of this reason, the LPM method is also limited to the main-group elements.

Table 1 compares the characteristics of four experimental methods: PES, LPT, LPM, and SEVI. Both PES and SEVI methods have a large dynamic range for measuring the kinetic energy of photoelectrons. Therefore, PES and SEVI methods can obtain a rough EA value for an element with an unknown EA value at a preliminary measurement. The advantage of SEVI is that the EA value can be further accurately determined by selecting a specific photodetachment channel. LPT and LPM conduct the EA measurement near the threshold. Therefore, LPT and LPM need to know the EA value in advance. Otherwise, LPT and LPM need many tries to pin down the threshold for the element with an unknown EA value. Compared with the threshold measurement, SEVI usually has a much higher photoelectron count rate since it can conduct the measurement at $E_k \sim 10$ meV. This is a very important advantage for a p-wave photodetachment due to the Wigner threshold law. There are a few other methods that have been occasionally used to measure EA values: resonant multiphoton detachment of negative ions,^{45,46} stimulated Raman scattering detachment spectroscopy,⁴⁶ and accelerator mass spectrometry (AMS).⁴⁷ Brief descriptions of these methods can be found in the previous review.³ Each of these methods has its own limitations and is rarely used. In summary, SEVI has a high energy resolution, a large dynamic range, and a high photoelectron count rate. These features make SEVI the right choice to measure the EA values of the transitional, lanthanide, and actinide elements.

Figure 2 shows the schematic diagram of our SEVI apparatus used for investigating the electronic structures of negative ions. The detailed descriptions of our spectrometer can be found in our previous work.^{37,48} A brief description is given here. Negative ions were generated by focusing a 532-nm Nd:YAG pulsed laser onto a translating and rotating metal disk. The negative ions were then accumulated and confined in an octupole radio-frequency (rf) ion trap, where they thermally equilibrated with a burst of cold buffer gas by sufficient collisions. The typical buffer gas was a mixture of 20% H₂ and 80% He. The ion trap was mounted on a cryogenic refrigerator with a temperature controlled in the range 5-300 K. The negative ions usually were stored in the trap for 45 ms and then were ejected out via pulsed potentials applied on its end caps. The ejected ions were analyzed by a Wiley-McLaren type TOF mass spectrometer.^{49,50} Ions of interest were selected via a mass gate and then photodetached by a tunable laser in the interaction zone of the VMI system. Outgoing photoelectrons formed a spherical shell and were projected onto a microchannel-plate enhanced phosphor screen. The weighted centers of electron hitting positions were recorded in an event-count mode via a charge-coupled-device camera and accumulated for typically 50 000 laser shots. The radius r can be obtained by summing the intensity over all angles and then

TABLE 1. Comparison of four different experimental methods used for EA measurements

Methods ^a	Resolving power (two adjacent transitions)	Typical accuracy	Dynamic range	Applicability
PES	Discrete peaks if gap >10 meV	~10 meV	A few eV	Elements with simple electronic structures
LPT	Overlapped spectrum, excellent resolution for s-wave, but poor for p-wave	0.001–1 meV	~10 meV	Main group elements and partial late transitional elements
LPM	Overlapped interference patterns, only s-wave photodetachment with $E_k \sim 0.1 \text{ meV}$	0.001-0.01 meV	~0.1 meV	Elements in main groups IIIA-VIIA
SEVI	Discrete peaks if gap >1 meV	0.01-0.1 meV	A few eV	All elements

^a Abbreviations: PES, photoelectron energy spectrometry; LPT, laser photodetachment threshold; LPM, laser photodetachment microscopy; SEVI, slow-electron velocity-map imaging.



FIG. 2. Schematic diagram of the cryo-SEVI apparatus at Tsinghua University.⁶⁴ The anisotropy parameter β is 2 for the plotted PAD.

finding the peak center by a Gaussian function fitting. The repetition rate of the laser system was 20 Hz. The linewidth of our dye laser system was 0.06 cm^{-1} , and its wavelength was monitored by a HighFinese WS6-600 wavelength meter with an accuracy of 0.02 cm^{-1} .

In a typical SEVI experiment, the photodetachment laser has a linear polarization parallel to the phosphor screen. In the case of one-photon detachment by a linear polarized laser, the photoelectron angular distribution (PAD) is given by 51-57

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{tot}}{4\pi} [1 + \beta P_2(\cos\theta)], \tag{5}$$

where σ_{tot} is the total photodetachment cross section; Ω is the solid angle; $P_2(\cos \theta)$ is the second-order Legendre polynomial, $(3\cos^2 \theta)$ (-1)/2; θ is the angle between the velocity of the emitted photoelectron and the electric field of the laser; and β (varies from -1 to 2) is the anisotropy parameter. β depends on the kinetic energy of photoelectrons and the symmetry of the electronic state. Since the distribution of outgoing photoelectrons has a cylindrical symmetry about the polarization axis, the photoelectron distribution can be reconstructed from the projected imaging via an inverse Abel transformation^{58,59} or the maximum entropy velocity Legendre reconstruction (MEVELER) method.^{60,61} MEVELER is used more often in our group since it can reliably reconstruct the distribution without the annoying central-noise problem. PAD can provide helpful information for the state assignment of experimental spectra. β is equal to 2 for the photodetachment of an s-subshell electron. For photodetachment of a p electron, β is close to zero near the threshold, gradually decreases to -1, and then increases as E_k increases due to the interference between s and d partial waves. For the photodetachment of a d electron, β is close to 0.2 near the photodetachment threshold, gradually decreases to -1, and then increases as $E_{\mathbf{k}}$ increases.

We tested our cryo-SEVI machine using the atomic anions of main-group elements because of their easy production and simple electronic structures. We scanned the photon energy hv above the EA value with a typical step 0.5 cm⁻¹. The kinetic energy of photoelectrons E_k was proportional to the radius squared r^2 of the photoelectron image, and r was obtained by a fitting procedure from the reconstructed photoelectron distribution. The BE was extracted by BE = $hv - \alpha r^2$, and α is a calibration coefficient, which can be obtained by changing the photon energy hv or measuring an atomic anion with a well-known EA. As shown in Fig. 3, the measured r^2 was plotted versus the photon energy hv. The EA value and its uncertainty were determined by a best linear fitting, where we have

considered the uncertainty of the intercept to be essentially the one that remains, once the slope has been fixed at its most probable value when ideally possible variations of both parameters should be considered simultaneously. For example, we previously found [115] large isotope shifts for 206Pb (-0.40(12) cm⁻¹) and 207Pb (+0.12(20) cm⁻¹) compared to 208Pb that are significantly larger than the estimated value (less than 0.02 cm⁻¹) for the whole 206 to 208 structure by Bresteau et al. [116]. The determinations of electron affinities by the SEVI method and their uncertainties may be impacted as well by systematic uncertainties in our measurements and analysis. In 2015, we measured the EA value of iodine (I) using our first-generation apparatus and obtained $EA(I) = 24672.94(10) \text{ cm}^{-1}$, which is consistent with 24 672.874(29) cm⁻¹ reported by the Blondel group using the LPM method. 62 In 2018, we determined the EA value of S to be 16 753.00(7) cm⁻¹ using our second-generation apparatus, which had a higher energy resolution than our first apparatus. Our result is in excellent agreement with the LPM result [16752.9753(41) cm⁻¹].63 The slight difference (0.025 cm^{-1}) remains within the limits set by the linewidth of the dye laser (0.06 cm^{-1}) and the accuracy of the wavelength meter (0.02 cm⁻¹). Figure 3 shows a typical photoelectron energy spectrum obtained with our second-generation machine at an imaging voltage of -150 V. The energy resolution [the full width at half maximum (FWHM)] is 0.53 cm⁻¹ (0.066 meV) for the peak with a kinetic energy $E_k = 1.08 \text{ cm}^{-1}$. The energy resolution decreases as the kinetic energy increases. For example, it is 5.1 cm⁻¹ for $E_{\rm k}$ = 93.6 cm⁻¹. The feature of SEVI with an energy resolution of a few cm⁻¹ for $E_k \sim 100 \text{ cm}^{-1}$ is crucial for measuring EAs of the transition elements since the fine structures can be resolved and the photodetachment cross section is much higher than that of LPT and LPM near the threshold.

It should be pointed out that a cold ion trap^{48,66-68} is also an important tool for measuring the EAs of transitional elements, lanthanides, and actinides. The advantages of a cold ion trap are as follows: (1) It can effectively enhance the intensity of the negative ion beam. This is an important feature for acquiring a strong enough negative ion beam for elements with a very low EA value. (2) It is helpful for identifying the excited states with a lifetime of tens of milliseconds since their intensity will change during the trapping period. The energy spectra of atomic anions of lanthanides are extremely complicated. The different initial states can be identified according to the intensity changing trends when the trapping time changed. Moreover, some metastable states can be quenched by the buffer gas in the ion trap, and the quenching efficiency may be significantly different when a different buffer gas is used, such as He, H₂, and CH₄.^{69,70} This also provides helpful information for identifying the excited states. (3) The cold ion trap can effectively cool molecular anions down to a temperature as low as ~10 K, which can substantially improve the sharpness and cleanness of the photoelectron energy spectra of polyatomic molecular anions. It is crucial for an atomic anion if its mass is accidentally the same as that of a molecular anion. Otherwise, the energy spectrum of molecular anions is almost a continuous distribution due to the thermal broadening and hot bands since the ions are usually very hot from the laser ablation ion source. The molecular spectrum may overlap with the spectrum of the atomic anion. Consequently, the signal-to-noise ratio is not good enough for an accurate measurement.

To demonstrate the features of our cryo-SEVI method, we present here the EA measurement of La as an example. La⁻ has a



FIG. 3. Test of our cryo-SEVI apparatus using negative ions of sulfur S^{-,65} (a) The photon energy hv vs the squared radius r^2 of the photoelectron spherical shell for the photodetachment from the ground state of S⁻ ($3s^23p^5 {}^2P_{3/2}$) to the ground state of S ($3s^23p^4 {}^3P_2$). The solid line is the linear least-squares fitting. The intercept 16 753.00 cm⁻¹ is the BE of the photodetachment channel. The error bars are for r^2 . The uncertainty of the slope α was given by the line regression. (b) Deviations of the binding energy from the least-squares fit extrapolated value as a function of the kinetic energy of photoelectrons. The dashed lines indicate the estimated uncertainty of $\pm 0.07 \text{ cm}^{-1}$. The red solid line represents the BE obtained via our SEVI method. The LPM result is also plotted as a blue dotted line for comparison. (c) Photoelectron energy spectrum obtained at $hv = 16754.08 \text{ cm}^{-1}$. The averaged kinetic energy is 1.08 cm^{-1} . The energy resolution (FWHM) is 0.53 cm^{-1} (0.066 meV).

very complicated electronic structure and has attracted great interest for being a candidate for laser cooling negative ions.⁷¹ ⁸ Figure 4 shows the photoelectron energy spectra of La⁻ at the photon energy $hv = 11595.57 \text{ cm}^{-1}$. In Fig. 4(a), La⁻ ions were stored in the trap for 45 ms, so only states with lifetimes comparable with 45 ms can appear in the spectrum. In Fig. 4(b), more peaks were observed when the ion trap was turned off. The extra peaks were related to the shortlived excited states. In the trap-off mode, La⁻ ions took 0.4 ms to fly from the ion source to the photodetachment zone. Therefore, the short-lived excited states had more chance to survive compared with the trap-on mode. The energy levels of neutral atom La are well known with a high accuracy, which can be taken as the fingerprint for the state assignment. Therefore, according to the trends of the peak intensity, the energy levels of La,²⁰ and the well-known energy gaps of La⁻ determined by the infrared resonant spectroscopy, as well as the calculations by Pan and Beck,⁷¹ most of the peaks observed in Fig. 4 can be identified. See Fig. 5 for details. The peak s is from the ground state ${}^{3}F_{2}^{e}$ of La⁻ to the ground state $5d6s^{2}D_{3/2}$ of La. Its BE is the EA value of La. However, an infrared laser would be required if we measure its BE directly around its threshold. Instead, the strong peak a, which corresponds to the transition $La({}^{2}F_{5/2}^{e})$ \leftarrow La⁻⁽³ F_2^e), was chosen to measure the EA of La because its photodetachment threshold was in the tuning range of our dye laser. To determine the BE of peak a as accurately as possible, the photon energy hv was scanned from 11 525 to 11 575 cm^{-1} with a step

~10 cm⁻¹, slightly above the threshold of the transition. Then, a linear fitting procedure was used to determine the BE. As shown in Fig. 6, the BE of transition $La({}^{2}F_{5/2}^{e}) \leftarrow La^{-}({}^{3}F_{2}^{e})$ was determined to be 11 508.88 ± 0.20 cm⁻¹.⁷⁹ The uncertainty of the radius *r* was the main error source. The error bars were not plotted in Fig. 6(a) because it is too small to be visible. As a result, the EA value of La was determined to be 4496.97(20) cm⁻¹ or 0.557 553(25) eV by subtracting the level energy 7011.909 cm⁻¹ of the final neutral La state $5d^{2}6s^{2}F_{5/2}^{e}$ from 11 508.88 ± 0.20 cm⁻¹.²⁰ Later, Blondel optimized this value via a global optimization analysis and obtained 4496.91(17) cm⁻¹ or 0.557 546(20) eV⁸⁰ since multiple transitions were observed in our experiment and the energy gaps among the bound excited states of La⁻ were determined by the infrared resonant spectroscopy.⁷³⁻⁷⁶

4. Survey of Electron Affinity

4.1. Main-group elements

The electronic structure of atomic anions for the elements in group IA (H–Cs) of the Periodic Table is a closed shell ${}^{1}S_{0}$.^{3,81} No fine-structure splitting and easily generating strong negative ion beams make them good targets for the LPT method. Among them, the H⁻ ion is the simplest negative ion, an interesting three-body atomic system. The elaborate numerical calculations have yielded a very accurate EA value of H, 0.754 203 832(4) eV,^{3,82,83} which is a



FIG. 4. Photoelectron energy spectra of La⁻ at photon energy $h\nu$ = 11595.57 cm⁻¹ obtained with the trap-on mode (a) and the trap-off mode (b).⁷⁹ In the trap-on mode, the ions were trapped for 45 ms and were then thrown out for further analysis. In the trap-off mode, the ions directly flew through the ion trap as the trap was turned off. The red curve shows the weak peaks multiplied by a factor of 6 for a clearer view. The sticks below the spectra indicate the BE of photodetachment channels from the states labeled on the left or right sides. The related transitions are illustrated in Fig. 5.

few orders of magnitude more accurate than the best experimental value available 0.754 195(19) eV.84 For elements in group IIA, Be and Mg have no stable negative ions,^{5,85} ^{,86} while Ca⁻, Sr⁻, Ba⁻, and ^{4,47,87–89} The extra electron is weakly bounded in its Ra⁻ are stable.^{5,} p subshell. Their EA values were accurately measured using a resonant LPT method via an s-wave photodetachment,^{24,87–89} except for Ra. Based on the AMS method, Nadeau et al. estimated EA(Ra) as 0.17 eV.⁹⁰ It has been theoretically and experimentally established that Be⁻ exists as a long-lived metastable anion,^{85,91-93} but the existence and nature of such metastable Mg⁻ ions are uncertain.⁸ The detection of a metastable Mg⁻ ion has so far been unsuccessful. The p-block elements (group IIIA-VIIA) form atomic negative ions via the attachment of an electron to their p subshell. Both LPT and LPM methods have been used to determine their EA values with a high accuracy because of an s-wave photodetachment.^{3,97-100} Note that the nitrogen atom is an exception. It has been well established that the nitrogen atom cannot form a stable negative ion N⁻. The AMS ¹⁴C dating method has taken advantage of this fact to get rid of the inference of ¹⁴N.^{5,101} The group VIIIA elements (noble gas elements He-Rn) cannot form stable negative ions because their neutral atoms have a closed-shell ground state 1S0. He⁻ and Ar⁻ can exist as long-lived metastable anions (observable in a mass spectroscopy)^{9,10,102-104} but no evidence for long-lived metastable Ne⁻ and Kr⁻.¹⁰²⁻¹⁰⁴ The existence of a long-lived Xe⁻ ion is uncertain. The claimed observation of the signal of Xe⁻ might be due to an unknown molecular contamination. ^{5,102,105,106}

The EA values of most main-group elements had been accurately measured and were well summarized in the previous review.³ The accuracy of EA values of the p-block elements was further improved by the Blondel group by using the LPM method during the past 20 years. For example, they obtained EA(³²S) = 2.077 104 2(6) eV.⁶³ The uncertainty is only 0.6 μ eV. It should be pointed out that the accuracies of the EA values of Ga, In, Tl, As, and Pb were quite low at that time.^{3,107} The EA values of Ga, In, Tl, As, and Pb were 0.41(4),¹⁰⁸ 0.404(9),¹⁰⁹ 0.377(13),¹¹⁰ 0.814(8),¹¹¹ and 0.364(8) eV,¹¹² respectively, as recommended in the previous review, which were obtained using the PES method. The reason for the much lower accuracy of the five elements compared with other main group elements might be due to that a tunable infrared laser was required if directly measuring their EAs around photodetachment thresholds. These EA values have been greatly improved recently. Walter et al. obtained EA(As) = 0.8048(2) eV in 2009¹¹³ and EA(In) = 0.38392(6) eV in 2010 via the LPT method.¹¹⁴ In 2016, we measured the binding energies of the photodetachment channel ${}^{4}S_{3/2} \rightarrow {}^{3}P_{2}$ of ${}^{206}Pb$, ²⁰⁷Pb, and ²⁰⁸Pb separately using the SEVI method and obtained an EA value 0.356743(16) eV for the isotope m = 208.¹¹⁵ In 2019, Bresteau et al. measured the isotope-averaged BE of the photodetachment channel ${}^{4}S_{3/2} \rightarrow {}^{3}P_{1,2}$, and obtained 0.356721(2) eV.¹¹⁶ The reason behind the slight discrepancy between the two results is not clear. In 2019, Gibson et al. reported an improved result EA(Ga) = 0.301 20(11) eV via the LPT method,¹¹⁷ and slightly later, we determined it to be 0.301 166(14) eV via the SEVI method.⁶⁵ In 2020, Walter et al. obtained EA(Tl) = 0.320 053(19) via the LPT method.¹¹⁸ Recently, the EA value of radioactive element astatine (At) was measured to be 2.41578(7) eV by Leimbach et al. via the LPT method.¹¹⁹ Based on the tandem accelerator mass spectrometry (AMS), Nadeau et al. estimated that EA(Ra) = 0.17 eV.^{90,120} Up until now, only Po, Fr, and artificially prepared elements (Z = 113-118) in the main group have no experimental EA value.¹²¹⁻¹²³ Finney and Peterson predicted EA(Po) = 1.483(26) eV with a relativistic coupled-cluster version of the Feller-Peterson-Dixon composite method in 2019.¹²⁴ Bahrim and Thumm predicted EA(Fr) = 0.492(10) eV in 2000,¹²⁵ which was further improved as 0.491(5) eV by Eliav et al. in 2015.¹²⁶

4.2. Transitional elements

The late transitional elements have been measured partially by the LPT method because of their high EA values and relatively simple electronic structures.³ However, the uncertainty of EA values of many transitional elements remained ~10 meV,^{32,127,128} and these experimental data were mainly obtained using the PES method by Feigerle *et al.* in 1981.³² For Hf and Re, even no experimental value was available in the previous reviews.^{3–5} The difficulties for measuring the EA of transitional elements were as follows: (1) The low photodetachment cross sections due to a p-wave photodetachment since their outer valence electrons occupy either *d* or *s* subshell. (2) The complicated electronic structures due to the partially filled *d* subshell. (3) The difficulty in producing a strong enough negative ion beam due to their low EA value, and an infrared laser system was required for measuring their EA values at the



FIG. 5. Partial energy levels of La and La⁻. The transitions' labels correspond to the peaks observed in Fig. 4. Transition *a* is used to measure the EA value of La.⁷⁹



FIG. 6. Measurement of the EA of La using the SEVI method.⁷⁹ (a) The photon energy hv versus the squared radius r^2 of the measured electron spherical shell for the photodetachment channel a used for EA measurement. The solid line is the linear least-squares fitting. The intercept 11 508.88 cm⁻¹ is the BE of photodetachment channel a. Channel a is La⁻ $({}^{3}F_{2}^{e}) \rightarrow La({}^{2}F_{5/2}^{e})$. The error bars are for r^2 . The uncertainties are too small to see the minus and plus bars separately. ${}^{3}F_{2}^{e}$ is the ground state of atomic anion La⁻, and ${}^{2}F_{5/2}^{e}$ is the excited state of neutral atom La. (b) Deviations of the binding energy of channel a from the least-squares fit extrapolated value as a function of the kinetic energy of photoelectrons. The dashed lines indicate the uncertainty of $\pm 0.20 \text{ cm}^{-1}$.

photodetachment threshold, which was expensive or not available. (4) The high reactivity-the negative ions generated via the laser ablation ion source were dominantly their oxides and hydrides due to the reaction with the residual gas in the vacuum. In particular, the negative hydride ions can form a noisy background due to the close mass. Recently, these difficulties have been overcome using the cryo-SEVI method because of the following: (1) SEVI can operate at energies where the ion has a relatively large photodetachment cross section since the typical E_k is a few meV, much higher than the threshold method. (2) The high energy resolution to resolve the congested photodetachment channels. An infrared laser system is no longer necessary for measuring their EA values since the energy levels of neutral atoms are well known with a high accuracy. Other than the photodetachment channel from the anion ground state to the neutral ground state, many channels to the neutral excited states can be chosen for the EA measurement. This option is especially important for the elements with a low EA value. A channel in the near-optical region (230 < λ < 2000 nm) is preferred since it is covered by a commercially available laser system. (3) The ion trap can significantly enhance the intensity of the ion beam via accumulation. (4) Buffer cooling makes the spectra of the hydride anions simpler and cleaner at a low temperature down to 5 K, thus no overlapping with that of atomic anions. An accuracy better than 0.1 meV has been achieved for most transitional elements via the cryo-SEVI method by our group. It should be pointed out that we have successfully measured EA values of Re and Hf with this method for the first time. It has been well established that Mn⁻ does not exist as a stable ion due to the half-filled d subshell of Mn.^{3,90} The ground-state configuration of Mn is $3d^54s^2 {}^6S_{5/2}$. It was ever believed that the rhenium anion Re⁻ was not stable, just like Mn⁻. However, our recent work unambiguously showed that Re⁻ was stable, and EA(Re) = 60.396(63) meV.¹²⁹ For the element hafnium, several groups tried to produce Hf⁻ and measure its EA value,^{32,90,130} and Pan and Beck predicted that Hf⁻ has one bound state $5d^26s^26p$ j = 5/2 and EA is 0.114 eV using relativistic configuration-interaction (RCI) calculations.¹³¹ However, the lack of definitive experimental evidence for its stability persisted in the previous reviews. The difficulties in measuring the EA value of Hf were the weak intensity of its anion beam and the contamination of its hydride anions HfH⁻ and HfH2⁻, which were the dominant signals in our mass spectra. The natural abundance of isotopes of hafnium are ¹⁷⁶Hf 5%, ¹⁷⁷Hf 19%, ¹⁷⁸Hf 27%, ¹⁷⁹Hf 14%, and ¹⁸⁰Hf 35%. Therefore, the pure ¹⁷⁶Hf⁻ was very weak. With the cryo-SEVI method, we acquired the energy spectra of anions with m = 177, 180, 181, and 182 and unambiguously determined EA(Hf) to be 0.1780(6) eV through the comparison.68

Up until now, among transitional elements, only Tc has no EA experimental data due to its radioactivity. The EA of Tc was 0.55(20) eV obtained by the semiempirical method in the previous review. O'Malley and Beck revised this value to 0.658 eV based on the relativistic configuration-interaction theory and their own semiempirical estimation in 2002.¹³² The ground-state configurations of Zn, Cd, and Hg are nd^{10} $(n + 1)s^2$ ¹S₀, n = 3–5. No stable negative ion can form due to the closed-shell structure.³ The experimental limit for their EA values established by the AMS method is ≤ 0.005 eV.^{90,120} Among atomic anions of transitional elements, it was found that Os⁻ has bound states of opposite parity.^{71,133–136} It is very rare in atomic anions.

Since the LPT method cannot well resolve congested p-wave photodetachment channels, some fine-structure splittings of atomic anions were not available, although their EA values were measured via the LPT method. For example, EA(Co) = 663.3(6) meV was obtained via the LPT method by Scheer *et al.*,¹³⁷ but the energy interval between Co⁻ (${}^{3}F_{2}$) and Co⁻ (${}^{3}F_{4}$) was not measured in Ref. 137. Recently, we measured Co⁻ using the SEVI method and found that there was a notable discrepancy between our result and that by Scheer *et al.* Our result EA(Co) = 662.256(46) meV via SEVI was not well consistent with 663.3(6) meV by Scheer *et al.* via LPT. The discrepancy between the measured fine-structure splittings was even more notable. The interval between Co⁻ (${}^{3}F_{3}$) and Co⁻ (${}^{3}F_{4}$) was 875(15) cm⁻¹ via LPT, while it was 920.9(6) cm⁻¹ via SEVI. Moreover, we also determined the interval of Co⁻ (${}^{3}F_{2}$) and Co⁻ (${}^{3}F_{4}$)



FIG. 7. 7Photoelectron spectra of U⁻.⁶⁴ (a) Photoelectron image and spectrum of ions with m = 238 at photon energy 11 590 cm⁻¹. The strong peaks c, g, and j are from U⁻. The inset is the photoelectron imaging. The double-headed arrow indicates the laser polarization. (b) Photoelectron spectra of anions with m = 238 (red) and 239 (black). It is a result of piecing together spectra at photon energies 5000, 11 590, and 15 750 cm⁻¹. The spectra with m = 238 include signals of U⁻ and UH⁻ ions due to contaminations from the strong UH⁻ signals, and the spectra with m = 239 are contributed only by UH⁻. Peaks a-q that appear only in the spectrum with m = 238 belong to U⁻. The blue vertical spikes under the spectrum of U⁻ indicate the energy levels of the neutral U atom. The assignment of peaks a-q can be found in Ref. 64.

to be 1550.3(9) cm⁻¹. The performance of SEVI was further compared with LPT in the EA(Ir) experiment. Ir has a higher EA value, 1.564 36(15) eV, determined via the LPT method by Bilodeau *et al.*,¹³⁸ so it is pretty easy to get a high experimental signal-to-noise ratio due to the strong ion beam. Two photodetachment channels can be used to measure the EA value of Ir via the SEVI method within the tuning range of our dye laser. The EA(Ir) value was measured to be 12 615.01(11) cm⁻¹ or 1.564 062(14) eV via the channel Ir⁻³ $F_4 \rightarrow$ Ir $a^4F_{9/2}$. The BE of another channel Ir⁻⁵ d^86s^2 ${}^3F_4 \rightarrow$ Ir $5d^86s$ $b^4F_{9/2}$ was determined to be 15 449.90(12) cm⁻¹. The excited state $b^4F_{9/2}$ is 2834.98 cm⁻¹ above the ground state $a^4F_{9/2}.^{20}$ Therefore, EA(Ir) = 12 614.92(12) cm⁻¹ can be obtained via this channel by subtracting 2834.98 cm⁻¹ from 15 449.90(12) cm⁻¹. Moreover, we also determined the BE of the channel Ir⁻⁵ d^86s^2 3F_4 \rightarrow Ir $5d^86s$ $b^4F_{9/2}$ to be 15 450.22(40) cm⁻¹ via the threshold law. The three EA(Ir) values obtained via different channels or different methods are in excellent agreement.¹³⁹ Our weighted average EA(Ir) is 12 614.97 \pm 0.09 cm⁻¹, which does not agree well with 12 617.4(12) cm⁻¹ by Bilodeau *et al.*¹³⁸ The discrepancy is either due to the poor ability of the LPT method to distinguish two adjacent p-wave photodetachment channels or the non-Wigner-threshold-law behavior. A resonance or a non-constant background contributed by a different photodetachment channel or by a different negative ion with the same mass can cause a deviation from the Wigner threshold law. The better accuracy of SEVI over LPT motivated us to measure more transitional elements that had been measured via the LPT method before. Among them, we obtained EA values of Cr,¹⁴⁰ Co,¹³⁷ Ni,¹³⁷ Mo,¹⁴⁰ Ru,¹⁴¹ W,¹⁴² Os,¹³³ and Ir¹³⁸ with a higher accuracy than previous LPT results. Therefore, our SEVI data were recommended in Table 3 for these elements.

TABLE 2. Comparison of theoretical and	I experimental EA v	values of lanthanides and actinides
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Z	Atom	Atomic state	Neg. ion state	Theoretical EA (eV) ^a	Experimental EA (eV) ^b
57	La	$5d6s^2 {}^2D_{3/2}$	$5d^26s^2 {}^3F_2$	0.545	0.557546(20)
58	Ce	$4f5d6s^{2\ 1}G_4$	$4f5d^26s^2 {}^4H_{7/2}$	0.660	0.600 160(26)
59	Pr	$4f^36s^2 {}^4I_{9/2}$	$4f^36s^2 6p {}^5K_5$	0.177	0.10923(46)
60	Nd	$4f^46s^{2}{}^5I_4$	$4f^46s^26p^6K_{9/2}$	0.167	0.097 48(31)
61	Pm	$4f^56s^2 {}^6H_{5/2}$	$4f^{5}6s^{2} 6p^{7}I_{3}$	0.154	
62	Sm	$4f^{6}6s^{2} {}^{7}F_{0}$	$4f^{6}6s^{2} 6p^{8}G_{1/2}$	0.130	
63	Eu	$4f^76s^2 {}^8S_{7/2}$	$4f^76s^2 6p {}^9P_3$	0.117	0.116(13)
64	Gd	$4f^75d6s^2 {}^9D_2$	$4f^75d6s^26p^{10}F_{3/2}$	0.234	0.212(30)
65	Tb	$4f^96s^2 {}^6H_{15/2}$	$4f^85d6s^26p^9G_7$	0.088	0.13131(79)
66	Dy	$4f^{10}6s^2 {}^5I_8$	$4f^{10}6s^26p^6H_{15/2}$	0.063	0.0155(25)
67	Ho	$4f^{11}6s^2 \ {}^4I_{15/2}$	$4f^{11}6s^26p\ ^5H_7$	0.050	< 0.005
68	Er	$4f^{12}6s^2 {}^3H_6$	$4f^{12}6s^26p \ {}^4G_{11/2}$	0.038	< 0.005
69	Tm	$4f^{13}6s^2 {}^2F_{7/2}$	$4f^{13}6s^26p\ ^3D_3$	0.022	0.032(7)
70	Yb	$4f^{14}6s^{2} S_0$		<0	< 0.003 6
71	Lu	$5d6s^2 {}^2D_{3/2}$	$5d6s^26p \ ^1D_2$	0.353	0.23882(62)
89	Ac	$6d7s^2 {}^2D_{3/2}$	$6d7s^2 7p^3F_2$	0.491	
90	Th	$6d^27s^2 {}^3F_2$	$6d^37s^2 {}^4F_{3/2}$	0.599 ^a	0.607690(60)
91	Pa	$5f^2 6d7s^2 {}^4K_{11/2}$	5f ² 6d7s ² 7p ⁵ L ₆	0.384	> 0.05
92	U	$5f^36d7s^2 {}^5L_6$	$5f^36d7s^27p^6M_{13/2}$	0.373	0.31497(9)
93	Np	$5f^46d7s^2 {}^6K_{11/2}$	5f ⁴ 6d7s ² 7p ⁷ M ₆	0.313	
94	Pu	$5f^67s^2 {}^7F_0$	$5f^67s^27p^8G_{1/2}$	0.085	> 0.05
95	Am	$5f^77s^2 {}^8S_{7/2}$	$5f^77s^27p^9P_3$	0.076	
96	Cm	$5f^{7}6d7s^{2}{}^{9}D_{2}$	$5f^7 6d7s^2 7p^{10}F_{3/2}$	0.321	
97	Bk	$5f^97s^2 {}^6H_{15/2}$	5f ⁹ 7s ² 7p ⁷ G ₇	0.031	
98	Cf	$5f^{10}7s^2 {}^5I_8$	$5f^{10}7s^27p^{6}H_{15/2}$	0.018	
99	Es	$5f^{11}7s^2 {}^4I_{15/2}$	$5f^{11}7s^27p^5H_7$	0.002	
100	Fm	$5f^{12}7s^2 {}^3H_6$		<0	
101	Md	$5f^{13}7s^2 {}^2F_{7/2}$	$5f^{13}7s^27p^5F_3$	0.169 ^a	
102	No	$5f^{14}7s^{2} {}^{1}S_0$		<0	
103	Lr	$5f^{14}7s^27p^2P_{1/2}$	$5f^{14}6d7s^27p^3P_0$	0.465	

^aTheoretical results for lanthanides are from Refs. 155 and 156 and actinides from Ref. 157, except Th and Md. The theoretical EA(Th) is from Ref. 165 and EA(Md) from Ref. 173. Nadeau *et al.* have detected Pa^- and Pu^- by AMS and established EA(Pa) > 0.05 eV and EA(Pu) > 0.05 eV.⁹⁰

^bSee the references in Table 3 for the experimental results.

4.3. Lanthanides and actinides

Lanthanides and actinides are f-block elements, which have even more complicated electronic structures than the transitional elements. Thompson and co-workers measured the EA of several of the lanthanides via the hemispherical type PES method.^{130,143–148} However, most of their obtained EA values were significantly higher than the theoretical predictions.¹³⁰ For example, they experimentally determined EA(Pr) to be 0.926(24) eV,¹⁴⁵ while Dinov and Beck predicted EA(Pr) = 0.128 eV.¹⁴⁹ Their high EA value of Pr was not consistent with the low yield of the ion beam Pr⁻ either.²³ Their experimental result turned out to be problematic. Recently, our highresolution experiment determined EA(Pr) to be 0.109 23(46) eV.¹⁵⁰ The reason for the large discrepancy is not clear. It may be due to an incorrect assignment of their observed spectra. The partially filled f-subshell, significant electron correlation effects, and substantial relativistic contributions make lanthanides and actinides the most challenging groups of elements for electronic structure theories. Theoretical calculations predicted that the attachment of a 6p(7p) or 5d(6d) electron rather than a 4f(5f) electron has contributed to the formation of lanthanide (actinide) atomic anions due to the strong correlation effects.^{72,151-160} Theoretical calculations and experimental observations have shown that atomic anions of lanthanides and actinides usually have more than one bound state. For example, the high-level RCI calculations by O'Malley and Beck predicted that La⁻ has 15 bound states, and among them, 14 bound states have been confirmed experimentally.^{71-78,161} The multiple bound states of anions pose a practical difficulty to resolving all photodetachment channels. It is a nontrivial task to reliably assign the observed spectra since many photodetachment channels were opened at a higher photon energy. To resolve the conundrums, the tunable range of our dye laser system was further extended to the infrared region via a difference frequency generation (DFG) system recently. The infrared laser was produced by a nonlinear DFG effect between a dye laser and a 1064 nm laser beam, which was the residual fundamental output of the pump laser. The residual 1064 nm laser was mixed with the dye laser in a nonlinear LiNbO3 crystal, producing infrared light with a frequency corresponding to the difference between the frequencies of the 1064 nm and the dye laser. The tuning range of our DFG system was 1.5-4.2 μ m, and the linewidth of the DFG light was 1 cm⁻¹ limited mainly by the linewidth of the unseeded 1064-nm laser. Figure 7 shows the photoelectron energy spectra of U⁻ at different photon energies. It can be seen that the weak peaks in the region of low binding energies become much sharper at a lower photon energy. Since a strong UH⁻ (m = 239) signal and a much weak U^- (m = 238) signal were observed in the mass spectra, the photoelectron energy spectrum of UH⁻ was also measured in comparison to check the possible contamination. The extension of our laser system to the infrared band significantly enhanced our ability to resolve the complicated electronic structures. For U, we determined its EA to be 0.314 97(9) eV and observed two bound excited states of its anion.⁶⁴ Recently, Ciborowski et al. reported EA(U) = 0.309(25) eV via the VMI method.¹⁶²

With the cryo-SEVI method, we successfully measured EA values of La, Ce, Pr, Nd, Tb, and Lu among lanthanide elements^{69,79,150,163} and Th and U among actinides.^{64,164,165} We also tried Sm, Eu, Gd, Dy, Ho, and Tm. It was very difficult to generate strong enough negative ion beams of these elements with our laser ablation ion source. For Gd, we can estimate its EA value to

be 0.212(30) eV or 1712(240) cm⁻¹ based on a preliminary measurement. For other elements, we cannot obtain a decent energy spectrum with a definite assignment. Pm and other actinides were not tried in our laboratory due to their radioactivity. Based on tandem accelerator mass spectrometry,^{90,120,166,167} Nadeau et al. set the limits of their EA values: EA(Sm) > 0.05 eV, EA(Eu) > 0.05 eV, $EA(Ho) \le 0.005 \text{ eV}, EA(Er) \le 0.005 \text{ eV}, EA(Pa) > 0.05 \text{ eV}, and$ EA(Pu) > 0.05 eV and estimated EA values of Tm and Dy: EA(Tm) $= 0.032(7) \text{ eV}, \text{EA}(\text{Dy}) = 0.015(3) \text{ eV}.^{90,120}$ Cheng *et al.* determined EA(Eu) to be 0.116(13) eV with the VMI method in 2015.¹⁶⁸ Ytterbium (Yb) atom has a closed 4f shell. Its ground configuration, $4f^{14}6s^{2-1}S_0$ is similar to the alkaline earth elements and may be expected to form negative ions by attachment of a 6*p* electron rather than a 5d electron. In 1991, the Toronto AMS group claimed the observation of Yb⁻ via the AMS method,¹⁶⁹ and later EA(Yb) was determined to be 0.010(3) eV by the same group.90,120 However, Andersen *et al.* could not observe the signal of stable or metastable Yb⁻ via a double charge exchange of Yb⁺ (30 or 100 keV) beam in an alkali metal vapor cell.^{5,170} Theoretical calculations also suggested that the negative ytterbium ion most likely was unbound.^{155,171} Recently, the Toronto AMS group searched for the elusive Yb⁻ again and concluded that Yb⁻ has not yet been observed by AMS using a Cs⁺ sputter ion source.¹⁷² Therefore, it is reasonable to conclude that Yb cannot form stable negative ion Yb⁻. No experimental data of EA values are available for trans-uranium elements (Z > 92). O'Malley and Beck performed the valence calculations of lanthanide and actinide anion binding energies using the relativistic configuration-interaction method.^{155,157} Their calculated EA values are compared with experimental results in Table 2. It can be seen that their theoretical EA values agree well with the experimental results. Therefore, it is reasonable to conclude that the elaborated calculations can make reliable predictions for the properties of lanthanides and actinides. Recently, Li and Dzuba predicted the EA value of Md (Z = 101) to be 0.169 eV via the configuration interaction and perturbation (CIPT) method.¹⁷³ It is well known that the noble gas



FIG. 8. The decay branches from the ${}^2S^o_{1/2}$ excited state in Th^{-.164} The red arrow indicates the pumping direction for laser cooling. The thicknesses of the blue arrows, which are indicative of branching fractions, and energies are not to scale.

TABLE 3. Summar	ry of the recommende	d atomic electron	affinity (EA) values
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Z	Atom	Atomic state	Neg. ion state	$EA (cm^{-1})^{a}$	EA (eV)	Method ^b	References
1	Н	$1s^2 S_{1/2}(F=0)$	$1s^{2} S_0$	6083.064 145(30) ^c	$0.754203832(4)^{\circ}$	Calc.	3 and 82
2	He	$1s^{2} S_0$		<0	<0	Calc.; SE	3
3	Li	$2s^2S_{1/2}$	$2s^{2} S_0$	4984.90(17)	0.618 049(22)	LPT	198
4	Be	$2s^{2} S_0$		<0	<0	Calc., SE	3
5	В	$2p^2 P_{1/2}$	$2p^{2} {}^{3}P_{0}$	2256.12(20)	0.279 723(26)	LPT	199
6	С	$2p^{2} {}^{3}P_{0}$	$2p^{3} {}^{4}S_{3/2}$	10 179.705(10)	1.262 122 6(12)	LPM	7
7	Ν	$2p^{3} {}^{4}S_{3/2}$		<0	<0	DEA, Calc.	3
8	0	$2p^{4} {}^{3}P_{2}$	$2p^{5} {}^{2}P_{3/2}$	11784.676(7)	1.461 113 6(9)	LPM	29
9	F	$2p^{5} {}^{2}P_{3/2}$	$2p^{6} S_0$	27 432.446(19)	3.401 189 8(24)	LPT/LPM	200/201
10	Ne	$2p^{6} S_0$	1	<0	<0	Calc., SE	3
11	Na	$3s^2S_{1/2}$	$3s^{2} S_0$	4419.32(20)	0.547 926(25)	LPT	3
12	Mg	$3s^{2} S_0$		<0	<0	Calc.; e ⁻ scatt.	3
13	Al	$3p^2 P_{1/2}$	$3p^{2} {}^{3}P_{0}$	3491.0(4)	0.43283(5)	LPT	202
14	Si	$3p^{2} {}^{3}P_{0}$	$3p^{3} {}^{4}S_{3/2}$	11 207.244(6)	1.389 521 2(7)	LPM	29
15	Р	$2p^{3} {}^{4}S_{3/2}$	$2p^{4} {}^{3}P_{2}$	6021.81(8)	0.746 609(9)	LPM	203
16	S	$2p^{4} {}^{3}P_{2}$	$2p^{5} P_{3/2}$	16752.9753(41)	2.077 104 2(6)	LPM	63
17	Cl	$3p^{5} {}^{2}P_{3/2}$	$3p^{6} {}^{1}S_{0}$	29 138.59(22)	3.612 725(28)	LPT	204
18	Ar	$3p^{6} {}^{1}S_{0}$	1 0	<0	<0	Calc., SE	3
19	К	$4s^2S_{1/2}$	$4s^{2} S_0$	4044.54(10)	0.501 459(13)	LPT	205
20	Ca	$4s^{2}$ ¹ So	$4s^2 4p^2 P_{1/2}$	198.0(9)	0.02455(10)	LPT	2.4
21	Sc	$3d4s^{2} D_{3/2}$	$3d4s^2 4p^{-1}D_2$	1446.80(18)	0.179380(22)	SEVI	206
22	Ti	$3d^24s^{2} {}^{3}F_{2}$	$3d^34s^{2/4}F_{3/2}$	609.29(34)	0.07554(5)	SEVI	48
23	V	$3d^34s^2 {}^4F_{2/2}$	$3d^44s^{2} {}^5D_0$	4255 9(16)	0.527.66(20)	SEVI	207
24	Cr	$3d^54s^7S_2$	$3d^54s^2 {}^6S_{5/2}$	5451 73(21)	0.675.928(27)	SEVI	206
25	Mn	$3d^54s^2 {}^6S_{5/2}$	500 15 05/2	<0	<0	Calc /AMS	3/90
26	Fe	$3d^{6}4s^{2} {}^{5}D_{4}$	$3d^74s^{24}F_{0/2}$	1235 93(28)	0.153236(34)	SEVI	208
20	Co	$3d^74s^2 {}^4F_{0}$	$3d^84s^{2} {}^3F_4$	5341.45(37)	0.662255(47)	SEVI	200
28	Ni	$3d^84s^{2} {}^3F_4$	$3d^94s^{2/2}D_{5/2}$	9334 80(46)	1.157.368(58)	SEVI	205
20	Cu	$3d^{10}4s^2S_{12}$	$3d^{10}4s^{2}$	9967 2(3)	1.137 500(50) 1.235 78(4)	I PT	140
30	Zn	$3d^{10}4s^2 {}^{1}S_{0}$	5u 1 3 00	<0	<0	e ⁻ scatt /AMS	3/90
31	Ga	$4s^2 4p^2 P_{1/2}$	$4s^2 4p^2 {}^3P_0$	2429.07(12)	0 301 166(15)	SEVI	65
32	Ga	$4s^2 4p^2 {}^3 P_2$	45 4p 10 $4s^2 4p^3 4 Seve$	9942,206(10)	1,232,676,4(12)	IDM	210
32	As	$45 + \mu = 10$ $4s^2 4b^3 + S_{2}c_{1}$	$4s^2 4p^4 {}^3 P_2$	6491 1(17)	0.8048(2)	LI IVI I DT	113
34	rs Se	$4s^{2} 4p^{4} {}^{3} P_{2}$	$43 4p 1_2$ $4s^2 4p^{5 2} P_{2} p_{3}$	16207276(0)	2.020.604.7(11)	LI I I DM	211
35	Br	43 4p 12 $4c^2 4p^5 2 P_{\rm eff}$	43 4p 13/2	10297.270(9) 27129170(15)	2.0200047(11) 2.362588(3)		200
36	DI Kr	$43 4p F_{3/2}$	43 4p 30	2/ 129.1/0(13)	2.303 388(3)	CF 1	200
27	NI Dh	$43 4p 3_0$	E_{c}^{2} 1 c	<0	<0		212
20	KU Su	$53 \ 5_{1/2}$	$55 \ 5_0$	410.0(5)	0.465910(21)		212
20 20	Sr V	$58 \ 50$	$55 5p P_{1/2}$	419.9(5)	0.05200(0) 0.21120(21)	LPI	215
39	1	$4055 D_{3/2}$	$4055 5p D_2$	2510.7(17)	0.51129(21)	SEVI	200
40	Zr Nh	$4a 55 F_2$	$4a^{-}5s^{-}F_{3/2}$	5494.67(72) 7200.25(51)	0.455 285(89)	SEVI	214
41	ND	$4a 55 D_{1/2}$	$4a 55 D_0$	/399.35(51)	0.91740(7)	SEVI	3/
42	Mo	$4a^{-}5s^{-}S_{3}$	$4a^{-}5s^{}S_{5/2}$	6026.85(58)	0.74723(8)	SEVI	206
43	lc	$4d^{2}5s^{-2}S_{5/2}$	$4d^{-}5s^{}D_{4}$	5130	0.636	Calc., SE	132
44	Ru	$4d'5s^{3}F_{5}$	$4d'5s^{2}F_{9/2}$	8438.74(16)	1.046 270(20)	SEVI	206
45	Kh	$4d' 5s^2 F_{9/2}$	$4d^{\circ}5s^{2}F_{4}$	9218.0(15)	1.142 89(20)	LPT	137
46	Pd	$4d^{-5} S_0$	$4d^{-5}5s^{-5}S_{1/2}$	4534.0(10)	0.562 14(12)	LPT	137
47	Ag	$4d^{10} 5s^2 S_{1/2}$	$4d^{10} 5s^{2-1}S_0$	10 521.3(2)	1.304 47(2)	LPT	140
48	Cd	$4d^{10}5s^{2}S_{0}$	2 2 2	<0	<0	e ⁻ scatt./AMS	3/90
49	In	$5s^2 5p^2 P_{1/2}$	$5s^{2} 5p^{2} P_{0}$	3096.5(5)	0.383 92(6)	LPT	114
50	Sn	$5s^{2} 5p^{2} P_{0}$	$5s^2 5p^{3/4}S_{3/2}$	8969.447(13)	1.112 070(2)	LPM	215

Z	Atom	Atomic state	Neg. ion state	EA $(cm^{-1})^{a}$	EA (eV)	Method ^b	References
51	Sb	$5s^2 5p^{3} {}^4S_{3/2}$	$5s^2 5p^{4} {}^3P_2$	8447.86(15)	1.047 401(19)	LPT	46
52	Те	$5s^2 5p^{4} {}^3P_2$	$5s^2 5p^{5} {}^2P_{3/2}$	15 896.18(5)	1.970 875(7)	LPT	216
53	Ι	$5s^2 5p^{5} {}^2P_{3/2}$	$5s^2 5p^{6} S_0$	24672.874(29)	3.059 046 5(36)	LPM	62
54	Xe	$5s^2 5p^{6-1}S_0$		<0	<0	SE	3
55	Cs	$6s^{2}S_{1/2}$	$6s^{2} S_0$	3803.92(20)	0.471 626(25)	LPT	3, 217, and 218
56	Ba	$6s^{2} S_0$	$6s^2 6p {}^2P_{1/2}$	1166.4(5)	0.144 62(6)	LPT	89
57	La	$5d6s^2 {}^2D_{3/2}$	$5d^26s^2 {}^3F_2$	4496.91(17)	0.557 546(20)	SEVI	79 and 80
58	Ce	$4f5d6s^{2} G_4$	$4f5d^26s^2 {}^4H_{7/2}$	4840.62(21)	0.600 160(26)	SEVI	69
59	Pr	$4f^36s^2 {}^4I_{9/2}$	$4f^{3}6s^{2} 6p^{5}K_{5}$	881.0(37)	0.10923(46)	SEVI	150
60	Nd	$4f^46s^{2}{}^5I_4$	$4f^46s^2 6p {}^6K_{9/2}$	786.3(26)	0.097 48(31)	SEVI	150
61	Pm	$4f^56s^2 {}^6H_{5/2}$	$4f^56s^2 6p^7I_3$	1242	0.154	Calc.	155
62	Sm	$4f^{6}6s^{2} {}^{7}F_{0}$	$4f^{6}6s^{2} 6p^{8}G_{1/2}$	1049	0.130	Calc.	155
63	Eu	$4f^76s^2 {}^8S_{7/2}$	$4f^{7}6s^{2}$ 6p ${}^{9}P_{3}$	936(105)	0.116(13)	VMI	168
64	Gd	$4f^{7}5d6s^{2}{}^{9}D_{2}$	$4f^{7}5d6s^{2}6p^{10}F_{3/2}$	1712(240)	0.212(30)	SEVI	206
65	Tb	$4f^96s^2 {}^6H_{15/2}$	$4f^85d6s^26p^9G_7$	1059.1(64)	0.13131(80)	SEVI	150
66	Dy	$4f^{10}6s^{2} {}^{5}I_{8}$	$4f^{10}6s^26p^{6}H_{15/2}$	125(24)	0.015(3)	AMS	90
67	Ho	$4f^{11}6s^2 {}^4I_{15/2}$	$4f^{11}6s^26p^5H_7$	<40	< 0.005	AMS	90
68	Er	$4f^{12}6s^2 {}^{3}H_6$	$4f^{12}6s^26p^4G_{11/2}$	<40	< 0.005	AMS	90
69	Tm	$4f^{13}6s^{2}F_{7/2}$	$4f^{13}6s^26p^3D_3$	258(56)	0.032(7)	AMS	90
70	Yb	$4f^{14}6s^{2}S_0$		<0	< 0.0036	AMS/Calc.	172/155
71	Lu	$5d6s^2 {}^2D_{3/2}$	$5d6s^26p \ ^1D_2$	1926.2(50)	0.238 82(62)	SEVI	163
72	Hf	$5d^26s^{2\ 1}G_4$	$5d^26s^26p^4G_{5/2}$	1436(5)	0.1780(6)	SEVI	68
73	Та	$5d^36s^2 {}^4F_{3/2}$	$5d^46s^{2} {}^5D_0$	2652.43(18)	0.328 859(22)	SEVI	206
74	W	$5d^46s^{2} {}^5D_0$	$5d^56s^2 {}^6S_{5/2}$	6585.52(66)	0.816 500(82)	SEVI	206
75	Re	$5d^56s^2 {}^6S_{5/2}$	$5d^{6}6s^{2} {}^{5}D_{4}$	487.13(51)	0.060 396(63)	SEVI	129
76	Os	$5d^{6}6s^{2} {}^{5}D_{4}$	$5d^76s^2 {}^4F_{9/2}$	8691.92(19)	1.077 661(24)	SEVI	206
77	Ir	$5d^76s^2 {}^4F_{9/2}$	$5d^86s^{2}F_4$	12614.97(9)	1.564 057(11)	SEVI	139
78	Pt	$5d^86s^2 {}^3D_3$	$5d^96s^2 {}^2D_{5/2}$	17 140.1(4)	2.125 10(5)	LPT	138
79	Au	$5d^{10}6s^2S_{1/2}$	$5d^{10}6s^{2} {}^{1}S_{0}$	18 620.2(2)	2.308 61(3)	LPT	3
80	Hg	$5d^{10}6s^{2} S_0^{10}$	Ŭ	<0	<0	e ⁻ scatt./AMS	3/90
81	Tl	$6s^2 6p^2 P_{1/2}$	$6s^26p^2 {}^3P_0$	2581.40(15)	0.320 053(19)	LPT	118
82	Pb	$6s^26p^3P_0$	$6s^26p^3 {}^4S_{3/2}$	2877.149(15)	0.356721(2)	LPM	116
83	Bi	$6s^26p^{3} {}^{4}S_{3/2}$	$6s^26p^{4} {}^{3}P_2$	7600.66(10)	0.942 362(13)	LPT	219
84	Ро	$6s^26p^{4} {}^{3}P_2$	$6s^26p^{5} {}^2P_{3/2}$	11 965(210)	1.483(26)	Calc.	124
85	At	$6s^26p^{5} {}^2P_{3/2}$	$6s^26p^{6-1}S_0$	19 484.6(6)	2.41578(7)	LPT	119
86	Rn	$6s^26p^{6-1}S_0$	I II	<0	<0	SE	3
87	Fr	$7s^2S_{1/2}$	$7s^{2}$ ¹ S ₀	3960(41)	0.491(5)	Calc.	126
88	Ra	$7s^{2}$ ¹ So	$7s^2 7p^2 P_{1/2}$	1371	0.17	AMS	90
89	Ac	$6d7s^{2} D_{2/2}$	$6d7s^2 7p^3 F_2$	3960	0.491	Calc	157
90	Th	$6d^27s^{2/3}F_2$	$6d^37s^{2/4}F_{2/2}$	4901.35(48)	0.607 690(60)	SEVI	165
91	Pa	$5f^2 6d7s^{2/4}K_{11/2}$	$5f^2 6d7s^2 7p^5 L_{4}$	3097	0.384	Calc	157
92	U	$5f^{3}6d7s^{2}{}^{5}L_{6}$	$5f^{3}6d7s^{2}7p^{6}M_{13/2}$	2540.4(7)	0.314 97(9)	SEVI	64

TABLE 3. (Continued)

^aThe energy conversion factor between eV and cm⁻¹ is 1 eV/hc = 8065.543 937... cm⁻¹ as recommended by CODATA 2018.¹⁸³ The EA value obtained via the LPM method is for the most abundant isotope.

^bAbbreviations: Calc., *ab initio* calculations; LPT, laser photodetachment threshold; LPM, laser photodetachment microscopy; SEVI, slow-electron velocity-map imaging; DEA, dissociative electron attachment; SE, semiempirical extrapolation (isoelectronic extrapolation and/or horizontal analysis); AMS, accelerator mass spectrometry; e⁻ scatt., electron scattering resonance.

^cThe calculated EA value of H in eV has been changed from 0.754 203 75(3) to 0.754 203 832(4) eV due to the newly recommended fundamental physical constants according to the suggestion from one anonymous reviewer. The latest experimental EA(H) value is 6082.99(15) cm⁻¹ or 0.754 195(19) eV reported by Lykke *et al.* in 1991 using the LPT method.⁸⁴

Ζ	Anionic state	Energy level (cm ⁻¹)	Method ^a	References
	$B^{-}(2p^{2}{}^{3}P_{0})$	0		
5	${}^{3}P_{1}$	3.23(15)	LPT	199
	${}^{3}P_{2}$	8.41(20)	LPT	199
	$C^{-}(2p^{3} {}^{4}S_{3/2})$	0		
6	$^{2}D_{3/2}$	9914(8)	LPT	3 and 8 ^b
	${}^{2}D_{5/2}$	9917(8)	LPT	3 and 8 ^b
	$\Omega^{-}(2p^{5/2}P_{3/2})$	0		
8	$^{2}P_{1/2}$	177.09(2)	LPM	98
	$Al^{-}(3p^{2})^{3}P_{0}$	0	DI III	20
	^{3}p	227(3)	I PT	202
13	$\frac{1}{3}D$	68.4(3)		202
	I_2	2679(91)	DEC	112
	D_2	20/8(81)	PES	112
	$(3p \ S_{3/2})$	0	I DT	220
14	$^{-}D_{3/2}$	6954.81(21)	LPI	220
	$^{2}D_{5/2}$	6968.89(16)	LPT	220
	$^{2}P_{j=1/2,3/2}$	10973(41)	PES	221
	$P^{-}(3p^{4} {}^{5}P_{2})$	0		
15	${}^{3}P_{1}$	180.887(5)	LPM	203
	${}^{3}P_{0}$	263.863(7)	LPM	203
16	$S^{-}(3p^{5} {}^{2}P_{3/2})$	0		
10	${}^{2}P_{1/2}$	483.5352(34)	LPM	222
20	$Ca^{-}(4s^{2}4p^{2}P_{1/2})$	0		
20	$^{2}P_{3/2}$	39.24(11)	LPT	88
	$Sc^{-}(3d4s^{2}4p^{-1}D_{2})$	0		
21	^{3}D	1190(230)	PES	127
	$Ti^{-}(3d^{3}4s^{2} {}^{4}F_{3/2})$	0		
	${}^{4}F_{5/2}$	70.0(6)	SEVI	48
22	$\frac{4}{F_{7/2}}$	165 4(6)	SEVI	48
	$\frac{4}{F_{0/2}}$	285 2(13)	SEVI	48
	$V^{-} (3d^{4}4s^{2} {}^{5}D_{0})$	0	OL VI	10
	$\sqrt{(50.45)}$ $D_0)$	35 5(21)	SEVI	207
23	${}^{5}D_{2}$	103.4(18)	SEVI	207
20	$^{5}D_{2}$	203 8(17)	SEVI	207
	⁵ D.	3301(16)	SEVI	207
	$E_{e}^{-} (3d^{7}4s^{2} + F_{e})$	0	OL VI	207
	$4E_{-1}$	520.9(11)	SEVI	208
26	1.7/2 4 E	320.9(11)	SEVI	208
	F 5/2 4 D	901.0(14)	SEVI	208
	$F_{3/2}$	1160.8(15)	SEVI	208
27	$Co (3a^{3}4s^{-1}F_{4})$	0		• • • •
27	F_3	920.9(6)	SEVI	209
	F_2	1550.3(9)	SEVI	209
28	Ni ⁻ $(3d^{3}4s^{2} D_{5/2})$	0		
	$^{2}D_{3/2}$	1485(3)	LPT	137
	$Ga^{-}(4s^{2} 4p^{2} {}^{3}P_{0})$	0		
31	${}^{3}P_{1}$	187.31(22)	SEVI	65
	${}^{3}P_{2}$	502.70(28)	SEVI	65
	$Ge^{-}(4s^2 4p^{3} {}^4S_{3/2})$	0		
32	${}^{2}D_{3/2}$	6704.3(9)	LPT	220
	$^{2}D_{5/2}$	6896.9(6)	LPT	220

TABLE 4. Summary of the recommended energy levels of atomic anions

Z	Anionic state	Energy level (cm ⁻¹)	Method ^a	References
	$As^{-}(4s^{2} 4p^{4} {}^{3}P_{2})$	0		
33	${}^{3}P_{1}$	1029.2(16)	LPT	113
	${}^{3}P_{0}$	1325.2(81)	LPT	113
	$Se^{-}(4s^{2} 4p^{5} {}^{2}P_{3/2})$	0		
34	${}^{2}P_{1/2}$	2278.2(2)	SRS	223
	$Sr^{-}(5s^{2}5p^{2}P_{1/2})$	0		
38	${}^{2}P_{3/2}$	160.4(3)	LPT	88
	$Y^{-}(4d5s^{2}5p^{-1}D_{2})$	0		
39	$^{3}D_{1}$	1150(220)	PES	127
	$Zr^{-}(4d^{3}5s^{2}F_{3/2})$	0	120	
	$\frac{4}{F_{5/2}}$	251 0(37)	SEVI	214
40	${}^{4}F_{7/2}$	579 6(8)	SEVI	211
	$\frac{4}{F_{0,0}}$	971 7(12)	SEVI	211
	$Mb^{-} (4d^45c^{2}{}^5D_c)$	0	SE VI	214
	$^{5}D.$	1361(10)	SEVI	37
41	$^{5}D_{2}$	3771(10)	SEVI	37
11	$^{5}D_{2}$	7005(10)	SEVI	37
	^{5}D	1258 2(20)	SEVI	37
	D_4 $P_{11}^{-} (A d^7 5 c^2 {}^4 F_{ev})$	1238.2(30)	SEVI	57
	4π $(4\pi$ 35 $F_{9/2})$	0	CEVI	206
44	F7/2	1444.2(7)	SEVI	206
	F 5/2	2047.0(10)	SEVI	206
	$F_{3/2}$	2831	Calc.	141
45	$\operatorname{Rn} \left(4a^{2}5s^{2}F_{4}\right)$	0	DEC	
45	F_3	2370(65)	PES	32
	F_2	3370(65)	PES	32
46	$Pd^{-}(4d^{10}5s^{2}S_{1/2})$	0		
	$4d^{2} 5s^{2} D_{5/2}$	1127(4)	SEVI	70
	$In^{-}(5s^{2} 5p^{2} P_{0})$			
49	${}^{3}P_{1}$	613.47(56)	LPT	114
	$^{3}P_{2}$	1375.98(48)	LPT	114
	$\operatorname{Sn}^{-}(5s^{2} 5p^{3} {}^{4}S_{3/2})$	0		
50	$^{2}D_{3/2}$	5762.45(8)	RTP	220
	$^{2}D_{5/2}$	6512.40(7)	RTP	220
	$Sb^{-}(5s^{2} 5p^{4} {}^{3}P_{2})$	0		
51	${}^{3}P_{1}$	2684.37(15)	RTP	46
	${}^{3}P_{0}$	2800.8(6)	LPT	46
	$^{1}D_{2}$	7392.55(15)	RTP	46
50	$Te^{-}(5s^{2} 5p^{5} {}^{2}P_{3/2})$	0		
52	${}^{2}P_{1/2}$	5005.36(10)	SRS	224
E6	$Ba^{-} (6s^2 6p {}^2P_{1/2})$	0		
30	${}^{2}P_{3/2}$	443.8(8)	LPT	89
57	$La^{-}(5d^{2}6s^{23}F_{2}^{e})$	0		
	${}^{3}F_{3}^{e}$	677.03(16)	RTP/SEVI	73, 79, and 80
	${}^{3}F_{4}^{e}$	1394.28(21)	RTP/SEVI	73, 79, and 80
	${}^{1}D_{2}^{e}$	2389.26(34)	SEVI	79 and 80
	${}^{3}P_{0}^{e}$	3091.6(27)	SEVI	79 and 80
	${}^{3}P_{1}^{e}$	3430(60)	SEVI	79
	${}^{3}P_{2}^{e}$	4045(60)	SEVI	79
	$5d6s^2 6 D^{-1} D_2^0$	1789.7 (64)	LPT	73 and 80
	${}^{3}F_{0}^{2}$	2772.021(13)	RTP	73 and 80

TABLE 4. (Continued)

Z	Anionic state	Energy level (cm ⁻¹)	Method ^a	References
	${}^{3}F_{3}^{o}$	3096.17(20)	RTP	73 and 80
	${}^{3}D_{1}^{o}$	3221.9628(25) ^c	RTP	76
	${}^{3}D_{2}^{o}$	3795.19(21)	RTP	73 and 80
	${}^{3}F_{4}^{o}$	4002.04(23)	RTP	73 and 80
	${}^{3}P_{0}^{o}$	4424.8	Calc.	76
	${}^{3}D_{3}^{o}$	4345.74(18)	RTP	73 and 80
	$Ce^{-}(4f5d^{2}6s^{24}H^{o}_{7/2})$	0		
	${}^{4}H_{9/2}^{o}$	788.41(32)	RTP	179
	${}^{4}I_{9/2}^{o'}$	1083(6)	SEVI	69
	${}^{2}G_{7/2}^{o}$	1355(88)	SEVI	69
	${}^{4}H_{0}^{0}$	1944	Calc	154
	${}^{2}G^{o}$	1954(2) SEV		69
	$4 \mu^{o}$	2648(7)	SEVI	69
	$\frac{11_{13/2}}{4D^{0}}$	2040(7)	Cala	154
	$D_{1/2}^{2}$	2887	Calc.	154
	$F_{5/2}^{-}$	2564(3)	SEVI	69
	$^{2}F_{7/2}^{0}$	3452	Calc.	154
58	${}^{4}D^{o}_{3/2}$	3460	Calc.	154
	${}^{4}I^{o}_{13/2}$	3274(2)	SEVI.	69
	${}^{2}H_{9/2}^{o}$	4307	Calc.	154
	${}^{4}D_{5/2}^{o'}$	4315	Calc.	154
	${}^{4}F_{3/2}^{o}$	4468	Calc.	154
	$4 I_{0}^{0}$	4630	Calc.	154
	${}^{2}S_{0}^{0}$	4734	Calc	154
	$4 F^{o}$	4888	Calc.	154
	$\frac{1}{5/2}$	2402(100)	Cale.	60
	$4530050pH_{9/2}$	2402(100)	SEV1	154
	$G_{7/2}^{2}$	5651	Calc.	154
	$-G_{5/2}^{-}$	4065	Calc.	154
	$^{2}D^{e}_{3/2}$	4186	Calc.	154
	${}^{4}H^{e}_{7/2}$	4654	Calc.	154
	${}^{2}H^{e}_{11/2}$	4710	Calc.	154
	${}^{4}I^{e}_{9/2}$	4960	Calc.	154
	$Pr^{-}(4f^{3}6s^{2}6p^{5}K_{5})$	0		
59	${}^{5}I_{4}$	352(2)	SEVI	150 and 154
	$4f^25d^26s^2$ 5L_6	818(5)	SEVI	150
60	Nd ⁻ $(4f^46s^26p^6K_{9/2})$	0		
00	⁶ I _{7/2}	577(2)	SEVI	150
65	$Tb^{-} (4f^85d^16s^26p^9G_7)$	0		
05	${}^{9}G_{6}$	270(6)	SEVI	150
	$Lu^{-}(5d6s^{2}6p^{1}D_{2}^{o})$	0		
71	$6s^2 6p^2 {}^3 P_o^e$	1326.3(70)	SEVI	163
	$5d6s^26p\ {}^3F_2^o$	1383.4 (70)	SEVI	163
	$Ta^{-}(5d^{4}6s^{2} {}^{5}D_{0})$	0		
73	${}^{5}D_{1}$	1169.97(31)	SEVI	206
, 5	${}^{5}P_{0}$	1736.7(10)	SEVI	206
	$^{5}D_{2}$	2320.5(21)	SEVI	206
	$Os^{-}(5d^{7}6s^{24}F^{e}_{9/2})$	0		
76	${}^{4}F^{e}_{7/2}$	4231(25)	LPT	133
	$5d^{6}6c^{2}6p^{6}D^{0}$	8600 3227(12) ^d	RPT	135

TABLE 4. (Continued)

Z	Anionic state	Energy level (cm ⁻¹)	Method ^a	References
	$Ir^{-}(5d^{8}6s^{2}{}^{3}F_{4})$			
77	$a^{3}P_{2}$	$4163.24(16)^{e}$	SEVI	139
//	${}^{3}F_{3}$	7087.27(33)	SEVI/RTP	139/45
	$b^{3}P_{2}$	11983 ^d	Calc.	192
	$Pt^{-}(5d^{9}6s^{2} {}^{2}D_{5/2})$	0		
78	${}^{2}D_{3/2}$	9740.9(5)	RTP	45
	${}^{2}S_{1/2}$	10 289(13)	LPT	225
83	$Bi^{-}(6s^{2}6p^{4}{}^{3}P_{2})$	0		
05	${}^{3}P_{0}$	4591.47(24)	RTP	226
	$Th^{-} (6d^{3}7s^{24}F^{e}_{3/2})$	0		
	${}^{4}F^{e}_{5/2}$	1657(6)	SEVI	164
	${}^{4}F_{7/2}^{e}$	2896(10)	SEVI	164
	${}^{4}F_{9/2}^{e'}$	3637	Calc.	164
	${}^{4}P_{3/2}^{e'}$	4284	Calc.	164
90	${}^{4}P_{1/2}^{e'}$	4940	Calc.	164
	$6d^27s^27p^4G^o_{5/2}$	401	Calc.	164
	${}^{4}F_{3/2}^{o}$	3033	Calc.	164
	${}^{2}S_{1/2}^{o}$	4118.0(10)	RTP	164
	${}^{4}F_{7/2}^{o}$	3974	Calc.	164
	${}^{4}F^{o}_{5/2}$	4592.6(10)	RTP	164
	${}^{4}D_{3/2}^{o}$	4445	Calc.	164
	${}^{4}D_{1/2}^{3/2}$	4618.1(10)	RTP	164
	$U^{-}(5f^{3}6d7s^{2}7p^{6}M^{e}_{12/2})$	0		
92	$5f^{3}6d^{2}7s^{2}{}^{6}M^{0}_{12/2}$	674(84)	SEVI	64
	$5f^{3}6d7s^{2}7p^{6}L^{e}_{11/2}$	1291(92)	SEVI	64

TABLE 4. (Continued)

^aAbbreviations: Calc., *ab initio* calculations; LPT, laser photodetachment threshold; LPM, laser photodetachment microscopy; SEVI, slow-electron velocity-map imaging; SRS, stimulated Raman spectroscopy; RTP, Resonant two-photon detachment. ^bThe order of the fine-structure splitting of the ²D term of C⁻ was determined by an *ab initio* calculation.²²⁸ Note the isoelectronic species N I, O II, F III, and Ne IV all have the J = 5/2 level below the J = 3/2 one.

^cFor hyperfine states $F = 11/2 \leftarrow F = 9/2$ of La.

^dFor isotope ¹⁹²Os.

^eThe symbol terms of Ir⁻ used in Ref. 192 are different from the literature.^{45,139} We label them as $a^{3}P_{2}$ and $b^{3}P_{2}$ in agreement with the literature.^{45,139} The state $b^{3}P_{2}$ has been experimentally observed, and its lifetime is 172(35) ms.

elements have no stable negatively atomic ions. However, in contrast to the lighter noble gas elements, theories predicted that the superheavy element Og (Z = 118) has a positive EA value ~0.095 eV due to the relativistic and quantum electrodynamic (QED) effects. $^{174-177}$

Recently, atomic anions of lanthanides have aroused the interest of researchers in that there exist electric dipole (E1) bound-tobound transitions in La⁷¹⁻⁷⁸ and Ce^{178,179} anions, which may pave the way for sympathetically cooling antiprotons.^{134,164,180-182} The parity of a *p* electron is odd and even for a *d* electron. Therefore, the atomic anions of lanthanides and actinides potentially have bound states with an opposite parity due to the attachment of a *p* or *d* electron. Indeed, besides La⁻ and Ce⁻, we found that Th⁻ and U⁻ also have bound states with an opposite parity.^{64,164,165} In particular, Th⁻ is a laser-cooling candidate of negative ions since it has a fast electric dipole (E1) transition.^{164,165} The resonant frequency of the laser-cooling transition was determined to be v = 123.455(30) THz $[\lambda = 2428.4(6) \text{ nm}]$. The transition rate was calculated as A = 1.17 × 10⁴ s⁻¹. Figure 8 shows the laser cooling transition and related decay branches. Since the branching fraction to dark states is negligible, 1.47×10^{-10} , this represents an ideal closed cycle in Th⁻ for laser cooling. Another advantage of Th⁻ over La⁻ is that the nuclear spin of ²³²Th⁻ is zero, while the nuclear spin of ¹³⁹La⁻ is 7/2. This makes the laser system for cooling Th⁻ much simpler than that for La⁻. Before conducting the laser-cooling experiment, an experimental determination of the absolute transition rates, the photodetachment loss, and the resonant frequency of the cooling of Th⁻ is planned in the near future in our laboratory. In principle, once one kind of negative ion is laser-cooled, other negative-ion species can be sympathetically cooled by confining them simultaneously in a trap. In addition, ultracold neutral atoms or molecules can be acquired via threshold photodetachment of the corresponding ultracold negative

 TABLE 5. Experimental lifetimes, binding energies, and fine-structure splittings of long-lived metastable states of negative ions

Z	Ion	J	Lifetime (µs)	Binding energy $(cm^{-1})^a$	Binding energy (eV) ^a	Splitting (cm ⁻¹) ^b	References
2	He ⁻ (1 <i>s</i> 2 <i>s</i> 2 <i>p</i> ⁴ <i>P</i>)	5/2 3/2 1/2	345(10) 11(2) 9(2)	625.21(5) [He 1 <i>s</i> 2 <i>s</i> ³ <i>S</i> ₁]	0.077 516(6) [He 1 <i>s</i> 2 <i>s</i> ³ <i>S</i> ₁]	0.027 508(27) [5/2→3/2] 0.2888(18) [5/2→1/2]	3, 9, 12, and 16 3, 11, 12, and 16 3, 16, and 19
4	$Be^{-}(2s2p^{2}{}^{4}P)$	1/2 3/2 5/2	0.73(8) 42.07(12) 0.33(6)	2344.9(8) [Be $2s2p^{3}P_{0}$]	0.29074(10) [Be $2s2p^{3}P_{0}$]	$0.74(7) [1/2 \rightarrow 3/2]$ $0.59(7) [3/2 \rightarrow 5/2]$	92 92, 93, and 227 92
18 56	Ar ⁻ $(3p^54s4p \ {}^4S)$ Ba ⁻ $(5d6s6p \ {}^4F)$	3/2 9/2	0.26(3) ~5000	262(8) [Ar 3 <i>p</i> ⁵ 4 <i>s</i> ³ <i>P</i> ₂] 1163(4) [Ba 5 <i>d</i> 6 <i>p</i> ³ <i>D</i> ₃]	0.0325(10) [Ar 3 <i>p</i> ⁵ 4 <i>s</i> ³ <i>P</i> ₂] 0.1442(5) [Ba 5 <i>d</i> 6 <i>p</i> ³ <i>D</i> ₃]	.,	103 and 104 85 and 89

^aThe BE is relative to the neutral state in the brackets.

^bRelated angular momentums J and J' are given in the brackets.

ions. Since electron mass (m_e) is much less than the mass of the neutral atom or molecule (M), the kinetic energy of the neutral atom or molecule is much less than the kinetic energy of the photoelectron E_k after photodetachment. For example, if $E_k = 1$ meV and M = 100 u, the kinetic energy of the neutral atom or molecule after photodetachment is (m_e/M) $E_k = 5.5 \times 10^{-6}$ meV, which is corresponding to a temperature ~60 μ K. Therefore, laser cooling of anions not only creates a new quantum system but also provides a general method to create cold atoms and molecules via threshold photodetachment. This method may play an important role to acquire ultracold atoms or molecules that cannot be directly laser-cooled in the future.

5. Recommended Values for Atomic Electron Affinities

Table 3 lists the recommended EA values for elements H–U (Z = 1-92). Since the LPM method can determine EA value with an extremely high accuracy, and it even can observe the isotope shift, i.e., the EA values of different isotopes are slightly different. In this case, only the EA value for the most abundant isotope is listed in Table 3 for conciseness. For example, Bresteau *et al.* reported that EA(12 C) = 1.262 122 6(11) eV and EA(13 C) = 1.262 113 6(12) eV.⁷ The EA value for carbon listed in Table 3 is for the isotope 12 C. The energy conversion factor between eV and cm⁻¹ is 1 eV/hc = 8065.543 937... cm⁻¹ as recommended by CODATA 2018.¹⁸³

Although some sophisticated theories have predicted EA values for elements with Z > 92, no experimental data are available to our knowledge. The development of theoretical calculations is very rapid. Therefore, Table 3 does not include those elements. Some information and reference on theoretical work were mentioned in Sec. 3.3.

6. Recommended Values for Energy Levels of States in Atomic Negative Ions

Table 4 presents the recommended values of energy levels of bound states in atomic negative ions relative to their ground states. Most atomic anions have only one bound state with a few fine-structure splittings due to the weak and short-range nature of the polarization potential. However, there are a few exceptions, such as Os⁻, La⁻, Ce⁻, Th⁻, and U⁻. Theories and experiments have shown that they possess a lot of bound states with opposite parity, and there

exist electric dipole (E1) bound-to-bound transitions. The parity of the bound states is indicated by the superscript o or e if their parity is different. Here, *o* is for the odd parity and *e* for even. The energy levels listed in Table 4 are for the bound states that have been experimentally observed, but theoretic predictions for La⁻, Ce⁻, and Th⁻ are also included for completeness. Table 5 lists the experimental lifetimes, binding energies, and fine-structure splittings of long-lived metastable states of negative ions. These states are embedded in the detachment continuum and can decay via autodetachment. This table is duplicated from Ref. 3. The interested readers can acquire the related knowledge of metastable negative ions in the excellent review by Andersen.⁵ Recently, lifetimes of bound excited states of several atomic anions have been measured in a cryogenic electrostatic storage ring.^{184–193} The development in this subfield is not included in this Review because the fast progress will make the summarization outdated very soon.

7. Conclusions

Through the efforts of several generations, the negative ion properties of most elements in the Periodic Table have been known. The goal toward the completion of the Periodic Table of the negative ions, at least for the naturally occurring elements, has almost been achieved. So far, for elements from H to U (Z = 1-92), only Tc, Pm, Sm, Ho, Er, Po, Fr, Ac, and Pa have no experimental EA value available, and among them, experiments have set EA limits for Sm, Ho, and Er: EA(Sm) > 0.05 eV, $EA(Ho) \le 0.005 \text{ eV}$, EA(Er) \leq 0.005 eV. Further experiments to improve EA values of nonradioactive elements Sm, Ho, and Er may come soon. The experiment for the EA measurement of radioactive elements is still a challenge. How to efficiently produce negative ions of these radioactive elements is the main obstacle for their EA measurements, especially for the elements with a very low EA value. The isotope separation on-line technique is a well-established method for the production of radioactive ion beams. A pulsed proton beam with an energy of ~1 GeV actuates the spallation, fragmentation, and fission reactions by bombarding thick targets. As demonstrated by Leimbach et al., the radioactive ion beam of At was produced with this method and was then converted into At⁻ in a negative surface ion source.¹¹⁹ The radioactive elements with low EA values can be converted into negative ions by using a double charge exchange in an alkaline vapor cell.

However, such an experiment for radioactive elements is expensive and hazardous. The development of theoretical models that can make reliable predictions may be a more practical way. With the rapid development of computer technology and the sophisticated relativistic computational methods with QED corrections, some elaborated calculations have been able to make reliable predictions for properties of actinides and even superheavy elements $(Z \ge 104)$.^{122,126,194} One interesting prediction is that the superheavy noble gas element Og (Z = 118) has a positive EA 0.095 eV, $^{174-177,19}$ which is an anomaly in the group of noble gas elements. The theoretical calculations also predicted that the EA value of Rg (Z = 111) is 1.565 eV¹⁹⁴ and 0.68 eV for Nh (Z = 113)¹⁹⁶ and no stable negative ion of Fl (Z = 114, Pb-like).¹⁹⁷ Borschevsky et al. predicted electron affinities of the superheavy elements 115-117 to be EA(Mc) = 0.313 eV (Z = 115), EA(Lv) = 0.776 eV (Z = 116), and EA(Ts) $= 1.602 \text{ eV Ts} (Z = 117).^{122}$

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8. Author Declarations

8.1 Conflict of Interest

The authors have no conflicts to disclose.

9. Data Availability

The data that support the findings of this study are available within the article and its supplementary material. Data for Figs. 3(a), 3(b), 6(a), and (6b) and Tables 2–5 are included in the supplementary material.

10. References

¹H. Hotop and W. C. Lineberger, "Binding energies in atomic negative ions," J. Phys. Chem. Ref. Data **4**, 539 (1975).

²H. Hotop and W. C. Lineberger, "Binding energies in atomic negative ions: II," J. Phys. Chem. Ref. Data 14, 731 (1985).

³T. Andersen, H. K. Haugen, and H. Hotop, "Binding energies in atomic negative ions: III," J. Phys. Chem. Ref. Data **28**, 1511 (1999).

⁴J. C. Rienstra-Kiracofe, G. S. Tschumper, H. F. Schaefer, S. Nandi, and G. B. Ellison, "Atomic and molecular electron affinities: Photoelectron experiments and theoretical computations," Chem. Rev. **102**, 231 (2002).

⁵T. Andersen, "Atomic negative ions: Structure, dynamics and collisions," Phys. Rep. **394**, 157 (2004). ⁶W. C. Lineberger, "Once upon anion: A tale of photodetachment," Annu. Rev. Phys. Chem. **64**, 21 (2013).

⁷D. Bresteau, C. Drag, and C. Blondel, "Isotope shift of the electron affinity of carbon measured by photodetachment microscopy," Phys. Rev. A **93**, 013414 (2016).

⁸D. Feldmann, "Infrared photodetachment measurements near thresholds of C⁻," Chem. Phys. Lett. **47**, 338 (1977).

⁹P. Kristensen, U. V. Pedersen, V. V. Petrunin, T. Andersen, and K. T. Chung, "Binding energy of the metastable He⁻ ion," Phys. Rev. A **55**, 978 (1997).

¹⁰P. Kristensen, U. V. Pedersen, V. V. Petrunin, T. Andersen, and K. T. Chung, "Erratum: Binding energy of the metastable He⁻ ion [Phys. Rev. A 55, 978 (1997)]," Phys. Rev. A 56, 1674 (1997).

¹¹L. M. Blau, R. Novick, and D. Weinflash, "Lifetimes and fine structure of the metastable autoionizing (1s2s2p)⁴ P_1 states of the negative helium ion," Phys. Rev. Lett. **24**, 1268 (1970).

¹²T. Andersen, L. H. Andersen, P. Balling, H. K. Haugen, P. Hvelplund, W. W. Smith, and K. Taulbjerg, "Metastable-ion lifetime studies utilizing a heavy-ion storage ring: Measurements on He⁻," Phys. Rev. A **47**, 890 (1993).

¹³S. J. Buckman and C. W. Clark, "Atomic negative-ion resonances," Rev. Mod. Phys. 66, 539 (1994).

¹⁴C. W. Walter, J. A. Seifert, and J. R. Peterson, "Reexamination of the He⁻ 1s2 p^{2} ⁴ P^{e} shape resonance: Details of its properties and a precise electron affinity for He 2 ³S," Phys. Rev. A **50**, 2257 (1994).

¹⁵U. V. Pedersen, M. Hyde, S. P. Møller, and T. Andersen, "Lifetime measurement of He⁻ utilizing an electrostatic ion storage ring," Phys. Rev. A 64, 012503 (2001).
¹⁶A. Wolf, K. G. Bhushan, I. Ben-Itzhak, N. Altstein, D. Zajfman, O. Heber, and M. L. Rappaport, "Lifetime measurement of He⁻ using an electrostatic ion trap," Phys. Rev. A 59, 267 (1999).

 17 G. Miecznik, T. Brage, and C. Froese Fischer, "Autoionization studies of the 1*s*2*s*2*p* $^4P_{5/2}$ levels in He⁻, Li I, and Be II," Phys. Rev. A **47**, 3718 (1993).

¹⁸T. Brage and C. F. Fischer, "Autodetachment of negative ions," Phys. Rev. A 44, 72 (1991).

 19 F. R. Simpson, R. Browning, and H. B. Gilbody, "An experimental study of the decay of the He⁻ ion," J. Phys. B: At. Mol. Phys. 4, 106 (1971).

²⁰A. Kramida, Y. Ralchenko, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database, SRD 78 (version 5.9), https://www.nist.gov/pml/atomic-spectra-database, 2021. (version 5.9), https://physics.nist.gov/as, 2021.

²¹J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong, and C. M. Whitehouse, "Electrospray ionization for mass spectrometry of large biomolecules," Science 246, 64 (1989).

²² R. Middleton, "A versatile high intensity negative ion source," Nucl. Instrum. Methods Phys. Res. 214, 139 (1983).

²³ R. Middleton, A Negative Ion Cookbook (University of Pennsylvania Press, Philadelphia, 1989).

²⁴ V. V. Petrunin, H. H. Andersen, P. Balling, and T. Andersen, "Structural properties of the negative calcium ion:binding energies and fine-structure splitting," Phys. Rev. Lett. **76**, 744 (1996).

²⁵R. S. Berry, J. C. Mackie, R. L. Taylor, and R. Lynch, "Spin-orbit coupling and electron-affinity determinations from radiative capture of electrons by oxygen atoms," J. Chem. Phys. 43, 3067 (1965).

²⁶W. C. Lineberger and B. W. Woodward, "High resolution photodetachment of S⁻ near threshold," Phys. Rev. Lett. **25**, 424 (1970).

²⁷E. P. Wigner, "On the behavior of cross sections near thresholds," Phys. Rev. 73, 1002 (1948).

²⁸D. M. Neumark, K. R. Lykke, T. Andersen, and W. C. Lineberger, "Laser photodetachment measurement of the electron affinity of atomic oxygen," Phys. Rev. A **32**, 1890 (1985).

²⁹W. Chaibi, R. J. Peláez, C. Blondel, C. Drag, and C. Delsart, "Effect of a magnetic field in photodetachment microscopy," Eur. Phys. J. D 58, 29 (2010).

³⁰P. Kruit and F. H. Read, "Magnetic field paralleliser for 2π electron-spectrometer and electron-image magnifier," J. Phys. E: Sci. Instrum. **16**, 313 (1983).

³¹L.-S. Wang, C.-F. Ding, X.-B. Wang, and S. E. Barlow, "Photodetachment photoelectron spectroscopy of multiply charged anions using electrospray ionization," Rev. Sci. Instrum. **70**, 1957 (1999).

J. Phys. Chem. Ref. Data **51**, 021502 (2022); doi: 10.1063/5.0080243

REVIEW

³²C. S. Feigerle, R. R. Corderman, S. V. Bobashev, and W. C. Lineberger, "Binding energies and structure of transition metal negative ions," J. Chem. Phys. 74, 1580 (1981).

³³A. T. J. B. Eppink and D. H. Parker, "Velocity map imaging of ions and electrons using electrostatic lenses: Application in photoelectron and photofragment ion imaging of molecular oxygen," Rev. Sci. Instrum. 68, 3477 (1997).

³⁴A. Osterwalder, M. J. Nee, J. Zhou, and D. M. Neumark, "High resolution photodetachment spectroscopy of negative ions via slow photoelectron imaging," J. Chem. Phys. **121**, 6317 (2004).

 ³⁵D. M. Neumark, "Slow electron velocity-map imaging of negative ions: Applications to spectroscopy and dynamics," J. Phys. Chem. A 112, 13287 (2008).
 ³⁶I. León, Z. Yang, H.-T. Liu, and L.-S. Wang, "The design and construction of a high-resolution velocity-map imaging apparatus for photoelectron spectroscopy studies of size-selected clusters," Rev. Sci. Instrum. 85, 083106 (2014).

³⁷Z.-H. Luo, X.-L. Chen, J.-M. Li, and C.-G. Ning, "Precision measurement of the electron affinity of niobium," Phys. Rev. A 93, 020501 (2016).

³⁸Yu. N. Demkov, V. D. Kondratovich, and V. N. Ostrovskii, "Interference of electrons resulting from the photoionization of an atom in an electric field," Sov. J. Exp. Theor. Phys. Lett. **34**, 403 (1981).

³⁹C. Blondel, C. Delsart, and F. Dulieu, "The photodetachment microscope," Phys. Rev. Lett. 77, 3755 (1996).

⁴⁰C. Blondel, C. Delsart, F. Dulieu, and C. Valli, "Photodetachment microscopy of O⁻," Eur. Phys. J. D **5**, 207 (1999).

⁴¹C. Blondel, S. Berge, and C. Delsart, "Physical and unphysical phases of uniformly accelerated particles," Am. J. Phys. **69**, 810 (2001).

⁴²C. Delsart, F. Goldfarb, and C. Blondel, "Molecular photodetachment microscopy," Phys. Rev. Lett. 89, 183002 (2002).

⁴³C. Blondel, W. Chaibi, C. Delsart, C. Drag, F. Goldfarb, and S. Kröger, "The electron affinities of O, Si, and S revisited with the photodetachment microscope," Eur. Phys. J. D 33, 335 (2005).

⁴⁴W. Chaibi, C. Blondel, C. Delsart, and C. Drag, "Do fringes and trajectories shift equally in matter-wave interferometers? The example of photodetachment microscopy in a magnetic field," Europhys. Lett. **82**, 20005 (2008).

⁴⁵J. Thøgersen, M. Scheer, L. D. Steele, H. K. Haugen, and W. P. Wijesundera, "Two-photon detachment of negative ions via magnetic dipole transitions," Phys. Rev. Lett. **76**, 2870 (1996).

⁴⁶M. Scheer, H. K. Haugen, and D. R. Beck, "Single- and multiphoton infrared laser spectroscopy of Sb⁻: A case study," Phys. Rev. Lett. **79**, 4104 (1997).

⁴⁷M.-J. Nadeau, X.-L. Zhao, M. A. Garwan, and A. E. Litherland, "Ca negative-ion binding energy," Phys. Rev. A **46**, R3588 (1992).

⁴⁸ R. Tang, X. Fu, and C. Ning, "Accurate electron affinity of Ti and fine structures of its anions," J. Chem. Phys. **149**, 134304 (2018).

⁴⁹W. C. Wiley and I. H. McLaren, "Time-of-flight mass spectrometer with improved resolution," Rev. Sci. Instrum. 26, 1150 (1955).

⁵⁰W. A. de Heer and P. Milani, "Large ion volume time-of-flight mass spectrometer with position- and velocity-sensitive detection capabilities for cluster beams," Rev. Sci. Instrum. **62**, 670 (1991).

⁵¹C. N. Yang, "On the angular distribution in nuclear reactions and coincidence measurements," Phys. Rev. 74, 764 (1948).

⁵²J. Cooper and R. N. Zare, "Angular distribution of photoelectrons," J. Chem. Phys. 48, 942 (1968).

⁵³J. Cooper and R. N. Zare, "Erratum: Angular distribution of photoelectrons," J. Chem. Phys. 49, 4252 (1968).

⁵⁴D. Hanstorp, C. Bengtsson, and D. J. Larson, "Angular distributions in photodetachment from O⁻," Phys. Rev. A **40**, 670 (1989).

⁵⁵C. M. Oana and A. I. Krylov, "Cross sections and photoelectron angular distributions in photodetachment from negative ions using equation-of-motion coupled-cluster Dyson orbitals," J. Chem. Phys. **131**, 124114 (2009).

⁵⁶A. Sanov, "Laboratory-frame photoelectron angular distributions in anion photodetachment: Insight into electronic structure and intermolecular interactions," Annu. Rev. Phys. Chem. 65, 341 (2014).
 ⁵⁷Y. Liu and C. Ning, "Calculation of photodetachment cross sections and pho-

⁵⁷Y. Liu and C. Ning, "Calculation of photodetachment cross sections and photoelectron angular distributions of negative ions using density functional theory," J. Chem. Phys. **143**, 144310 (2015). ⁵⁸V. Dribinski, A. Ossadtchi, V. A. Mandelshtam, and H. Reisler, "Reconstruction of Abel-transformable images: The Gaussian basis-set expansion Abel transform method," Rev. Sci. Instrum. 73, 2634 (2002).

⁵⁹G. A. Garcia, L. Nahon, and I. Powis, "Two-dimensional charged particle image inversion using a polar basis function expansion," Rev. Sci. Instrum. **75**, 4989 (2004).

⁶⁰B. Dick, "Inverting ion images without Abel inversion: Maximum entropy reconstruction of velocity maps," Phys. Chem. Chem. Phys. **16**, 570 (2014).

⁶¹B. Dick, "MELEXIR: Maximum entropy Legendre expanded image reconstruction. A fast and efficient method for the analysis of velocity map imaging or photoelectron imaging data," Phys. Chem. Chem. Phys. **21**, 19499 (2019).

⁶² R. J. Peláez, C. Blondel, C. Delsart, and C. Drag, "Pulsed photodetachment microscopy and the electron affinity of iodine," J. Phys. B: At., Mol. Opt. Phys. 42, 125001 (2009).

⁶³T. Carette, C. Drag, O. Scharf, C. Blondel, C. Delsart, C. Froese Fischer, and M. Godefroid, "Isotope shift in the sulfur electron affinity: Observation and theory," Phys. Rev. A 81, 042522 (2010).

⁶⁴R. Tang, Y. Lu, H. Liu, and C. Ning, "Electron affinity of uranium and bound states of opposite parity in its anion," Phys. Rev. A **103**, L050801 (2021).

⁶⁵R. Tang, X. Fu, Y. Lu, and C. Ning, "Accurate electron affinity of Ga and fine structures of its anions," J. Chem. Phys. **152**, 114303 (2020).

⁶⁶C. Hock, J. B. Kim, M. L. Weichman, T. I. Yacovitch, and D. M. Neumark, "Slow photoelectron velocity-map imaging spectroscopy of cold negative ions," J. Chem. Phys. 137, 244201 (2012).

⁶⁷X.-B. Wang and L.-S. Wang, "Development of a low-temperature photoelectron spectroscopy instrument using an electrospray ion source and a cryogenically controlled ion trap," Rev. Sci. Instrum. **79**, 073108 (2008).

⁶⁸R. Tang, X. Chen, X. Fu, H. Wang, and C. Ning, "Electron affinity of the hafnium atom," Phys. Rev. A **98**, 020501 (2018).

⁶⁹X.-X. Fu, R.-L. Tang, Y.-Z. Lu, and C.-G. Ning, "Accurate electron affinity of atomic cerium and excited states of its anion," Chin. Phys. B **29**, 073201 (2020).

⁷⁰R. Tang, X. Fu, Y. Lu, and C. Ning, "Ground-state Pd anions react with H₂ much faster than the excited Pd anions," J. Phys. Chem. Lett. **10**, 702 (2019).

⁷¹ L. Pan and D. R. Beck, "Candidates for laser cooling of atomic anions: La⁻ versus Os⁻," Phys. Rev. A 82, 014501 (2010).

⁷²S. M. O'Malley and D. R. Beck, "Lifetimes and branching ratios of excited states in La⁻, Os⁻, Lu⁻, Lr⁻, and Pr⁻," Phys. Rev. A **81**, 032503 (2010).

⁷³C. W. Walter, N. D. Gibson, D. J. Matyas, C. Crocker, K. A. Dungan, B. R. Matola, and J. Rohlén, "Candidate for laser cooling of a negative ion: Observations of bound-bound transitions in La⁻," Phys. Rev. Lett. **113**, 063001 (2014).

⁷⁴A. Kellerbauer, G. Cerchiari, E. Jordan, and C. W. Walter, "High-resolution laser spectroscopy on bound-bound transitions in La⁻," Phys. Scr. **90**, 054014 (2015).

⁷⁵E. Jordan, G. Cerchiari, S. Fritzsche, and A. Kellerbauer, "High-resolution spectroscopy on the laser-cooling candidate La⁻," Phys. Rev. Lett. **115**, 113001 (2015).

⁷⁶G. Cerchiari, A. Kellerbauer, M. S. Safronova, U. I. Safronova, and P. Yzombard, "Ultracold anions for high-precision antihydrogen experiments," Phys. Rev. Lett. **120**, 133205 (2018).

⁷⁷C. W. Walter, N. D. Gibson, N. B. Lyman, and J. Wang, "Photodetachment spectroscopy of quasibound states of the negative ion of lanthanum," Phys. Rev. A 102, 042812 (2020).

⁷⁸ M. S. Safronova, C. Cheung, M. G. Kozlov, S. E. Spielman, N. D. Gibson, and C. W. Walter, "Predicting quasibound states of negative ions: La⁻ as a test case," Phys. Rev. A **103**, 022819 (2021).

⁷⁹Y. Lu, R. Tang, X. Fu, and C. Ning, "Measurement of the electron affinity of the lanthanum atom," Phys. Rev. A **99**, 062507 (2019).

⁸⁰C. Blondel, "Comment on 'Measurement of the electron affinity of the lanthanum atom," Phys. Rev. A **101**, 016501 (2020).

⁸¹ J. J. De Groote and M. Masili, "Electron affinity of the sodium atom within the coupled-channel hyperspherical approach," J. Chem. Phys. **120**, 2767 (2004).

⁸²G. W. F. Drake, M. M. Cassar, and R. A. Nistor, "Ground-state energies for helium, H⁻, and Ps⁻," Phys. Rev. A 65, 054501 (2002).

REVIEW

 83 G. W. F. Drake, "High precision variational calculations for the 1s² ¹S state of H⁻ and the 1s² ¹s, 1s2s ¹s and 1s2s ³s states of helium," Nucl. Instrum. Methods Phys. Res., Sect. B **31**, 7 (1988).

⁸⁴ K. R. Lykke, K. K. Murray, and W. C. Lineberger, "Threshold photodetachment of H⁻," Phys. Rev. A 43, 6104 (1991).

⁸⁵T. Andersen, H. H. Andersen, P. Balling, P. Kristensen, and V. V. Petrunin, "Structure and dynamics of the negative alkaline-earth ions," J. Phys. B: At., Mol. Opt. Phys. **30**, 3317 (1997).

⁸⁶ M. Nemouchi, A. Taleb, and M. Godefroid, "Isotope shift in the electron affinity of beryllium," J. Phys. B: At., Mol. Opt. Phys. **37**, 865 (2004).

⁸⁷C. W. Walter and J. R. Peterson, "Shape resonance in Ca⁻ photodetachment and the electron affinity of Ca(¹*S*)," Phys. Rev. Lett. **68**, 2281 (1992).

⁸⁸P. Kristensen, C. A. Brodie, U. V. Pedersen, V. V. Petrunin, and T. Andersen,
 "State-selective depletion spectroscopy of negative ions: First observation of the
 ⁴P state in Ca⁻ and Sr⁻," Phys. Rev. Lett. **78**, 2329 (1997).

⁸⁹V. V. Petrunin, J. D. Voldstad, P. Balling, P. Kristensen, T. Andersen, and H. K. Haugen, "Resonant ionization spectroscopy of Ba⁻: Metastable and stable ions," Phys. Rev. Lett. **75**, 1911 (1995).

⁹⁰M.-J. Nadeau, M. A. Garwan, X.-L. Zhao, and A. E. Litherland, "A negative ion survey; towards the completion of the periodic table of the negative ions," Nucl. Instrum. Methods Phys. Res., Sect. B **123**, 521 (1997).

⁹¹ P. Balling, L. H. Andersen, T. Andersen, H. K. Haugen, P. Hvelplund, and K. Taulbjerg, "Metastable ion lifetime studies utilizing a heavy-ion storage ring: Measurements on Be⁻," Phys. Rev. Lett. **69**, 1042 (1992).

⁹²H. H. Andersen, P. Balling, V. V. Petrunin, and T. Andersen, "State-selective stepwise two-photon detachment study of the Be⁻ ion," J. Phys. B: At., Mol. Opt. Phys. **29**, L415 (1996).

⁹³L. Knoll, K. G. Bhushan, N. Altstein, D. Zajfman, O. Heber, and M. L. Rappaport, "Lifetime measurement of Be⁻ $(2s2p^{2} {}^{4}P_{3/2})$ using an electrostatic ion trap," Phys. Rev. A **60**, 1710 (1999).

⁹⁴K. Bethge, E. Heinicke, and H. Baumann, "On the existence of negative beryllium and magnesium ions," Phys. Lett. 23, 542 (1966).

⁹⁵D. R. Beck, "Three lowest bound states of Mg⁻," Phys. Rev. A 30, 3305 (1984).
⁹⁶T. Andersen, J. O. Gaardsted, L. E. Srensen, and T. Brage, "Optical transition in the negative magnesium ion," Phys. Rev. A 42, 2728 (1990).

⁹⁷ P. Andersson, A. O. Lindahl, C. Alfredsson, L. Rogström, C. Diehl, D. J. Pegg, and D. Hanstorp, "The electron affinity of phosphorus," J. Phys. B: At., Mol. Opt. Phys. 40, 4097 (2007).

⁹⁸C. Blondel, C. Delsart, C. Valli, S. Yiou, M. R. Godefroid, and S. Van Eck, "Electron affinities of ¹⁶O, ¹⁷O, ¹⁸O, the fine structure of ¹⁶O⁻, and the hyperfine structure of ¹⁷O⁻," Phys. Rev. A **64**, 052504 (2001).

⁹⁹ M. R. Godefroid and C. F. Fischer, "Isotope shift in the oxygen electron affinity," Phys. Rev. A 60, R2637 (1999).

¹⁰⁰J. E. Wells and J. N. Yukich, "Photodetachment spectroscopy from the lowest threshold of S⁻," Phys. Rev. A 80, 055403 (2009).

 101 Y. Su, R. Si, K. Yao, and T. Brage, "The structure and radiative lifetimes of negative ions homologous to N⁻," J. Phys. B: At., Mol. Opt. Phys. **52**, 125002 (2019).

¹⁰²Y. K. Bae, J. R. Peterson, A. S. Schlachter, and J. W. Stearns, "Observation of the metastable negative argon ion Ar⁻," Phys. Rev. Lett. **54**, 789 (1985).

¹⁰³I. Ben-Itzhak, O. Heber, I. Gertner, and B. Rosner, "Production and meanlifetime measurement of metastable Ar⁻ ions," Phys. Rev. A **38**, 4870 (1988).

¹⁰⁴U. V. Pedersen, H. H. Andersen, T. Andersen, and L. Veseth, "Binding energy of the metastable Ar⁻ ion," Phys. Rev. A **58**, 258 (1998).

¹⁰⁵H. Haberland, T. Kolar, and T. Reiners, "Negatively charged xenon atoms and clusters," Phys. Rev. Lett. **63**, 1219 (1989).

¹⁰⁶C. A. Nicolaides and G. Aspromallis, "Binding of an electron by He and Xe," Phys. Rev. A 44, 2217 (1991).

107 R. Si, S. Schiffmann, K. Wang, C. Y. Chen, and M. Godefroid, "Ab initio multiconfiguration Dirac-Hartree-Fock calculations of the In and Tl electron affinities and their isotope shifts," Phys. Rev. A 104, 012802 (2021).

¹⁰⁸W. W. Williams, D. L. Carpenter, A. M. Covington, M. C. Koepnick, D. Calabrese, and J. S. Thompson, "Laser photodetachment electron spectrometry of Ga⁻," J. Phys. B: At., Mol. Opt. Phys. **31**, L341 (1998). ¹⁰⁹W. W. Williams, D. L. Carpenter, A. M. Covington, J. S. Thompson, T. J. Kvale, and D. G. Seely, "Fine-structure-resolved laser-photodetachment electron spectroscopy of In⁻," Phys. Rev. A 58, 3582 (1998).
¹¹⁰D. L. Carpenter, A. M. Covington, and J. S. Thompson, "Laser-

photodetachment-electron spectroscopy of Tl⁻," Phys. Rev. A **61**, 042501 (2000).

 111 T. P. Lippa, S.-J. Xu, S. A. Lyapustina, J. M. Nilles, and K. H. Bowen, "Photoelectron spectroscopy of As⁻, As₂⁻, As₃⁻, As₄⁻, and As₅⁻," J. Chem. Phys. **109**, 10727 (1998).

¹¹²C. S. Feigerle, R. R. Corderman, and W. C. Lineberger, "Electron affinities of B, Al, Bi, and Pb," J. Chem. Phys. **74**, 1513 (1981).

¹¹³C. W. Walter, N. D. Gibson, R. L. Field, A. P. Snedden, J. Z. Shapiro, C. M. Janczak, and D. Hanstorp, "Electron affinity of arsenic and the fine structure of As⁻ measured using infrared photodetachment threshold spectroscopy," Phys. Rev. A **80**, 014501 (2009).

¹¹⁴C. W. Walter, N. D. Gibson, D. J. Carman, Y. G. Li, and D. J. Matyas, "Electron affinity of indium and the fine structure of In⁻ measured using infrared photodetachment threshold spectroscopy," Phys. Rev. A **82**, 032507 (2010).

¹¹⁵X. Chen and C. Ning, "Accurate electron affinity of Pb and isotope shifts of binding energies of Pb⁻," J. Chem. Phys. **145**, 084303 (2016).

¹¹⁶D. Bresteau, C. Drag, and C. Blondel, "Electron affinity of lead," J. Phys. B: At., Mol. Opt. Phys. **52**, 065001 (2019).

¹¹⁷N. D. Gibson, C. W. Walter, C. Crocker, J. Wang, W. Nakayama, J. N. Yukich, E. Eliav, and U. Kaldor, "Electron affinity of gallium and fine structure of Ga⁻: Experiment and theory," Phys. Rev. A **100**, 052512 (2019).

¹¹⁸C. W. Walter, N. D. Gibson, and S. E. Spielman, "Electron affinity of thallium measured with threshold spectroscopy," Phys. Rev. A **101**, 052511 (2020).

¹¹⁹D. Leimbach, J. Karls, Y. Guo, R. Ahmed, J. Ballof, L. Bengtsson, F. Boix Pamies, A. Borschevsky, K. Chrysalidis, E. Eliav, D. Fedorov, V. Fedosseev, O. Forstner, N. Galland, R. F. Garcia Ruiz, C. Granados, R. Heinke, K. Johnston, A. Koszorus, U. Köster, M. K. Kristiansson, Y. Liu, B. Marsh, P. Molkanov, L. F. Pašteka, J. P. Ramos, E. Renault, M. Reponen, A. Ringvall-Moberg, R. E. Rossel, D. Studer, A. Vernon, J. Warbinek, J. Welander, K. Wendt, S. Wilkins, D. Hanstorp, and S. Rothe, "The electron affinity of astatine," Nat. Commun. 11, 3824 (2020).

¹²⁰M.-J. Nadeau, A. E. Litherland, M. A. Garwan, and X.-L. Zhao, "Electric dissociation of negative ions—II," Nucl. Instrum. Methods Phys. Res., Sect. B **92**, 265 (1994).

¹²¹ J. Li, Z. Zhao, M. Andersson, X. Zhang, and C. Chen, "Theoretical study for the electron affinities of negative ions with the MCDHF method," J. Phys. B: At., Mol. Opt. Phys. 45, 165004 (2012).

¹²² A. Borschevsky, L. F. Pašteka, V. Pershina, E. Eliav, and U. Kaldor, "Ionization potentials and electron affinities of the superheavy elements 115–117 and their sixth-row homologues Bi, Po, and At," Phys. Rev. A **91**, 020501(R) (2015).
 ¹²³ R. Si and C. F. Fischer, "Electron affinities of At and its homologous elements

¹²³ R. Si and C. F. Fischer, "Electron affinities of At and its homologous elements Cl, Br, and I," Phys. Rev. A 98, 052504 (2018).

¹²⁴B. A. Finney and K. A. Peterson, "Beyond chemical accuracy in the heavy p-block: The first ionization potentials and electron affinities of Ga–Kr, In–Xe, and Tl–Rn," J. Chem. Phys. **151**, 024303 (2019).

¹²⁵C. Bahrim and U. Thumm, "Low-lying ${}^{3}P^{o}$ and ${}^{3}S^{e}$ states of Rb⁻, Cs⁻, and Fr⁻," Phys. Rev. A **61**, 022722 (2000).

¹²⁶E. Eliav, S. Fritzsche, and U. Kaldor, "Electronic structure theory of the superheavy elements," Nucl. Phys. A 944, 518 (2015).

 127 C. S. Feigerle, Z. Herman, and W. C. Lineberger, "Laser photoelectron spectrometry of Sc⁻ and Y⁻: A determination of the order of electron filling in transition-metal anions," J. Electron Spectrosc. Relat. Phenom. **23**, 441 (1981).

¹²⁸D. G. Leopold and W. C. Lineberger, "A study of the low-lying electronic states of Fe₂ and Co₂ by negative ion photoelectron spectroscopy," J. Chem. Phys. **85**, 51 (1986).

¹²⁹X. Chen and C. Ning, "Observation of rhenium anion and electron affinity of Re," J. Phys. Chem. Lett. 8, 2735 (2017).

¹³⁰V. T. Davis, J. Thompson, and A. Covington, "Laser photodetachment electron spectroscopy studies of heavy atomic anions," Nucl. Instrum. Methods Phys. Res., Sect. B 241, 118 (2005).

¹³¹L. Pan and D. R. Beck, "Calculations of Hf⁻ electron affinity and photodetachment partial cross sections," J. Phys. B: At., Mol. Opt. Phys. 43, 025002 (2009). ¹³²S. M. O'Malley and D. R. Beck, "Binding energies of 4*d*⁶5*s*² states in Tc⁻," Phys. Rev. A 65, 064502 (2002).

¹³³ R. C. Bilodeau and H. K. Haugen, "Experimental studies of Os⁻: Observation of a bound-bound electric dipole transition in an atomic negative ion," Phys. Rev. Lett. **85**, 534 (2000).

¹³⁴A. Kellerbauer and J. Walz, "A novel cooling scheme for antiprotons," New J. Phys. 8, 45 (2006).

¹³⁵U. Warring, M. Amoretti, C. Canali, A. Fischer, R. Heyne, J. O. Meier, Ch. Morhard, and A. Kellerbauer, "High-resolution laser spectroscopy on the negative osmium ion," Phys. Rev. Lett. **102**, 043001 (2009).

¹³⁶ A. Fischer, C. Canali, U. Warring, A. Kellerbauer, and S. Fritzsche, "First optical hyperfine structure measurement in an atomic anion," Phys. Rev. Lett. **104**, 073004 (2010).

¹³⁷M. Scheer, C. A. Brodie, R. C. Bilodeau, and H. K. Haugen, "Laser spectroscopic measurements of binding energies and fine-structure splittings of Co⁻, Ni⁻, Rh⁻, and Pd⁻," Phys. Rev. A 58, 2051 (1998).

¹³⁸R. C. Bilodeau, M. Scheer, H. K. Haugen, and R. L. Brooks, "Near-threshold laser spectroscopy of iridium and platinum negative ions: Electron affinities and the threshold law," Phys. Rev. A **61**, 012505 (1999).

¹³⁹Y. Lu, J. Zhao, R. Tang, X. Fu, and C. Ning, "Measurement of electron affinity of iridium atom and photoelectron angular distributions of iridium anion," J. Chem. Phys. **152**, 034302 (2020).

¹⁴⁰R. C. Bilodeau, M. Scheer, and H. K. Haugen, "Infrared laser photodetachment of transition metal negative ions: Studies on Cr⁻, Mo⁻, Cu⁻ and Ag⁻," J. Phys. B: At., Mol. Opt. Phys. **31**, 3885 (1998).

¹⁴¹ P. L. Norquist, D. R. Beck, R. C. Bilodeau, M. Scheer, R. A. Srawley, and H. K. Haugen, "Theoretical and experimental binding energies for the $d^7 s^{2} + F$ levels in Ru⁻, including calculated hyperfine structure and M1 decay rates," Phys. Rev. A **59**, 1896 (1999).

¹⁴²A. O. Lindahl, P. Andersson, C. Diehl, O. Forstner, P. Klason, and D. Hanstorp, "The electron affinity of tungsten," Eur. Phys. J. D 60, 219 (2010).

¹⁴³ A. M. Covington, D. Calabrese, J. S. Thompson, and T. J. Kvale, "Measurement of the electron affinity of lanthanum," J. Phys. B: At., Mol. Opt. Phys. 31, L855 (1998).

¹⁴⁴V. T. Davis and J. S. Thompson, "Measurement of the electron affinity of cerium," Phys. Rev. Lett. **88**, 073003 (2002).

¹⁴⁵V. T. Davis and J. S. Thompson, "Measurement of the electron affinity of praseodymium," J. Phys. B: At., Mol. Opt. Phys. **35**, L11 (2001).

¹⁴⁶V. T. Davis and J. S. Thompson, "An experimental investigation of the atomic europium anion," J. Phys. B: At., Mol. Opt. Phys. **37**, 1961 (2004).

¹⁴⁷V. T. Davis and J. S. Thompson, "Measurement of the electron affinity of thulium," Phys. Rev. A 65, 010501 (2001).

¹⁴⁸V. T. Davis and J. S. Thompson, "Measurement of the electron affinity of lutetium," J. Phys. B: At., Mol. Opt. Phys. **34**, L433 (2001).

¹⁴⁹K. Dinov and D. R. Beck, "Electron affinities of 6p electrons in Pr⁻," Phys. Rev. A 51, 1680 (1995).

¹⁵⁰X. Fu, Y. Lu, R. Tang, and C. Ning, "Electron affinity measurements of lanthanide atoms: Pr, Nd, and Tb," Phys. Rev. A **101**, 022502 (2020).

¹⁵¹ D. Datta and D. R. Beck, "Electron affinities of opposite-parity bound states in Th⁻: Relativistic-configuration-interaction studies," Phys. Rev. A 50, 1107 (1994).
 ¹⁵² K. D. Dinov and D. R. Beck, "Electron affinity of Pa by 7*p* attachment and hyperfine structure constants for Pa⁻," Phys. Rev. A 53, 4031 (1996).

 153 K. D. Dinov and D. R. Beck, "Electron affinities and hyperfine structure for U⁻ and U I obtained from relativistic configuration-interaction calculations," Phys. Rev. A **52**, 2632 (1995).

¹⁵⁴S. M. O'Malley and D. R. Beck, "Calculation of Ce⁻ binding energies by analysis of photodetachment partial cross sections," Phys. Rev. A 74, 042509 (2006).

¹⁵⁵S. M. O'Malley and D. R. Beck, "Valence calculations of lanthanide anion binding energies: 6p and 6s attachments to $4f^m(5d + 6s + 6p)^3$ thresholds," Phys. Rev. A **79**, 012511 (2009).

¹⁵⁶S. M. O'Malley and D. R. Beck, "Valence calculations of lanthanide anion binding energies: 6p attachments to $4f^n 6s^2$ thresholds," Phys. Rev. A **78**, 012510 (2008).

¹⁵⁷S. M. O'Malley and D. R. Beck, "Valence calculations of actinide anion binding energies: All bound 7*p* and 7*s* attachments," Phys. Rev. A 80, 032514 (2009). ¹⁵⁸Z. Felfli, A. Z. Msezane, and D. Sokolovski, "Simple method for electron affinity determination: Results for Ca, Sr and Ce," J. Phys. B: At., Mol. Opt. Phys. **41**, 041001 (2008).

¹⁵⁹X. Cao and M. Dolg, "Electron affinity of Ce and electronic states of Ce⁻," Phys. Rev. A **69**, 042508 (2004).

¹⁶⁰J. Felton, M. Ray, and C. C. Jarrold, "Measurement of the electron affinity of atomic Ce," Phys. Rev. A **89**, 033407 (2014).

¹⁶¹L. Pan and D. R. Beck, "La⁻ binding energies by analysis of its photodetachment spectra," Phys. Rev. A **93**, 062501 (2016).

¹⁶²S. M. Ciborowski, G. Liu, M. Blankenhorn, R. M. Harris, M. A. Marshall, Z. Zhu, K. H. Bowen, and K. A. Peterson, "The electron affinity of the uranium atom," J. Chem. Phys. **154**, 224307 (2021).

¹⁶³X.-x. Fu, R.-l. Tang, Y.-z. Lu, and C.-g. Ning, "Measurement of electron affinity of atomic lutetium via the cryo-SEVI method," Chin. J. Chem. Phys. **32**, 187 (2019).

 164 R. Tang, R. Si, Z. Fei, X. Fu, Y. Lu, T. Brage, H. Liu, C. Chen, and C. Ning, "Observation of electric-dipole transitions in the laser-cooling candidate Th⁻ and its application for cooling antiprotons," Phys. Rev. A **103**, 042817 (2021).

¹⁶⁵R. Tang, R. Si, Z. Fei, X. Fu, Y. Lu, T. Brage, H. Liu, C. Chen, and C. Ning, "Candidate for laser cooling of a negative ion: High-resolution photoelectron imaging of Th⁻," Phys. Rev. Lett. **123**, 203002 (2019).

¹⁶⁶X.-L. Zhao, M.-J. Nadeau, M. A. Garwan, L. R. Kilius, and A. E. Litherland, "Observation of the negative ions: Ra⁻, Pa⁻, and Pu⁻," Phys. Rev. A 48, 3980 (1993).

¹⁶⁷D. Berkovits, E. Boaretto, O. Heber, G. Hollos, G. Korschinek, W. Kutschera, and M. Paul, "Study of weakly-formed negative ions by laser photodetachment and accelerator mass spectrometry," Nucl. Instrum. Methods Phys. Res., Sect. B **92**, 254 (1994).

¹⁶⁸S.-B. Cheng and A. W. Castleman, "Direct experimental observation of weaklybound character of the attached electron in europium anion," Sci. Rep. **5**, 12414 (2015).

¹⁶⁹A. E. Litherland, L. R. Kilius, M. A. Garwan, M.-J. Nadeau, and X.-L. Zhao, "Observation of Yb⁻ by accelerator mass spectrometry," J. Phys. B: At., Mol. Opt. Phys. **24**, L233 (1991).

¹⁷⁰H. H. Andersen, T. Andersen, and U. V. Pedersen, "Search for stable or metastable negative Yb ions," J. Phys. B: At., Mol. Opt. Phys. **31**, 2239 (1998).

¹⁷¹V. A. Dzuba and G. F. Gribakin, "Yb⁻ 6*p*_{1/2}—Low-lying shape resonance rather than a bound state," J. Phys. B: At., Mol. Opt. Phys. **31**, L483 (1998).

¹⁷²X.-L. Zhao, A. E. Litherland, W. E. Kieser, and R. J. Cornett, "Yb⁻ and 236 UF₅⁻—Two case studies of E/q and EM/q² interferences in AMS," Nucl. Instrum. Methods Phys. Res., Sect. B **455**, 224 (2019).

¹⁷³J. Li and V. Dzuba, "Theoretical study of the spectroscopic properties of mendelevium (Z = 101)," J. Quant. Spectrosc. Radiat. Transfer **247**, 106943 (2020). ¹⁷⁴P. Pyykko, "Relativistic effects in structural chemistry," Chem. Rev. **88**, 563 (1988).

¹⁷⁵E. Eliav, U. Kaldor, Y. Ishikawa, and P. Pyykkö, "Element 118: The first rare gas with an electron affinity," Phys. Rev. Lett. 77, 5350 (1996).
 ¹⁷⁶I. Goidenko, L. Labzowsky, E. Eliav, U. Kaldor, and P. Pyykkö, "QED correc-

¹⁷⁶I. Goidenko, L. Labzowsky, E. Eliav, U. Kaldor, and P. Pyykkö, "QED corrections to the binding energy of the eka-radon (Z = 118) negative ion," Phys. Rev. A **67**, 020102 (2003).

¹⁷⁷B. G. C. Lackenby, V. A. Dzuba, and V. V. Flambaum, "Atomic structure calculations of superheavy noble element oganesson (Z=118)," Phys. Rev. A **98**, 042512 (2018).

¹⁷⁸C. W. Walter, N. D. Gibson, C. M. Janczak, K. A. Starr, A. P. Snedden, R. L. Field III, and P. Andersson, "Infrared photodetachment of Ce⁻: Threshold spectroscopy and resonance structure," Phys. Rev. A **76**, 052702 (2007).

¹⁷⁹C. W. Walter, N. D. Gibson, Y. G. Li, D. J. Matyas, R. M. Alton, S. E. Lou, R. L. Field, D. Hanstorp, L. Pan, and D. R. Beck, "Experimental and theoretical study of bound and quasibound states of Ce⁻," Phys. Rev. A **84**, 032514 (2011).

180 P. Yzombard, M. Hamamda, S. Gerber, M. Doser, and D. Comparat, "Laser cooling of molecular anions," Phys. Rev. Lett. 114, 213001 (2015).

¹⁸¹S. Gerber, J. Fesel, M. Doser, and D. Comparat, "Photodetachment and Doppler laser cooling of anionic molecules," New J. Phys. 20, 023024 (2018).

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¹⁸²G. Gabrielse, X. Fei, L. A. Orozco, R. L. Tjoelker, J. Haas, H. Kalinowsky, T. A. Trainor, and W. Kells, "Cooling and slowing of trapped antiprotons below 100 meV," Phys. Rev. Lett. 63, 1360 (1989).

¹⁸³E. Tiesinga, P. J. Mohr, D. B. Newell, and B. N. Taylor, The 2018 CODATA Recommended Values of the Fundamental Physical Constants, http://physics.nist.gov/constants.

¹⁸⁴H. K. Haugen, L. H. Andersen, T. Andersen, P. Balling, N. Hertel, P. Hvelplund, and S. P. Möller, "Storage-ring experiments with 10–100-keV Ca⁻ beams: Role of blackbody radiation," Phys. Rev. A 46, R1 (1992).

¹⁸⁵D. J. Pegg, "Structure and dynamics of negative ions," Rep. Prog. Phys. 67, 857 (2004).

¹⁸⁶A. Ellmann, P. Schef, P. Lundin, P. Royen, S. Mannervik, K. Fritioff, P. Andersson, D. Hanstorp, C. Froese Fischer, F. Österdahl, D. J. Pegg, N. D. Gibson, H. Danared, and A. Källberg, "Radiative lifetime of a bound excited state of Te⁻," Phys. Rev. Lett. **92**, 253002 (2004).

¹⁸⁷P. Andersson, K. Fritioff, J. Sandström, G. Collins, D. Hanstorp, A. Ellmann, P. Schef, P. Lundin, S. Mannervik, P. Royen, K. C. Froese Fischer, F. Österdahl, D. Rostohar, D. J. Pegg, N. D. Gibson, H. Danared, and A. Källberg, "Radiative lifetimes of metastable states of negative ions," Phys. Rev. A 73, 032705 (2006).

¹⁸⁸E. Bäckström, D. Hanstorp, O. M. Hole, M. Kaminska, R. F. Nascimento, M. Blom, M. Björkhage, A. Källberg, P. Löfgren, P. Reinhed, S. Rosén, A. Simonsson, R. D. Thomas, S. Mannervik, H. T. Schmidt, and H. Cederquist, "Storing keV negative ions for an hour: The lifetime of the metastable ${}^{2}P^{ol/2}$ level in ${}^{32}S^{-}$," Phys. Rev. Lett. **114**, 143003 (2015).

¹⁸⁹M. Kamińska, V. T. Davis, O. M. Hole, R. F. Nascimento, K. C. Chartkunchand, M. Blom, M. Björkhage, A. Källberg, P. Löfgren, P. Reinhed, S. Rosén, A. Simonsson, R. D. Thomas, S. Mannervik, P. A. Neill, J. S. Thompson, H. T. Schmidt, H. Cederquist, and D. Hanstorp, "Lifetime of the bound excited level in Ni⁻," Phys. Rev. A **93**, 012512 (2016).

¹⁹⁰K. C. Chartkunchand, M. Kamińska, E. K. Anderson, M. K. Kristiansson, G. Eklund, O. M. Hole, R. F. Nascimento, M. Blom, M. Björkhage, A. Källberg, P. Löfgren, P. Reinhed, S. Rosén, A. Simonsson, R. D. Thomas, S. Mannervik, V. T. Davis, P. A. Neill, J. S. Thompson, D. Hanstorp, H. Zettergren, H. Cederquist, and H. T. Schmidt, "Radiative lifetimes of the bound excited states of Pt⁻," Phys. Rev. A **94**, 032501 (2016).

¹⁹¹ R. Si, C. Y. Zhang, K. Yao, T. Brage, C. Y. Chen, and Y. M. Zou, "Persistent discrepancy between experimental and theoretical lifetimes for Ni⁻," Phys. Rev. A 95, 042504 (2017).

¹⁹²M. K. Kristiansson, S. Schiffmann, J. Grumer, J. Karls, N. de Ruette, G. Eklund, V. Ideböhn, N. D. Gibson, T. Brage, H. Zettergren, D. Hanstorp, and H. T. Schmidt, "Experimental and theoretical studies of excited states in Ir⁻," Phys. Rev. A **103**, 062806 (2021).

¹⁹³D. Müll, F. Grussie, K. Blaum, S. George, J. Göck, M. Grieser, R. von Hahn, Z. Harman, Á. Kálosi, C. H. Keitel, C. Krantz, C. Lyu, O. Novotný, F. Nuesslein, D. Paul, V. C. Schmidt, S. Singh, S. Sunil Kumar, X. Urbain, A. Wolf, and H. Kreckel, "Metastable states of Si⁻ observed in a cryogenic storage ring," Phys. Rev. A 104, 032811 (2021).

¹⁹⁴E. Eliav, U. Kaldor, and A. Borschevsky, "Electronic structure of the transactinide atoms," in *Encyclopedia of Inorganic and Bioinorganic Chemistry* (John Wiley & Sons Ltd, Chichester, 2018), pp. 1–16.

¹⁹⁵Y. Guo, L. F. Pašteka, E. Eliav, and A. Borschevsky, "Chapter Five—Ionization potentials and electron affinity of oganesson with relativistic coupled cluster method," Adv. Quantum Chem. **83**, 107–123 (2021).

¹⁹⁶E. Eliav, U. Kaldor, Y. Ishikawa, M. Seth, and P. Pyykkö, "Calculated energy levels of thallium and eka-thallium (element 113)," Phys. Rev. A 53, 3926 (1996).
 ¹⁹⁷A. Borschevsky, V. Pershina, E. Eliav, and U. Kaldor, "Electron affinity of

element 114, with comparison to Sn and Pb," Chem. Phys. Lett. **480**, 49 (2009). ¹⁹⁸G. Haeffler, D. Hanstorp, I. Kiyan, A. E. Klinkmüller, U. Ljungblad, and D. J. Pegg, "Electron affinity of Li: A state-selective measurement," Phys. Rev. A **53**, 4127 (1996).

¹⁹⁹M. Scheer, R. C. Bilodeau, and H. K. Haugen, "Negative ion of boron: An experimental study of the ³*P* ground state," Phys. Rev. Lett. **80**, 2562 (1998).

²⁰⁰C. Blondel, P. Cacciani, C. Delsart, and R. Trainham, "High-resolution determination of the electron affinity of fluorine and bromine using crossed ion and laser beams," Phys. Rev. A 40, 3698 (1989).

²⁰¹C. Blondel, C. Delsart, and F. Goldfarb, "Electron spectrometry at the μ eV level and the electron affinities of Si and F," J. Phys. B: At., Mol. Opt. Phys. **34**, L281 (2001).

²⁰²M. Scheer, R. C. Bilodeau, J. Thøgersen, and H. K. Haugen, "Threshold photodetachment of Al⁻: Electron affinity and fine structure," Phys. Rev. A **57**, R1493 (1998).

²⁰³R. J. Peláez, C. Blondel, M. Vandevraye, C. Drag, and C. Delsart, "Photodetachment microscopy to an excited spectral term and the electron affinity of phosphorus," J. Phys. B: At., Mol. Opt. Phys. 44, 195009 (2011).

²⁰⁴U. Berzinsh, M. Gustafsson, D. Hanstorp, A. Klinkmüller, U. Ljungblad, and A.-M. Mårtensson-Pendrill, "Isotope shift in the electron affinity of chlorine," Phys. Rev. A 51, 231 (1995).

²⁰⁵K. T. Andersson, J. Sandström, I. Y. Kiyan, D. Hanstorp, and D. J. Pegg, "Measurement of the electron affinity of potassium," Phys. Rev. A 62, 022503 (2000).

²⁰⁶S. Li, Y. Z. Lu, R. L. Tang, X. X. Fu, X. L. Chen, H. Wang, and C. G. Ning (unpublished).

 207 X. Fu, Z. Luo, X. Chen, J. Li, and C. Ning, "Accurate electron affinity of V and fine-structure splittings of V⁻ via slow-electron velocity-map imaging," J. Chem. Phys. **145**, 164307 (2016).

²⁰⁸X. Chen, Z. Luo, J. Li, and C. Ning, "Accurate electron affinity of iron and fine structures of negative iron ions," Sci. Rep. 6, 24996 (2016).

²⁰⁹X.-L. Chen and C.-G. Ning, "Accurate electron affinity of Co and fine-structure splittings of Co⁻ via slow-electron velocity-map imaging," Phys. Rev. A **93**, 052508 (2016).

²¹⁰D. Bresteau, P. Babilotte, C. Drag, and C. Blondel, "Intra-cavity photodetachment microscopy and the electron affinity of germanium," J. Phys. B: At., Mol. Opt. Phys. **48**, 125001 (2015).

²¹¹M. Vandevraye, C. Drag, and C. Blondel, "Electron affinity of selenium measured by photodetachment microscopy," Phys. Rev. A **85**, 015401 (2012).

²¹² P. Frey, F. Breyer, and H. Holop, "High resolution photodetachment from the rubidium negative ion around the Rb(5p_{1/2}) threshold," J. Phys. B: At. Mol. Phys. 11, L589 (1978).

²¹³H. H. Andersen, V. V. Petrunin, P. Kristensen, and T. Andersen, "Structural properties of the negative strontium ion: Binding energy and fine-structure splitting," Phys. Rev. A 55, 3247 (1997).
²¹⁴X. Fu, J. Li, Z. Luo, X. Chen, and C. Ning, "Precision measurement of electron

²¹⁴X. Fu, J. Li, Z. Luo, X. Chen, and C. Ning, "Precision measurement of electron affinity of Zr and fine structures of its negative ions," J. Chem. Phys. **147**, 064306 (2017).

²¹⁵M. Vandevraye, C. Drag, and C. Blondel, "Electron affinity of tin measured by photodetachment microscopy," J. Phys. B: At., Mol. Opt. Phys. 46, 125002 (2013).
 ²¹⁶G. Haeffler, A. E. Klinkmüller, J. Rangell, U. Berzinsh, and D. Hanstorp, "The electron affinity of tellurium," Z. Phys. D: At., Mol. Clusters 38, 211 (1996).

²¹⁷J. Slater, F. H. Read, S. E. Novick, and W. C. Lineberger, "Alkali negative ions. III. Multichannel photodetachment study of Cs⁻ and K⁻," Phys. Rev. A **17**, 201 (1978).

²¹⁸M. Scheer, J. Thøgersen, R. C. Bilodeau, C. A. Brodie, H. K. Haugen, H. H. Andersen, P. Kristensen, and T. Andersen, "Experimental evidence that the 6*s*6*p* ${}^{3}P_{j}$ states of Cs⁻ are shape resonances," Phys. Rev. Lett. **80**, 684 (1998).

²¹⁹R. C. Bilodeau and H. K. Haugen, "Electron affinity of Bi using infrared laser photodetachment threshold spectroscopy," Phys. Rev. A **64**, 024501 (2001).

²²⁰M. Scheer, R. C. Bilodeau, C. A. Brodie, and H. K. Haugen, "Systematic study of the stable states of C⁻, Si⁻, Ge⁻, and Sn⁻ via infrared laser spectroscopy," Phys. Rev. A 58, 2844 (1998).

²²¹ A. Kasdan, E. Herbst, and W. C. Lineberger, "Laser photoelectron spectrometry of the negative ions of silicon and its hydrides," J. Chem. Phys. 62, 541 (1975).

²²²C. Blondel, W. Chaibi, C. Delsart, and C. Drag, "The fine structure of S and S⁻ measured with the photodetachment microscope," J. Phys. B: At., Mol. Opt. Phys. 39, 1409 (2006).

223 J. Thøgersen, L. D. Steele, M. Scheer, H. K. Haugen, P. Kristensen, P. Balling, H. Stapelfeldt, and T. Andersen, "Fine-structure measurements for negative ions: Studies of Se⁻ and Te⁻," Phys. Rev. A 53, 3023 (1996).

²²⁴M. Scheer, R. C. Bilodeau, and H. K. Haugen, "Observation of the magneticdipole fine-structure transition in the tellurium negative ion," J. Phys. B: At., Mol. Opt. Phys. **31**, L11 (1998).

²²⁵P. Andersson, A. O. Lindahl, D. Hanstorp, and D. J. Pegg, "Observation of the ${}^{2}S_{1/2}$ metastable state in Pt⁻," Phys. Rev. A **79**, 022502 (2009).

(2009).
 ²²⁶C. W. Walter, S. E. Spielman, R. Ponce, N. D. Gibson, J. N. Yukich, C. Cheung, and M. S. Safronova, "Observation of an electric quadrupole transition

in a negative ion: Experiment and theory," Phys. Rev. Lett. 126, 083001 (2021).

 227 P. Kristensen, V. V. Petrunin, H. H. Andersen, and T. Andersen, "Laser spectroscopy of the Be $^-$ ion: Binding energies of metastable states," Phys. Rev. A 52, R2508 (1995).

²²⁸T. Carette and M. R. Godeforid, "Theoretical study of the C⁻⁴ $S_{3/2}^{o}$ and $^{2}D_{3/2,5/2}^{o}$ bound states and C ground configuration: Fine and hyperfine structures, isotope shifts, and transition probabilities," Phys. Rev. A **83**, 062505 (2011).