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Measurement of the electron affinity of lanthanum

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Abstract. The electron affinity of lanthanum has been measured using laser photoelectron energy spectroscopy. This is the first electron affinity measurement for lanthanum and one of the first measurements of an electron affinity of a rare-earth series element. The electron affinity of lanthanum was measured to be 0.47 ± 0.02 eV. At least one bound excited state of La^- was also observed in the photoelectron spectra, and the binding energy relative to the ground state of lanthanum was measured as 0.17 ± 0.02 eV. The present experimental measurements are compared to a recent calculation.

The experimental study of negative ions has been a field of intense interest in atomic physics for a number of years. Reviews of negative ion research [1–3] illustrate the breadth of the field and bring forth the depth of atomic physics research conducted with negative ions. The importance of experimentally determined parameters such as electron affinities is crucial to the understanding of the electron–electron interactions which are responsible for the existence of negative ions. Although the inclusion of electron correlation in a negative ion structure calculation results in a small correction to the total energy, the correlation energy is usually the critical term in determining whether bound states are predicted. Negative ion structure calculations are difficult, and approximations are typically used in the calculations to reduce the number of terms contributing to the energy levels so the calculation is tractable. Experimental verification of the existence of the predicted negative ion structure is therefore necessary to judge the validity of the approximations. The present work is the first electron affinity measurement for lanthanum and as such, is the first experimental test of the recently predicted La^- energy level structure, which included predictions of bound excited states in La^- [4].

A number of semi-empirical estimates [5–7] and a Hartree–Fock–Slater calculation [8] have been used to estimate the electron affinities of lanthanum and the rare-earth series elements. The semi-empirical estimates led to a recommended value of 0.5 ± 0.3 eV for the electron affinity of lanthanum, with the ground state configuration of La^- predicted as $[Xe]5d^26s^2$ in a review [1]. Recently, Vosko *et al* [4] reported a theoretical investigation of La^- using a Hartree–Fock system method of density functional theory with J-independent relativistic contributions added perturbatively. This structure calculation for La^- predicted that the ground state of La^- is formed in the $[Xe](5d6s^26p)\ ^1D^o$ state with the electron affinity of La in the range between 0.27 and 0.41 eV. Three bound excited states were also

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predicted for La^-: odd parity states of [Xe](5d6s^{2}6p) $^3F^o$ (binding energy (BE) relative to the La ground state between 0.1 and 0.2 eV), [Xe](5d6s^{2}6p) $^3D^o$ (BE between 0.1 and 0.2 eV) and an even parity state of [Xe](5d^{2}6s^2) ^3F (BE between 0.1 and 0.3 eV). This calculation was the first prediction of bound states of a negative ion of both odd and even parities.

Previous experimental investigations of rare-earth negative ions using accelerator mass spectrometry have reported ion production yields for rare-earth negative ions [9]. The reported negative ion production yields for La^- and Ce^- were much higher than for the other atomic rare-earth anions, indicating that either the electron affinities of lanthanum and cerium are greater than other rare-earth atoms, or La^- and Ce^- have more than one bound state [9]. Nadeau *et al* have reported measurements of the electron affinities of Tm, Yb and Dy using an electric field dissociation technique [10]. A subsequent experimental investigation [11] disputed these results, observing no evidence for a stable or metastable state of Yb^- with a binding energy greater than 3 meV.

A detailed description of the experimental apparatus has been given elsewhere [12, 13], but a brief description follows. A continuous La^- beam was produced by a caesium-sputter negative ion source. A solid lanthanum pellet in a copper holder was used as a sputter target to produce the La^- beam. The ion source was held at a potential of -10 kV, accelerating the negative ions toward the extraction electrode which was held at ground potential. A 90°, double-focusing, bending magnet was used to momentum select the $^{139}La^-$ beam for the measurements. The mass resolution of the magnet ($\Delta m/m$) was approximately 1:200. Copper dimer anions ($^ACu_2^-$, $A = 126, 128, 130$) produced from sputtering of the target holder were used as mass markers to identify the $^{139}La^-$ beam. The total flight length of the beam line was 6.4 m and the pressure in the beam line was of the order of 1×10^{-6} Pa. Typical ion beam currents were in the range of 80–150 pA for La^- and 2–5 nA for Cu^- when measured in a 6 mm diameter Faraday cup in the experimental chamber.

After entering the experimental chamber, the ion beam was crossed at 90° by a laser-produced, continuous photon beam. The plane formed by the ion and photon beams coincided with the horizontal plane. A 25 W Ar^+ laser operated in a linearly polarized, single-line (488.0 or 514.5 nm) mode provided the photon beam for the measurements. Before intersecting the ion beam, the laser beam passed through a Glan-laser polarizing prism and a double-Fresnel rhomb. The polarizing prism set the degree of linear polarization to greater than 10^5:1, and the double-Fresnel rhomb was used to rotate the linear polarization vector of the laser beam. Following the intersection of the ion and photon beams, the power output of the laser was monitored with a power meter. The power of the photon beam was set between 8.6 and 9.7 W at the 514.5 nm wavelength output and was set to 7.6 W at the 488.0 nm wavelength output.

An electrostatic 160° spherical-sector electron kinetic energy analyser with a channel electron multiplier (CEM) detector was used to detect the photoelectrons resulting from the absorption of laser-produced photons by negative ions in the beam. The entrance aperture of the electron kinetic energy analyser was located at an angle of 45° vertically below the velocity vector of ions in the ion beam. The interaction region, where the ion and photon beams crossed, was approximately 2.5 cm from the entrance aperture of the electron kinetic energy analyser. The interaction region and electron kinetic energy analyser were enclosed in a μ-metal box, and a set of mutually perpendicular circular coils enclosed the experimental chamber to reduce the intensity of the Earth's and stray magnetic fields in the interaction region. The operating pressure in the experimental chamber was 1×10^{-7} Pa.

The electron energy analyser was operated at a constant pass energy. The electron acceleration voltage was decreased in steps by a computer-based digital-to-analogue

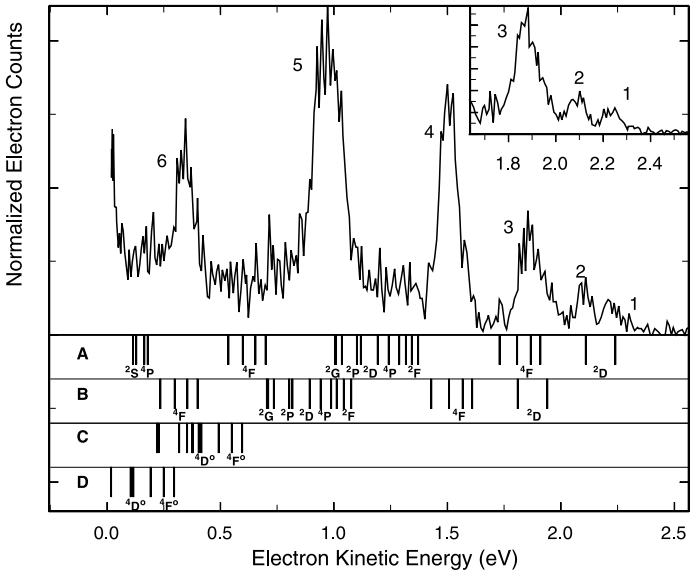

Figure 1. Typical photoelectron kinetic energy spectrum for photodetaching La^-. The ion beam energy was 10 keV and the photon wavelength was 514.5 nm (2.410 eV) for this spectrum. The smaller graph in the upper right-hand corner is a photoelectron kinetic energy spectrum for photodetaching La^- over the energy range 1.6–2.6 eV at twice the accumulation time per data point. The peaks in the spectra are labelled for further identification in the text. The energy level diagrams (labelled A, B, C and D) are discussed in the text.

converter. Electron counts were accumulated for a specified time at each acceleration voltage to create an electron kinetic energy spectrum as a function of the acceleration voltage. The ion beam intensity was monitored with an electrometer connected to a Faraday cup in the experimental chamber. Voltage output signals from both the laser power meter and the electrometer were digitized with a voltage-to-frequency converter and collected for normalization of the electron signal.

A typical photoelectron kinetic energy spectrum for La^- is shown in figure 1. The kinetic energy of the La^- ions in the beam for this spectrum was 10 keV, and the ion current, measured in the experimental chamber, was 150 pA. The photon wavelength was 514.5 nm and the laser output power was 8.6 W. The polarization vector of the laser beam was rotated so the vector pointed toward the entrance aperture of the electron energy analyser for this particular spectrum. The data accumulation time for each data point was 60 s and the spectrum took approximately 4 h to complete. The inset in figure 1 is a separate photoelectron kinetic energy spectrum over the three highest energy peaks in the spectrum with an accumulation time of 120 s per data point. The laser power for this spectrum was 9.7 W and the La^- ion beam current, measured in the experimental chamber, was 100 pA.

The energy scale for the La^- photoelectron kinetic energy spectra was determined using the photoelectron energy spectra of Cu^-. Electron energy spectra were taken for the photodetachment of Cu^- with either 488.0 or 514.5 nm wavelength laser light before and after each La^- photoelectron spectrum was accumulated. The electron affinity of Cu is well determined by laser photoelectron energy spectroscopy [14]. Ion beam currents of Cu^- were typically 2–5 nA, and with laser powers of approximately 8.5 W, produced photoelectron energy spectra with signal-to-noise ratios of approximately 3500:1. The data accumulation

time for each data point was 2 s, and each photoelectron spectrum of Cu^- was accumulated in approximately 5 min. The kinetic energy of the photoelectrons from $^{63}Cu^-$ as measured in the laboratory frame was determined using the following equation:

$$E_\ell = \left(\sqrt{\epsilon}\cos\theta_\ell + \sqrt{E_c - \epsilon\sin^2\theta_\ell}\right)^2 \tag{1}$$

where E_ℓ is the laboratory frame energy of the photoelectrons, and θ_ℓ is the angle between the velocity vector of an ion in the ion beam and the collection direction for the photoelectrons. The term ϵ is the kinetic energy of an electron with the same speed as the ions, i.e. $\epsilon = (m_e/m_i)E$, where m_e and m_i are the masses of an electron and the negative ion, respectively, and E is the kinetic energy of the negative ions in the ion beam. E_c is the kinetic energy of the photoelectrons in the rest frame of the negative ion and is given by $E_c = E_\gamma - E_a$, where E_γ is the photon energy and E_a is the electron affinity of the atoms associated with the negative ion beam species. The value of the energy centroid of the Cu^- photoelectron peak was determined using a weighted least-squares fit to a Gaussian function with a linear background, and the fitted value of the energy centroid was assigned the value of E_ℓ for photoelectrons from Cu^- for the experimental conditions.

The energy scale for the La^- photoelectron spectra in the laboratory frame was then referenced to the Cu^- photoelectron spectra. The La^- photoelectron spectra were transformed into the rest frame of the ion using the following formula:

$$E_c = E_\ell + \epsilon - 2\sqrt{\epsilon E_\ell}\cos\theta_\ell \tag{2}$$

where E_c is the energy of the photoelectrons resulting from La^- photodetachment in the ion rest frame. This technique was tested for this experimental apparatus by measuring the electron affinity of Cu using O^- [3] as the reference photoelectron spectrum, which yielded an electron affinity of copper (1.241 ± 0.011 eV) in excellent agreement with the accepted value (1.235 ± 0.005 eV) [14].

The feature near 0 eV in the electron kinetic energy spectrum shown in figure 1 is consistent with electrons that have the same speed as the La^- ions in the beam. These electrons were produced by aperture scattering of the ion beam and collisional detachment with background gas, and were present in the electron kinetic energy spectra when the photon beam did not interact with the ions. The energy value of the centre of the peak corresponds to the energy ϵ which is 0.0395 eV for a 10 keV beam of $^{139}La^-$. The peak is well defined in the laboratory frame spectra, but due to the instrumental width of the peak, the lower energy side of the peak does not transform into the ion reference frame. Also, the contribution to the background from collisional detachment and aperture scattering in the La^- photoelectron energy spectra was negligible for energies greater than 0.15 eV. This indicates that the electron signal measured with energies greater than 0.15 eV resulted from the photodetachment of La^-.

After the La^- photodetachment spectra were transformed into the ion rest frame using the Cu^- photoelectron spectra as a reference, the spectra were interpreted using spectroscopic data for the lanthanum atom [15]. The energy separation of the photoelectron peaks corresponds to the initial and final states for the process $h\nu + La^- \rightarrow La + e^-$, where La and La^- can be in excited states. Conservation of energy requires that the kinetic energy of the photoelectron, E_c is given by

$$E_c = E_\gamma - E_e^a - E_a + E_e^n, \tag{3}$$

where E_γ is the photon energy, E_e^a is the excitation energy of the final state of the atom, E_a is the electron affinity, and E_e^n is the excitation energy of the initial negative ion state.

The photoelectron peaks labelled 1 and 2 in figure 1 were fitted to a Gaussian function using a weighted least-squares technique to determine the energy centroid of each peak. The measured energy separation between peaks 1 and 2 (0.139 ± 0.011 eV) was equal to the energy difference between the $^2D_{3/2}$ and $^2D_{5/2}$ fine structure levels in the ground state of lanthanum (0.130 eV) [15]. The energy level diagram labelled A in figure 1 represents the final even parity energy levels of the lanthanum atom following photodetachment using photoelectron peaks 1 and 2 as the signature of the photodetachment channels leaving the lanthanum atom in the $^2D_{3/2,5/2}$ levels. Clearly, as can be seen in figure 1, the photoelectron peaks labelled 4, 5 and 6 cannot be explained by the energy level diagram labelled A.

An investigation of the photoelectron angular distribution of peak 3, and its width, indicated that peak 3 was composed of photoelectrons from more than one photodetachment channel. Therefore, peak 3 was fit to Gaussian functions at the energy positions of the ^4F (near 1.7 eV) levels in diagram A and two Gaussian functions with the energy separation of the $^2D_{3/2,5/2}$ levels in lanthanum. The energy level diagram of even states, with the $^2D_{3/2,5/2}$ levels identified in this manner, is labelled B in figure 1. The energy level diagram labelled B has photodetachment channels that correspond to photoelectron peaks 4, 5 and 6. The energy level diagram labelled C contains the odd parity states in lanthanum with the same energy shift as the even parity energy level diagram labelled A. The energy level diagram labelled D contains the odd parity states in lanthanum with the same energy shift as the even parity energy level diagram labelled B. The photon-dependent increase in photoelectron signal below $\sim$1.7 eV in the electron energy spectrum is a result of the large number of final state fine structure levels in the lanthanum atom that open below this energy. Therefore, the analysis of the photoelectron spectra shows that La^- has at least two bound states. The ground state of La^- produced the photoelectrons corresponding to photodetachment channels in the energy level diagrams labelled B and D. The bound excited state of La^- produced the photoelectrons corresponding to the energy level diagrams labelled A and C.

Twenty-one La^- photoelectron spectra were recorded using the 514.5 nm photon wavelength of the laser, along with Cu^- photoelectron spectra using either 514.5 nm or 488.0 nm photon wavelengths, which proceeded or followed each La^- photoelectron spectrum. The electron affinity of La($^2D_{3/2}$) was determined to be 0.47 ± 0.02 eV. The data also show that La^- has at least one bound excited state with a binding energy of 0.17 ± 0.02 eV relative to the $^2D_{3/2}$ ground state of the lanthanum atom. The bound excited state of La^- must be long lived since the flight time to the interaction region for an ion in the beam was approximately 54 μs. The reported uncertainty in the measurements represents one standard deviation of the mean. The uncertainties include statistical and systematic contributions due to the photoelectron count rates for La^- and fitting the data to Gaussian functions for the La^- and Cu^- photoelectron energy spectra, the uncertainty in the electron affinity of Cu, and the determination of the ion beam energy. The reported uncertainty was dominated by the variance in the energy centroids resulting from fitting the data to Gaussian functions for peaks in the La^- photoelectron spectra. This variance was due to the relatively low photoelectron count rates experienced in the La^- photoelectron spectra.

In summary, the electron affinity of lanthanum has been measured using laser photoelectron energy spectroscopy. The electron affinity of La($^2D_{3/2}$) was determined to be 0.47 ± 0.02 eV. The photoelectron spectra of La^- indicated at least one bound excited state of La^- exists with a binding energy of 0.17 ± 0.02 eV relative to the $^2D_{3/2}$ ground state of lanthanum. The present measurements indicate that the electron affinity of lanthanum is greater than that predicted by Vosko *et al* [4], who predicted the electron affinity of La to be between 0.27 and 0.41 eV. Three bound negative ion excited states were also predicted by Vosko *et al* [4] with binding energies between 0.1 and 0.3 eV relative to the ground state of

lanthanum. The present experiment does support the existence of at least one excited, bound, long-lived state in La^-. However, the present experimental resolution was insufficient to determine the existence of more than one of the predicted excited, bound states. Further experiments are underway to resolve this issue, and to investigate the electron affinities of other rare-earth atoms.

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