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LETTER TO THE EDITOR

Laser photodetachment electron spectrometry of Ga^-

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Abstract. We report the first experimental determination of the electron affinity of gallium. The experiment was performed using the laser photodetachment electron spectrometry technique. Photoelectron kinetic energy spectra from Cu^- and O^- were used to calibrate the energy scale for the Ga^- photoelectron energy spectra. The electron affinity was determined to be 0.43 ± 0.03 eV. This measurement is compared to several recent calculations of the electron affinity of gallium.

Numerous studies of negative-ion structure have been reported, and a cursory investigation of review articles [1] and compilations [2] shows that for most elements, electron affinities have been measured or calculated. In fact, for a majority of the elements, theoretical predictions of electron affinities can be compared with measurements. The group-13 elements represent one of the few columns in the periodic table where experimental measurements are not available for comparison with theoretical predictions for all members of the group.

Boron and aluminium are the only members of the group-13 elements for which electron affinities have been measured. The electron affinity of boron (0.277 ± 0.010 eV) [3] was measured using the laser photodetachment spectrometry technique. Recently, a very precise measurement of the electron affinity of aluminium (0.432 83(5) eV) [4] using tunable infrared laser spectroscopy, was reported. The recommended value for the electron affinity of gallium (0.30 ± 0.15 eV) [1] was determined using the results of a semiempirical extrapolation [5] and a photodetachment threshold experiment [6] that was unable to reach the energy threshold for the photodetachment of Ga^-.

Three theoretical investigations of the electron affinities of the group-13 elements, using different techniques, have reported calculations of the electron affinity of gallium. Arnau *et al* used a form of the multireference single- and double-configuration-interaction method (CIPSI) to predict the electron affinity of gallium to be 0.29 eV [7]. Eliav *et al* predicted the electron affinity of gallium to be 0.301 eV using a relativistic coupled-cluster method [8]. In addition, Wijesundera predicted the electron affinity of gallium to be 0.305 eV using the multiconfiguration Dirac–Fock method [9].

In this letter, we report the first experimental determination of the electron affinity of gallium. The measurements were made using the laser photodetachment spectrometry technique. A detailed description of the experimental apparatus has been given previously [10, 11], but a brief description follows. Negative ions used in the experiment were produced

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with a caesium-sputter negative-ion source. In this ion source, energetic Cs^+ ions (2–6 keV) were accelerated and focused onto a target, where negative ions were sputtered from the target material. The target for this experiment was a pressed pellet of gallium–vanadium powder with a 10% stoichiometric mixture of copper powder. The negative ions were extracted from the ion source by applying a bias voltage of either -10 or -20 kV to the ion source, which accelerated the negative ions toward ground potential. The extracted negative-ion beam was focused onto the entrance slit of a 90°, double-focusing, bending magnet that momentum selected the negative-ion beam for the experiment. The mass resolution of the bending magnet was approximately 1:200 ($\Delta m/m$). The pressure in the beam line was of the order of 1×10^{-6} Pa and the total flight length of the beam line was 6.4 m. The flight time for reaching the experimental chamber for a Ga^- ion in the beam was 27 or 38 μs, depending on the ion source acceleration voltage used for these measurements. Typical ion beam currents were 100 pA for Ga^-, 100 nA for Cu^- and 10 nA for O^- when measured in the 6 mm diameter Faraday cup in the experimental chamber.

After entering the experimental chamber, the negative-ion beam was crossed at 90° with a linearly polarized photon beam produced by a 25 W argon ion laser. Photon wavelengths of 514.5 nm (2.41 eV) and 488.0 nm (2.54 eV) were used in these experiments. The photon beam traversed a Glan-laser polarizer and a double-Fresnel rhomb ($\lambda/2$ retarder) before crossing the negative-ion beam. The polarizer set the linear polarization of the laser light with an extinction ratio of at least 10^5 to 1 and the double-Fresnel rhomb was used to rotate the linear polarization vector of the light. The laser beam was monitored with a thermopile power meter following the crossing of the ion and laser beams. Typical laser powers were 8.5 W at 514.5 nm and 6.0 W at 488.0 nm.

Photodetached electrons were energy analysed with an electrostatic 160° spherical-sector spectrometer and detected with a channel-electron multiplier (CEM). The entrance aperture of the spectrometer was located at 45° relative to the ion beam velocity vector and located in the plane perpendicular to the plane containing the ion and photon beams. The ion and laser beams crossed approximately 2.5 cm from the entrance aperture to the spectrometer. The spectrometer and the photon–negative-ion interaction region were enclosed in a μ-metal box, and a set of mutually perpendicular coils enclosed the experimental chamber to reduce the intensity of the Earth's and stray magnetic fields in the experimental chamber. Typical pressure in the experimental chamber was 2×10^{-7} Pa.

The electron energy analyser was operated at a constant pass energy. A voltage was applied to the entrance aperture of the analyser to accelerate electrons to the pass energy. The electron acceleration voltage was decreased in steps by a computer-based digital-to-analogue converter, and 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. Electrons with energies within the band of pass energies for transmission through the analyser were detected with the CEM. The output signal from the CEM was amplified, and a discriminator was used to eliminate electronic noise. The resulting output pulses from the discriminator were recorded by a computer-based counter. 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 voltage-to-frequency converters and recorded for normalization of the electron signal.

A typical photoelectron kinetic energy spectrum for Ga^- is shown in figure 1. The kinetic energy of the Ga^- ions in the beam was 10 keV for this spectrum, and the ion current measured in the experimental chamber was approximately 100 pA. The photon wavelength was 488.0 nm and the power of the photon beam was 7 W. The double-Fresnel rhomb was set so that the polarization vector of the laser light pointed toward the entrance

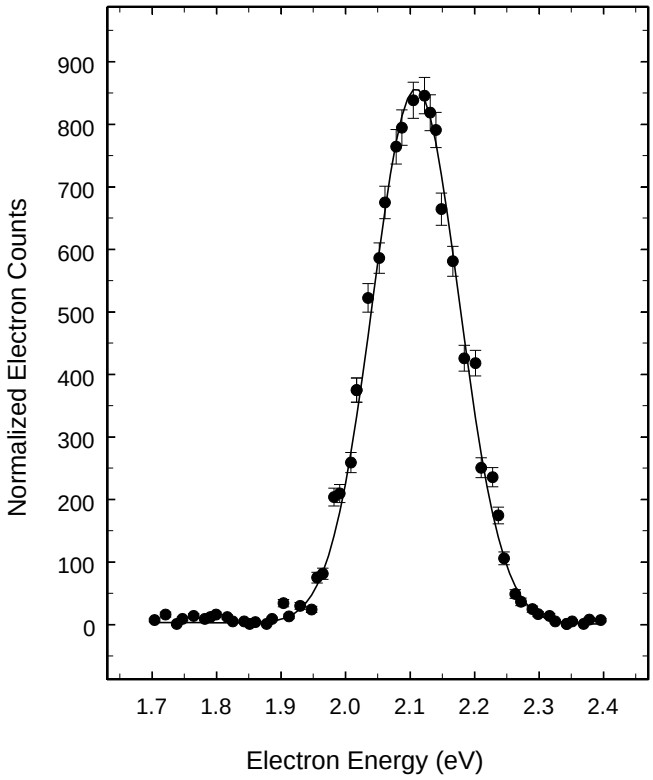

Figure 1. Photoelectron kinetic energy spectrum for Ga^-. The ion beam energy was 10 keV and the laser wavelength was 488.0 nm. The error bars on the data points represent counting statistics at one standard deviation. The full curve represents a Gaussian fit to the data with a linear background. The energy scale was determined by comparison to a reference photodetachment spectrum (see text for details).

aperture of the electron spectrometer. The data accumulation time for each data point was 60 s and the spectrum took ~ 50 min to complete. The data points are plotted with error bars that represent the uncertainty related to counting statistics at one standard deviation. The full curve represents a weighted least-squares fit to a Gaussian function with a linear background. Typical drifts during the accumulation of data for a photoelectron kinetic energy spectrum were less than 1% for the laser power, and less than 20% for the ion beam current. Only one peak was observed in the photoelectron kinetic energy spectrum for Ga^-. The excitation energy for the lowest-lying excited state in gallium ($(4s^24p)^2P^o \rightarrow (4s^25s)^2S$) is approximately 3.074 eV [12]. This excitation energy is greater than the energies of the photons used for these measurements, making photodetachment into the excited states of gallium energetically impossible. Furthermore, the fine-structure splitting in the ground state of gallium ($^2P^o_{1/2\rightarrow 3/2}$) is 0.102 eV [12] and the estimated fine-structure splitting in the gallium anion ($^3P_{0\rightarrow 2}$) is 0.072 eV [1], which could not be resolved by the apparatus.

The energy scale for the Ga^- photoelectron kinetic energy spectra was determined using the photoelectron energy spectra of Cu^- or O^-. Photoelectron kinetic energy spectra of Cu^- and/or O^- were taken using either 488.0 or 514.5 nm laser light before and after each Ga^- photoelectron energy spectrum was collected. The electron affinities of

Cu (1.235 ± 0.005 eV) [13] and O ($1.461\,1103 \pm 0.000\,0007$) [14] have been determined by laser photodetachment spectrometry and laser photodetachment threshold techniques, respectively. Typical signal-to-noise ratios for photoelectron kinetic energy spectra of Cu^- were 2000:1 and 20:1 for O^-. The technique for determining the energy scale for the Ga^- photoelectron energy scale was the same for both O^- and Cu^- reference ions and is described as follows. The kinetic energy of the photoelectrons from the reference ion, as measured in the laboratory frame, was determined using the 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 is the angle between the velocity vector of an ion in the beam and the collection direction for the photoelectrons (45° for this experiment). The term ϵ is the kinetic energy of an electron with the same velocity as the ions in the beam, i.e. $\epsilon = (m_e/m_i)E$, where m_e and m_i are the masses of an electron and an ion in the beam, respectively, and E is the kinetic energy of an ion in the beam. E_c is the kinetic energy of the photodetached electrons in the rest frame of the 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 associated with the reference atom. The laboratory frame energy, E_ℓ, for photoelectrons from the reference ions was determined using equation (1). The value of the energy centroid of the reference ion photoelectron peak was determined using a weighted least-squares fit to a Gaussian function with a linear background. The fitted value of the energy centroid was then assigned the value of E_ℓ for photoelectrons from the reference ion for the experimental conditions.

The energy scale for the Ga^- photoelectron spectra in the laboratory frame was then referenced to either O^- or Cu^- photoelectron spectra. The Ga^- photoelectron spectra were then transformed into the rest frame of the gallium anion using the 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 photodetachment of Ga^- in the ion rest frame. The electron affinity of gallium was then determined using the equation, $E_c = E_\gamma - E_a$. The technique was tested by measuring the electron affinity of Cu using the photoelectron spectrum of O^- as a reference. The electron affinity of Cu was measured to be 1.240 ± 0.011 eV in this manner, which is in excellent agreement with the accepted value [13].

Twenty-two photoelectron spectra of Ga^- were collected and reference photoelectron spectra of O^- and/or Cu^- were collected before and after each Ga^- spectrum. This technique yielded the electron affinity of gallium to be 0.43 ± 0.03 eV. The total uncertainty in the electron affinity is reported at one standard deviation. Included in the total uncertainty were the uncertainties in the electron affinities of the reference ions, the uncertainty in determining the ion beam energy and the uncertainty in determining the energy centroid of the photoelectron peaks in the spectra. The total uncertainty was dominated by the uncertainty in determining the energy centroid of the Ga^- photoelectron peak in each spectrum, which was directly related to the signal-to-noise ratio in the spectrum.

The measured electron affinity of Ga($^2P^o$), 0.43 ± 0.03 eV, is in reasonable agreement with the previously reported calculations [7–9] and in good agreement with the recommended value, 0.3 ± 0.15 eV, of Hotop and Lineberger [1]. Planned improvements in the experimental apparatus should increase the signal-to-noise ratio and lead to fine-structure resolution in photoelectron spectra. The fine-structure-resolved electron affinity of gallium could then be determined. Future investigations of In^- and Th^- are planned so that a

complete set of experimentally determined electron affinities of the group-13 elements will be available for comparison with theoretical predictions.

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