

Electron affinity of selenium measured by photodetachment microscopy

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The electron affinity ${}^eA(\text{Se})$ of selenium is measured by photodetachment microscopy on a cesium-sputtering-produced Se^- ion beam using a single-mode CW dye laser. The measured value of the electron affinity is $16\,297.276(9)\text{ cm}^{-1}$, or $2.020\,604\,6(11)\text{ eV}$, which improves the accuracy of this atomic quantity by a factor of 60.

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Introduction. Selenium, which is essentially known in the world of quantum physics as an ingredient of the CdSe quantum dots [1,2] and PbSe [3] or TlSe [4] IR detectors, also forms an anion Se^- of some interest for atomic photodetachment studies. The electron affinity ${}^eA(\text{Se})$ of selenium is of the order of 2.0 eV, which is quite similar to the electron affinity of tellurium and just a little less than that of sulfur (the elements just below and above Se in the Periodic Table [5]). Therefore, threshold photodetachment with a dye laser can be performed relatively easily using one of the very effective rhodamine dyes.

In 1973, Hotop *et al.* [6] performed laser threshold spectroscopy on a Se^- ion beam to measure the electron affinity of selenium and found ${}^eA(\text{Se}) = 16\,297(2)\text{ cm}^{-1}$. Edge *et al.* [7,8] later used a tunable laser working with rhodamine 640 to deplete the Se^- ion cloud contained in a Penning trap, and they claimed a ten times better accuracy, with ${}^eA(\text{Se}) = 16\,297.8(2)\text{ cm}^{-1}$. A subsequent laser photodetachment study [9] provided a similar result, ${}^eA(\text{Se}) = 16\,297.7(4)\text{ cm}^{-1}$. We report on a significantly more accurate measurement, which brings the accuracy of ${}^eA(\text{Se})$ to an order of magnitude of $1\ \mu\text{eV}$, namely 0.009 cm^{-1} .

Hotop *et al.* [6] also investigated the fine structure of Se^- , which is an inverted ${}^2P_{3/2}$ doublet, using five different Xe-lamp pumped laser dyes. Thøgersen *et al.* [9] used the Raman scheme they had first developed on Te^- [10] to measure the energy of the upper (${}^2P_{1/2}$) level, the radiative lifetime of which was measured in an ion storage ring [11]. The limited amount of time we had available to work on selenium before major changes had to be done on the experimental setup did not allow us to change dyes nor to implement multiphoton excitation schemes, so the present work has dealt only with the ground-state-to-ground-state ${}^2P_{3/2} \rightarrow {}^3P_2$ photodetachment channel, leading to a direct measurement of the electron affinity.

Experimental setup. The usual scheme of photodetachment microscopy [12] is applied to a beam of Se^- ions. The ions are extracted from a SNICS II [13] cesium sputtering ion source with an initial kinetic energy of 9 keV. The beam, as it exits the source, is immediately decelerated to 1.2 keV and then decelerated again down to 300 eV just before entering the photodetachment chamber. This results in a relatively low ion

current of typically 60 pA within 0.5 mm diameter in the laser-ion interaction region, which has at least the advantage of making space-charge effects negligible. Photodetachment microscopy could actually be very sensitive to space charge, as it relies on the observation of the electron interferogram naturally produced when photodetachment occurs in the presence of an electric field F [12]. This interferogram has shown to be very robust, at least as concerns its internal phase, with respect to macroscopic perturbations such as the presence of an external magnetic field [14]. It is thus a very reliable tool to measure the ejection energy of the electron with a μeV accuracy. Accurate electron affinity measurements can, in principle, be performed at a single wavelength of the excitation photon, in contradistinction to the laser photodetachment threshold technique, which requires a quantitative monitoring of the photodetachment yield as the laser wavelength is scanned across the threshold [5,15]. Excitation is provided by a Spectra 380A CW ring dye laser. Selenium has spectral terms quite similar to those of sulfur [16], but with (roughly) four times larger fine-structure intervals. It is thus no longer possible to explore all six fine-structure thresholds with the same laser dye. Rhodamine 640 was used in the present study to explore the ground-state to ground-state ${}^2P_{3/2} \rightarrow {}^3P_2$ photodetachment threshold. The wave number of the laser is measured by an Ångström WS-U lambdameter, with an accuracy better than $2 \times 10^{-3}\text{ cm}^{-1}$.

Data analysis. Figure 1 gives an example of a pair of interferograms obtained from a double pass of the laser on the ion beam. The relatively low background level is all the more striking because these interferograms are necessarily superimposed on the larger-energy photoelectron background produced by photodetachment of the ${}^2P_{1/2}$ excited Se^- ions either to the ground 3P_2 or to the first fine-structure excited 3P_1 level, 1989.5 cm^{-1} higher in energy [17]. Within a 364.5 V/m electric field, however, these 2279 and 289 cm^{-1} photoelectrons are expected to spread in the detector plane on disks of 42 and 15 mm in radius, respectively, thus leading to a reduced electron current density. Quantitatively, since the Wigner law [18] predicts s -wave detachment cross sections to vary like the square root of the photoelectron energy ϵ , and because the photoelectron current spreads on a surface proportional to ϵ , one expects the more energetic contributions to the photoelectron current density to scale down as $1/\sqrt{\epsilon}$. In addition, every contribution must be weighted according to a specific branching ratio and to the relative population of the initial level. As for the latter factor, a fine structure

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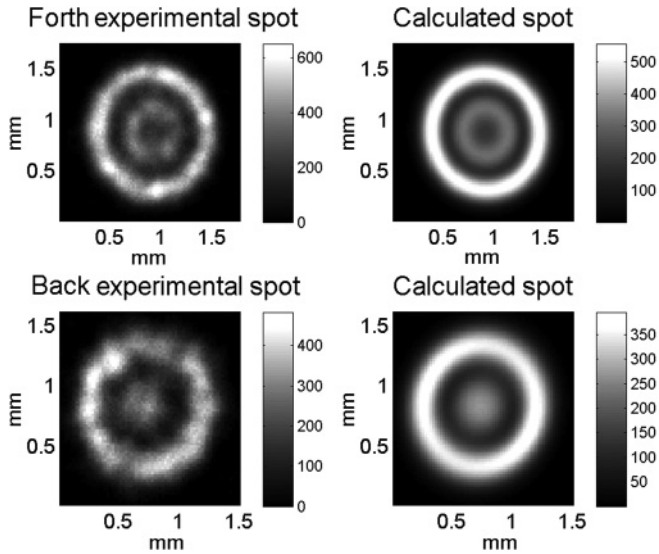


FIG. 1. A pair of spots produced at a laser wave number of $16\,297.757(2)\text{ cm}^{-1}$. Photodetachment takes place in an electric field $F = 364.5\text{ V m}^{-1}$. The fitting procedure yields the kinetic energy ϵ of the detached electron, $0.525(1)$ and $0.447(1)\text{ cm}^{-1}$ for the upper and lower spot, respectively. Note the slight difference in the actual size of the spots, due to the fact that their diameter scales as the initial velocity of the ejected electron, i.e., $\sqrt{\epsilon}$.

as high as $2278.2(2)\text{ cm}^{-1}$ [9] very likely makes the thermal population of the $^2P_{1/2}$ level much smaller than in S^- . All these factors together explain the nearly total absence of the higher-energy background in the Se^- photodetachment signal.

Another striking feature of these Se^- interferograms is the very good contrast of the interference fringes, despite the fact that our Wien velocity filter has a resolution too low to select one single isotope of this relatively heavy element. Hyperfine structure is not expected to blur the interferograms so much, since the even isotopes, 74, 76, 78, 80, and 82, constitute 92% of the sample, and have no nuclear spin. The only naturally present odd isotope, 77, has a spin 1/2 with a not especially large g factor [19,20]. This does not prevent ^{77}Se , however, from being of some use in nuclear magnetic resonance studies [21].

The isotopic dependence of the electron affinity is thus expected to be the major source of energy broadening. For sulfur, this dependence was recently found to be very small [22]. In the same column, however, oxygen exhibits an anomalous electron-affinity isotope shift of $-0.074(18)\text{ cm}^{-1}$, between isotopes 16 and 18 [23], which is not quite negligible as far as the contrast of a superposition of interferograms is concerned. Yet the relative mass variation, from ^{78}Se to ^{80}Se (the most abundant Se isotopes), is much smaller than from ^{16}O to ^{18}O , and the normal mass shift scales as this relative variation divided by the mass number itself. This may explain why selenium photodetachment interferograms appear so robust with respect to isotopic mixing, and fully justifies that a measurement of the electron affinity of selenium remains meaningful, even with an accuracy better than $1\text{ }\mu\text{eV}$, without isotopic selection.

The laser beam is not set exactly at right angles with the ion beam, but rather at a 93° angle, in order not to shine on the electron detector. This setting produces a slightly positive Doppler shift. The laser beam is then reflected by a concave mirror that refocuses it back on the ion beam, either downstream or upstream of the first interaction zone. A second source of photoelectrons is produced in this way, which produces in turn a second photoelectron spot, a few millimeters away from the first one, always with a negative Doppler shift. Combining the photoelectron energies ϵ and ϵ' of the two interferograms produced in this forth-and-back illumination scheme makes a Doppler-free measurement possible, provided one also takes into account the smaller, though not quite negligible, corrections due to (i) the necessary deviation of the incidence angle of the laser from 90° on the reflecting mirror, and (ii) the deviation of the ion beam itself by the electric field, between the two laser-ion interaction zones [23].

In principle, one pair of electron spots, recorded in a single photodetachment experiment, is enough to measure the electron affinity eA . The difference between the Doppler-corrected photon energy and the mean electron kinetic energy $\bar{\epsilon} = \frac{1}{2}(\epsilon + \epsilon')$ provides a (first-order) measurement of how much energy was required to reach the detachment threshold. However, because the quantitative analysis of every interferogram is only a measure of the $\frac{\epsilon^{3/2}}{F}$ ratio, any discrepancy between the estimated and actual values of the electric field F in the photodetachment region produces a systematic shift in the photoelectron energy measurement, with the relative error of the latter just 2/3 of the relative error of the former. Since the relative error appears to be constant, extrapolating the measured electron affinity down to zero initial kinetic energy, i.e., actually to the detachment threshold, may circumvent the electric-field uncertainty [24,25]. Two series of measured electron affinities recorded at two different values of the applied electric field are represented in Fig. 2.

A remarkable feature of these series is that they appear distributed around the same affine function with a -1.6% slope, which corresponds to a 2.5% error made when estimating the electric field present in the photodetachment

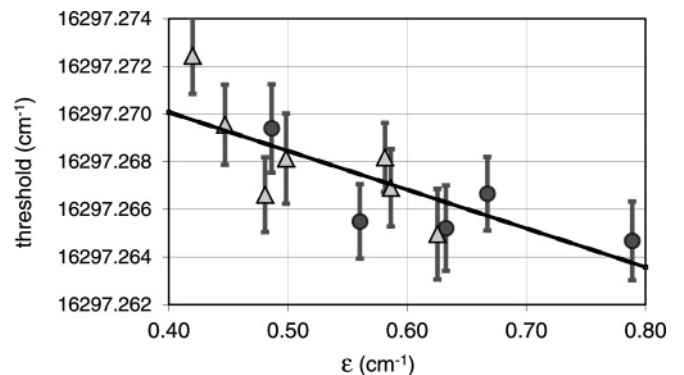


FIG. 2. Linear regression of the measured detachment threshold as a function of the mean photoelectron energy $\bar{\epsilon}$. Triangles (circles) correspond to measurements performed in a 254.1 (364.5) V m^{-1} electric field. The pair of spots shown in Fig. 1 produces the circle at abscissa $\bar{\epsilon} = 0.486\text{ cm}^{-1}$.

region. A similar observation has been made in all previous photodetachment microscopy experiments for the past seven years, with a bias of 2.4% in the case of I^- [26] and even more than 3% for some S^- photodetachment series [16]. In the latter case, observation of a larger bias coincided with the replacement of the electrode spacers, which confirms that a relative error on the electric field is a very clear possible cause of variation of the apparent photodetachment threshold as a function of the photoelectron energy.

In a more recent experiment on phosphorus, however, the apparent electric-field error was only -0.3% [27]. Such a change of bias, from one ion to the other, may result from a change of the laser and ion beam setting. In a given electrostatic configuration, all ions are supposed to follow the same trajectory, irrespective of their mass, but the faster the ion, the larger the transverse drift of the photoelectron between the detachment point and the electron detector. Because the interaction zone must be placed so as to keep the terminal point of the electron trajectory on the detector, the actual value of the electric field at the detachment point may vary from one ion to the other. Simion[®] calculations, however, do not predict that the electric field will vary locally more than by a few 10^{-3} . In addition, for the very element that suggested the largest error (sulfur), a more recent study exhibited nothing but a very small bias (-0.3%) [22]. The dependence of the apparent threshold as a function of the electron energy, as measured by photodetachment microscopy, thus remains partially a mystery. Extrapolating the threshold down to zero kinetic energy, however, should not be made unreliable as a result of this unknown.

Results. The experimental electron affinity of selenium, obtained as the intercept of the linear regression just described, is $16\,297.276(9)\text{cm}^{-1}$. The statistical part of the indicated error bars is twice the standard deviation. The error bars also include a systematic $\pm 2 \times 10^{-3}\text{cm}^{-1}$ uncertainty on the laser wave-number measurements. The result corresponds to an increase of the electron-affinity accuracy by a factor of 25 at least. Because the 1985 measurement appears to have been off the real value by more than 2.5 times its error bar, telling of a 60-fold increase would seem more appropriate.

Neither publication of the 1985 measurement [7,8] actually tells whether the attached 0.2cm^{-1} half-error bar must be taken as an expanded uncertainty or as a standard deviation. In the latter case, the 1985 measurement at $16\,297.8(2)\text{cm}^{-1}$ would not appear to disagree that much with our $16\,297.276(9)\text{cm}^{-1}$ result. Regardless, this would not change our conclusion of the previous paragraph on the accuracy improvement factor. Analyzing the reasons for a possible overestimation of detachment thresholds in the Penning trap-depletion method is of course beyond the scope of the present paper. On the other hand, our result appears to be quite compatible with the 1995 measurement [9] at $16\,297.7(4)\text{cm}^{-1}$ and sits in the middle of the uncertainty interval of the 1973 value at $16\,297(2)\text{cm}^{-1}$.

In electronvolts, taking the 2.5×10^{-8} relative uncertainty of the cm^{-1} -to-eV conversion factor into account [28], the measured value of the electron affinity of selenium is $2.020\,604\,6(11)\text{eV}$.

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