AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **145**, 084303 (2016); doi: 10.1063/1.4961654
View online: http://dx.doi.org/10.1063/1.4961654
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/145/8?ver=pdfcov
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Accurate electron affinity of Pb and isotope shifts of binding energies of Pb^-

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(Received 22 June 2016; accepted 13 August 2016; published online 26 August 2016)

Lead (Pb) was the last element of the group IVA whose electron affinity had a low accuracy around 10 meV before the present work. This was due to the generic threshold photodetachment measurement that cannot extent well below 0.5 eV due to the light source limitation. In the present work, the electron affinity of Pb was determined to be 2877.33(13) cm^{-1} or 0.356 743(16) eV for the isotope $m = 208$. The accuracy was improved by a factor of 500 with respect to the previous laser photodetachment electron spectroscopy. Moreover, remarkable isotope shifts of the binding energy of Pb^- $6p^3\ ^4S_{3/2}$– Pb $6p^2\ ^3P_2$ were observed for $m = 206$, 207, and 208. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4961654]

I. INTRODUCTION

Electron affinity (EA) is a fundamental parameter of atoms and molecular. The EA of lead (Pb) has received substantial experimental and theoretical investigations.[1–10] The first experimental determination of EA(Pb) was reported by Zandberg *et al.* via the surface ionization method.[1] The obtained value was 1.1 ± 0.2 eV. Politzer predicted the value of EA(Pb) as 1.79 eV,[3] while Zollweg gave the value of EA(Pb) as 1.03 eV.[4] In 1975, Chen and Wentworth predicted the electron affinity of Pb to be 1.05 ± 0.09 eV.[5] However, Feigerle *et al.* determined EA(Pb) as 0.365 ± 0.008 eV by the laser photodetachment spectroscopy in 1981.[6] Brunot *et al.* confirmed this value by the mass spectrometry in 1983.[7] Later, Hotop and Lineberger updated the value as 0.364 ± 0.008 eV.[8] This was the latest experimental determination of EA(Pb) before the present work. Recently, Tatewaki *et al.* predicted the EA of Pb to be 0.403 eV using the four-component relativistic multi-configurational quasi-degenerate perturbation method.[9] Melton *et al.* calculated EA(Pb) to be 0.417 ± 0.007 eV using the quantum Monte Carlo method.[10] The EAs of the lighter congeners (C, Si, Ge, and Sn) of Pb in the periodic table were 1.2629 eV, 1.385 eV, 1.2 eV, and 1.2 eV, respectively.[8] Later, these values were largely improved by Scheer *et al.* via the laser photodetachment threshold (LPT) method in 1998.[11] Recently, Blondel and co-workers have improved the accuracy of these values to the μeV level via the laser photodetachment microscopy (LPM).[12–15] The latest values are EA(C) = 1.262 122 6(11) eV,[12] EA(Si) = 1.389 521 0(7) eV,[13] EA(Ge) = 1.232 676 4 (12) eV, and EA(Sn) = 1.112 070(2) eV.[15] It is urgent to improve the EA(Pb) = 0.364(8) eV, which was reported 30 years ago. The sharp decrease of EA value at Pb is due to the large spin-orbit splitting in the neutral Pb atom.[16] The spin–orbit interaction induces splitting in the $3P$ state, and the resulting lowest state ($^3P_0$) descends toward the Pb^- $^4S_{3/2}$ state. In contrast with the steadily improved accuracy of the EA measurements of C, Si, Ge, Sn, there is no improvement for EA(Pb) during the past 30 years. This is due to the generic threshold photodetachment measurement that cannot extent well below 0.5 eV because of the light source limitation.

The present work aims at improving the accuracy of EA(Pb) to the sub-cm^{-1} accuracy. Our recent works showed that the slow-electron velocity-map imaging (SEVI) method can measure the low EA values by using the visible laser, without needing the infra-red laser.[17–19] The SEVI technique was previously developed by Neumark and co-workers.[20,21] SEVI has a supper high energy resolution for slow electrons.[17–27] This feature means that SEVI can resolve the different photodetachment channels. Since the energy levels of neutral atoms are well known with a high accuracy, this gives a freedom to choose the photodetachment final neutral state for measuring electron affinities. This flexibility is crucial for the current Pb study and other elements with a low EA value, such as Ca with a very low EA value of 24.55(10) meV.[28]

II. METHODS

The experiment was conducted using a slow-electron velocity-map imaging apparatus equipped with a laser ablation ion source. The detailed description of the spectrometer has been reported previously.[17,19] Briefly, the Pb^- anion beam was produced by focusing the second-harmonic output of a Nd:YAG laser (532 nm, ~10 mJ/pulse) onto a continually rotating and translating Pb metal disk. After a skimmer, the anions were extracted perpendicularly into a time-of-flight (TOF) mass spectrometer.[29] The anionic species were accelerated to 900 eV by a high voltage pulse and then were guided by a set of deflectors and focused by a set of einzel lens into a 1.4-m-long TOF tube. To clearly resolve the different isotopes $m = 206$, 207, and 208 of Pb, a smaller skimmer with a diameter of 5 mm was used instead of the previously

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used one (8 mm in diameter). After this modification, the mass resolution ($M/\Delta M$) became 500 for $M \sim 200$. The Pb^- anions were selected by a Wiley-McLaren type TOF mass spectrometer. Then, the selected ions were perpendicularly crossed by the detachment laser beam in the interaction zone. The photodetachment laser was from a Spectra-Physics dye laser system (400–920 nm, linewidth 0.06 cm^{-1} at 625 nm) pumped by a Quanta-Ray Pro 290 Nd:YAG laser (20 Hz, 1000 mJ/pulse at 1064 nm). The photon energy ($h\nu$) was monitored by a HighFinesse WS6-600 wavelength meter with an accuracy of 0.02 cm^{-1}. The detached photoelectrons were projected onto a phosphor screen intensified by micro-channel plates and recorded by a CCD camera. Each photoelectron imaging was an accumulated result of 50 000 laser shots. The imaging voltage was −650 V for recording the full spectrum and was −150 V for the EA measurement. The photoelectron spectrum was reconstructed from the accumulated image using the maximum entropy velocity Legendre reconstruction (MEVELER) method.[30]

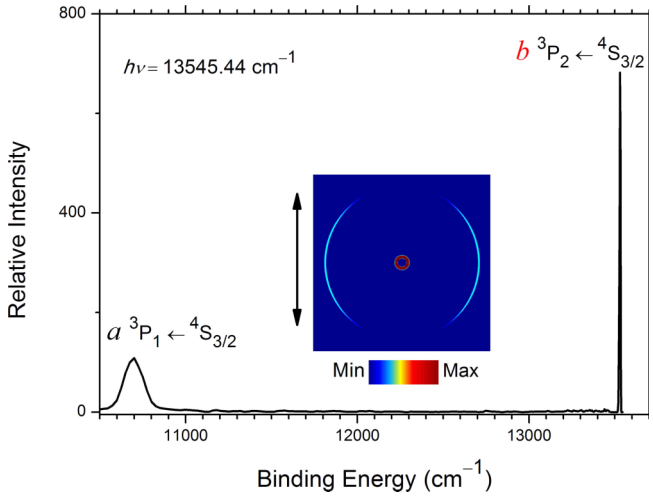

FIG. 2. Photoelectron image and spectrum of Pb^- ions obtained with 13 545.44 cm^{-1} photons. The double arrow indicates the laser polarization. Peak b is related to the $Pb(^3P_2) \leftarrow Pb^-(^4S_{3/2})$ transition, which is used to measure the electron affinity of Pb in the present work.

III. RESULTS AND DISCUSSION

Figure 1 shows the energy levels of Pb^- and Pb related to the present measurement of EA(Pb). The transition Pb $6p^2\ ^3P_0 \leftarrow Pb^-\ 6p^3\ ^4S_{3/2}$ was not measured since it is far out of the tuning range of our dye laser system. As shown in Fig. 2, the energy spectrum of Pb^- measured at the photon energy $h\nu$ = 13 545.44 cm^{-1} has two peaks under the imaging voltage −650 V. The broad peak a is related to transition Pb $6p^2\ ^3P_1 \leftarrow Pb^-\ 6p^3\ ^4S_{3/2}$. The photoelectron imaging shows a perpendicular angular distribution (PAD),[31] which is the interference result of the s and d waves. The sharp peak b is related to transition Pb $6p^2\ ^3P_2 \leftarrow Pb^-\ 6p^3\ ^4S_{3/2}$. The angular distribution of peak b is almost isotropic since the d wave is suppressed near the photodetachment threshold. For one-photon detachment with linearly polarized light, the photoelectron angular distributions can be described by the asymmetry parameter β.[31] The value of β ranges from −1 to 2, which depends on the electronic state and the kinetic energy of the photoelectron. In Fig. 2, $\beta = -0.88$ for peak a, and $\beta = 0.18$ for peak b at photon energy $h\nu$ = 13 545.44 cm^{-1}. The uncertainty was estimated as 0.1 in the present experiment.

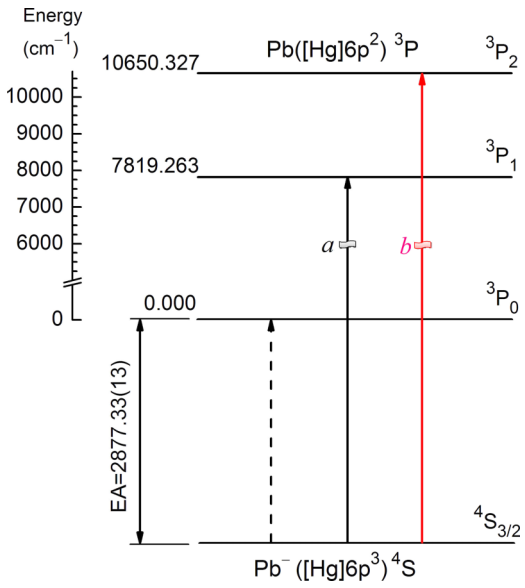

FIG. 1. Energy levels of Pb and Pb^- related to the present measurement. The ground state of Pb is $^3P_0$. The ground state of Pb^- is $^4S_{3/2}$. The labels of each transition are the indexes of the observed peaks in Fig. 2. The transition b is used for the present electron affinity measurement. The transition from Pb^- ($^4S_{3/2}$) to Pb ($^3P_0$) indicated by the dash line was not measured.

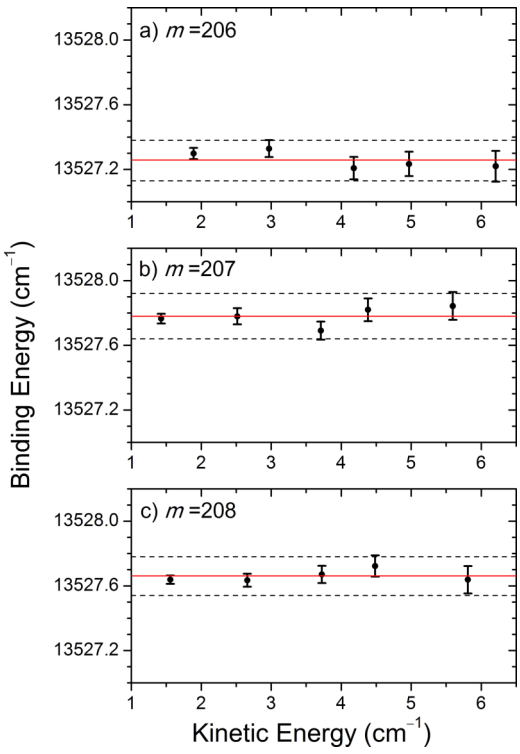

FIG. 3. Binding energy of transition $Pb(^3P_2) \leftarrow Pb^-(^4S_{3/2})$ measured as a function of the photoelectron kinetic energy for (a) isotope $m = 206$, (b) $m = 207$, and (c) $m = 208$. The dotted lines indicate the measured uncertainties.

The transition b Pb $6p^2\ ^3P_2 \leftarrow$ Pb$^-$ $6p^3\ ^4S_{3/2}$ was selected as the target channel for the present EA measurement.

The binding energy of peak b is determined to be 13 528 cm^{-1} from Fig. 2. To accurately determine EA(Pb), the imaging voltage −150 V was used. The energy scale of velocity-map imaging (VMI) system was carefully calibrated for the transition b. The photon energy was scanned from 13 529 to 13 534 cm^{-1} with a 1-cm^{-1} step. Hence, the photoelectron energy E_k for channel b roughly varied from 1 to 5 cm^{-1}. The centers of these observed peaks were obtained using a Gaussian function fitting procedure. Lead has three primary isotopes, m = 206 (abundance 24%), m = 207 (22%), and m = 208 (52%). The binding energy of transition b for three isotopes was measured individually. Fig. 3 shows the binding energy of the transition b plotted as a function of E_k for the different isotopes. The mean binding energy of the peak b for m = 208 is 13 527.66 cm^{-1} with an uncertainty ±0.13 cm^{-1}. By subtracting the energy 10 650.327 cm^{-1} of Pb($^3P_2$, m = 208),[32] the electron affinity of Pb(m = 208) is determined to be 2877.33(13) cm^{-1} or 0.356 743(16) eV, which is consistent with the previously reported value 0.364(8) eV,[8] but the accuracy is improved by a factor of 500. Similarly, the mean binding energy of peak b for m = 206 is 13 527.26(13) cm^{-1}, and 13 527.78(15) cm^{-1} for m = 207. However, to our best knowledge, the accurate energy levels of Pb($^3P_2$) for m = 206 and 207 are not known. Therefore, the EA values for m = 206 and 207 cannot be accurately determined. For the convenience of discussion, the isotope shift δ was defined as the difference of the binding energy between ^{m}Pb and ^{208}Pb, i.e., $\delta_m \equiv$ BE(^{m}Pb) − BE(^{208}Pb). The isotope shift for m = 206 is −0.40(18) cm^{-1}. This is a large isotope shift as compared with the isotope shift −0.073(6) cm^{-1} of the electron affinity for carbon 12 and carbon 13.[12] Similarly, the isotope shift for m = 207 is 0.12(20) cm^{-1}. The Pb atom is much heavier than C atom. The heavier the atom is, the smaller the isotope shift is. Therefore, the observed shift is not a normal mass shift. The mechanism behind the large shift is not clear now. It may be due to the different nuclear charge distribution. The values of the isotope shifts that we observed are comparable with the isotope shifts of the resonant 283.3-nm line ($6p^2\ ^3P_0 - 6p\,7s\ ^3P_1$). The isotope shift of the 283.3-nm line is 0.0745(6) cm^{-1} for m = 206, 0.1001(7) cm^{-1} for m = 207 (F = 3/2 hyperfine component), and −0.3402(7) cm^{-1} for m = 207 (F = 1/2).[33]

In Table I, the measured electron affinity of Pb was also compared with the reported calculations. It can be seen that the latest calculation still has a 60-meV deviation. The accurate EA(Pb) value determined in this study could serve as a benchmark for developing more accurate theoretical methods for heavy elements.

TABLE I. Measured binding energies of Pb$^-$ and electron affinities of Pb.

Peak	*Levels* (Pb ← Pb$^-$)	Binding energy (cm^{-1})
a	$^3P_1 \leftarrow {}^4S^o$	10 699(5)
b (m = 206)	$^3P_2 \leftarrow {}^4S^o$	13 527.26(13)
b (m = 207)	$^3P_2 \leftarrow {}^4S^o$	13 527.78(15)
b (m = 208)	$^3P_2 \leftarrow {}^4S^o$	13 527.66(13)

Electron affinities of Pb

Value	Reference
1.79 eV	Politzer[3] (calculated)
1.03 eV	Zollweg[4] (calculated)
1.05(9) eV	Chen and Wentworth[5] (calculated)
0.403 eV	Tatewaki *et al.*[9] (calculated)
0.417 eV	Melton *et al.*[10] (calculated)
1.1(2) eV	Zandberg *et al.*[1] (measured)
0.365(8) eV	Feigerle *et al.*[6] (measured)
0.364(8) eV	Hotop *et al.*[8] (measured)
0.356 743(16) eV or 2877.33(13) cm^{-1}	This work, for ^{208}Pb (measured)

IV. CONCLUSIONS

In summary, the electron affinity of the element lead (Pb) and the isotope shifts of the binding energy Pb$^-$ $6p^3\ ^4S_{3/2}$ − Pb $6p^2\ ^3P_2$ for m = 206, 207, and 208 have been measured via the slow-electron velocity-map imaging method. The electron affinity of Pb was determined to be 2877.33(13) cm^{-1} or 0.356 743(16) eV for m = 208. The accuracy was improved by a factor of 500 with respect to the previous measurement.

ACKNOWLEDGMENTS

This work is supported by National Natural Science Foundation of China (NSFC) (Grant No. 91336104) and Ministry of Science and Technology of China (MOST) (Grant No. 2013CB922004) of the National Key Basic Research Program of China.

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