

Photoelectron spectroscopy of anions at 118.2 nm: Observation of high electron binding energies in superhalogens MCl_4^- ($M=Sc, Y, La$)

Jie Yang, Xue-Bin Wang, Xiao-Peng Xing, and Lai-Sheng Wang^{a)}

Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99354 and Chemical and Materials Sciences Division, Pacific Northwest National Laboratory, MS K8-88, P.O. Box 999, Richland, Washington 99352, USA

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High energy photon is needed for photoelectron spectroscopy (PES) of anions with high electron binding energies, such as superhalogens and O-rich metal oxide clusters. The highest energy photon used for anion PES in the laboratory has been 157 nm (7.866 eV) from F₂ excimer lasers. Here, we report an anion PES experiment using coherent vacuum ultraviolet radiation at 118.2 nm (10.488 eV) by tripling the third harmonic output (355 nm) of a Nd:YAG laser in a Xe/Ar cell. Our study focuses on a set of superhalogen species, MCl_4^- ($M=Sc, Y, La$), which were expected to possess very high electron binding energies. While the 157 nm photon can only access the ground state detachment features for these species, more transitions to the excited states at binding energies higher than 8 eV are observed at 118.2 nm. The adiabatic detachment energies are shown to be, 6.84, 7.02, and 7.03 eV for $ScCl_4^-$, YCl_4^- , and $LaCl_4^-$ eV, respectively, whereas their corresponding vertical detachment energies are measured to be 7.14, 7.31, and 7.38 eV. © 2008 American Institute of Physics. [DOI: 10.1063/1.2938390]

I. INTRODUCTION

Electron affinity (EA), defined as the energy released when an extra electron is attached to a neutral atom or molecule, is an important atomic and molecular property related to their electronic structure, chemical stability, and reactivity. The EAs of most atoms or molecules are positive, i.e., they form stable anions upon electron attachment.¹ Molecules with high EAs are strong oxidizing agents. For example, the oxidative power of PtF_6 is dramatically shown by its ability to pull an electron from Xe to form the first chemical compound $Xe^+[PtF_6]^-$ of the supposedly inert rare gas by Bartlett in 1962.² In 1981, Gutsev and Boldyrev³ coined the term “superhalogen” to describe molecular species that possess EAs higher than the halogens—atoms with the highest EAs. In particular, they proposed an empirical formula, MX_{k+1} , for superhalogens, where M is an electropositive atom, X is a halogen atom, and k is the highest oxidation state of M. Many superhalogens have since been studied theoretically,^{4–10} and a number of them have been observed experimentally^{11–16} and shown to possess EAs much higher than the highest EA among the atoms (Cl: 3.613 eV).¹ EAs of some superhalogens have been predicted theoretically to be larger than 10 eV,^{17–20} i.e., higher than the ionization energies of all metal atoms in the periodic table, though there have not been direct experimental measurements of such high EAs.²¹ Additionally, we have recently found that certain O-rich metal oxide clusters can also exhibit extremely high EAs.^{22–24}

Anions of such high EA species require high energy photons for electron detachment in photoelectron spectroscopy (PES). However, because of the low number densities asso-

ciated with anion beams, intense photon sources coming from lasers are needed for anion PES experiments.²⁵ The 157 nm (7.866 eV) output of F₂ excimer lasers is the highest energy UV laser available for anion PES experiments heretofore.^{22–24,26–29} Very recently, vacuum ultraviolet (vuv) radiations from a free-electron laser at 32 nm has been demonstrated for electron detachment from lead cluster anions,³⁰ although the relatively low photon flux only allowed signals from the *5d* core levels to be observed because of their high cross sections.

On the other hand, the theory and technology of generating coherent vuv radiations by nonlinear four-wave mixing (NFWM) have been well developed over the past three decades.^{31–41} Radiations between 60 and 185 nm (7 and 20 eV) with laser-level properties have been generated by NFWM processes in rare gases (Ne, Ar, Kr, and Xe) or metal vapors (Hg). By nonresonant NFWM processes in rare gases, 118.2 nm (10.488 eV) radiation has been generated by tripling the third harmonic output (355 nm) of a Nd:YAG (yttrium, aluminum garnet) laser.^{42–46} The 118 nm radiation source is widely used in chemical physics, such as in high-resolution ion-pair photodissociation spectroscopy,^{47–50} photoionization mass spectrometry and chemical dynamic studies of cations and neutral molecules,^{51–56} and high sensitivity plasma diagnostics.⁵⁷ However, the 118 nm radiation from the NFWM processes has not been used for anion PES. The moderate photon flux of $\sim 10^{12}$ photons/pulse from such a source is still one or two orders of magnitude too low relative to a laser source for anion PES, but it may be feasible for anion systems with high ion intensities and high detachment cross sections.

In the current Communication, we report an anion PES study using 118.2 nm, which is generated using a homebuilt

^{a)}Electronic mail: ls.wang@pnl.gov.

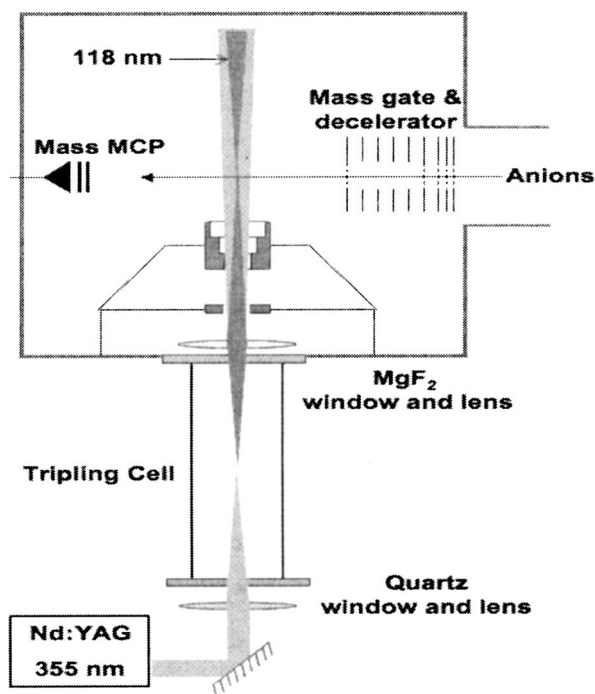


FIG. 1. Schematic diagram of the tripling cell and optics to generate coherent vuv at 118.2 nm and details of the electron detachment chamber. The magnetic-bottle photoelectron analyzer is perpendicular to the page (Ref. 58).

Xe/Ar cell by tripling the 355 nm output of a Nd:YAG laser. Our experiment was done on a set of superhalogens, MCl_4^- ($\text{M}=\text{Sc}, \text{Y}, \text{La}$). These anions are ideal for our initial 118 nm experiment because (1) they have high electron binding energies, (2) they can be produced with relatively high intensities from our electrospray ion source, and (3) they have relatively high detachment cross sections.

II. EXPERIMENTAL METHOD

A. The 118.2 nm radiation source

A sketch of our homebuilt tripling cell for the 118.2 nm source and the experimental arrangement is shown in Fig. 1. The vuv coherent radiation at 118.2 nm is generated by a nonresonant NFWM process in a phase-matched rare gas cell. The 355 nm output from a Nd:YAG laser (Coherent, Infinity 40-100) is focused by a quartz lens ($f=216.4$ mm at 355 nm) into the tripling cell (305 mm in length) containing a mixed gas of Xe/Ar in 1:10 ratio. Under our experimental conditions (≤ 40 mJ/pulse at 355 nm), the optimal conversion efficiency is achieved at a total pressure of ~ 50 Torr. A MgF_2 window is used to separate the tripling cell and the high vacuum photodetachment chamber. A MgF_2 lens ($f=75.9$ mm at 118 nm), mounted above the MgF_2 window inside the vacuum chamber, is used to focus the 118.2 nm output into the interaction zone of the photodetachment center. Since the focal length of the MgF_2 lens is longer at 355 nm, the primary beam is diverging after the lens and is not focused at the interaction zone. No efforts are made to separate the 118 nm output from the primary 355 nm beam. A 3.8 mm diameter aperture and a ladderlike tube are used to align the light path and minimize scattered 118 nm photons

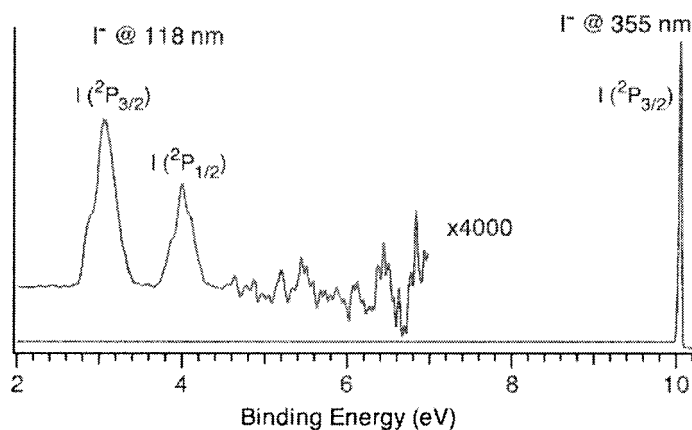


FIG. 2. Photoelectron spectrum of I^- at 118.2 nm (10.488 eV). The dominating feature at 10 eV corresponds to an electron kinetic energy of 0.437 eV, which was due to detachment of I^- by the primary 355 nm beam because the UV and vuv beams were not separated.

from reaching the interaction zone. In the current work, we typically use about 35 mJ/pulse of the primary beam: single-longitudinal mode at 355 nm and pulse width of 3 ns. Using a conversion efficiency of $(1-2) \times 10^{-5}$,^{45,56} we estimate ~ 5 μJ /pulse (or $\sim 10^{12}$ photons/pulse) 118.2 nm radiation with a pulse width of ~ 4 ns.

B. Photoelectron spectroscopy

The experiment was performed with our magnetic-bottle PES apparatus equipped with an electrospray ion source, a room-temperature ion trap, and a time-of-flight mass spectrometer.⁵⁸ The MCl_4^- anions were produced by electrospray of 1 mM solutions of the corresponding MCl_3 salts ($\text{M}=\text{Sc}, \text{Y}, \text{La}$) in a water/methanol mixed solvent (1/3 volume ratio). Anions from the electrospray source were guided by a radio-frequency quadrupole into a three-dimensional Paul trap operated at room temperature. The anions were accumulated for 100 ms before being pulsed out into the extraction zone of a time-of-flight mass spectrometer. The anions of interest, MCl_4^- ($\text{M}=\text{Sc}, \text{Y}, \text{La}$), were mass selected and decelerated before being intercepted by a detachment photon beam in the interaction zone of the magnetic-bottle PES analyzer (Fig. 1). In addition to the 118.2 nm photon source described above, PES spectra were also taken at 157 nm (7.866 eV) from an F2 excimer laser. Photoelectron time-of-flight spectra were recorded and then converted to kinetic energy spectra, calibrated by the known spectra of I^- . The electron kinetic energy resolution ($\Delta\text{KE}/\text{KE}$) was $\sim 3\%$ for the high energy photons and deteriorated somewhat for very high energy electrons. The electron binding energy spectra presented were obtained by subtracting the kinetic energy spectra from the detachment photon energies.

III. RESULTS AND DISCUSSION

A. PES spectra of I^- at 118 nm

Figure 2 shows the 118 nm spectrum of I^- , which is used as calibration at the vuv wavelength. Since the EA of I^- (3.059 eV) is below the photon energy of 355 nm, the dominating feature in Fig. 2 is due to detachment from the pri-

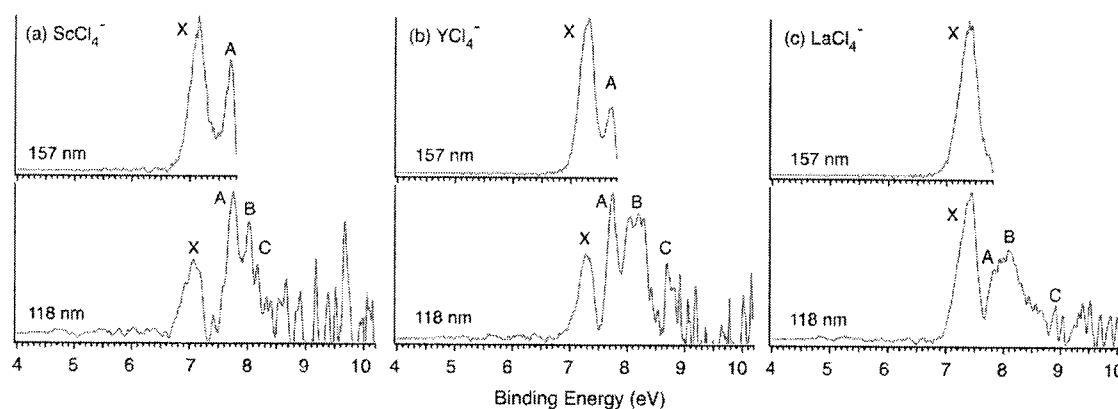


FIG. 3. Photoelectron spectra of (a) $ScCl_4^-$, (b) YCl_4^- , and (c) $LaCl_4^-$ at 157 nm (7.866 eV) and 118 nm (10.488 eV).

mary 355 nm laser beam, yielding the $I^2P_{3/2}$ ground state with a KE of 0.437 eV (the 10.051 eV peak in Fig. 2). The 118 nm detachment signals from I^- were much weaker due to the weak intensity of the 118 nm radiation and the competition from the primary 355 nm detachment, which effectively depleted the I^- beam. The peak width of the $I^2P_{3/2}$ feature from 118 nm (KE: 7.429 eV) is about 0.290 eV. Significant noises were present at KE less than 6 eV due to the scattered 118 nm radiation; and careful alignment and baffling of the vuv output, as shown in Fig. 1, were essential to minimize the noise level.

B. PES spectra of MCl_4^- (M = Sc, Y, La)

The spectra of $ScCl_4^-$, YCl_4^- , and $LaCl_4^-$ are displayed in Fig. 3 at both 157 and 118 nm. The 157 nm spectra show a ground state band (X) for all three species, as well as the onset of a second band (A) in the cases of $ScCl_4^-$ and YCl_4^- . The onset of the X band defines the EA for the neutral MCl_4 or the adiabatic detachment energy (ADE) of MCl_4^- : 6.84 ± 0.10 ($ScCl_4^-$), 7.02 ± 0.10 (YCl_4^-), and 7.03 ± 0.10 ($LaCl_4^-$) eV. The 118 nm spectra revealed a number of higher binding energy features in each case. The signal-to-noise ratio for the $ScCl_4^-$ spectrum at 118 nm was relatively poor due to its lower detachment cross section, which increases with the atomic numbers of the metal atoms. At 118 nm, the first excited state band (A) was clearly resolved and became the most intense band in the spectra of $ScCl_4^-$ and YCl_4^- . The A band was also observed in the case of $LaCl_4^-$ at 118 nm, but it was much weaker and was congested with the band B, which seems to contain unresolved

fine features. Two higher binding energy bands (B and C) were clearly resolved for $ScCl_4^-$ and YCl_4^- at 118 nm. The B band of YCl_4^- also appeared to contain unresolved features. At higher binding energies, a band C could be tentatively identified for both YCl_4^- and $LaCl_4^-$. The ADE for the ground state band and the vertical detachment energies (VDEs) for all the observed bands are summarized in Table I.

The chemical bonding in the MCl_4^- species is ionic in nature and they can be viewed as $M^{3+}(Cl^-)_4$. Thus, all the observed PES features should be due to detachment from Cl-based molecular orbitals. The extra charge in MCl_4^- is thus delocalized in the highly electronegative ligands, giving rise to their extremely high ADEs, which are the highest that we have observed experimentally for superhalogens. It was expected that the corresponding fluoride superhalogens MF_4^- may possess even higher ADEs due to the higher electronegativity of F relative to Cl. We tried unsuccessfully to take PES spectra for these fluoride species mainly due to their lower detachment cross sections and their weak ion signals from our electrospray source because the fluorides have very low solubility in aqueous solutions.

IV. CONCLUSIONS

In conclusion, we have demonstrated the feasibility of using vuv radiations from tripling the 355 nm output of a Nd:YAG laser as a photon source for anion PES. Our experiment was performed on a set of superhalogens MCl_4^- (M = Sc, Y, La), which all have extremely high electron binding energies. It is anticipated that further improvements of the nonlinear four-wave mixing technique may allow it to become a routine photon source for anion PES, opening the door to study anions with extremely high electron binding energies or to probe tightly bound valence electrons or inner shell electrons for molecular anions or size-selected atomic clusters.

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TABLE I. The measured adiabatic detachment energy (ADE) and vertical detachment energy (VDE) for $ScCl_4^-$, YCl_4^- , and $LaCl_4^-$. All energies are in eV. (The numbers in the parentheses represent the uncertainty in the last digit.)

		$ScCl_4^-$	YCl_4^-	$LaCl_4^-$
ADE	X	6.84(10)	7.02(10)	7.03(10)
	X	7.14 (5)	7.31 (6)	7.38 (5)
	VDE	A	7.75 (6)	7.74 (6)
	B	8.04 (5)	~8.1	~8.1
	C	8.17 (5)	8.71 (6)	8.91 (6)

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