EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Proposal to the ISOLDE and Neutron Time-of-Flight Committee

(Following ISOLDE Letter of Intent I-148)

Determination of the electron affinity of astatine and polonium by laser photodetachment

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Abstract: We propose to conduct the first electron affinity (EA) measurements of the two elements astatine (At) and polonium (Po). Collinear photodetachment spectroscopy will allow us to measure these quantities with an uncertainty limited only by the spectral linewidth of the laser. We plan to use negative ion beams of the two radioactive elements At and Po, which are only accessible on-line and at ISOLDE. The feasibility of our proposed method and the functionality of the experimental setup have been demonstrated at ISOLDE in off-line tests by the clear observation of the photodetachment threshold for stable iodine. This proposal is based on our Letter of Intent I-148 [1].

Requested shifts: 16 shifts

1 Introduction

The electron affinity (EA) is the energy gained when an additional electron is attached to a neutral atom forming a negative ion. This energy is, just like the ionization potential (IP), a fundamental property of an element. The EA and IP determine the chemical reactivity of an element and, indirectly, the compounds it forms as well as the stability of its chemical bonds [2]. The few radioactive elements along the periodic table for which only short-lived isotopes exist are the most difficult elements to investigate from a chemists point of view. The main experimental difficulty is that they are available only in ultra-trace amounts. Correspondingly, often only rudimentary studies have been performed and many fundamental properties still remain unknown.

In a recent work by Borschevsky *et al.* [3], the EA's of astatine (At) and polonium (Po) as well as their superheavy homologues were calculated using state-of-the-art quantum mechanical methods and the values obtained were compared to previous theoretical work. Figure 1 shows an overview of this comparison. Experimental data for the EA(At) and EA(Po) would validate their approach and give confidence in the EA predictions for the superheavy elements ununseptium (Uus, Z-117) and livermorium (Lv, Z=116), which in turn would be crucial for tailoring experimental conditions for the experimental determination of EA(Uus) and EA(Lv).

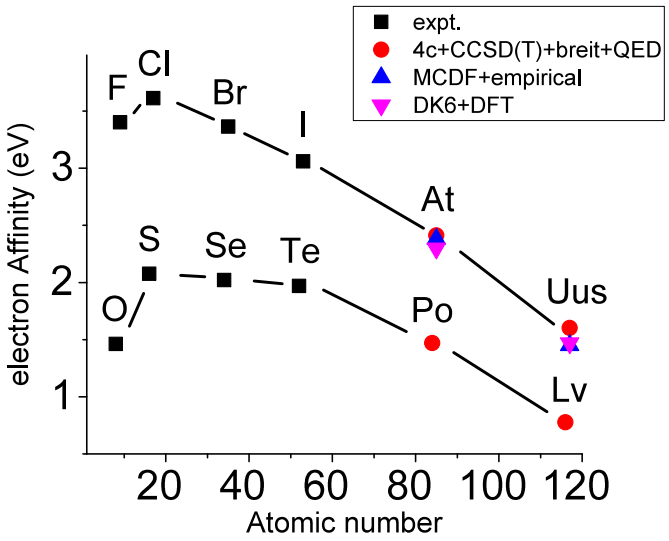

Figure 1: Trends of measured EAs (squares) of the chalcogens and halogens and predictions for At and Po as well as their superheavy homologues Ununseptium (Uus) and Livermorium (Lv) from recent theoretical calculations. Data taken from [3].

2 Motivation

2.1 Astatine

Astatine, element 85, is among the rarest of the naturally occurring elements on Earth. One of its longest-lived isotopes, ^{211}At (half-life = 7.21 h), is of considerable interest as a radiotherapeutic agent for the future of targeted alpha therapy in nuclear medicine [4, 5]. For the enigmatic element astatine, the measurement of the EA would be an indisputable advance to determine its chemical behavior [6]. It is well recognized that the lack of basic chemical studies on At to date hinders the development of its efficient use in radiotherapy [6]. As a recent and valuable step in this field, its IP was determined experimentally for the first time at ISOLDE (subject to the INTC-I-086 [7]). This work has been published in Nature Communications [8]. Like the IP, the significance of the EA determination for the astatine chemistry is twofold: First, both properties are related to the redox potential of astatine in solution [9] as well as its electrophilicity, hardness and electronegativity. The latter serve as figures of merit for the prediction of the nature of chemical bonds and their properties [10]. Secondly, due to the availability of only minute quantities of ^{211}At produced in cyclotrons, i.e. 10^{-13} to 10^{-9} g, computational chemistry is to date the main and an almost exclusive tool to gain an insight, at the molecular level, into the chemistry of this "invisible"element [11, 12]. However, a knowledge of the fundamental atomic properties, with the IP and EA being the most important ones, is needed to benchmark these quantum mechanical methods [13].

2.2 Polonium

The second element of interest is polonium (Po, Z=84). The isotope ^{210}Po (half-life = 138.4 d), that occurs naturally in the decay of uranium, is known for being one of the most toxic radionuclides in natural samples due to its high specific activity (166 TBq/g). It is also considered as an important component of natural radiation affecting humans [14]. Although Pierre and Marie Curie made the discovery of polonium more than a century ago, many of its characteristics still today remain unknown. The knowledge of the basic physico-chemical properties of Po is crucial for developing efficient "decorporation treatments "in medicine, and for understanding its behavior in natural systems, e.g. in the frame of the long-term management of abandoned uranium mines [15]. Following the ISOLDE work on At, the same technique was applied for Po and its IP was measured with high precision at ISOLDE [16]. Also here the EA remains completely unknown.
Po is a direct neighbour of At; being the last members of the chalcogen and the halogen families, respectively and together they are members of the 6th row of the periodic table. For both elements the existence of thermodynamically stable negative ions is predicted, i.e. the EAs are expected to be non-vanishing and thus could and should be determined by laser spectroscopy.

3 Experimental details

3.1 Technique

The laser photodetachment threshold (LPT) method [17] is the standard technique for precision determination of electron affinities. Among many other elements, this method was applied successfully for studies on tellurium (Te) [18] and iodine (I) [19] which are the lighter homologues of Po and At.

The EA of an element can be determined from the threshold photon energy required for inducing a photodetachment process on the negative ion. This represents a transition from the ground-state of the negative ion to the ground-state of the neutral atom, thereby releasing a photo-electron [17]. For such an LPT measurement, a beam of negative ions is overlapped in a preferably large interaction volume with a laser beam, e.g. in a collinear geometry. The collinear geometry has the advantage that the resolution in the experiment is improved by the so called Doppler compression [20]. Neutral atoms generated in the detachment process are detected while the laser frequency is scanned across the threshold region. If the photon energy exceeds the electron affinity, the photodetachment cross-section increases following the Wigner-law [21]. This law states that the cross-section scales to the power of $I + 1/2$, where I is the angular momentum of the outgoing electron. For negative ions with a p-valence electron, which is the case for At^- and Po^-, the outgoing electron will be either an s or a d electron. The centrifugal barrier close to the threshold only allows s-wave detachment. The resulting angular momentum of $I = 0$, gives rise to a very sharp onset of the increase in cross-section. This, in turn, makes it possible to accurately measure the onset of the photodetachment and thereby determine the electron affinity of the element under investigation. The relative detachment cross-section is measured as the neutralization rate. [19]
Following our Letter of Intent INTC-I-148 [1] we have successfully demonstrated the feasibility of the laser photodetachment technique under ISOLDE operating conditions with a negative ion beam of stable iodine obtained from a negative ion source at the GPS front-end. The results are discussed in the shift requirements section. A schematic layout of the setup is shown in Figure 2.

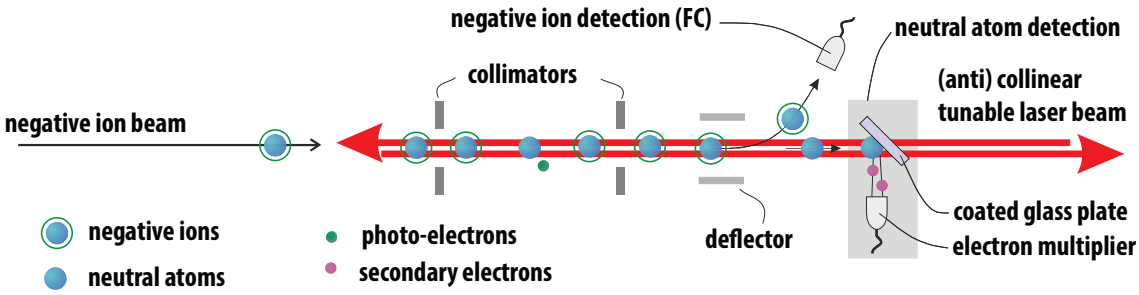

Figure 2: Schematic layout of the experimental setup. Negative ions, extracted from an ISOLDE target, are overlapped (anti)collinearly with the detachment laser beam. Undetached ions are deflected to a Faraday cup. The neutral atoms impinge on a coated glass substrate and create secondary electrons which are detected by an electron multiplier.

3.2 Experimental setup

In the frame of the I-148 campaign we have constructed and tested a transportable collinear laser spectroscopy setup, designed to be mounted at the GLM beam line. The setup, named GANDALPH (Gothenburg ANion Detector for Affinity measurements by Laser PHotodetachment), is based on the design of the negative ion beam apparatus GUNILLA (Gothenburg University Negative Ion Laser LAboratory) [22] which has been successfully used to measure the EAs of several elements (e.g. tungsten, [23]). The setup consists of the following components:

- differential pumping section
- laser ion merging section
- laser/ion interaction region
- neutral detector
- tunable laser system
- data acquisition

The differential pumping system enables adequate vacuum conditions (design goal 10^{-9} mbar) in the laser/ion interaction region while the apparatus is connected to the GLM beamline at $\approx 10^{-6}$ mbar. Laser/ion overlap is achieved by a 10° electrostatic bend. The laser/ion interaction region is defined by two collimators. The neutralized fraction of the beam is detected in the neutral detector where secondary electrons are generated upon impact of the fast atomic fraction onto the detector plate which are then extracted and detected by a channeltron detector. The photo-electrons generated when the laser pulse strikes the detector plate are suppressed by a fast-switching deflector plate [24]. The laser system is part of the ISOLDE RILIS installation. The data acquisition system is built upon the modular and well established RILIS DAQ format commonly used for in-source laser spectroscopy [25].

3.3 Laser requirements

In accordance with the most recent theoretical predictions, the scan range for At and Po has to be 510-518 nm and 833-855 nm respectively. These wavelengths are available at RILIS using UV pumped Coumarin 152 dye in ethyl or isopropyl alcohol and the grating based Ti:Sapphire laser, respectively. The spectral linewidth of the pulsed lasers of <20 GHz (≈0.1 meV) is sufficiently small. The optical beam path from RILIS to GLM has already been established and allows safe transport of the class 4 laser beams to the experimental beamline. The neutral signal will be obtained by integrating the events from the electron multiplier within a time window corresponding to the time of flight of the atoms, which is given by the length of the interaction region, its distance from the detector and the accelerating voltage of the ions. The background signal will be obtained simultaneously from the integral of the events in a delayed time window with the same length. The residual ion beam intensity will be recorded for normalization using the Faraday cup installed after the deflector.

4 Shift requirements

4.1 Astatine

The estimates made here are based on our experience during our I-148 campaign with negatively charged beams of stable iodine. The results given in Figure 3 show the laser photodetachment threshold measurements obtained with the GANDALPH setup at different initial beam intensities. The data plotted in Figure 3 a) was obtained with an ion current of 28 pA measured at the negative ion deflector Faraday cup at the detector flange at the end of the collinear beamline. These data were recorded with a pressure of 10^{-8} mbar.
A tenfold reduction in vacuum pressure is expected after baking of the vacuum chamber, giving the corresponding reduction in the background level. In order to estimate the minimum required beam intensity for astatine and polonium, the beam intensity was reduced to below the detection limit of our Faraday cup of 1 pA (conservatively). This resulted in a neutral rate above threshold of 70 events/s (4 counts average in 500 samples from the gated time-to-digital converter (TDC) over 30 s). The results shown in a) and b) were obtained in less than 10

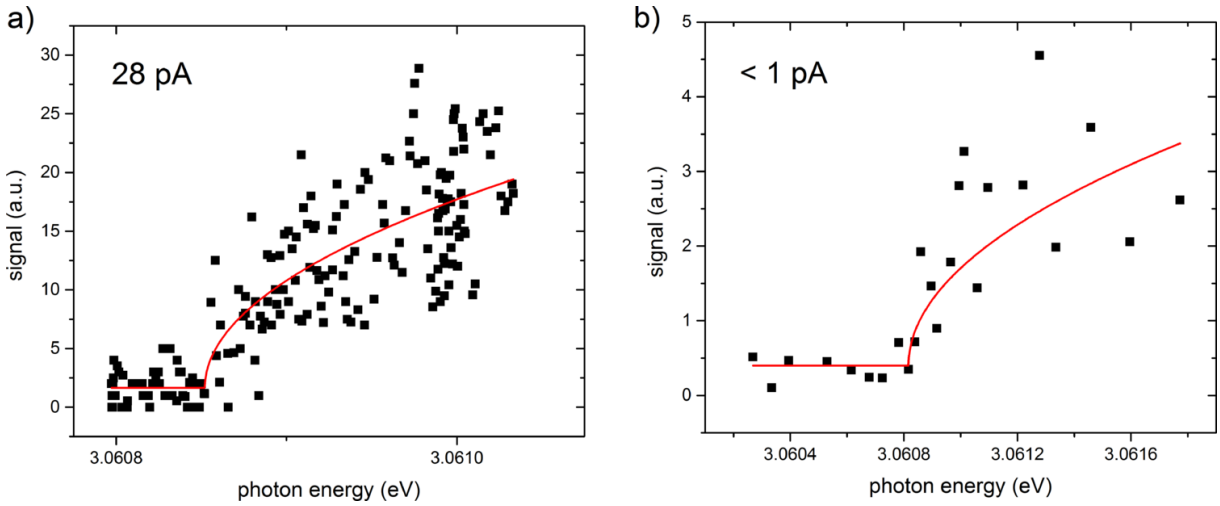

Figure 3: Photodetachment threshold measurement for iodine obtained during the 2015 negative ion run at ISOLDE for the I-148 campaign. The raw data and the Wigner-fit are shown. Two measurements were performed: a) With a measured current of 28 pA I^- at the end of the collinear beamline. b) The ion beam intensity was reduced to below the detection limit of the Faraday cup. The statistics are severely reduced, but are sufficient to determine the onset and therefore the EA.

minutes each. Note that no attempt was made to record and substract the background in the initial tests. The transmission efficiency from GLM through our collinear beamline was 8%. This could be improved by adding a pair of Einzel lenses in the region between the GLM exit port and the detection chamber.

The preparation of the collinear beam line requires at least seven days (preferably ten) during which the GLM beam line would be occupied. Most of the time is required for pumping and baking the system to achieve good vacuum conditions. The initial ion beam setup (4 shifts) will be performed with a beam of stable negative iodine ions (no protons required).

Iodine will also be the reference element. We shall request 1 shift during the run for reference scans where no protons are required. Before attempting a detailed scan one has to narrow down the threshold region. As the theoretical predictions could be far off, the laser setup may have to be modified (changing laser dye to access a different wavelength region). We will require 4 shifts to initially search for the energy region of the threshold for photodetachment of At.

The *conservative estimate* for the expected negative ion beam intensity of ^{211}At is ≈2 pA, based on the published yields in the ISOLDE yield database [26] and assuming 1.6 µA average proton intensity on the target. To obtain similar (low) statistics as in Figure 3 a) one would require a factor of 175 longer data acquisition time which would amount to ≈ 3.5 shifts (28 pA / 8% / 2 pA × 10 min). The fine laser scan should also be repeated in the anticollinear geometry in order to correct for the large Doppler shift that is inherent when studying fast ion beams in a collinear geometry. In an *optimistic estimate* one can obtain up to 80 pA of $^{205}At^-$, based on the observed 200 pA $^{205}At^{1+}$ using RILIS and an estimated laser ionization efficiency of ≪10% as reported in [8] which is in the same order as the efficiency of the negative ion source. Any increase in yield would improve the statistics.

4.2 Polonium

The experimental requirements for Po are similar to those for At. Without measurements of the yields however, it is difficult to estimate beam time requirements. We would therefore propose to attempt searching for the threshold region during the At beam time, which would require 4 shifts. The shift requirement for the precision threshold measurement of EA(Po) will then be subject of an addendum to this proposal once the negative polonium yields are measured. If the ion beam intensity of Po^- is too low, other methods (e.g. double charge exchange of Po^+) will have to be developed, as suggested in the Letter of Intent I-148 (Stage 2) [1].

4.3 Summary of requested shifts

We request a total number of **16 shifts** preceded by 4 shifts for the offline setup and initial reference scans.

Description	Element	Number of shifts (off-line)	Protons
stable beam tuning	iodine	(4)	no
determining threshold region	astatine	4	yes
fine scan collinear	astatine	3.5	yes
reference scans	iodine	1	no
fine scan anticollinear	astatine	3.5	yes
attempt threshold region	polonium	4	yes

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Appendix

The experimental setup comprises:

Part	Availability	Design and manufacturing
RILIS	☒ Existing	☒ To be used without any modification
GANDALPH detector chamber	☒ Existing	☐ To be used without any modification ☒ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing

HAZARDS GENERATED BY THE EXPERIMENT

Additional hazards:

Hazards	RILIS	GANDALPH	-
Thermodynamic and fluidic			
Vacuum		10^{-9} mbar	
Electrical and electromagnetic			
Static electricity		5000 V	
Ionizing radiation			
Target material			
Beam particle type (e, p, ions, etc)		negative ions	
Beam intensity		100 pA	
Beam energy		10-30 kV	
Cooling liquids		water	
Non-ionizing radiation			
Laser	class 4, 500-1000 nm	class 4, 500-1000 nm	

Hazard identification:

Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): 5 kW