

Lanthanide negative ion detection using accelerator mass spectrometry

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Accelerator mass spectrometric methods have been used in the detection of the negative ions of the lanthanides. All of the lanthanide negative ions (La^- – Lu^-) have been observed except Pm^- , Ho^- , and Er^- . The heavy element analysis line at the IsoTrace Laboratory was used to count the positive ions resulting from the atomic negative ions produced in a Cs sputter ion source and passed through the tandem accelerator. Because of its very low electron affinity, Dy^- had a terminal voltage dependent yield, and its study required the reduction of the electric field gradients used to accelerate the ions. The relative negative ion yields among the lanthanides will be discussed. Both Yb^- and Lu^- have recently been theoretically predicted to exist in negative parity ground states.

1. Introduction

The atomic negative ions have been studied over the recent years [1]. Knowledge about the creation, properties and dissociation of negative ions proved to be of importance from two points of view. The first is due to the widespread use of tandem accelerators in basic and applied research using accelerator mass spectrometry (AMS) [2]. The second is that the configurations and binding energies of those ions have implications for the understanding of the atomic shell structure, especially for the correlations of the electrons.

About one third of the elements in the periodic table have uncertain or unknown negative ion parameters [1]. Group II elements and the rare earths are the main groups with missing or incomplete negative ion data [3].

The laser photoelectron spectroscopic work of Feigerle et al. on Sc^- and Y^- [4], found the ground state configurations of these ions to be $3d4s^24p$ and $4d5s^25p$ respectively. Then two reports (an experimental and a theoretical) simultaneously attributed a stable negative ion to Ca. In the experimental work, Pegg et al. [5] concluded that the Ca^- was in the $4s^24p$ configuration rather than the commonly expected $3d4s^2$ configuration. The measured electron affinity from this experiment for Ca^- was claimed to be 43 ± 7 meV. However, in two very recent and independent experiments a lower value for the Ca^- electron affinity has been reported. Nadeau et al. [6] using electric dissociation and AMS obtained a value of $17.5^{+3.5}_{-1.5}$ meV, and

Walter and Peterson [7] using photodetachment spectroscopy obtained 18.4 ± 2.5 meV for the Ca^- electron affinity. The theoretical work of Fischer et al. [8] used both multiconfiguration Hartree–Fock and density functional theory in the calculations on Ca and Ca^- . This calculation predicted the Ca^- to be mainly in the $4s^24p$ state. The calculated electron affinity of Ca^- in this case was 45 meV.

Vosko et al. [9] in theoretical work also predicted stable Sr^- , Ba^- , and Ra^- . The calculations of Vosko et al., with density-functional theory using the Hartree–Fock method, placed the ground states of Sr^- , Ba^- and Ra^- also in the ns^2np ($n = 5, 6, 7$) configuration. The negative ions of Sr, Ba, and Ra; have been observed experimentally using AMS [10,11].

Very little has been known about the negative ions of the lanthanides and the actinides. Zollweg [12] predicted stable negative ions for a few of the lanthanides. However, a conflicting report by Sen et al. [13] argued that none of the lanthanides is likely to form stable negative ions. Since the early eighties, better theoretical techniques have been employed to probe the stability of the negative ions of the lanthanides and the actinides. Cole and Perdew [14] performed calculations on the binding energy of atomic negative ions ($Z < 86$) using a self-interaction correction to the local spin density approximation. In the lanthanide series, Cole and Perdew performed their calculations only on Ce^- , Pr^- , Nd^- , and Gd^- ; the four elements concluded by Zollweg to have bound negative ions. They assumed an extra 5d electron for all of the four cases, and their results agreed with Zollweg's on these ions and on the order of their binding energies. Bratsch [15] estimated the electron affinities of the lanthanides by extrapolation according to the energy variation associated with

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the filling of the 4f orbital. He predicted the ground state electron affinities to be within the range of -0.3 – 0.5 eV, with five of the lanthanides having positive values. Vosko et al. [16] very recently performed more sophisticated calculations to study the negative ions of La. They used density functional theory to which the relativistic contributions are added perturbatively, and predicted La^- to be bound in two configurations, an even-parity state of $[\text{Xe}]5d^26s^2$ and the odd-parity state of $[\text{Xe}]5d^16s^26p^1$. They estimated the binding energy of the even-parity state to be 0.108 – 0.270 eV, and that of the odd-parity state to be 0.108 – 0.405 eV. In another work Vosko et al. [17] also predicted Yb^- to be stable in the odd parity $[\text{Yb}]6p$ configuration. More recently, Vosko and Chevary [18] studied Lu^- theoretically. They performed calculations based on density functional theory and the Dirac Hartree–Fock method, and showed the bound state of Lu^- to be the odd-parity state $[\text{Xe}]4f^{14}5d^16s^26p^1$. They also pointed to the similarity between Lu^- , Sc^- and Y^- . The same work [18] also shows that the formerly thought to be bound even-parity state of Lu^- , $[\text{Xe}]4f^{14}5d^26s^2$ [13,15,19] is actually unbound by about 1 eV.

Answering the challenge of these recent predictions on some of the lanthanides, and searching for prospects among the lanthanides for possible future applications based on their negative ion properties; this work used AMS to study the negative ions of the lanthanides.

2. Experimental procedure

The accelerator mass spectrometry equipment of the IsoTrace Laboratory at the University of Toronto was used in performing these experiments. The laboratory facility and the heavy element analysis line have been described elsewhere [20–23]. Some of the procedures in the detection of atomic negative ions have already been reported recently [10].

The lanthanide targets used in this work were mostly pure metallic samples or mixtures of equal volume amounts of a lanthanide fluoride and another metallic powder (niobium powder most of the time). Lanthanum hexaboride was used as a target material for lanthanum.

The analysis leading to the detection of the atomic negative ions of the lanthanides consisted of three stages: analysis at the low energy section followed by acceleration to higher energy (6–14 MeV), and final analysis at the high energy section.

The low energy analysis starts by the use of the Cs^+ sputter source to produce the negative ions of interest, which are extracted and then energetically analyzed by a 45°C electric analyzer with a resolution of $E/\Delta E \approx$

400. The beam of the negative ions is then analyzed for the mass of interest to be injected into the tandem. This mass analysis is performed by a 90° analyzing magnet of a resolution of $M/\Delta M \approx 250$.

A tandem accelerator was used in accelerating the negative ions to higher energies. The acceleration voltages used in the lanthanide experiments varied from 0.75 to 2 MV depending on the nature of the species being accelerated (as will be discussed in the results section). Molecular species are destroyed in the Ar stripper gas midway inside the accelerator, where also a spectrum of positive charge states is generated and further accelerated prior to analysis by the high energy AMS section.

A +3 or higher charge state is usually chosen for analysis by the high energy section. This analysis begins by choosing the charge state of interest, based on its energy, using a 15° electric analyzer having a resolution of $E/\Delta E \approx 200$. The highest discrimination in the high energy section is accomplished by a 15 ton, 90° analyzing magnet. This magnet has a mass resolution of $M/\Delta M \approx 2600$ and a bending power of ~ 120 amu MeV. After the magnet the beam is electrically analyzed again through a 45° electric analyzer having resolution of $E/\Delta E \approx 900$. The ions to be detected then terminate in a gas ionization detector where the energy proportional pulses are collected in a personal computer (PC) based data acquisition station. For all of the lanthanides (except La and Ce) the negative ion yield was beyond the detection limit (≤ 1 pA) in the low energy system. Calibration of the whole AMS system is usually performed using strong beams of negative ions (e.g. $^{127}\text{I}^-$, $^{197}\text{Au}^-$). However, the fine tune calibration of the high energy system in the immediate range for the ion of interest was usually performed using an isobar of an element known to form negative ions, or a molecular fragment having almost the same electric and magnetic rigidities.

Since ^{176}Lu is an isobar with ^{176}Hf , this Hf isotope was used in tuning the system for the detection of $^{176}\text{Lu}^-$. The setting of the high energy magnet (B2) for detecting $^{176}\text{Hf}^{3+}$ from $^{176}\text{Hf}^-$ was found to be at $B2 = 0.975086$ T, and the peak of $^{176}\text{Lu}^{3+}$ from $^{176}\text{Lu}^-$ was found to be centered at $B2 = 0.975052$ T. The difference in B2 due to the mass defect difference of the two isotopes ($M/\Delta M \geq 10^5$) is beyond the resolution of the high energy magnet. The experimental difference in B2 between the two values corresponds to $B/\Delta B \geq 25\,000$, which is well within the resolution of the magnet ($B/\Delta B \approx 5200$).

The existence of Lu^- was confirmed by scanning the other Lu isotope. The yield of $^{175}\text{Lu}^{3+}$ from $^{175}\text{Lu}^-$ was more than 30 times greater than the corresponding yield of $^{176}\text{Lu}^{3+}$, that reflects the greater isotopic abundance of ^{175}Lu (97.40%), and confirms that Lu^- was the species injected into the accelerator.

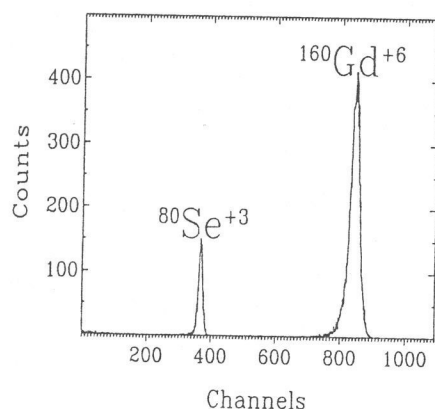


Fig. 1. Energy spectrum of $^{80}\text{Se}^{3+}$ from $^{80}\text{Se}_2^-$ and $^{160}\text{Gd}^{6+}$ from $^{160}\text{Gd}^-$ from a gas ionization chamber.

Fig. 1 shows a typical energy spectrum from the final ionization chamber. The energy gained by the ion during tandem acceleration is proportional to its charge and this enables the discrimination against the ions having electric and magnetic rigidities differing by small amounts beyond the resolution of the high energy electric and magnetic analyzers.

3. Results and discussion

The negative ions of all the lanthanides except Ho and Er have been detected using the AMS experimental procedures described in the last section. The yield of negative ions varied widely among the lanthanides.

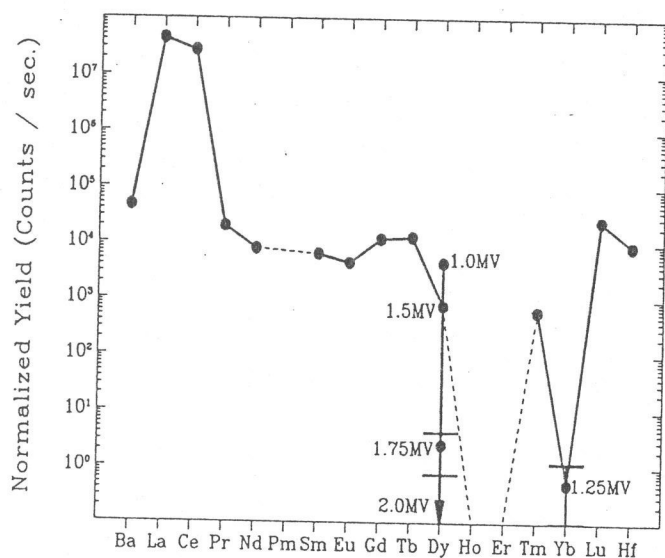


Fig. 2. Negative ion yield of the lanthanides. Except where indicated the yield measurement took place at a terminal voltage of 1.5 MV or higher. Dysprosium and ytterbium were the only elements that have a terminal voltage dependent negative ion yield.

Fig. 2 shows the normalized yield of negative ions for the lanthanides, barium, and hafnium. The yield data was normalized with respect to isotopic abundance so that the figure reflects the yield counts per second from a 100% abundant isotope. The signal collection point was the same for all of the data except for La^- and Ce^- , where they had yields that were possible to read on the last Faraday cup in the system. Fig. 2 displays a ranking order for the yields of negative ions among the lanthanides.

The general trend depicted in fig. 2 shows the higher yields of the negative ions of the lanthanides of lower Z number, especially La^- and Ce^- . This is an indication of relatively high negative ion binding energies for that region of the lanthanides assuming the yield is given by the tunneling theory of sputtering of Norskov and Lundqvist [24]. This trend is broken by the dissociation of Dy^- when higher acceleration fields are used. The yield of Dy^- is shown for a few acceleration voltages in fig. 2. The drastic change of the Dy^- counting rate with acceleration voltage indicates not only its lower binding energy, but it also hints at the configuration of the removed electron in this decay [25,26]. The preliminary comparison of the rate at which the Dy^- counting rate changes with acceleration voltage suggests that a $p_{1/2}$ electron is removed with a binding energy of ≈ 15 meV. This strongly supports the Dy^- configuration to be in the $4f^{10}6s^26p$ state, similar to a low lying state of its isoelectronic HoI.

The detection of Dy^- by lowering the acceleration voltages leaves the Yb^- as the most fragile negative ion observed in this work, and helps in the understanding of the difficulties surrounding its detection. Detecting Yb^- at the lowest terminal voltages (0.75–1.25 MV) resembles very much trying to detect Dy^- at 1.75–1.8 MV, where minor variations in the system can add to the destruction of the ions of interest and cause the signal not to be observed (like the higher vacuum pressure during one of the Yb experiments). Also the copious interfering hydrides of Yb add to the challenge of detecting Yb^- above the background created by that interference. The Yb^- binding energy is definitely lower than the binding energy of Dy^- . This suggests an electron affinity for Yb^- (estimated at present to be ~ 8 meV) below the theoretically calculated value of 54 ± 27 meV [17].

An electric dissociator [26] used to study the dissociation of Ca^- can exploit electric field gradients much higher than the gradients normally present in the accelerator or the ion source. This was used to test the vulnerability of the negative ions of the other lanthanides to as high an electric field (≈ 5 MV/m) as the dissociator can go. In addition to the dissociation of Dy^- , the only lanthanide negative ion that showed any measurable attenuation so far was Tm^- , a sign that this ion, although more bound than both Yb^- and

Dy⁻, is the next in line in its vulnerability to be dissociated, hence adds to the information of ranking the binding energies of these species.

4. Conclusions

In conclusion, the results from the search for the atomic negative ions of the lanthanides can be summarized as follows:

This work reports the detection of the negative ions of all of the lanthanides except Ho and Er (Pm was not investigated).

The Yb⁻ is the most fragile negative ion detected in this work. Due to its extremely low binding energy and metastable hydride interference, minor deviations in the system conditions can interfere with the experiments on its detection, even at the lowest possible operational electric field. More experimental work is required to improve its background and yield.

The dissociation of Dy⁻ in the electric field of the accelerator, and the verification of this phenomenon using the electric dissociator, gave an estimate of its binding energy; i.e. ≈ 15 meV [26].

The failure to observe Ho⁻ and Er⁻, guided by the results for Yb⁻ and Dy⁻, cannot prove the non-existence of those ions. However, it provides an upper bound for their binding energies of ≤ 5 meV.

The exceptionally high yield of both La⁻ and Ce⁻, indicates that they may have relatively high binding energies (≥ 600 meV), several excited states, or both.

The present experimental results together with the theoretical predictions suggest that the role of the 6p electron in the lanthanide negative ions may be an important one.

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