International Journal of Mass Spectrometry 359 (2014) 12–18

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Feasibility of photodetachment isobar suppression of WF_5^- with respect to HfF_5^-

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ARTICLE INFO

Article history:
Received 31 August 2013
Received in revised form 5 December 2013
Accepted 13 December 2013
Available online 24 December 2013

Keywords:
Negative ions
Photodetachment
Isobar suppression
Accelerator mass spectrometry
Absolute cross section

ABSTRACT

The feasibility of using laser photodetachment as a means for isobar suppression in accelerator mass spectrometry has been investigated for the special case of HfF_5^-/WF_5^-. A method for absolute photodetachment cross section measurements was applied and the cross sections of tungsten pentafluoride and hafnium pentafluoride negative ions were measured. The measurements indicate that the photodetachment cross section for WF_5^- is at least 100 times larger than for HfF_5^- at the wavelength of the fourth harmonic of the Nd:YAG laser at 266 nm. The absolute cross section for WF_5^- at this photon energy was found to be $(2.8 \pm 0.3) \times 10^{-18}$ cm^2, while an upper limit of 2×10^{-20} cm^2 was obtained for the HfF_5^- cross section. The measured cross sections indicate that an optical filtering scheme for isobar suppression in accelerator mass spectrometry for the case of ^{182}Hf should be feasible.

1. Introduction

^{182}Hf is a cosmologically interesting radioactive trace isotope with a half life of 9.6 million years. Detection of ^{182}Hf on earth would give direct evidence of a supernova event in the vicinity of our solar system [1]. There are reports of a discovery of a similar supernova indicator, ^{60}Fe, in the deep sea crust [2]. However, questions have been raised about the reliability of these findings [3]. A search for the occurrence of any ^{182}Hf traces is thus of considerable interest. Vockenhuber et al. [1] showed that the abundance of ^{182}Hf from a supernova relative to the abundance of stable ^{180}Hf in deep sea sediments is expected to be on the order of 10^{-13}. The most sensitive method for measuring such low abundances is accelerator mass spectrometry (AMS). A major problem in AMS measurements of ^{182}Hf, however, is the strong interference of the stable isobar ^{182}W. To a certain extent, the contamination of ^{182}W can be suppressed by several independent techniques. For example, hafnium and tungsten have different chemical properties which allows rejection of ^{182}W by chemical separation. Furthermore, ^{182}W can be suppressed by several orders of magnitude [1] by using a suitable molecule that has different production yields for the W and Hf containing species in the negative ion source of the AMS facility. So far, using pentafluoride negative ions achieved the highest suppression of ^{182}W. By injecting HfF_5^- into the AMS tandem accelerator, the corresponding isobar, WF_5^-, is sufficiently reduced to yield a detection limit of about 10^{-11} for the isotope ratio ^{182}Hf/^{180}Hf [1]. A recent reassessment of the detection limit, which devoted sufficient time to a thorough optimization of beam parameters, produced a limit of 10^{-12} for the ^{182}Hf/^{180}Hf ratio [4]. Most of the remaining ^{182}W contamination originates from the ion source and not the sample. Thus, an additional suppression of one to two orders of magnitude is required to access the abundance level of 10^{-13} as expected in the deep sea crust. It has been shown that selection of isobars in the detection stage by their individual energy loss in gases is an efficient method [5]. However, this method gets less effective as the mass of the ion of interest increases, and new suppression methods in the injection stage are therefore highly desirable.

As demonstrated by Berkovits et al. [6,7], laser photodetachment can be used to remove unwanted isobars in AMS systems. This technique naturally requires that the interfering isobar has

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http://dx.doi.org/10.1016/j.ijms.2013.12.010

a lower electron affinity than the species of interest. In addition, substantial depletion of the interfering isobar can only be achieved by a high photon flux or long interaction time. For this purpose a collinear overlap geometry of laser and ion beams can be applied. Berkovits et al. used a pulsed laser which delivered a high photon flux during pulses but the duty cycle of the experiment was low. For practical use in AMS, however, the duty cycle must be close to 100%. This can be achieved by decelerating the fast ion beam to allow for a long interaction time with a laser. Either a continuous wave laser or, alternatively, a high repetition rate pulsed laser operating in the 10 kHz regime can be used. Liu et al. [8] have demonstrated the latter approach by using a linear gas filled Radio Frequency Quadrupole (RFQ) as an ion guide to confine a decelerated ion beam of only a few electronvolt of kinetic energy. A buffer gas in the ion guide cools the beam, both translationally and internally [9]. During the extraction from the RFQ, the beam is re-accelerated to its original kinetic energy. The translational cooling in the ion guide results in reduced emittance and energy spread of the ions. By applying this technique, i.e. overlapping the laser beam collinearly with the slow ion beam along the RFQ structure, Andersson et al. demonstrated a suppression of more than 99.99% of a Co^- beam, corresponding to a suppression factor of 10^4 [10].

The main motivation for this work is the proof of principle of this technique for the interference of WF_5^- to HfF_5^- and the search for a suitable photon energy where WF_5^- is photodetached efficiently while HfF_5^- is unaffected. Laser photodetachment depletion would then provide the additional suppression needed to measure lowest $^{182}Hf/^{180}Hf$ ratios with AMS. To the authors knowledge there are no measurements or theoretical calculations of absolute photodetachment cross sections for these species published in literature. However, theoretical calculations for the binding energies of pentafluorides have been reported. Dyall gave an electron affinity for WF_5 of 2.5 eV [11], while Chen et al. published a vertical detachment energy of 3.9 eV for WF_5^- and 8.8 eV for HfF_5^- [12]. The theoretical work thus indicates that isobar suppression with lasers should be energetically possible. A successful implementation of the laser suppression method requires that a commercial laser system producing the needed photon energy with sufficient power is available. Currently, the most promising candidate is the Nd:YAG laser, representing a well proven laser type which delivers high power while still retaining optimum beam properties. Continuous or quasi-continuous Nd:YAG lasers available today generate a broad selection of emitted radiation with wavelengths of 1064, 512, 355 or 266 nm. Hence, this study has focused on probing the suitability of different wavelengths produced by Nd:YAG lasers.

The isotope shift of the photodetachment cross section of HfF_5^- is several orders of magnitude smaller than the difference between the HfF_5^- and WF_5^- cross sections and is insignificant to this application. Hence, instead of using the trace isotope $^{182}HfF_5^-$, any stable isotope can be used to determine the photodetachment cross section, and in particular the most abundant one.

2. Photodetachment basics

In the photodetachment process, absorption of one or several photons by an atomic or molecular negative ion leads to emission of an electron. Atomic and molecular negative ions are, in general, loosely bound compared to the isoelectronic neutral or positive ion. The Electron Affinity (EA) is defined as the energy difference between the ground state of the negative ion and the ground state of the corresponding neutral. If the photon energy is equal to or larger than the EA, the photodetachment process

$$X^- + h\nu \rightarrow X + e^- \qquad (1)$$

can occur. The Wigner law [13] describes the energy dependence of the photodetachment cross section in the vicinity of a state threshold of an atomic negative ion. The photodetachment cross section below the ground state threshold is vanishing, unless there are populated excited states. In that case, it most often can be approximated by a constant. Therefore the shape described by the Wigner law can easily be fitted, and a high precision EA value can be extracted.

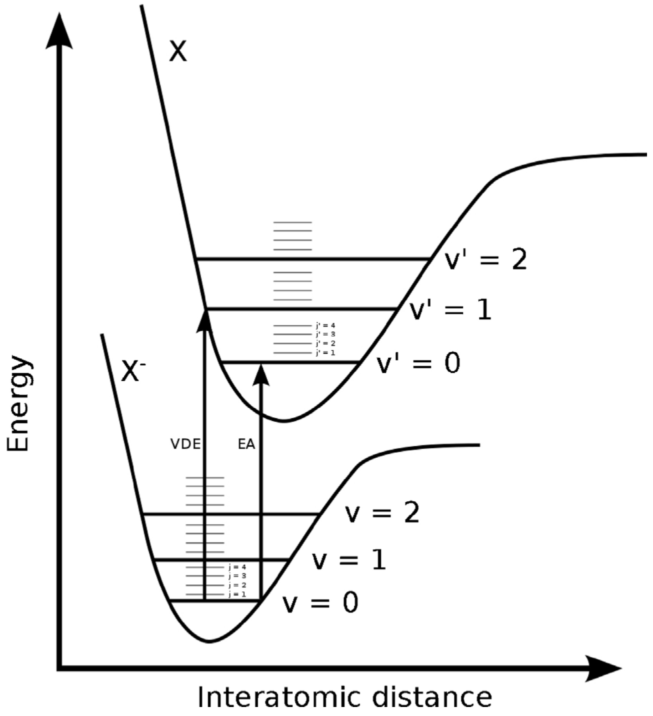

Fig. 1. Schematic representation of the energy potentials for a neutral and negatively charged prototype molecule. The smaller dashes represent rotational state multitudes associated with every vibrational state $v = 0, 1, 2, \ldots$.

Molecular negative ions have a much more complex structure than atomic negative ions, as illustrated in Fig. 1. In addition to the electronic states, a molecule also has vibrational and rotational states. In the Born–Oppenheimer approximation, the nucleus will be motionless during an electronic transition, thus allowing only vertical transitions during photon absorption or emission. The EA of a molecular negative ion is defined as the transition between the lowest electronic, vibrational and rotational state in the negative ion to the lowest electronic, vibrational and rotational state in the neutral. Usually, the transition that corresponds to the EA value of a molecular negative ion is not the transition with the highest probability. Instead, the transition from the negative ion ground state with the largest Franck–Condon factor is designated as the vertical detachment energy (VDE).

Correspondingly, the determination of an EA from an observed photodetachment cross section for a molecular negative ion is complex. Molecular negative ions are usually produced with a thermal distribution among vibrational and rotational states. This will produce a photodetachment cross section that is a superposition of a large number of channels, stemming from energetically allowed transitions between different vibrational and rotational states in the negative ion and the neutral. As the photon energy increases, the number of possible transitions will grow, and the total photodetachment cross section rises gradually without any sharp structures. It will not be possible to determine the energy for individual thresholds and absolute determinations of the EA and the VDE cannot be made, but a rough estimate may be derived. A suitable approach to accurately determine the EA and VDE for a molecular negative ion is to cool the ion beam considerably to