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Feasibility of photodetachment isobar suppression of \mathbf{WF}_5^- with respect to \mathbf{HfF}_5^-

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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 $(2.8 \pm 0.3) \cdot 10^{-18}$ cm², while an upper limit of $2 \cdot 10^{-20}$ cm² 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.

INTRODUCTION

¹⁸²Hf is a cosmologically interesting radioactive trace isotope with a half life of 9.6 million years. Detection of ¹⁸²Hf 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, ⁶⁰Fe, 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 ¹⁸⁰Hf 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 ¹⁸²Hf, 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 ¹⁸²W by chemical separation. Furthermore, ¹⁸²W 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 $^{182}\mathrm{W}.$ 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 ¹⁸²Hf/¹⁸⁰Hf [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 ¹⁸²Hf/¹⁸⁰Hf ratio [4]. Most of the remaining ¹⁸²W 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 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 eV 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-continous 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 mag-

nitude 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.

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

$$X^- + h\nu \to X + e^- \tag{1}$$

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. Molecular negative ions have a much more complex structure than atomic negative ions, as illustrated in Figure 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 negative ion to the lowest of 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



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 ...

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 reduce the number of populated states. Alternatively, methods that do not use the shape of the photodetachment cross section, such as photodetachment electron spectroscopy, might also be used.

EXPERIMENTAL DETAILS

The GUNILLA negative ion beam laser apparatus

The experiments discussed here were performed at GUNILLA (Gothenburg University Negative Ion Laser LAboratory), schematically shown in Figure 2. A detailed description of the apparatus can be found in [14]. Abbreviations used in the text refer to parts shown in Figure 2. A cesium sputter ion source produces negatively charged ions which are accelerated to a kinetic energy of 6 keV. Thereafter, the ions are mass separated using a 90 degree sector magnet. Several electrostatic ion optical elements guide the ion beam to one of the two interaction regions. GUNILLA can be operated in either a collinear or a crossed beams geometry. For measurements using the collinear beams geometry, the first quadrupole deflector (Q1) deflects the ion beam by 90 degrees into the collinear interaction region. Two 3 mm apertures placed 610 mm apart define this interaction region in which a laser beam is overlapped collinearly with the ion beam. Behind the interaction region, two vertically aligned rods are used to create an electrostatic field that deflects the ion beam into a Faraday cup (FC1). Laser photodetachment in the interaction region produces neutral atoms or molecules, indicated by dotted lines in Figure 2. These neutrals continue unaffected through the electrostatic rods. They are then detected by a neutral particle detector, situated in the forward direction. The neutral particle detector is designed to be transparent in order to allow the laser light to pass through. This is a necessity when collinear laser photodetachment experiments are performed. The main parts of the neutral particle detector, described in detail elsewhere [15], is a glass plate coated with transparent Tin-doped Indium Oxide (ITO) and a Channel Electron Multiplier (CEM). Fast atoms or molecules hit the glass plate and emit secondary electrons, which are then detected with the CEM. The ITO coated glass plate in the neutral particle detector has a transmission window that lies in the visible region. For wavelengths shorter than 340 nm, the transmission of ITO coated glass plate drops sharply. Similarly, absorption in the IR wavelength region is observed, but the cut off is not as sharp as in the UV region. The collinear beams geometry cannot be used for wavelengths outside this transmission window. For such wavelengths the crossed beams geometry is used instead. For the crossed beams geometry, Q1 is turned off, and the second electrostatic quadrupole deflector (Q2) deflects the ion beam by 90 degrees into the second interaction



FIG. 2. Schematic drawing of the experimental setup at GUNILLA. By using either the first or the second quadrupole deflector (Q1 or Q2) it is possible to examine negative ions of interest in collinear or in crossed beams geometry. The Channel Electron Multipliers (CEM1 and CEM2) and two Faraday cups (FC1 and FC2) are used for detection.

region. A 3 mm entrance aperture and a 1 mm exit aperture placed 150 mm downstream define this interaction region, in which the laser beam crosses the ion beam perpendicularly. The volume where the two beams intersect defines the effective interaction region, which is in the order of 10 - 30 mm³. After the interaction region, electrostatic plates deflect the ion beam into the second Faraday cup (FC2) while neutral atoms or molecules produced in the interaction region continue straight forward for detection by a neutral particle detector similar to the one used in the collinear beams geometry. The last mirror, used to guide the laser beam into the interaction region, is mounted on a linear stage which is controlled by a stepper motor. This allows the vertical position of the laser beam to be shifted over a range of 10 mm.

 WF_5^- ions were produced from a cathode material consisting of tungsten powder mixed with AgF₂ powder. In the case of the HfF₅⁻, a mix of HfF₄ and Ag powders was used. The cathodes were baked at a temperature of about 100°C for several hours to minimize the oxygen content. The measured ion current in the Faraday cups behind both interaction regions was typically 10 - 100 pA.

The pulsed laser light used in this study was produced by two laser systems available at GUNILLA. Both systems are based on optical parametric oscillators/optical parametric amplifiers pumped by pulsed Nd:YAG lasers. They produce 6 ns pulses with a repetition rate of 10 Hz. The bandwidths of both lasers are 0.2 cm^{-1} , and the energy of each pulse is of the order of 1 mJ, measured after passing through the interaction region. The combined output from the two systems provides continuous tunable radiation over the region of 220 - 5000 nm.

Experimental procedure

Collinear and crossed beams geometries are complementary, and the choice of geometry is determined by a number of key parameters. At wavelengths shorter than 340 nm only the crossed beams geometry can be used as mentioned above. The collinear beams geometry gives the highest sensitivity due to the large interaction volume, and it can therefore be used to measure extremely small cross sections. However, variations in the overlap between laser and ion beam give large uncertainties for the measurements of absolute cross sections. With the crossed beams geometry, on the other hand, absolute cross section measurements are straightforward, as will be described below. This advantage comes at the cost of reduced sensitivity due to the smaller interaction volume.

For both geometries neutral particles produced by photodetachment are detected and counted for each laser pulse. With the laser pulse duration of 6 ns and the velocity of the ions being in the order of 0.1 mm per ns or less, the ions can be considered stationary during the duration of the laser pulse. The neutrals can hence be treated as if they were produced in a well defined volume and will arrive at the detector during a fixed time period after the laser pulse. It is therefore possible to gate the data acquisition. The aim is to select only those neutral particles that were created during passage of the laser pulse through the interaction region. Neutrals created by collisional detachment with residual gas make up the background noise. Time gating leads to a reduction in duty cycle to 10^{-4} and 10^{-7} for the collinear and crossed beams geometry, respectively. Furthermore, a background correction can be performed via the neutral particle rate outside the selected time window. A LabVIEW based data acquisition system was used to record the signals from the neutral particle detectors, the laser power and the ion current in the Faraday cup. For the crossed beams geometry, also the position of the translation mirror was registered.

Cross section measurement - Collinear beams geometry

The cross section as a function of the photon energy E_{γ} for the collinear beams geometry is derived from the definition of the cross section

$$\sigma_{\omega} = \frac{n}{N_I / A \cdot n_{\gamma}} \,, \tag{2}$$

which assumes homogeneous beams and a complete overlap. Here, n and n_{γ} are the number of reactions per second and the photons per second, and N_I/A the number of ions per area. N_I is given by the particle flux $\frac{I}{ev}$ times length L of the interaction region, with the ion current I, ion velocity v and elementary charge e. A is the area in cross-section of the interaction region. For a pulsed beams experiment it is useful to go from photons per second to photons per pulse, which is given by \bar{E}_L/E_{γ} , where \bar{E}_L is the average laser pulse energy and E_{γ} the photon energy. With the average number of reactions per pulse \bar{N} , the total cross section in a collinear beams geometry is given by

$$\sigma(E_{\gamma}) = \frac{\bar{N} \cdot A \cdot e \cdot v \cdot E_{\gamma}}{\bar{I} \cdot L \cdot \bar{E}_L} \,. \tag{3}$$

This expression is valid if either the ion or the laser beam is uniform perpendicular to the beam axis over the whole length of the the interaction region. The 610 mm length and 3 mm in diameter of the interaction region ensures an almost parallel ion beam. Likewise, an unfocused laser beam at the entrance of the interaction region will ensure that the laser beam is uniform.

Cross section measurement - Crossed beams geometry

For cross sections measurements in the crossed beams geometry, the animated beams method, first developed by Defrance *et al.* [16], was applied. For this method the laser beam axis is translated vertically through the ion beam. In this way, the effective overlap between laser and ion beam is indirectly measured. Measuring the beam overlap directly would



FIG. 3. Sketch of the experimental method in the crossed beams geometry. The ion beam (red) passes two apertures to obtain a well defined, parallel beam in the interaction region. The laser beam (blue) is displaced vertically by movement of the final mirror. Both beams interact between the two apertures in a well defined interaction volume. The produced neutral particles (green) travel straight to the CEM, while the ions are deflected into a Faraday cup behind the second aperture.

in principle also be possible, but requires much more experimental effort and nevertheless would be the prominent source of uncertainty.

The original experiment by Defrance *et al.* used continuous ion and electron beams. Later experiments, e.g. described in [17], used continuous ion and laser beams. It is straightforward to transform the expression used in these experiments to be valid for a pulsed laser beam, too. The geometry of the ion beam traveling in the y-direction and the laser beam intersecting in x-direction is shown in Figure 3.

The ion and laser beam density in the direction of the laser can be projected onto the y-z-plane. The ion beam is assumed to be constant in time during a pulse. Consequently, the two dimensional ion density $\rho_I(y, z)$ is independent from y. Integration along the z-axis yields a constant one dimensional ion density, depending only on the particle flux I/e and

the ion velocity v:

$$\int_{-\infty}^{\infty} \rho_I(y, z) dz = \rho_I(y) = \frac{I}{ev}$$
(4)

As the ion density does not depend on y, the photon distribution in this dimension does not affect the result and can be considered as constant. Correspondingly, integration of the photon density ρ_{ω} over z yields the total photon number per laser pulse N_{ω} :

$$\int_{-\infty}^{\infty} \rho_{\omega}(z) \mathrm{d}z = N_{\omega} \tag{5}$$

For homogeneous beams overlapping completely, the cross section σ_{ω} is given by Equation (2). For a pulsed beams experiment, the number of reactions per second and number of photons per second are replaced by the number of reactions per pulse and number of photons per pulse. For heterogeneous beams an overlap integral of the particle densities has to be evaluated. Correspondingly, $N_I/A \cdot n_{\gamma}$ becomes $\int_{-\infty}^{\infty} \rho_I(z) \rho_{\omega}(z) dz$ with the aforementioned normalization. This yields the number of reactions per laser pulse of

$$N = \sigma_{\omega} \int_{-\infty}^{\infty} \rho_I(z) \rho_{\omega}(z) \mathrm{d}z.$$
(6)

By the translation of one beam in z-direction and integration of the number of reactions per pulse over this displacement \tilde{z} the overlap integral is separated into easily measurable quantities

$$\int_{-\infty}^{\infty} N \mathrm{d}\tilde{z} = \sigma_{\omega} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho_I(z) \rho_{\omega}(z+\tilde{z}) \mathrm{d}z \mathrm{d}\tilde{z}.$$
(7)

Using the normalization in (4) and (5), the integration can be performed sequentially. If the integral over \tilde{z} in Equation (7) is evaluated first one obtains for the absolute cross section

$$\sigma_{\omega} = \frac{ev}{N_{\omega}I} \int_{-\infty}^{\infty} N \mathrm{d}\tilde{z}.$$
(8)

In the experiment it is not necessary to perform the integration, i.e. the scan of the laser beam, all the way from minus to plus infinity. N will be zero when the two beams do not overlap. In our case, the laser beam is moved over a range of about 8 mm. Due to the very low reaction rates several hundred scans have to be performed to acquire the necessary statistics.

For the evaluation a Matlab based script was used. All events, i.e. laser shots, and their recorded experimental data are binned according to their vertical displacement \tilde{z} . The average number of counts is normalized with ion current and pulse energy for each bin. A numerical integration is performed and scaled with natural constants and the transmission of the window at the respective wavelength.

RESULTS

Figure 4 (a) shows the measured mass spectrum, i.e. the ion current in the region of WF_5^- recorded in FC2 as a function of the magnetic field of the sector magnet. The mass resolution of the apparatus during this experiment was $m/\Delta m > 600$. A newly inserted cathode only showed the expected WF_5^- mass peaks at 277 u, 278 u, 279 u and 281 u, corresponding to the pentafluorides of ^{182}W , ^{183}W , ^{184}W and ^{186}W , during the first minutes of operation. With time a considerable amount of oxidized molecules were created in the ion source and the mass spectrum became contaminated with WF_4O^- and $WF_3O_2^-$ ions. These contributions affect the WF_5^- peak at mass 278 u, hence the measurements were performed at masses 279 u and 281 u, representing anyhow the species with the highest natural abundance. A fit was applied to the observed mass spectrum to verify the correctness of the assumption of the oxidized contamination alone. As shown in Figure 4 (b), it matches the shape of the mass spectrum, reproducing the relative abundance for each mass.



FIG. 4. (a) Mass spectrum of the tungsten cathode in the mass region around the WF_5^- molecules, recorded in FC2. The peak assignment is according to the color coded fit of (b). (b) Simulated mass spectrum with WF_5^- , WF_4O^- and $WF_3O_2^-$. At this point in time the observed abundance ratio for the three different molecules was 21.5 % : 35.5 % : 43 %, respectively.

The recorded mass spectrum for the hafnium cathode shows, in contrast to tungsten, no contamination. The peaks seen in Figure 5 (a) agree perfectly with the natural abundances of the hafnium isotopes (b). Photodetachment cross section measurements were performed

at the 275 u peak to maximize the ion current. As mentioned before, neutrals created by photodetachment arrive in a fixed time window after the laser pulse and show a Gaussian distribution in time on top of the evenly distributed background counts. Even after several hours of data acquisition it was still not possible to detect a signal, i.e. see a peak in the time distribution of the neutral counts. Hence, only an upper limit of the cross section could be obtained.



FIG. 5. (a) Mass spectrum of the hafnium cathode in the mass region around the HfF_5^- molecules, recorded in FC2. The relative height of the peaks agree with the natural abundances of hafnium isotopes listed in (b).

In general, one of the remaining unknown parameters using the animated beams method is the detection efficiency of the neutral particle detector. Using an ITO coated glass plate of the same type as in the neutral particle detector as a Faraday cup, we compared the ion current with positive and negative suppression voltage on a collecting electrode. In this way it was possible to estimate the average number of electrons released per impact of a 6 keV ion on the glass plate with a relative statistical error of about 1 %. A survey on ions from over 30 atomic and molecular species showed that the secondary electron yield is strongly dependent on the ion species. The electron yield varied from 0.9 to 1.7 for most species, while a few lighter ion species showed a yield as high as 3. No further systematics on the ion mass have been found. The copper isotopes at 63 u and 65 u as well as the silver isotopes at 107 u and 109 u show a rather small yield with slightly less than one electron per impinging ion in average. Secondary electron yields for both ions of interest here, i.e. the pentafluorides of tungsten and hafnium, amounted to about 1.5 and 1.3, respectively. To ensure a reasonable detection efficiency for both, the element copper, which is easily producible with high currents in the sputter source, was chosen as test element and the photodetachment cross section of 63 Cu⁻ was measured and plotted versus the kinetic energy. For this measurement a shielding tube was installed around the crossed beams interaction region between the two apertures. By applying a positive potential on this tube it is possible to increase the overall ion beam energy from 6 up to 12 keV without changing any of the upstream ion optics parameters. Neutralized particles are unaffected by the ground potential aperture behind the interaction region and travel on with increased kinetic energy towards the detector. The measured cross sections, as given in Figure 6, show a saturation behavior which indicates that a detection efficiency close to 100% is reached at about 12 keV. Every ion with a secondary electron yield similar or higher than copper should thus also exhibit a detection efficiency close to unity at that kinetic energy. This is the case for both WF₅⁻ and HfF₅⁻ as stated above.

Assuming a Poisson distribution for the emission of secondary electrons the measured cross section σ_{exp} should be systematically too low, with the probability of releasing no electron on ion impact P(0) reducing the detection efficiency to 1 - P(0). Taking the average electron yield of copper at 6 keV as parameter λ in a Poisson distribution, there is a non-zero probability for zero electrons to be released. The calculated value of P(0) at 6 keV agrees perfectly with the ratio of the measured cross sections at 6 and 12 keV.

Photodetachment cross sections of HfF_5^- and WF_5^- were measured using the animated crossed beams method at the two different photon energies of 32051 and 37594 cm⁻¹, corresponding to 312 and 266 nm, respectively. The ion beam was accelerated to an energy of 12 keV to ensure a reasonable detection efficiency. More absolute cross sections were obtained in the collinear beams geometry at the three different photon energies of 22000, 23200, and 27184 cm⁻¹, corresponding to wavelengths 455, 431, 355 nm, by measuring the neutral particle count rate and applying Equation (3). The wavelengths of 355 and 266 nm correspond to the third and fourth harmonic of a Nd:YAG laser, while the other wavelengths were chosen to obtain a qualitative shape of the cross section versus wavenumber in that energy region. Figure 7 shows results given as absolute cross sections obtained by collinear and animated crossed beams method versus photon wavenumber for both HfF_5^- and WF_5^- . However, it is



FIG. 6. The photodetachment cross section for 63 Cu as function of ion beam energy. Saturation at high kinetic energies indicates full detection efficiency of the neutral particle detector.

only the data obtained with the crossed beams geometry where we claim to have measured absolute cross sections. The data taken with the collinear beam geometry is only shown to display the general trends of the cross sections. The cross section at lower photon energies is below or in the order of the detection limit for the crossed beams geometry. Therefore, the collinear beams geometry was used to measure these data. Above photon energies of 28200 cm⁻¹ the ITO glass plate in the neutral particle detector absorbs a significant portion of the laser light. Correspondingly, only the crossed beams geometry was used for the data points at 32051 cm⁻¹ and 37594 cm⁻¹. However, since the sensitivity is smaller, the low cross section of HfF_5^- was not measurable with the crossed beams geometry and only an upper limit in the order of $2 \cdot 10^{-20}$ cm² could be determined.

For WF_5^- the data presented in Figure 7 are in reasonable agreement with an exponential increase in cross section with photon energy. As we expect a similar behavior for HfF_5^- , a significant systematic error in the collinear beams measurement for HfF_5^- is assumed. Of special interest for the comparison between the two pentafluorides WF_5^- and HfF_5^- are their cross sections at 266 nm, where WF_5^- reaches the highest observed value. This data point was



FIG. 7. The photodetachment cross section for WF_5^- and HfF_5^- as measured at different photon energies. As shown in the spectra, the WF_5^- molecule exhibits a significantly higher cross section than the HfF_5^- molecule indicating lower vertical detachment energy for WF_5^- . On the left side of the figure, values obtained by using the collinear beams method are shown. On the right-hand side results of the animated beams method are plotted. The hatched area corresponds to the region where the cross section is too small to be detected in the noise level when measuring HfF_5^- .

therefore measured with high precision. The resulting cross sections are given in Table I. The

Molecule	Cross section
WF_5^-	$2.8(3) \cdot 10^{-18} \text{ cm}^2$
HfF_5^-	$< 2 \cdot 10^{-20} \ {\rm cm}^2$

TABLE I. Absolute photodetachment cross sections for WF_5^- and HfF_5^- at a wavelength of 266 nm.

uncertainty in the WF_5^- photodetachment cross section amounts to one standard deviation error calculated as the root square sum of the statistical and systematic errors present in the experimental setup. For the collinear beams geometry, the main contribution to the error is the uncertainty in overlap between laser and ion beam in the interaction region. Other errors, like the uncertainty in ion current and laser pulse energy are considerably smaller. While the relative precision is rather good, the absolute value should be considered as an estimate of the order of magnitude. Therefore we do not give error bars for the data obtained using the collinear beams geometry. For the crossed beams geometry, the statistical error due to low signal levels is dominating. Using the animated beams method described above eliminates most of the systematic errors. It consists mainly of the uncertainty in laser pulse energy in the interaction region and the uncertainty due to numerical integration which together are estimated to be about 10%. The statistical error is determined by the average number of neutrals detected (signal plus noise) as well as the average number of background counts only. The total relative error is estimated to be about 12%.

DISCUSSION

The feasibility of laser isobar suppression for ¹⁸²Hf in a correspondingly adapted AMS machine depends on the availability of commercial lasers that can deliver the right wavelength and high power. A reliable solution for the optical filtering in an AMS machine would be to use a harmonic frequency output of a Nd:YAG laser. These lasers deliver light with wavelengths of 1064 nm, 532 nm, 355 nm or 266 nm. The present data show that the photon energy at 355 nm (28169 $\rm cm^{-1})$ is too small to neutralize $\rm WF_5^-$ efficiently. Laser radiation at 266 nm (37594 cm⁻¹), however, might be sufficient to reach the VDE of WF_5^- . The measured cross section value for WF_5^- of $(2.8 \pm 0.3) \cdot 10^{-18} \text{ cm}^2$ at 266 nm is rather promising and could lead to a reasonable depletion of this contamination in the initial AMS negative ion beam. Using an ion cooler setup as demonstrated by Liu *et al.* [18] would enable an interaction time of approximately 30 ms for the heavy ions of interest here. There are commercial 266 nm lasers with output powers of 3W operating in a quasi-cw mode with a repetition rate of more than 20 kHz. This repetition rate is sufficiently high to approach a 100% duty cycle in an AMS machine that utilizes an ion cooler. A back of the envelope calculation of the suppression factor of the species can be made using the measured cross sections. Assuming that the size of the laser and ion beams is 2 mm and the losses in guiding the laser beam into the ion cooler is 20%, a depletion factor of 99.98% may be estimated for WF_5^- . The same calculation for HfF_5^- , using $2 \cdot 10^{-20}$ cm² as the upper limit for the cross section, yields a depletion factor that is less than 6%. This is consistent with the calculations of Chen *et al.* [12] in confirming that the ground state of HfF_5^- can not be detached with photons of 266 nm wavelength (4.7 eV photon energy).

At the level of the detection limit of AMS facilities, trace contaminations with other molecules at the same mass number can become a dominating background contribution. Then there are two possibilities. Either the considered molecule has a lower VDE than 4.66 eV (266 nm), in which case it will be photodetached efficiently. If it has a higher VDE photodetachment isobar suppression will not work for this molecule. However, this effect only becomes relevant if the background suppression has already been improved by several orders of magnitude.

Correspondingly, additional isobar suppression using optical filtering by laser photodetachment could become a useful method to deplete ${}^{182}WF_5^-$ in studies of ${}^{182}HfF_5^-$. However, as a prerequisite it must be demonstrated that the molecules will behave the same way within an ion cooler. Therein, the excited vibrational states will, at least to a large extent, be cooled down to the vibrational ground state. Thus, the photon energy of the laser must be sufficiently large to photodetach the WF₅⁻ molecules from the ground state. The experiments discussed here do not necessarily prove that this is the case.

Finally, it should be pointed out that we have only discussed the possibility to deplete WF_5^- ions, which is expected to be the primary isobaric contaminant when detecting HfF_5^- . There could, of course, be other interfering molecules at the same mass as $^{182}HfF_5^-$, such as $^{182}WF_4^{18}OH^-$. These ions could be the dominant background once the level of WF_5^- has been reduced. As described in this paper, the filtering method using 266 nm laser light will work for any molecule that has a VDE lower than 4.66 eV. It should then be pointed out that 4.66 eV is a large VDE for a molecular negative ion (Rienstra-Kiracofe et al. [19] tabulated the EA of more than 1000 molecules, and only 9 have EAs larger than 4.66 eV). It is hence quite likely that the optical filtering will work also for other interfering molecules. The next step, which will give the final answer of the applicability of the laser optical filter method for this case, is to perform the same experiment in an ion cooler at the detection levels achievable by an AMS facility.

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- C. Vockenhuber, M. Bichler, R. Golser, W. Kutschera, A. Priller, P. Steier, and S. Winkler, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 223, 823 (2004).
- [2] K. Knie, G. Korschinek, T. Faestermann, E. Dorfi, G. Rugel, and A. Wallner, Physical Review Letters 93, 171103 (2004).
- [3] C. Fitoussi, G. M. Raisbeck, K. Knie, G. Korschinek, T. Faestermann, S. Goriely, D. Lunney,
 M. Poutivtsev, G. Rugel, C. Waelbroeck, *et al.*, Physical Review Letters **101**, 121101 (2008).
- [4] O. Forstner, H. Gnaser, R. Golser, D. Hanstorp, M. Martschini, A. Priller, J. Rohlén, P. Steier,
 C. Vockenhuber, and A. Wallner, Nuclear Instruments and Methods in Physics Research
 Section B: Beam Interactions with Materials and Atoms 269, 3180 (2011).
- [5] S. Winkler, L. K. Fifield, S. Tims, and C. R. Morton, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 259, 256 (2007).
- [6] D. Berkovits, E. Boaretto, G. Hollos, W. Kutschera, R. Naaman, M. Paul, and Z. Vager, Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 281, 663 (1989).
- [7] D. Berkovits, E. Boaretto, G. Hollos, W. Kutschera, R. Naaman, M. Paul, and Z. Vager, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 52, 378 (1990).
- [8] Y. Liu, J. Liang, and J. Beene, Nuclear Instruments and Methods in Physics Research Section
 B: Beam Interactions with Materials and Atoms 255, 416 (2007).
- [9] A. Lindahl, D. Hanstorp, O. Forstner, N. Gibson, T. Gottwald, K. Wendt, C. C. Havener, and Y. Liu, Journal of Physics B: Atomic, Molecular and Optical Physics 43, 115008 (2010).
- [10] P. Andersson, A. Lindahl, D. Hanstorp, C. C. Havener, Y. Liu, and Y. Liu, Journal of Applied

Physics 107, 026102 (2010).

- [11] K. G. Dyall, The Journal of Physical Chemistry A 104, 4077 (2000).
- [12] H. Chen, P. Andersson, A. O. Lindahl, and D. Hanstorp, Chemical Physics Letters 511, 196 (2011).
- [13] E. P. Wigner, Physical Review **73**, 1002 (1948).
- [14] C. Diehl, K. Wendt, A. Lindahl, P. Andersson, and D. Hanstorp, Review of Scientific Instruments 82, 053302 (2011).
- [15] D. Hanstorp, Measurement Science and Technology 3, 523 (1992).
- [16] P. Defrance, F. Brouillard, W. Claeys, and G. Van Wassenhove, Journal of Physics B: Atomic and Molecular Physics 14, 103 (1981).
- [17] J. Blangé, X. Urbain, H. Rudolph, H. Dijkerman, H. Beijerinck, and H. Heideman, Journal of Physics B: Atomic, Molecular and Optical Physics 29, 2763 (1996).
- [18] Y. Liu, AIP Conference Proceedings 1390, 505.
- [19] J. Rienstra-Kiracofe, G. Tschumper, H. Schaefer, S. Nandi, and G. Ellison, Chemical Reviews 102, 231 (2002).