CERN-INTC-2017-031 / INTC-I-178
18/01/2017

Letter of Intent to the ISOLDE and N-Tof Experiments Committee (INTC)

Extraction of Refractory Elements by Laser Induced Breakup and ionisation of Molybdenum Carbonyls

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Abstract

With the ongoing development of new target techniques the extraction of refractory metals at ISOLDE has come within reach. At thick-target facilities such as ISOLDE the extraction of refractory species is challenging and has to be achieved by formation of a volatile molecules. Metal carbonyl $M(CO)_x$ compounds are a promising approach for a range of refractory metals such as molybdenum, technetium, ruthenium, rhodium, osmium and iridium [1] . For this LOI we will focus on molybdenum hexacarbonyl as a representative test case. One of the crucial

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factors during RIB production is the ionisation process which should be fast, efficient and enable ion extraction in a single charge state with low energy spread. The low binding energy of the carbonyl groups to the center metal atom is compatible with a the following ionisation procedure: non-resonant laser-induced dissociation of the carbonyl molecules followed by resonance laser ionisation of neutral fragments. The feasibility of both processes has been shown separately for $Mo(CO)_6$ in offline studies. As a next step we aim to investigate the combined process using the capacity of RILIS at ISOLDE with a dedicated target and ion source setup. We therefore request a total of 6 shifts during the offline period.

Requested shifts: 6 shifts during shutdown period, resources of workshop required

1 Introduction

The extraction of refractory elements with boiling point beyond 2000 °C is a long standing problem for thick-target ISOL facilities due to the reliance on diffusion of radioisotopes out of the target material and a random walk process through the target and transfer line setup. Losses due to condensation and chemical reactions can therefore occur. In some cases (e.g. C, B, Ti) this has been tackled by extracting these elements as volatile fluoride or oxide molecules [2][3]. For elements such as molybdenum, technetium, ruthenium,rhodium, osmium and iridium another approach is possible since these readily form carbonyl compounds which are known to be volatile at low temperatures. The formation of these molecules requires a dedicated target setup which is currently under development at ISOLDE as part of the PhD project of Jochen Ballof. A key process in the production of radioactive ion beams is the ionisation of these molecules, or the breakup of the molecule followed by ionisation and extraction of the species of interest as a singly charged ion. For ionisation of molecules usually FEBIAD or ECR ion sources are required. This is due to the fact that the maximum ionisation cross section for electron impact ionisation is typically at 4-5 [4] times the ionisation potential (this corresponds to approximately 70 eV for molecules such as CO, BF_3, TiF_4). However, the binding energies of the carbonyl groups to the core atom are as low as 1.5 eV[5]. This corresponds to a breakup energy within the accessible photon energy range of the RILIS laser system. Laser induced dissociation of carbonyl molecules with UV light is widely used in material science, where coatings of Mo are formed by exposing samples to UV light in a $Mo(CO)_6$ atmosphere [6]. Once all carbonyl groups are dissociated from the center molybdenum atom, the neutral molybdenum fragment with an ionisation potential of 7.092 eV [7] can be resonantly laser ionised. The figures below show a schematic of an ion source using a ns-range time delay between a first pulse of UV light and the laser pulses of the resonance ionisation scheme. Carefully synchronized laser pulse timing is essential to ensure that the neutral atoms emerging from the molecular breakup stage do not have time to leave the path of the ionisation lasers. Molecules entering the ion source volume will be dissociated on axis and the atomic molybdenum fragments resonantly ionised

thereafter. It is reasonable to expect a high extraction efficiency (close to 100%) of laser-ions if an ion source volume such as the one shown in figure 1 is used.

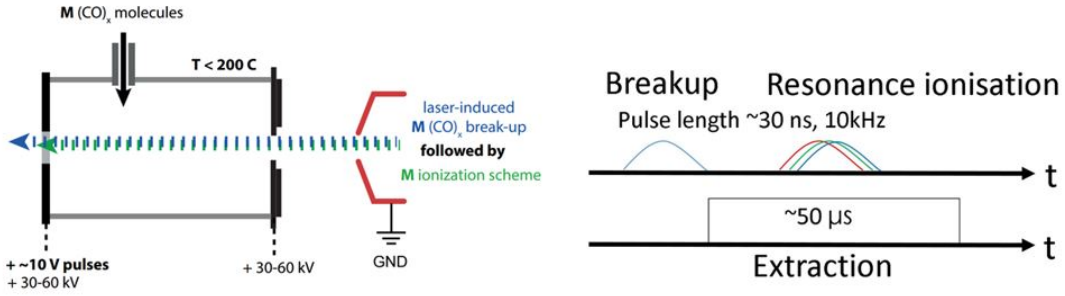

Figure 1: The figure shows a schematic of the target and ion source setup (l.) in RILIS mode. A non-resonant UV pulse is directed into the ion source to dissociate carbonyl groups from the center molybdenum atom. Immediately after the molybdenum fragments are ionised using a resonant ionisation scheme(r.).

The proposed laser dissociation and ionisation approach offers several crucial advantages over an approach based on electron impact dissociation and/or ionisation:

1. Laser-induced molecular breakup is pulsed and occurs on-axis, far from the cavity walls.
2. ionisation takes place immediately after molecular breakup: the neutral atom does not come into contact with the cold surfaces before having at least one opportunity to be ionized. The required ns-range timing synchronization is easily achievable.
3. The ion source does not rely on electron emission and therefore does not require any high temperature components that may cause thermal dissociation of the COx compound.
4. A high ion survival probability is achievable using a simple ion source design.
5. For a single interaction (set of laser pulses) the probability of laser ionization is expected to be greater than the probability of molecular breakup - which is a prerequisite for a high overall efficiency. Conversely, we expect that, for an electron impact based approach, the molecular break-up efficiency is likely to be higher than the ionisation efficiency, which would result in a higher efficiency loss factor due to wall sticking.

2 Physics interest in refractory metal beams

The physics interest in radioactive isotopes of refractory metals is manifold. Some examples are:

a.)RP-process

The availability of radioactive beams of ^{86}Mo would allow to study ^{86}Nb. The very neutron-deficient molybdenum isotopes and their electron-capture niobium daughters are traversed by the rapid-proton-capture (rp-) process of nucleosynthesis, which is thought to occur in the accretion disks of binary systems [8]. Long-lived isomeric states present in the neutron-deficient niobium isotopes can potentially affect the rp-process matter flow in the region and their properties (excitation energy, decay half-life) are a required input for network calculations. In particular, the initial claim of a 56 s isomer in ^{86}Nb [9] has not been confirmed in subsequent experiments [10] and is believed to be the result of contamination of the ground-state activity by that of another ^{86}Nb isomer, of unknown half-life or energy [11].

b.) Targeted radionuclide cancer therapy

After a proof of concept for the case of molybdenum the technique of extracting refractory elements as carbonyls can be expanded to other elements. For example osmium is an interesting candidate for targeted radionuclide therapy. DNA targeting Os compounds could act as vectors for Auger therapy with high specific activity ^{191}Os. ^{191}Os has great potential as therapeutic nuclide because among all beta emitters considered for medical application it has the lowest average electron energy and thus a very short mean free path for optimum targeting and minimum damage to healthy tissue [12].

Although the beam intensity considerations described in the following section are not conducive for on-line production of intense refractory metal beams for medical applications, the methods developed within this LOI may prove useful for future extraction and separation of reactor-produced samples[13].

c.) Laser spectroscopy

During the last decade, WM-RILIS collaboration carried out over 15 experimental campaigns in the lead region at ISOLDE, and completed IS/HFS measurements for long isotopic chains of Z=79-85 elements: Au, Hg, Tl, Pb [14], Po[15], At [16] and, in July 2016, Bi isotopes [17]. The neutron-deficient isotopes in this region provide some of the most spectacular examples of shape staggering and shape coexistence around N=104 As a natural continuation of this program, we wish to initiate a pioneering program for HFS/IS/radii measurements further below Z=82, in particular for the refractory elements such as Ta-Ir, which are expected to provide further interesting results on shape coexistence at low energy, and which were hardy studied so far by the laser spectroscopy.

In particular, our recent HFS/IS and nuclear spectroscopy studies of the Au isotopes showed a strong need for better understanding of the daughter Ir isotopes, for which no laser spectroscopy data exist and which can be developed within this LoI. The In-source RIS technique is the most sensitive spectroscopy method used at ISOLDE. Important results have been obtained with beam intensities as low as 0.01 ion per second. This application of refractory metal ion beams at ISOLDE is therefore still feasible, even if the eventual efficiency of overall ion beam production is lower than expected. This is a unique topic, not paralleled by any other research groups in the world.

3 Evaluating the efficiency requirements

To evaluate the ion source efficiency requirements for our proposed method of extracting M^+ beams from $M(CO)_x$ neutrals, the following components of the beam production must be considered:

Isotope recoil from target; $Mo(CO)_6$ formation before wall contact; Molecule transport to ion source; Laser-induced molecular breakup; Resonance ionisation; Ion extraction and transport.

For this LOI we intend to test the latter three of these steps of the Mo^+ beam production.

Refractory metal beams are readily available from thin target gas cell facilities such as the JYFL IGISOL. This is because reaction products are ejected immediately from the target foil after the driver beam impact, reduced to a single positive charge state in the collisional gas environment, and then extracted by differential pumping with little chemical dependence. The disadvantage of such an approach is the low in-target production rate imposed by the necessity of using a thin target and low intensity driver beam. The result is that the beam intensity for Mo isotopes is expected to be in the range of $10^3 - 10^4$ ions per second. At ISOLDE, the target made of rolled thin uranium foils would be used for the production of Mo isotopes which are generated by fission. The recoil effect allows propagation through the uranium foil and volatile metal carbonyl complexes are synthesized in-situ by thermalizing suitable transition metal atoms in carbon monoxide atmosphere. The latter is removed subsequently by cryogenic gas separation.

Based on FLUKA calculations, we estimate the in-target production rate for ^{105}Mo in a certain geometry containing 25 μm uranium foils to be in the order of $4 \cdot 10^8 \frac{1}{\mu C}$. Further stopping simulations using SRIM data indicate, that 11% of the fission fragments reach the foil surface and thereof 51% are stopped in a 1 bar carbon monoxide gas atmosphere. The chemical yield of carbonyl formation was investigated by Even et al by comparative transport studies. [1] Conservatively, a yield of 50% can be assumed for Mo based on this data, assuming another 50% efficiency for the gas separation results in a pre-ionisation yield in the order of $6 \cdot 10^6 \frac{1}{\mu C}$. For the extraction of competitive Mo^+ ion beams we can therefore afford losses of up to 3 orders of magnitude in the ion source volume itself, neglecting decay losses.

4 Current status

In preliminary offline tests conducted by the ISOLDE ISBM working group both laser induced breakup of $Mo(CO)_6$ and resonance ionisation of molybdenum have been achieved separately. In October 2016 dissociation of molybdenum carbonyl was achieved using the fourth harmonic of a Nd:YAG laser in a customized $Mo(CO)_6$ vapor vacuum assembly. A resonance ionisation scheme was determined in a separate off-line test at ISOLDE using the atomic vapour originating from the cathode of a VADIS ion source in November 2016. Having demonstrated these two prerequisites independently, the next step is to combine these processes in a further offline test using a customised laser breakup and resonance ionisation volume.

4.1 Laser induced molecular break-up

Figure 2 shows the absorption spectrum of $Mo(CO)_6$ (left figure, in red) and the achievable wavelengths by generation of the second, third and fourth harmonic of a Nd:Yag laser. It was shown that a breakup of $Mo(CO)_6$ can be achieved with the available 266 nm light. The results of this measurement are shown in figure 2 on the right. As expected from the absorption spectrum there is no effect when exposing the molecules to laser light with wavelengths of 355 nm and 532 nm. However, when exposing the molecules to laser light with a wavelength of 266 nm the signal of Mo drops significantly. This indicates a successful dissociation of the carbonyl groups from the $Mo(CO)_6$ molecule. With a laser power of 700 mW we are able to observe a drop of the Mo signal of 10-15 %. However with the higher laser powers available at RILIS a higher efficiency of the breakup can be expected. Furthermore, since this is a multiphoton process, we expect that, for a given laser power, considerable efficiency gains will be made by tuning a frequency tripled TiSa to the wavelength corresponding to the highest dissociation cross section (250 nm in figure 2).

4.2 Resonance ionisation

As indicated in figure 1 directly after the breakup of the molecule, laser pulses for the resonance ionisation of the neutral Mo fragments will be sent into the ion source. This has to happen before the fragments migrate from the location of breakup and out of the active volume for laser ionisation. To achieve efficient ionisation of molybdenum, a resonant ionisation scheme was recently developed at RILIS and several auto ionising states were identified (figure 3).

5 Experiment setup

Resonance laser ionisation of molybdenum combined with prior molecular breakup requires a dedicated laser setup with a total of 6 lasers. The required laser setup consists of:

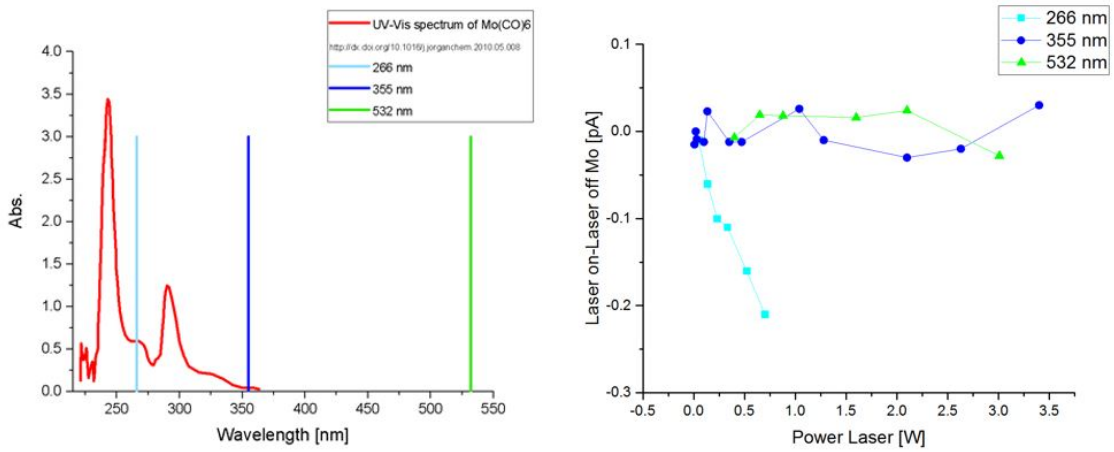

Figure 2: (l.) Absorption spectrum of $Mo(CO)_6$ molecules and achievable wavelength by generation of second, third and fourth harmonic of a Nd:Yag laser. (r)The reduction of a Mo signal in a quadrupole mass spectrometer due to exposure of $Mo(CO)_6$ to these wavelengths was tested. As expected dissociation of the molecule by exposure with 266 nm light was observed.

- Fourth harmonic of Nd:Yag laser, 266nm, or 3rd harmonic TiSa laser
- Resonant ionisation scheme: 3 pump lasers+3 tuneable lasers as indicated in fig 3

Such a setup is currently not available at the offline separator and thus the resources of the RILIS laboratory at ISOLDE are required. To conduct the experiment a dedicated prototype ion source setup is needed. As molybdenum carbonyls are thermally unstable at temperatures above approximately 150 °C a cold cavity made of an inert material such as quartz glass or PTFE with a cold pre-extraction electrode is required. For the alignment of the laser into the source an iris should be placed behind the rear end of the ion source, followed by a power meter. Furthermore we request the installation of two mass markers, one with a calibrated, and one with an excess sample of $Mo(CO)_6$. In this way a qualitative study could be performed followed by a measurement of the release efficiency. For the experiment a total of 6 offline shifts at the GPS separator with access to the central beam line is requested. This will enable the use of the installed MCP detector for time resolved release studies. For this experiment no protons are required.

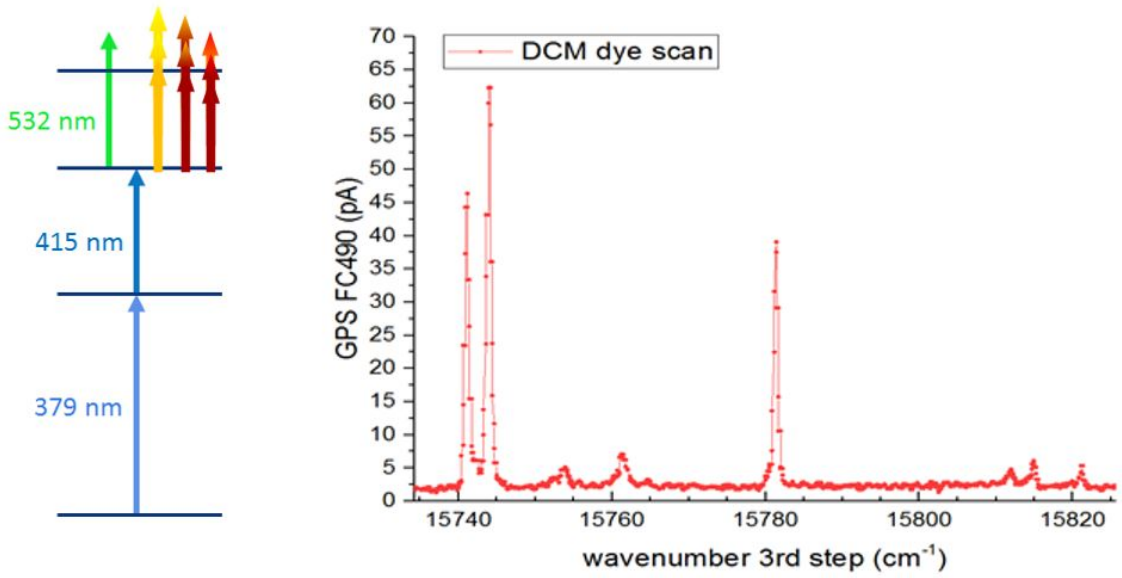

Figure 3: (l) Resonant laser ionisation scheme for Mo with alternative third steps. (r) Besides tests with a non resonant third step with 532 nm scans for auto ionising states using the wavelength range of DCM were performed. Several auto ionising states were identified with higher ionisation efficiencies in comparison to 532 nm light.

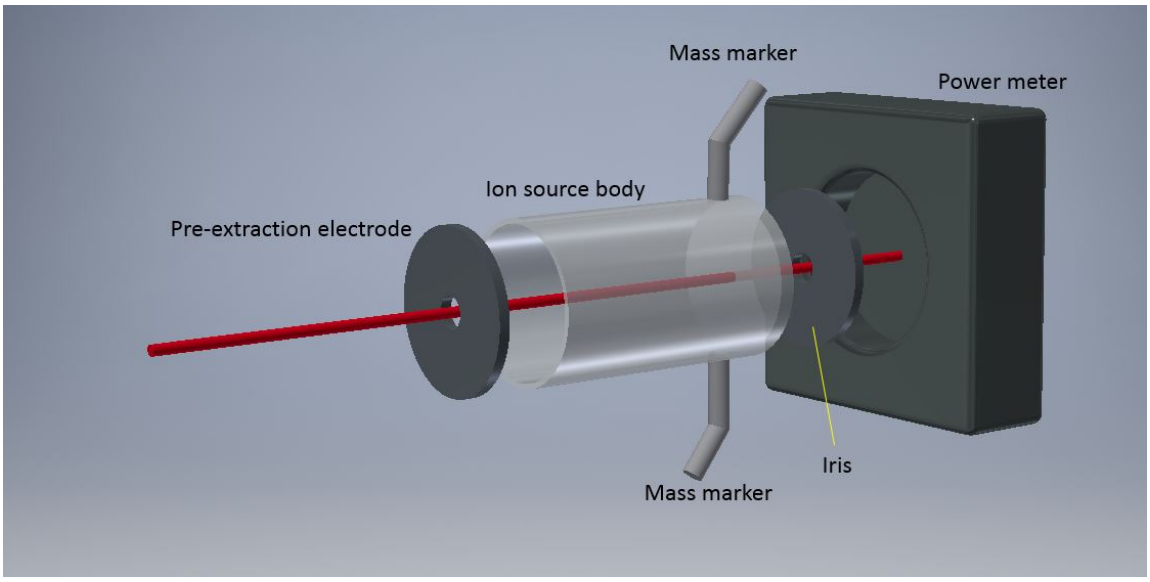

Figure 4: Proposed setup for the investigation of ionisation of $Mo(CO)_6$. To cope with the thermal instability of $Mo(CO)_6$ a cold cavity with chemically inert materials should be used. A pre-extraction electrode assures the efficient extraction after ionisation. The backside of the cavity should ressemble a window to allow the laser beams passing trough. For easier alignment of the laser beams an iris followed by a power meter [18]should be installed after the cavity. Two mass markers provide $Mo(CO)_6$ for the optimisation of the ionisation process and efficiency measurements.

6 Summary

We aim to investigate a method of laser induced breakup of molybdenum hexacarbonyl followed by resonance laser ionisation of elemental molybdenum fragments at ISOLDE. The measurement will allow us to determine the feasibility of this approach and to establish some insight into the overall efficiency. This LoI will also provide important elements for the production of $Mo(CO)_x$ molecular ions. We request a total of 6 offline shifts at the GPS separator with an ion source setup described in 5.

7 Acknowledgment

The authors would like to thank Vladimir Manea for the discussions on the physics case.

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