DEVELOPMENT OF RESONANT PHOTOIONIZATION MASS SPECTROMETER FOR DETERMINATION OF ISOTOPIC COMPOSITIONS OF KRYPTON.
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Introduction: Krypton isotope structures in extraterrestrial material record the physical properties of s-process sites and the irradiation history of the early solar system.

The isotopic structure of s-process krypton in presolar SiC grains is of particular interest because it is affected by two branching points (where an isotope's lifetime against neutron capture is comparable to its β-decay half-life). The branching ratio at ^{79}Se is sensitive to temperature as well as neutron flux since the nucleus has a low lying excited state, while that at ^{85}Kr depends only on neutron flux. Potentially, analyses of krypton in individual SiC grains thus allow both temperature and neutron flux of s-process to be investigated.

Cosmic ray spallation reactions cause a characteristic enrichment of specific noble gas isotopes in minerals [1-2]. A record of the irradiation environment of the early solar system may be accessible through analysis of the Kr system in irradiated chondrules.

To address these issues we are developing an ultrasensitive instrument for Kr isotopic analysis.

Experimental Procedure: The resonance photoionization mass spectroscopy method will be used for detection of Kr atoms. The development of the mass spectrometer benefits from its prototype 'RELAX (Refrigerator Enhanced Laser Analyser for Xenon)' [3] that has successfully been used for determination of isotopic ratios of Xe in various extraterrestrial samples [4-5]. As a result of step-heating or laser probe the atoms can be released from sample into a mass spectrometer volume where condensation at the localized cold spot (~80 K for Xe atoms) occurs. After desorption of condensate by 1064 nm Q-switched Nd:YAG laser Kr atoms are ionized by a resonant photoionization laser system and detected by electron multiplier or MCP detector. For calibration and adjustment purposes the known aliquots of air contained 10^5-10^6 atoms of interest can be used.

The Kr photoionization scheme (**Fig.1**) implies resonant excitation from ground state by 116.5 nm VUV light generated using four-wave non-linear mixing in Xe. The second resonant step is performed by 558.1 nm dye laser pumped by second harmonic (532 nm) of pulsed Nd:YAG laser. The part of fundamental 1064 nm light of a same Nd:YAG laser is used for ionization step.
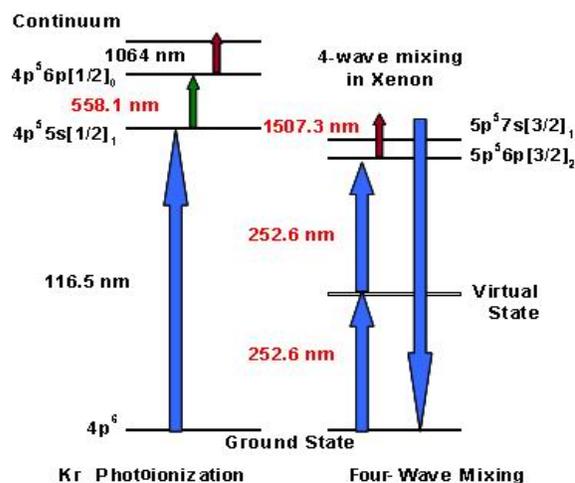

Figure 1: Kr photoionization scheme and levels used for four-wave mixing in Xe

Because of strongly allowed first VUV transition used (measured oscillator strength of ~0.2 [6]) the power density of only ~700 W/cm^2 [7] is required for transition saturation. For comparison 10^{10} W/cm^2 is needed to saturate a nearby two-photon allowed transition. To reach such a power density a strong focusing of laser light is required that would reduce the selectivity and efficiency due to non-resonant photoionization processes and decrease of saturated ionization volume.

VUV generation by four-wave mixing in Xe and Kr photoionization: The interaction of four coherent optical fields through the third order non-linear susceptibility known as four-wave mixing is well studied [8]. The application of this process for the resonant photoionization of Kr has been demonstrated at Institute of Rare Isotope Measurement, University of Tennessee [9].

In our experiments two ~0.5 mJ beams of 252.6 nm (obtained after doubling of 505 nm dye laser beam in BBO crystal) and 1507.3 nm (mixing of 632 nm dye laser beam with 1064nm of Nd:YAG laser in Lithium Niobate crystal) interact while passing through the small (180 mm x 19 mm) cylindrical gas cell. As a non-linear medium a Xe-Ar mixture is used (**Fig.1**). Because Xe is negatively dispersive and Ar is positively dispersive near 116 nm spectral region [10], the intensity of generated VUV light will peak if phase

matching condition $(\Delta k=2k_{(252.6nm)}+k_{(1507nm)}-k_{(116.5nm)}=0$, where $k(\lambda_i)$ is a wave vector depending on refractive index) is fulfilled.

Our mixing cell is attached to the ion source of mass-spectrometer via lithium fluoride viewport. From other side there are two home made cells divided by magnesium fluoride viewports and filled with ~10 Torr of nitric oxide (NO) and ~20 Torr of Kr respectively. These cells work as proportional counters and serve to monitor generation of VUV and Kr ionization. All photoionization and mixing laser beams are synchronized and made collinear.
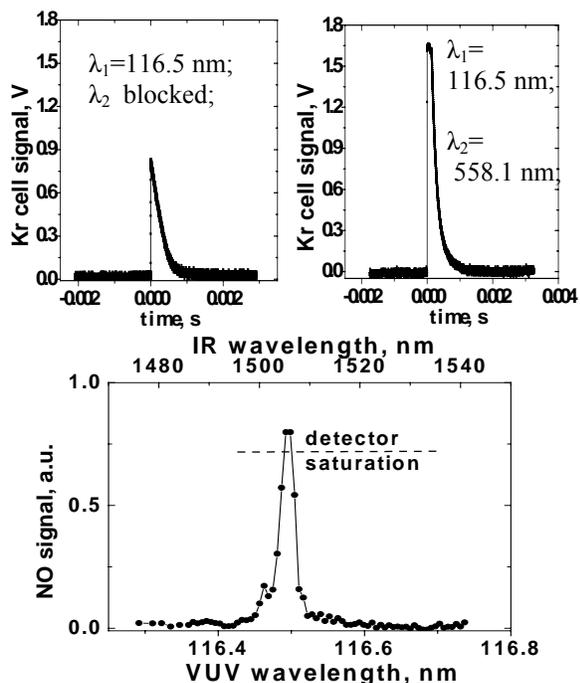

Figure 2: Kr cell photoionization signal with and without 558.1 nm beam and intensity of VUV produced.

The optimal ratio of partial pressures obtained within our experiments is $P_{Ar}/P_{Xe}\approx9$ ($P_{Xe}\approx50$ Torr; $P_{Ar}\approx450$ Torr) (**Fig.2**). At this value the intensity of generated 116.5 nm light is at maximum. Tuning of the VUV beam can be achieved by changing the wavelength of the IR laser beam. However if detuned more than 15 nm from 1507 nm the phase matching condition is not fulfilled and no VUV is produced. As soon as 116.5 nm light is generated the Kr in the monitoring cell becomes ionized, even when 558.1 nm and 1064 nm beams are blocked. Addition of only 558.1 nm wavelength increases the Kr ionization in the cell to such a level that in some cases the signal saturates.

Mass Spectrometer capabilities: At current stage of development we use Xe samples (~10^5 atoms) to optimize the mass-spectrometer and laser system parameters. The atoms are excited from ground state by two-photon absorption (252.6 nm, as used for frequency mixing) followed by the same wavelength ionization.

Because of high power density required for saturation of two-photon transition the possibility of using the second laser to increase the ionization efficiency was investigated. Using Xe reference cell (P_{Xe}=100 Torr) two resonant transitions (558.25 nm and 562.21 nm) starting from two-photon absorption level ($5p^5(^2P^0_{3/2})6p$, J=2) were found. In spite of gain in efficiency archived (the Xe signal increased by factor of ~4) it was too low to be used for Xe sample analysis in our current configuration.

The required power density is reached by focusing the UV laser beam into an ion source. The TOF spectra show good mass resolution; the Xe isotopic ratios correspond to the natural values (**Fig.3**).
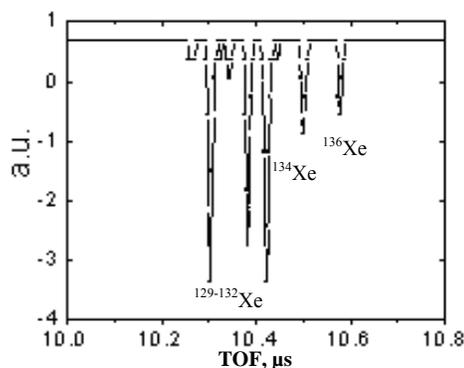

Figure 3: TOF spectrum of Xenon.

Conventional mass spectrometers typically require samples in excess of 200 mg for ^{81}Kr-Kr exposure age determinations — this is substantially more material than found in individual chondrules and SiC grains. The efficiency of proposed Kr photoionization scheme will allow analyzing the samples down to ~1 mg that makes such an analysis possible.

References:

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