

Rendiconti Accademia Nazionale delle Scienze detta dei XL Memorie e Rendiconti di Chimica, Fisica, Matematica e Scienze Naturali 141° (2023), Vol. IV, fasc. 2, pp. 341-350 ISSN 0392-4130 • ISBN 978-88-98075-56-0

Laser Isotope Selective Excitation techniques for efficient Atomic and Molecular Separation of isotopes in fusion and medical applications

ANTONIO PALUCCI¹ – PIETRO AGOSTINI² – PAOLO FAVUZZA² ANTONIO RASPA⁴ – FLAVIO CICCONI³*

- ¹ ENEA-FSN-TECFIS-DIM Frascati, Retired; OrcID 0009-0006-9442-1544 E-mail: palucci.antonio@gmail.com
- ² ENEA-FSN-ING Brasimone;
- ³ ENEA-FSN-ING Brasimone, OrcID 0000-0001-5895-4964 E-mail: cicconi.flavio@gmail.com
- ⁴ Luxinar Ltd
- * Author to whom correspondence should be addressed.

Abstract – Nowadays radionuclides have become more and more strategic materials in different fields of application with a relevant interest in medicine, for diagnosis and therapy of various cancers and cardiovascular disease, but also in electronic industry, for the production of semiconductors, low neutron capture isotopes to be used in nuclear reactors, as well as isotopes for industrial applications.

Many of these strategic isotopes, are produced in few nuclear reactors (USA, Canada, Russia, etc.) or in Calutrons (electromagnetic separators). Some of them, like Tc-99m, have a half-life of 6 hours, and therefore they cannot be stored but must be daily produced and used in a short supply chain, better local, in order to meet clinical demand.

The Laser Isotope Separation (LIS) technique has seen its golden age during the Uranium enrichment period, where different approaches have been investigated from Atomic Vapour LIS (AVLIS) to Molecular LIS (MLIS) in order to selectively excite and collect the selected isotope. The availability of high power, pulsed, tunable and narrow band laser allowed the experimentation of low impact methods.

Such new opportunities in radionuclides demand, have brought out the previous expertise in ENEA, that began with the studies of Prof. Anna Giardini, former head of the Molecular Spectroscopy and Laser Application Laboratory in Frascati, and her collaborators, who conducted experiments on molecules with a structure similar to UF_6 , such as SF_6 and other Freon gases, reaching the preindustrial demonstrator stage. These skills can still be used today in the new challenges to which the organization is preparing to contribute at a national and international level. In this work, the laser enrichment methods of various radionuclides are analyzed and discussed, in its AVLIS and MLIS declinations.

Keywords: Laser, Isotope, Radionuclide, Enrichment, Separation, Lithium, Uranium, Technetium

Riassunto - Oggigiorno è cresciuta la richiesta di radionuclidi per usi medicali, per l'industria elettronica nei semiconduttori, per i reattori a fusione e come traccianti nell'industria. Per la radiochimica medica le applicazioni rivestono principalmente la diagnostica per immagini e il trattamento di tumori localizzati. In questo campo riscuotono molto interesse isotopi quali Lu-177, Tc-99m, I-131, Cu-67, Ge-68, Ru-96, Ca-48, Xe-129, mentre in campo reattori di fusione c'è molta richiesta di Li-6. Questi elementi di difficile reperibilità, vengono prodotti principalmente da reattori a fissione veloci o lenti, che sono localizzati in paesi strategici tra cui la Russia. Inoltre c'è da sottolineare che la catena di approvvigionamento prevede, oltre alla produzione dei radionuclidi, anche la loro preparazione industriale per essere inviata ed utilizzata dagli ospedali. In alcuni casi, a causa di vite medie molto corte, i radioisotopi non possono essere conservati a lungo ma prodotti su scala giornaliera per essere utilizzati dall'utenza finale in tempi molto ravvicinati.

La tecnica di separazione isotopica via laser (LIS), proposta diversi anni fa per l'arricchimento isotopico dell'uranio, permette di ottenere l'arricchimento dell'isotopo di interesse in elevata purezza e a basso consumo. Il processo, sia quello in vapori atomici (AVLIS) che quello in gas molecolari (MLIS), è tipicamente condotto in fase vapore in reattori semplici da realizzare e a basso impatto ambientale.

Queste nuove opportunità hanno fatto riemergere competenze in ENEA iniziate con gli studi della prof.ssa Anna Giardini, allora responsabile del Laboratorio di Spettroscopia Molecolare e Applicazioni Laser di Frascati, e suoi collaboratori, che condussero esperimenti su molecole di struttura simili all'UF₆, quali l'SF₆ ed altri gas freon, con l'utilizzo di sorgenti laser di elevata potenza, sintonizzabili per righe di emissione a banda stretta per ottimizzare il processo di eccitazione fino alla dissociazione selettiva dell'isotopo di interesse.

Queste competenze possono ancora oggi essere utilizzate nelle nuove sfide a cui l'ente si appresta a contribuire in ambito nazionale ed internazionale.

In questo lavoro si analizzano i metodi di preparazione dei vari radionuclidi e si valuta la possibilità di applicare alle nuove richieste il processo LIS, nelle sue declinazioni AVLIS e MLIS.

Parole chiave: Laser, Isotopo, Radionuclide, Arricchimento, Separazione, Litio, Uranio, Tecnezio

Introduction

Back to basic, an isotope is an atom with the same number of protons but different number of neutrons, therefore also different in the atomic weight. Some of them are unstable and undergo radioactive decay (radioisotopes), to describe how quickly these atoms decay, a characteristic unit is used: Half-life (symbol t¹/₂) i.e., the time required for a quantity of the unstable isotope to reduce to half of its initial value. There are different types of decay: alpha, beta, and gamma decay, depending on how the decaying nucleus emits. The half-lives of different radioisotopes range from the order of the yoctoseconds to trillions of years. They can be therefore classified in short-lived and long-lived radioisotopes.

Stable isotopes are used to trace their variations in environmental studies, nutrition and forensics investigation.

Radioisotopes, emitting different particles and photons, find their useful application in many fields as medicine (radio diagnostic and radiopharmaceutical) [1], industry [2], agriculture [3], environmental tracing [4] and biological studies [5], as well as nuclear purposes [6].

In the last century, a lot of different processes for isotope separation have been investigated, from chemical to electromagnetic methods, or even gas diffusion, centrifugation and laser separation.

The efficiency and the applicability of these methods vary from isotope to isotope and are also dependent on the aggregation state of the specific compound.

The main focus of our study are the optical and laser methods, as they are selective par excellence and due to the rising demand of new different isotopes, especially for medical applications, where the selectivity is a crucial characteristic. Furthermore, the advancement in laser technology and the advent of solid-state lasers have made this kind of separation method much more feasible and economically advantageous.

Currently, the enrichment of Uranium-235 (U-235) is the most important segment of the global isotope market, there are about 2,000 tonnes of highly enriched Uranium in the world, produced mostly for civil nuclear power. However, it is expected that within the next fifty years the nuclear fusion energy will develop to a point that the demand of enriched Uranium will be replaced by the enriched Lithium-6 (Li-6) demand [7]. Unfortunately, the currently developed methods for the Uranium enrichment, which is a very heavy element, are not applicable to the separation of Lithium that is extremely light, for this reason many research groups are putting a lot of effort in the study of new methods for the separation of isotopes.

The enrichment in Li-6 has been realized for the first time during the early 50's, for the development of the Hydrogen Bomb at Oak Ridge Y-12 National Security Complex in Tennessee. Lithium was enriched via the COLEX process (stands for column exchange), which employed an enormous amount of liquid mercury, approximately 12 000 tonnes [8]. The environmental and toxicological impact of the facility was unprecedented and for this reason the United States stopped Lithium enrichment operations in 1963. It is clear that it will become more and more important to focus the scientific resources on less hazardous and more ecological methods of Lithium enrichment, and again the Laser Isotope Separation (LIS) it is a valuable candidate.

The other fundamental field of application of the isotope separation methods is nuclear medicine [9]. Many different radionuclides are used daily in hospitals for both diagnostic and therapeutic purposes. Unfortunately, the only few production routes of these radioisotopes are centralized in very specific nuclear reactors in Europe, North of America and Russia.

In fact, radioisotopes are artificially produced in research reactors and accelerators and less frequently are recovered from nuclear waste via gas centrifugation.

In the last decades, some supply chains were disrupted due to closure of many reactors and the Ukraine-Russia conflict has affected the export from Russia [10]. The radioisotope market is therefore extremely fragile and the price fluctuations of the medical radioisotopes can put at risk even the simplest hospital procedures.

For example, Molybdenum-99 (Mo-99), the precursor of Technetium-99*m* (Tc), is the most used radioisotope in diagnostic imaging, acting as tracer in single photon emission computed tomography (SPECT), which covers more than 80% of all the nuclear medicine diagnostic procedures worldwide [11]. In 2009, there was a global crisis of the Mo-99 supply which was caused by the simultaneous and unpredicted temporary shutdown of the two main fission reactors that were providing the 70% of the world demand of this isotope, namely HFR in Netherlands and the NRU in Canada [12].

The global shortage of Mo-99 led the scientific community to propose alternative production routes for Mo-99 that avoid the use of highly enriched U-235 for nonproliferation matter and fission reactors, because of maintenance issues of the main nuclear production plants.

Furthermore, both Tc-99m and Mo-99 (which is the parent radioisotope) have a very short half-life, 6 hours and 2.7 days respectively, for this reason the supply chain for this isotope must be very short and possibly close to the final usage.

For this specific purpose, the ENEA FSN department developed the SORGENTINA-RF project, with the main focus of the production of radiopharmaceutical precursors with a medium power 14 MeV fusion neutron source, relying on a rotating target and a deuterium/tritium ion accelerator. The D-T source will be used to irradiate about 10 kg of natural Molybdenum (10% natural enrichment in Mo-100) to make the ¹⁰⁰Mo (n,2n) ⁹⁹Mo reaction occur. [13]

For an innovative and more sustainable way of radioisotope production, a starting material with a high isotopic enrichment is necessary and again the laser separation technique can satisfy the needed requirements for many different radioisotopes.

For example, Gadolinium-157¹ (Gd-157), which is used as a burnable absorber for pressurized water reactors (PWR), has always been enriched via gaseous diffusion and gas centrifugation but, due to the extremely high costs for the enrichment, it is usually employed in its natural isotopic ratio [14].

Only since 1997 it was reported in literature the isotopic enrichment of Gd-155 and Gd-157 by double resonance laser ionization for the first time as an economic way to produce burnable nuclear reactor adsorber [15].

The Laser Isotope Separation (LIS)

The LIS method is based on the selective ionization of the hyperfine transitions, which derive from the different energy levels and ionization potentials of the different isotopes.

Schematically, the compound of interest with its natural isotopic abundance, is vaporized under vacuum and it is subsequently intersected by a laser beam, which promotes the nucleus-selective excitation and ionization of one of the isotopes, producing the positively charged species that will be collected, while the non-excited atomic vapor beam follows its path in the vacuum chamber [16].

Despite a simple conceptual scheme, the complexity is inherent both in the high-resolution spectroscopy of the investigated targets and in the laser source to be implemented for the successive selective excitation and dissociation.

Briefly, a LIS prototype consists of a reaction chamber, suitably equipped with gas dynamics components, pumps, collectors, optics and one or more specific laser systems for the excitation and/or for the vaporization of the element.

The LIS advantages are the collection of high purity specific nuclides, low energy consumption and its single stage production (i.e., no iterative processes) in contrast to the typical gas centrifugation and gas diffusion methods.

Several photoionization pathways of different isotopes of interest like Li-6, Gd-156, U-235, Mo-99 and

 $^{^1}$ Natural Gadolinium contains seven isotopes but only $^{155}{\rm Gd}$ and $^{157}{\rm Gd}$ are useful due to their very high neutron absorption cross sections

Lutetium-177 have been developed and demonstrated but due to the complexity of the apparatus the experimental results are usually limited to the spectroscopic measurements.

The LIS technique consists of two different types: Atomic Vapor LIS (AVLIS) and Molecular LIS (MLIS).

The high-resolution spectroscopy, both in AVLIS and MLIS, plays the role to identify the specific wavelengths for the selective excitation and such information is typically not disclosed in the open literature.

While in the AVLIS approach (Fig. 1), the laser photons interact with atoms in the vapor phase by exciting the electronic transitions implementing Ultraviolet or Visible region laser sources, in MLIS the process is shifted to the Infrared bands to exploit the molecular vibrational excitation of the compounds in the gas phase. The vibration bands and their combinations depend on the molecular mass and therefore on their isotopic composition.

In the MLIS the beam design is much more complex: a set of peculiar wavelengths with specific vibrational transitions, for the specific radionuclide, is the result from a deep preliminary spectroscopic investigation.

Nowadays, this kind of preliminary studies on the specific vibrational levels are much easier with the help of Density-Functional Theory (DFT), a powerful computational quantum mechanical modelling method used to investigate the electronic structure of molecules, atoms and crystals [17].

The design of the interaction chamber is the next step

to be faced, in which the proper interaction between the molecular gas and the laser photons must be assured. This task is critical due to the need to cool the gas in order to populate the fundamental states of the target molecule. For this reason, the molecular gas is usually diluted with an inert buffer gas to avoid interference phenomena, then a supersonic expansion is adopted with the mixing of the buffer gas and successively spatially separated by combining a nozzle and a collimator skimmer [18].

Immediately after, the interaction zone between the beam and the photons will be defined.

The key factor of the complexity of the MLIS lies in the difficult identification of the optimal molecular compound to use.

ENEA, under the direction of Professor Anna Giardini has already pursued extensively the research on MLIS, especially for the work of the Diagnostics and Metrology Laboratory of the FSN Department, between the end of the 70's and the beginning of the 80's. A research line of development led studies on the interaction of infrared laser radiation and polyatomic molecules in gas phase with the aim of understanding and applying the selective Multi-Photonic Dissociation (MPD) processes on molecules of strategic isotopic interest (Fig. 2). The scientific group of Professor A. Giardini put the bases to investigate in pulsed free jets the contribution of carrier gases in a single or dual laser excitation in order to increase the selective dissociation process [19].

The results, gained in the early 80's in Frascati,

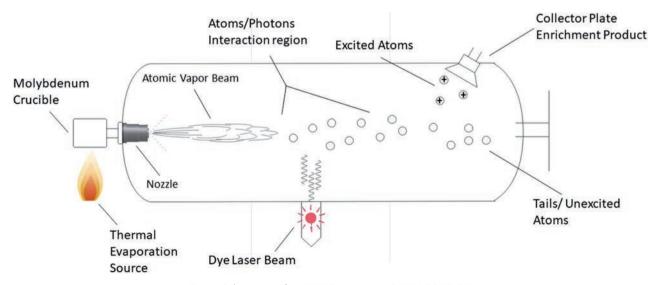


Fig. 1. Schematics of an AVLIS apparatus. OPEN SOURCE

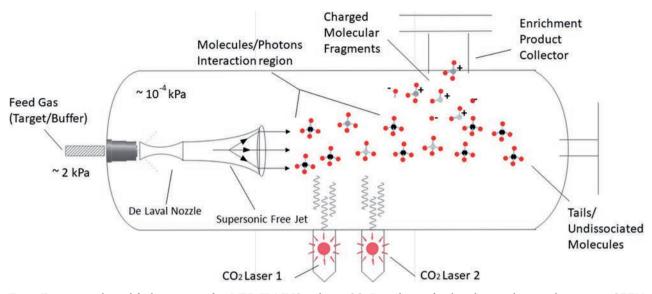


Fig. 2. Experimental simplified apparatus of an MPD-IR MLIS with two CO₂ Laser beams for the selective photonic dissociation. OPEN SOURCE

demonstrated the possibility of isotopic enrichment of specific substances as SF₆, CF₃Br, CF₃I and CF₃Cl, up to the realization of a prototype of a flow reactor for the isotope separation of Carbon-13 in CF₃Br [20]. Subsequently, a plant dedicated to the isotope separation of UF₆ was built, developing the ad-hoc laser source emitting in the 16 μ m wavelength range [21]. Recently, the Argentinian Comisión Nacional de Energía Atómica (CNEA), in collaboration with the nuclear company IN-VAP in Argentina, has realized a twin apparatus for the same purpose.

As an example, the spectroscopy of the octahedral SF_6 molecule was deeply investigated with the prospect of applying the results to the similar UF₆ molecule and thus obtaining indications on the most adequate instruments capable of selectively separating the isotopes asked by the nuclear plants applications, as we will describe in the next sections.

The technological and theoretical advancement that has been achieved for the laser enrichment processes of Uranium it is unmatched by any other element, essentially in view of the extremely strategic importance of Uranium in the last 70 years.

For example, regarding Li-6 enrichment, the situation is extremely different and only a few AVLIS applications are reported.

Duarte et al. [22] showed that the wavelengths of the transitions 2s–2p have been assigned as corresponding to 670.7764 nm for the Li-7 D2 line and 670.7915 nm for the Li-7 D1 line. The 2s–2p transitions for Li-6 D2

and D1 lines were assigned respectively to 670.7922 nm and 670.8073 nm, respectively. The frequency shift between the two lines corresponds to $\Delta\lambda = 0.0151$ nm. This value is crucial to identify the laser source to employ in the selective excitation process, because the bandwidth of the single emission wavelength, must result narrower than this spectral distance, otherwise it will not be a selective excitation. Therefore, this request demands for a high power, high resolution and narrow bandwidth emission wavelength at picometrical level.

Also V.K. Saini et al. studied the photoionization of Lithium isotopes via a two-step ionization method. They used a narrow band tunable dye laser in combination with mass spectrometer on tuning with Li-6 $(2s^2S_{1/2} \rightarrow 2p^2P_{1/2})$ and Li-7 $(2s^2S_{1/2} \rightarrow 2p^2P_{3/2})$ resonance levels that confirms high degree of isotope selectivity [23].

M. Saleem et al. used a similar set-up to perform the Lithium isotope separation, employing the two-step photoionization technique along with a narrow band dye laser in conjunction with a time-of-flight mass spectrometer. It is inferred that the concentration of the natural abundance (~7.5%) of the Li-6 isotope gets enhanced up to over 47% as the exciter dye laser is tuned to the $2s^2S_{1/2}\rightarrow 2p^2P_{1/2}$ transition of Li-6, even if the bandwidth of the exciter laser is not sufficiently narrow to excite only the specific isotope level. It is also noticed that the much higher energy density of the exciter laser limits the resolution of the fine structure levels of the Lithium isotopes, leading to a loss in the enrichment of Li-6 due to the power-broadening effect [24].

The MLIS has never been experimented for Lithium enrichment, due to the low electronegativity of Lithium and its monovalent nature. On the other hand, Alkyl-Lithium compounds form clusters containing multicentred bonds not only in the solid state and in liquid solution but also in the gas phase, making extremely difficult to apply the said technique due to the different possible combination of isotopes in the clusters.

For these reasons extensive spectroscopic studies should be performed in order to find the optimal compound, but some particular chemical moieties are already promising as they are stable in the gas phase and they do not form dimers or tetramers.

Few species such as Allyl-Lithium and Lithium Ferrocene do not aggregate in the gas phase and are therefore potentially viable for the formation of a monomeric molecular beam [25]. Nevertheless, as of today, no MLIS experimental or theoretical studies have yet been performed.

The strong tendency to form clusters and aggregates of Lithium compounds could also be exploited for different enrichment laser methods that rely on the selective repression of the clusterization of a specific isotope. The method is briefly described in the next paragraph.

MLIS and Low Energy Methods

For obvious reasons of costs and efficiency, AVLIS was easily surpassed by the MLIS techniques: it is much easier to produce molecular vapours instead of evaporating directly the solid metal; additionally, the overall laser energy required for the electronic transitions (UV region) to the excited state of the atoms is extremely higher than the one necessary for the excitation of the molecule vibrational levels (IR region).

The MLIS was therefore chosen as the preferred method, during the 80's, but at the time the laser technology was less developed and the experiments were carried out only with CO_2 lasers that are rather simple to operate and relatively inexpensive. The MLIS mode that had most success, as already mentioned earlier, was the selective multi-photon dissociation (MPD) of molecules by infrared radiation, and it was used successfully for the enrichment of Uranium, Boron, Sulphur, and Osmium isotopes [26].

The drawback of this method is the energy required for the dissociation of the excited molecule: the energy needed to dissociate UF_6 to UF_5^{+2} for example is high and the method development was therefore hindered by the high-power consumption and the lack of high-efficiency and high-power laser systems. For these specific reasons, the process had a lower efficiency compared with the traditional second-generation methods of gas centrifugation.

A different evaluation should be made for the lighter elements that could be possibly enriched much more easily with the MPD-IR MLIS methods. For example, it has been reported as a way to enrich Mo-100 by the dissociation of MoF₆ under cooled conditions (215 K). A selective excitation of the combination mode ($v_3 + v_5$) was obtained with the 9 µm band emission lines of a CO₂ laser, and an enrichment factor of ~1.12 for the case of Mo-100 was achieved [27].

Nevertheless, the need for a lower transition energy led to the so-called Low Energy Methods (LEM), where the activation energy must be extremely small i.e., << 1 eV.

Small energies like these are characteristic of very weak interactions like adsorption and desorption processes and for the dissociation and fragmentation of weakly bound dimers and clusters of non-ionic molecules that are known as Van der Waals molecules.

Being these interactions so small, this approach can potentially be applied to a variety of molecules, clusters, dimers, gas-molecules interaction and so on, but the most successful and experimented method is probably the Selective Laser-Assisted Repression of Condensation, also called MLIS-CR (Condensation Repression) or, in other works, clusterization suppression. [28]

The enrichment of a MX_6 molecule, like UF₆, MoF_6 or SF₆, requires that the target molecule is combined with an inert carrier gas G and expanded through a nozzle into a low-pressure chamber, as a supersonic jet. The jet that is generated is formed by van der Waals heteroor homodimers MX_6 -G and MX_6 : MX_6 if the temperature is sufficiently low (Below 150 K). The supersonic Van der Waals molecular jet is then irradiated with a tunable laser and the dimerization of the selectively excited isotopolougue MX_6 is suppressed (Fig. 3) [29].

This type of MLIS is intimately related to the next and last method that we are discussing: the SILEX.

The SILEX Technology

It is worthy of note that all the techniques we have dealt with in this dissertation, have been investigated only at a lab experimentation level, or even only at a theoretical one. However, there is an important exception: the SILEX technology.

 $^{^{2}}$ 235 UF₆ + hv \rightarrow 235 UF₅⁺ + F⁻, that costs 3 eV approximately.

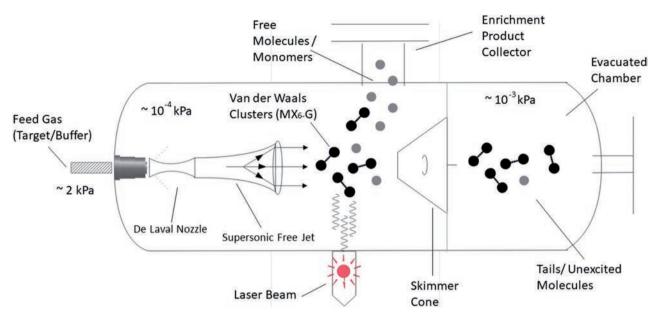


Fig. 3. Schematic of a MLIS-CR apparatus: The core gas made of Van der Waals condensed clusters, collected by the skimmer, is depleted while the excited free molecules get enriched. OPEN SOURCE

The Separation of Isotopes by Laser Excitation (SILEX) process is the only laser enrichment technology at an advanced stage of commercialisation.

SILEX is a third-generation Uranium enrichment method, the previous two methods being the now obsolete Gas Diffusion technique (1st generation) and the well-known Gas Centrifuge (2nd generation). The SILEX company claims that it provides a much higher enrichment process efficiency compared with these earlier methods, potentially offering significantly lower overall costs. It is estimated that, once it will reach a well-developed stage, its efficiency, in comparison with the gas centrifugation technique, will be 1.6 to 16 times higher [30].

The technology has also an extremely peculiar secrecy classification: it is a privately generated information that is nevertheless classified by the U.S. government. As a general rule, any kind of information or technology must be owned or controlled by the government in order to be eligible for classification in the first place. Nevertheless, on the peculiar terms of the Atomic Energy Act, the government may impose classification on «all» information concerning nuclear weapons and related matters that has not been previously declassified [31]. Since the new SILEX technology has never been declassified, it is *ipso facto* classified, despite the fact that it was generated by private and also foreign (Australian) researchers.

After 20 years of experimentation and 500 million dollars of investment, a pilot plant was built in Wilming-

ton, and a test cycle was completed in May 2013. The operability on industrial scale of the SILEX technology has been practically demonstrated.

Being a classified technology, the insights of the laser enrichment process are unknown, but some authors have suggested [29,28] that it employs either isotope-selective suppression of clusterization of UF₆ molecules or isotope-selective dissociation of dimers of UF₆ molecules, alone or mixed with the carrier gas.

The SILEX company has also launched a project to develop a process for the production at industrial scale of high-purity Zero-Spin Silicon (ZS-Si)^c, using the same technology with different excitation frequencies [32]. The project was announced in August 2023 to overcome the future needs for enriched Silicon as, after the Russian invasion of Ukraine, the supply chain was disrupted. The enriched silicon is extremely important for the development of quantum computers and almost the entirety of the world's supply came from Russia, which produced it with 2nd generation centrifuge technology³.

Nowadays, these sophisticated methods that we briefly discussed like MLIS-LEMs are much more effi-

³ ZeroSpin-Silicon is a key material for the silicon Quantum Computing processors. Natural Silicon consists of 3 isotopes: 92.2% Si-28, 3.1% Si-30 (each with zero electron spin state) and 4.7% Si-29 (with a spin state of ½). The lower the concentration of Si-29, the better a silicon quantum processor will perform in terms of computational power, accuracy and reliability.

cient and feasible thanks to the advent of new technologies in laser sources.

Innovative Laser Sources

The concept of laser isotope separation has been intertwined with the development and availability of laser sources. However, initial research efforts predominantly focused on dual-use applications, particularly in Uranium enrichment. This focus led to a relatively restricted dissemination of information. Despite these advancements, the field remains specialized and relatively niche, with a limited amount of circulating information. This work delved into the nuanced world of laser isotope separation, shedding light on significant advancements, the pivotal role of advanced laser technologies, and its critical applications in various industries.

Free Electron Lasers (FELs) [33] have emerged as stalwarts in this field, offering unparalleled tunability across a broad spectrum of wavelengths and the capability to meticulously align with the absorption lines of various isotopes. Despite their complexity and considerable cost, the potential gains in isotope separation efficiency are monumental. Ultrafast lasers, characterized by femtosecond pulse durations, bestow meticulous control over the excitation process, augmenting their effectiveness in AVLIS for example. These lasers produce ultrashort pulses with exceedingly high peak powers, crucial for ionization. isotope excitation and ionization. Advanced Gas Lasers, specifically excimer lasers, have seen enhancements in both efficiency and reliability, establishing themselves as indispensable tools in the future AVLIS process.

Conversely, MLIS concerns molecules, necessitating laser technologies capable of precisely targeting molecular transitions. Recent developments in laser technology have significantly expanded the capabilities of MLIS. Quantum Cascade Lasers (QCLs), semiconductor lasers operating in the mid-infrared region, seamlessly align with the vibrational modes of the molecules, enabling highly efficient excitation and ionization. This characteristic positions OCLs as pivotal technology in MLIS. Advanced Pulsed Lasers, encompassing femtosecond and picosecond lasers, have proven instrumental in MLIS, providing the high-energy pulses requisite for efficient molecular excitation and ionization. The precision and speed they offer have substantially improved the separation process. Additionally, Optical Parametric Oscillators (OPOs) and Optical Parametric Amplifiers (OPAs) furnish tunable, high-energy light in the mid-infrared region, critical for exciting vibrational modes, rendering them invaluable assets in MLIS.

In conclusion, the realm of laser isotope separation stands at the forefront of cutting-edge technology, with methodologies like AVLIS and MLIS showcasing remarkable efficiency and precision. Advanced laser technologies, ranging from Free Electron Lasers to Quantum Cascade Lasers, have propelled the field forward, enabling unprecedented control and targeting capabilities. These advancements have not only revolutionized isotope separation but also paved the way for the production of vital light radioisotopes with critical applications in medicine and industry. However, it is crucial to recognize that the integration of multidisciplinary competences is paramount for further progress. The synergy between atomic and molecular spectroscopy experts and high-level specialists in laser development is essential. This integration of knowledge and expertise will undoubtedly propel laser isotope separation into new realms of capability.

Conclusions

The possible reactions and strategies to enrich different isotopes via laser methods have been evaluated in detail. Many studies have been conducted since more than half a century, but they haven't led so far to the realization of a real large scale production plants with the only exception of the Uranium enrichment based on the SILEX process.

Currently, a group which is part of the KIT institution is working at the realization of a Li-6 production plant, based on the amalgamation process. This process is considered indeed one of the best enrichment processes, by comparing several possible methods on the basis of a full set of requirements, including the technical maturity of the process, its efficiency, its energy and equipment cost, its environment impact, its possible scalability to large productions; anyway it suffers the limit of employing large quantities of an extremely toxic material like mercury and, since its experimentation has just started, of not being able to lead to a large scale production of enriched Lithium before around two decades.

For all these reasons, it will be extremely important to also investigate the laser approach that could potentially step up the actual technologies by orders of magnitude. Li-6 is in fact essential for fusion energy production. Recently, EUROFUSION, the European Project that coordinates the efforts of European research institutions and industries in order to achieve the first Thermonuclear Fusion Demonstrator by 2050, has focused its attention on the Lithium fuel cycle of the Deuterium-Tritium fusion reactor. A rapid and effective technological development of the fuel cycle necessarily passes through the development of innovative isotope enrichment technologies.

Even though the LIS systems are still very far from becoming a feasible enrichment method of light isotopes, the extreme selectivity of the technique and the complete absence of chemical solvents and mercury makes it a clean process and surely worthy to be studied and experimented deeply. Indeed, achieving exceedingly precise and narrowband laser lines is a critical requirement, not limited solely to MLIS but also applicable to LEMs and AVLIS. This precision is indispensable for selectively exciting specific atomic or molecular transitions without inadvertently exciting neighbouring vibrational or electronic states. To meet this challenge, advanced laser technologies and meticulous control over laser parameters are essential.

The integration of advanced laser technologies in isotope separation systems extends beyond the realm of separation, playing a pivotal role in the production of light radioisotopes, which find critical applications in medicine and industry.

REFERENCES

- N. SINGH, Ed., Radioisotopes Applications in Bio-Medical Science. InTech, 2011. doi: 10.5772/1937.
- [2] DR. KHALID AL-NABHANI. Applications of Nuclear and Radioisotope Technology: For Peace and Sustainable Development. Elsevier Academic Press. 2021, ISBN 978-0-12-821319-3.
- [3] SIYAL, A.L.; HOSSAIN, A.; SIYAL, F.K.; JATT, T.; IRAM, S. Use of Radioisotopes to Produce High Yielding Crops in Order to Increase Agricultural Production. Chem. Proc. 2022, 10, 86.
- [4] VALKOVIĆ V., Radioactivity in the Environment. Elsevier 2019, https://doi.org/10.1016/C2017-0-03568-1
- [5] SLATER, ROBER J. Radioisotopes in biology (2nd ed.): (ed.) Biochemistry and Molecular Biology Education Volume 30, Issue 6 p. 336-336, 2006, https://doi.org/10.1002/bmb.2002. 494030069999
- [6] GREGORY CHOPPIN, JAN-OLOV LILJENZIN, JAN RYDBERG, CHRISTIAN EKBERG, Radiochemistry and Nuclear Chemistry 4th Edition - September 5, 2013, Hardback ISBN: 9780124058972 eBook ISBN: 9780123978684
- [7] GIGIERICH T., BATTES K., SCHWENZER J.C., DAY C. Development of a viable route for lithium-6 supply of DEMO and future fusion power plants, Fusion Engineering and Design, 149 (2019).
- [8] BROOKS' S. C., SOUTHWORTH R. S., History of mercury use and environmental contamination at the Oak Ridge Y-12 Plant, Environmental Pollution, Volume 159, Issue 1, January 2011, Pages 219-228.

- BOND, LEONARD Laser Isotope Enrichment for Medical and Industrial Applications - United States (2006) https://www.osti.gov/biblio/911877
- [10] NEA, N.E. The Supply of Medical Radioisotopes. 2018 Medical Isotope Demand and Capacity Projection for the 2018– 2023 Period. NEA/SEN/HLGMR. 2018. Available online: www.oecd-nea.org
- [11] CAPOGNI, M.; PIETROPAOLO, A.; QUINTIERI, L. 99mTc production via 100Mo(n,2n)99Mousing 14 MeV neutrons from a D-T neutron source: Discussion for a scientific case. In RT/2016/32/ENEA; ENEA: Rome, Italy, 2016.
- [12] GOULD P., Europe's isotope shortage will continue into 2009, Nature (2008) https://doi.org/10.1038/news.2008.1186
- [13] AGOSTINI P. and SRF COLLABORATION SORGENTINA-RF project: fusion neutrons for 99 Mo medical radioisotope, The European Physical Journal Plus volume 136, Article number: 1140 (2021).
- [14] BEJMER K., SEVEBORN O. ENRICHED GADOLINIUM AS BURN-ABLE Absorber for PWR - PHYSOR 2004 – The Physics of Fuel Cycles and Advanced Nuclear Systems: Global Developments Chicago, Illinois, April 25-29, 2004.
- [15] M. SANTALA, A. DAAVITTILA, H. LAURANTO, R. SALOMAA, Odd-isotope enrichment studies of Gd by double resonance laser-ionization for the production of burnable nuclear reactor poison, Appl. Phys. B 64, 339-347, 1997.
- [16] R.C. STERN, J.A. PAISNER, Atomic Vapor Laser Isotope Separation, First International Laser Science Conference Dallas, TX November 18-22, 1985.
- [17] DAVID S. SHOLL, JANICE A. STECKEL DFT Calculations of Vibrational Frequencies – Wiley (2009).
- [18] C.D. CANTRELL Multiple-Photon Excitation and Dissociation of Polyatomic Molecules – Springer DOI: 001: 10.1007/978-3-642-82292-6
- [19] R. FANTONI, E. BORSELLA, A. PALUCCI, A. GIARDINI. Laser e molecole: la stagione dei multifotoni a Frascati negli anni 70 e 80. Energia Innovazione multifotoni 2015. DOI: 10.12910/EAI2015-091.
- [20] E. BORSELLA, C. CLEMENTI, R. FANTONI, A. PALUCCI. Isotopic enrichment in laser-induced multiphoton dissociation: C13 separation from natural CF3Br in a flow system. Il Nuovo Cimento A Vol. 73A, N.4, 364 (1983). https://doi.org/10.1007/BF02724236. ISSN 1826-9869.
- [21] M. BERNARDINI, A. FERRARIO, M. GIORGI, S. MARCHETTI, A. PALUCCI. 1. Parametric study of a Raman p-H2 laser with over 30 MW emission at 16 mm. Il Nuovo Cimento D Vol 6, 520-528 (1984). https://doi.org/10.1007/BF02450957. ISSN 0392-6737.
- [22] IGNACIO E. OLIVARES, ANDRE S. E. DUARTE, EDUARDO A. SARAVIA, and FRANCISCO J. DUARTE. Lithium isotope separation with tunable diode lasers. APPLIED OPTICS 20 May 2002, Vol. 41, No. 15.
- [23] V. K. SAINI, S. TALWAR, V. V. SUBRAHMANYAM, R. K. MISHRA, P. K. SAINI and S. K. DIXIT - Laser isotope separation scheme of lithium by three-color photoionization. Phys. Scr. 95 (2020) 075403 (10pp) https://doi.org/10.1088/1402-4896/ab94d8.
- [24] M. SALEEM, SHAHID HUSSAIN, M. RAFIQ, and M. A. BAIGA. Laser isotope separation of lithium by two-step photoionization. J. Appl. Phys. 100, 053111 (2006); DOI: 10.1063/1.2338832

- [25] IRIGORAS A. The Ferrocene-Lithium Cation Complex in the Gas Phase - J. Am. Chem. Soc. 2001, 123, 5040-5043.
- [26] G. N. MAKAROV Towards molecular laser separation of uranium isotopes - Physics Uspekhi 65 (6) 531-566 (2022).
- [27] SAI PRASAD M. B., GHOSH A., DWIVEDI T. 98/100Mo enrichment by infrared multi-photon dissociation of MoF6 -Chemical Physics Letters Volume 787, January 2022, 139262
- [28] JEFF W. EERKENS, JAEWOO KIM Isotope separation by selective laser-assisted repression of condensation in supersonic free jets – AIChE Journal - Volume 56, Issue 9 September 2010.
- [29] G. N. MAKAROV Low energy methods of molecular laser isotope separation - Physics Uspekhi 58 (7) 670 700 (2015).

- [30] SILEX Uranium Enrichment, SILEX Annual Report 2023, https://clients3.weblink.com.au/pdf/SLX/02701979.pdf
- [31] Federation of American Scientist SECRECY NEWS from the FAS Project on Government Secrecy June 26, 2001 https://sgp.fas.org/news/secrecy/2001/06/062601.html
- [32] Official SILEX website https://www.silex.com.au/silex-technology/silex-zs-si-production-for-quantum-computing/
- [33] TETSUJI NODA, HIROSHI SUZUKI, HIROSHI ARAKI, JOHN L. LYMAN, BRIAN E. NEWNAM. Isotope separation of silicon and molybdenum using a free electron laser. Journal of Nuclear Materials 307-311 (2002) 715-718.