Isotope Separation by Selective Laser-Assisted Repression of Condensation in Supersonic Free Jets

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DOI 10.1002/aic.12212

Separation of gaseous molecules in supersonic free jets by laser-assisted selective condensation repression is reviewed. It is shown to have evolved from Becker's pre-laser "Nozzle Separator" concept of 1956 by simple addition of a laser. Although useful to separate mixtures of dissimilar gases, the technique has mostly been applied to isotope separation. To enrich $^{i}SF_6$ *for example,* SF_6 *mixed with an inert carrier gas G is expanded through a nozzle into a low-pressure chamber, where it forms a supersonic jet and creates van der Waals hetero- or homodimers* $SF_6{:}G$ *and* $SF_6{:}SF_6$ *if* $T < 150$ *K. By coaxial or cross irradiation of the free jet with a tunable laser, dimerization of selectively excited* $^{j}SF_6$ *is prevented. As radial out-of-the-jet-core diffusion depends on molecular mass, nondimerizable laser-excited* $^{j}SF_6$ *monomers enrich the background "rim" gases, which are separated by a skimmer from much heavier nonexcited* $^{i}SF_6{:}G$ *and* $^{i}SF_6{:}SF_6$ *dimers in the jet's core.* © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 2331–2337, 2010

Keywords: isotopes, separations, lasers, dimers, supersonic jets, uranium

Introduction

With the recent worldwide renaissance in nuclear power development, additional uranium enrichment capacity must be provided. This has prompted the nuclear industry in the US to start building four new enrichment plants, three of which will use advanced centrifuge technology and one planning to use laser enrichment. Currently, well-developed gas centrifuging is the technology of choice, but long-awaited laser enrichment may finally make its debut. A new GE subsidiary called Global Laser Enrichment (GLE) jointly financed by GE, Hitachi, and CAMECO is investing $500,000,000 in a pilot plant in Wilmington, North Carolina to evaluate the commercial viability of uranium laser enrichment.[1–4] Since the 1970s, many countries tried to develop more economic methods than the old gaseous diffusion plants (stamped out of the ground during WW-II), which are now unattractive because of high power consumption. Increased demands for medical (e.g., molybdenum) and industrial (e.g., silicon) isotopes have also arisen, many of which can be separated by the same general methods developed for uranium enrichment.

Among the many laser-driven uranium-hexafluoride enrichment techniques that were investigated in the last 40 years,[5] only molecular laser isotope separation (MLIS) using condensation repression (CR) in supersonic jets has survived.

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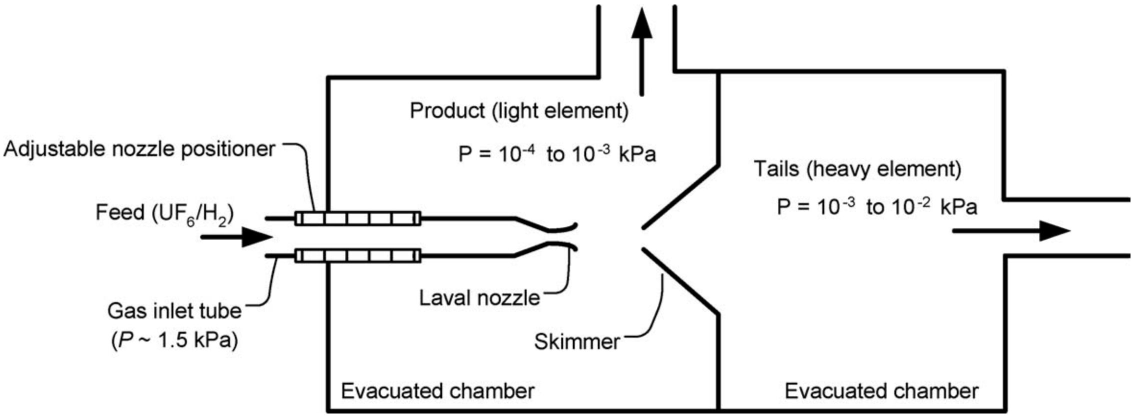

Figure 1. Diagram of Becker's nozzle scheme.

Most other MLIS enrichment programs have been terminated. A brief history of past LIS research is given later. Two surviving MLIS-CR methods using UF_6 have gone under the labels of CRISLA (Condensation Repression by Isotope Selective Laser Excitation) and SILEX (Separation of Isotopes by Laser Excitation). Although the SILEX process has been clouded in secrecy, sufficient information has been published[6] to indicate that it is an MLIS-CR scheme similar to that researched by Vandenbergh, who separated sulfur isotopes using SF_6 at the Ecole Polytechnique in Lausanne, Switzerland in 1985.[7] In hindsight, the MLIS-CR scheme actually evolved from Becker's pre-laser "Separation Nozzle" studies in 1955 at the University of Marburg in Germany.[8] By simple addition of a laser, separations are greatly improved.

Laser Isotope Separation by Condensation Suppression

Basic concept of MLIS-CR in supersonic free jets

As mentioned, the basic idea of MLIS-CR originated with Becker's pre-laser "Nozzle Process" of 1956 (Figure 1), which took advantage of mass difference effects in radial diffusion that cause $^{235}UF_6$ to flee out of the core of a nozzle-expanded supersonic free jet at a slightly faster rate than $^{238}UF_6$. The idea has similarities to the gaseous diffusion enrichment of UF_6 through porous walls developed during WW-II, where $^{235}UF_6$ escapes a little faster through the wall than $^{238}UF_6$. Except in a free jet, the resistance to outward migration from the supersonic jet core into the low-pressure subsonic background gases is due to collisions with other molecules instead of a solid matrix. After a gaseous feed stream enters a low-pressure chamber through a nozzle or orifice, the gas forms a supersonic jet. The adiabatic supersonic expansion causes downstream cooling of the jet, according to well-known gas dynamic relations[9] that can cause dimer formation of condensables below a certain temperature.

The gas flow in the supersonic core of the jet is separated from the chamber background gases by a skimmer placed some distance downstream from the nozzle (Figure 1). For jets of UF_6 + G mixtures (G = carrier gas), the background or "rim" gas is enriched with $^{235}UF_6$ while the core gas that is collected by the skimmer is depleted. Becker's observations of nozzle separation were confirmed in 1957 at UC-Berkeley, where one of us (Eerkens) measured 15% oxygen enrichments in the cores of supersonic free jets of air,[10,11] and established that mass-dependent radial pressure diffusion dominates the effect.[10–13] Becker built a small pilot plant to enrich U-235 in gaseous mixtures of 4% UF_6 and 96% H_2 via his nozzle process,[14] but got disappointing enrichment factors of only $\beta \sim 1.01$, that is, less than $\beta \sim 1.08$ obtainable with then-existing gas centrifuges.

Following the birth of the laser in 1960, studies showed that jet-expanded adiabatically cooled hexafluoride gases formed (earlier-than-expected) dimers downstream, attributable to attractive Van der Waals forces. Lee (1986 Nobel Laureate) and others at Los Alamos National Laboratory (LANL) suggested in 1977 to selectively photo-dissociate these dimers by isotope-targeted laser excitation, thus, achieving isotope separation.[15,16] As the mass of nonexcited dimerized $^{238}UF_6$:G or $^{238}UF_6$:UF_6 and laser-maintained $^{235}UF_6$ monomers now differ by $\Delta M = M_G + 3$ or $\Delta M = 355$ instead of by $\Delta M = 3$ as in Becker's scheme, differential radial escape rates of $^{235}UF_6$ from a free-jet core, which are proportional to ΔM, are greatly enhanced. Van der Waals binding energies ($\sim$0.01 eV) in dimers are much smaller than the energies of molecular vibrations ($\sim$0.1 eV), so the absorption of one IR laser photon by a dimer is all that is needed in an MLIS-CR scheme to cause a near-instant dimer break-up, according to molecular predissociation physics.[17,18] As discussed further below, dimer-forming attachment reactions due to attractive van der Waals forces can occur in low-velocity (low temperature) two-body gas-phase collisions for nonvibrating molecules.[19] Excess kinetic energy can be absorbed in that case by dimer rotation and perhaps by low-energy dimer wagging vibrations. This mechanism is much more probable than if three-body collisions would be required as conventional theory demands.[20] If a molecule is vibrationally excited by a photon however, the vibration destroys a van der Waals bond almost instantly (in nanoseconds) after some Lissajoux dancing motions.[17,18]

For optimum cooling and separations, heavy hexafluoride gases QF_6 are best mixed with a heavy carrier gas G, whose gas constant $\gamma = c_p/c_v$ is not too low to allow acceptable adiabatic cooling.[9,18] If necessary, the inlet gas mix can be

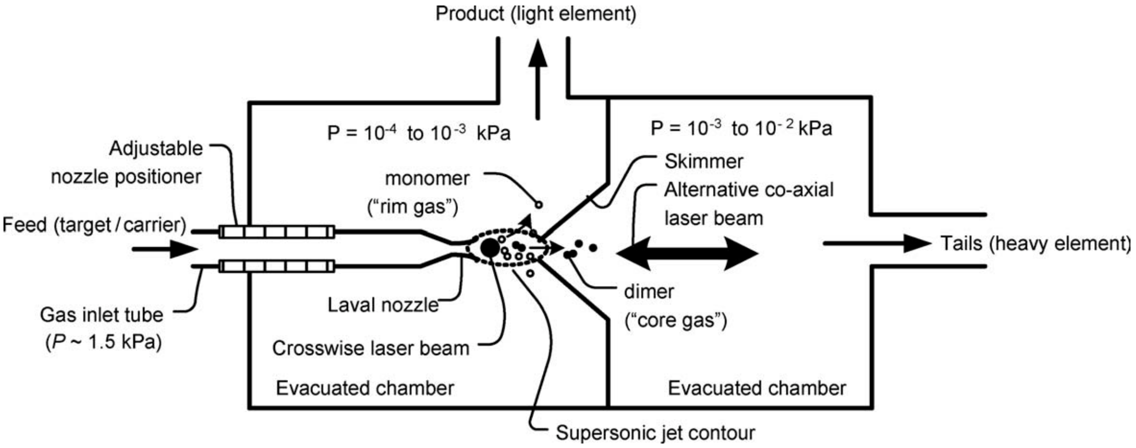

Figure 2. Simplified schematic of MLIS-CR process.

precooled to induce earlier downstream dimerization. To minimize undesirable vibration-to-vibration, energy transfers between different isotopomers $^{i}QF_6$ and $^{j}QF_6$, the concentration of QF_6 mixed in carrier gas G is generally kept below 10%. Suitable carrier gases G might be SF_6 ($M_G = 146$; $\gamma = 1.31$) or Xe ($M_G = 131$; $\gamma = 1.66$), which are heavy and thus promote high values of ΔM. M_G desirable for high separations, while their γ values provide adequate supersonic cooling.[9,21] These carrier gases also form beneficial nonreactive QF_6:G heterodimers.

Figure 2 illustrates the laser-improved nozzle-separator scheme for enriching UF_6 and other gaseous hexa- or tetrafluorides. Becker's 1955 nozzle separator was in essence similar to that in Figure 2 except there was no laser present and dimer formation was avoided. The special lasers and spectroscopic particulars required for selective isotope excitation of various hexafluorides were intensively investigated in the last few decades[5] and cannot be discussed here in detail. Some techniques are still proprietary or classified. Here, we examine primarily physico-chemical and gas-dynamic features.

The first experimental data proving that lasers can effectively suppress dimer formation in supercooled free jets to separate SF_6 isotopomers were published in 1985 by VandenBergh at the Ecole Polytechnique in Lausanne, Switzerland.[7] VandenBergh irradiated supersonically expanded free jets of SF_6/Ar mixtures with isotope-selective CO_2 laser photons and observed enrichments of $^{i}SF_6$ isotopomers. His results were somewhat unexpected since it had been assumed that dimerization could not occur as quickly downstream in supersonic jet expansions in earlier MLIS analyses. This was because prevailing theory demanded that three-body collisions were necessary.[20] However, published measurements by Kim et al. at Los Alamos [22] and by Human in South-Africa [23] showed that the onset of UF_6 dimer formation in supersonic free jets started much sooner during supersonic expansions than expected. The same phenomenon had been observed earlier for supersonic expansions of SF_6 and other gases,[18] but dimer formation in supersonic expansions of UF_6 had theretofore been avoided in MLIS experiments to preserve a sharp absorption spectrum.[24,25]

The importance of VandenBergh's experiments was not immediately recognized by most MLIS researchers. At the time, it appeared that the MOLIS (Molecular Obliteration Laser Isotope Separation) scheme[5,25] would be the winning MLIS technique as enrichment factors of $\beta > 5$ appeared feasible compared to only $\beta = 1.5$ to 2.5 for CR in free jets. However, after subsequent disappointments with MOLIS and chemically enhanced MLIS (CHEMLIS), the MLIS-CR approach was vigorously investigated by US CRISLA researchers[21] and by SILEX in Australia.[6] One key advantage is that the feed, product, and tails streams in the process are all unaltered UF_6 gas, allowing easy staging. Even though β factors are less for MLIS-CR than for some MOLIS schemes, because feed, product, and tails streams are all gaseous UF_6, direct staging without intermediate chemical reprocessing is possible as in existing centrifuge enrichment plants. With factors of $\beta \sim 2$, only three stages are needed for example to enrich natural uranium, for example, from 0.7 to 5.6% for power reactor fuels compared with 12 stages that would be required for centrifuging with $\beta = 1.2$.

In early 1986 CHEMLIS research by one of us (Eerkens) at Isotope Technologies (IT) in Los Angeles,[5] it was observed that on three separate independent occasions, unexpected small (but unequivocal) UF_6 enrichments were measured instead of expected depletions in cold traps that supposedly captured the tails stream.[26] This happened during runs in which inlet and outlet valves to the chilled irradiation chamber had accidentally failed to close, thereby producing supersonic free microjet flows at the feed inlets to the irradiation chamber and a near-vacuum in it. Normally this chamber was to hold stagnant UF_6 + HBr + Ar mixtures for one-minute laser irradiation periods.[5] After it was ascertained that the enrichment measurements were not due to experimental error, it was ascribed to dimerization or wall CR effects and the observations were set aside for a later "Plan B" investigation. Work was continued to search for a possible CHEMLIS or MOLIS scheme, which at the time promised greater enrichment factors. However, an examination was then begun of the physical details of dimer formation and nucleation in supersonic free jets.[19,27] Ultimately the theoretical analyses and experimental data indicated that the CHEMLIS approach would be futile and that a further investigation of "Plan B" might give better results.[21,28]

Diagnosis of supersonic MLIS-CR physics

To fully understand and utilize the small accidental microjet enrichments of UF_6 observed in 1986 and VandenBergh's published data on SF_6, it was found necessary to correct some existing theories of microscopic gas-phase mechanisms.[19,27,28] The key results were:

- Instead of requiring three-body collisions to allow simultaneous energy and momentum conservation as demanded by prevailing theory,[20] dimerization of cold QF_6 with itself or other gases was deduced to take place preponderantly by two-body collisions of molecules in the low-velocity part of the Boltzman distribution. Simultaneous energy and momentum conservation in such collisions can be accommodated by dimer rotation.[19] This two-body encounter theory increases equilibrium dimer populations and formation rates by orders of magnitude compared with a three-body theory, in agreement with observations.[18,22,23] It explains why UF_6/G mixtures experience dimer formation much earlier during supersonic jet expansion in self-cooling jets than what would be expected on the basis of a three-body theory. To facilitate the calculation of dimer formation rates, a model expression was also developed in Ref. 19 for quantized intermolecular van der Waals potentials.
- In self-cooling supersonic jet expansions of gas mixtures, the onset of irreversible nucleation and particle growth of condensables occurs somewhat later after a substantial increase in the equilibrium dimer concentration is established first, and only after a substantial concentration of oligomers of critical size is reached at low temperatures. The earlier Farkas–Becker–Doring–Volmer–Zeldovich theory of nucleation and particle growth required improvement and clarification.[27]
- Loss of laser-deposited vibrational energy in QF_6^* due to VT (Vibration→ Translation) energy transfer collisions as predicted by the well-established Schwartz–Slawsky–Herzfeld (SSH) theory,[29,30] correctly shows observed decreasing VT rates towards lower temperatures, but fails to explain a loss rate reversal and increase towards very low temperatures. By addition of another VT term to the SSH formula to account for two-body dimer-forming collisions coupled with near-instant predissociations, the observed reversal and increase of VT energy conversion rates at very low temperatures for excited QF_6^* is explained.[28]
- Although Los Alamos researchers suggested in 1977 that resonant laser excitation and dissociation of already-formed dimers could produce isotope separations,[15,16] it was found that resonant laser excitation of QF_6 monomers, which have a much higher absorption cross section is more efficient.[18,24] This was also observed by VandenBergh[7] in his sulfur isotope enrichment experiments with SF_6 and is explained by the theory in Ref. 19.

Summarizing, in the adiabatically cooled downstream portion of a supersonic expanding jet of UF_6/G gas, where condensation starts to set in, nonexcited heavy dimers ($^{238}UF_6$:G or $^{238}UF_6:UF_6$) tend to stay in the jet core and transit the jet chamber generally intact until they enter the skimmer (Figure 2). On the other hand, much lighter selectively laser-excited (warmed) $^{235}UF_6$ monomers that are prevented from forming dimers, migrate laterally out of the supersonic core into the subsonic background or "rim gases" (Figure 2) at a much faster pace than the much heavier dimers. The higher the mass of carrier gas G is, the higher the separation, which is proportional to $\Delta M = M_G + 3$. The $^{235}UF_6$ molecules acquire some additional kinetic energy during predissociation events when laser-deposited vibrational energy in transient $^{235}UF_6^*$:G dimers is almost instantly liberated and converted into translational recoil energy that enhances the out-of-jet-core escape rates of $^{235}UF_6$. This VT conversion driving force is in addition to the mass-dependent radial pressure gradient. Using improved relations developed in Refs. 19,27,28 for the bullet items listed above, MLIS-CR enrichment factors on the order of $\beta \sim 2$ were calculated in Ref. 21 for SF_6 and UF_6, and it was possible to explain the three accidental enrichments observed in 1986 at IT.

Subsonic MLIS-CR experiments

Besides CR with lasers in supersonic jets, there is another possibility to utilize laser-activated suppression of condensation to separate isotopes as reported first in 1976 by Gochelasvili et al.[31] In that method, a stream of gaseous isotopic molecules, such as $^iQF_6$ mixed with carrier gas G is passed subsonically through a chilled tube and coaxially irradiated with isotope-selective laser photons. The tube walls are cooled to a temperature just below the condensation point of QF_6, causing unexcited $^jQF_6$ to condense out on the wall but allowing laser-excited $^iQF_6^*$ to recoil from the surface after a VT conversion of its vibrational energy (V) into translation energy (T) on the wall. The $^iQF_6$ molecules recoiling from the wall thereby enrich the gas-stream flowing through the chilled tube, while causing isotope depletion in the wall condensate. The isotope effects for $^iBCl_3$ reported by the Russians[31] using cold-wall MLIS-CR were checked by Anderson and Lee at LANL, but they could not detect any significant isotope changes in selectively CO_2-laser-irradiated $^iBCl_3$.[32] Cold-wall MLIS-CR experiments were also conducted by the authors at the University of Missouri (MU). Their isotope-selective CO_2-laser-irradiations of $^iCHCl_3$ (chloroform) gave some positive but mostly ambiguous results.[33] On the other hand cold-wall MLIS-CR experiments at Idaho State University, which explored isotope separations of $^iSF_6$ using isotope-selective CO_2-laser-irradiations, seemed to show some observable isotope changes.[34]

A subsequent theoretical analysis of cold-wall MLIS-CR physics clarified the contradictory results that were observed for different molecules.[35,36] The laser-pumped vibrational energy quantum ε_L deposited in an excited isotopic molecule $^iQXZ^*$ must exceed the energy of the surface potential well-depth D_α of the condensate of QXZ to allow it to escape from the wall in a rebound upon VT conversion. Also the orientation of highly polar QXZ* molecules as they attach on the condensate surface layer is important. The CO_2-laser energy quantum of $\varepsilon_L \sim 0.12$ eV pumped into excited $^iCHCl_3^*$ or planar $^iBCl_3^*$ molecules cannot overcome the strong directional wall attractions ($D_\alpha \sim 0.13$ eV) they experience in their condensate surface layers. Even if $D_\alpha < \varepsilon_L$, the directions of atomic vibrations in polar molecules are usually not aligned along the attractive surface force perpendicular to the surface that must be overcome. The kinetic energy liberated in VT conversions of these molecules on condensate surfaces is then insufficient to allow them to escape from the attractive wall potential. For vibrationally excited symmetric $^{i}SF_6^*$ molecules however, the laser excitation energy $\varepsilon_L \sim 0.12$ eV does exceed the surface well-depth $D_\alpha \sim 0.08$ eV and allows $^{i}SF_6$ to escape from the wall after a VT conversion. On the other hand, for UF_6^* with $\varepsilon_L \sim 0.08$ eV and $D_\alpha \sim 0.14$ eV, escape from its condensate layer is not possible. Only on condensate-free surfaces with wall potentials $D_\alpha \sim 0.05$ eV (e.g., gold), is it possible to affect isotope separation during a very brief initial period when surface deposits do not yet cover the entire surface.[35,36]

Besides the $\varepsilon_L > D_\alpha$ requirement which few gaseous isotopomers can satisfy, low operating pressures are necessary to minimize gas-phase collisional VT losses for laser-excited $^{i}XYZ^*$ molecules diffusing to the wall. Low pressures and thus low flow rates makes the subsonic cold-wall MLIS-CR scheme unattractive. In comparison, free-jet MLIS-CR techniques can accommodate much higher flow rates due to supersonic speeds (1000 times subsonic speeds) even at low chamber operating pressures. They also do not have $\varepsilon_L > D_\alpha$ restrictions.

Brief History of Laser Isotope Separation Techniques

AVLIS, MOLIS and CHEMLIS

Although supersonic MLIS-CR seems now to have taken center stage over other MLIS techniques, it is worthwhile to examine previous LIS research efforts, which preceded the present status. Reference 5 is a compendium of 104 papers on various LIS research efforts written before 1994. After powerful lasers became available in the 1970s, there was a strong belief that laser technology could replace the old inefficient gaseous diffusion process for uranium enrichment. Two different approaches were explored, one called AVLIS (Atomic Vapor Laser Isotope Separation) using selective excitation of atomic uranium vapors, and the other MLIS (Molecular Laser Isotope Separation), which uses gaseous uranium hexafluoride (UF_6) as feed material.[5] In AVLIS, atomic uranium vapor is produced by an electron gun, and isotope-selective excitation and ionization (6.1 eV) of ^{235}U is carried out by three-color or two-color visible or ultraviolet laser irradiation. $^{235}U^+$ ions are collected by a negatively charged collector.[5] Successful pilot enrichments of atomic uranium using AVLIS were reported in the late 1980s by the Lawrence Livermore National Laboratory in the US and by the French Commissariat de l'Energie Atomique. Although more energy is needed and the generation/handling of corrosive uranium vapors is costly, the electron excitation spectroscopy of pure uranium atoms was well understood from the outset. In contrast, in the less expensive MLIS technique, the complex rovibrational laser excitation physics of molecular UF_6 required more exploratory investigations.

For MOLIS (Molecular Obliteration LIS), the most popular scheme was selective excitation and dissociation (2.7 eV) of $^{235}UF_6$ via the reaction $^{235}UF_6 + nh\nu \rightarrow {}^{235}UF_5 + F$. Reactant CH_4 was usually added to scavenge F atoms and inhibit the back reaction of UF_5–UF_6. This reaction can be induced by absorption of multiple $^{235}UF_6$-resonant 16 μm laser photons in intense pulses, a process referred to as multiphoton dissociation (MPD).[5] Because no high-power 16 μm infrared laser could be found to directly excite the fundamental photon-active ν_3-vibration of UF_6, the required 16 μm laser photons for MOLIS/MPD were produced in optically pumped para-H_2 gas by Raman conversion of 10 μm laser photons from a pulsed high-power CO_2 laser.[5]

Because the isotope shift $\Delta\nu_3$ between $^{235}UF_6$ and $^{238}UF_6$ is only 0.6 cm^{-1}, it was further necessary in MOLIS to cool UF_6 gas to a sufficiently low temperature to shrink and separate overlapping absorption bands of its ν_3 vibration around 16 μm ($\nu_3 \sim 626$ cm^{-1}) to promote selective excitation of $^{235}UF_6$.[5] To achieve this, one used supercooling supersonic free jets of UF_6 gas diluted in an inert buffer gas G (G = Ar, N_2, etc.). Gaseous UF_6 + G mixtures were self-cooled by adiabatic expansion after passing through a nozzle into a vacuum chamber, where the supersonic jet is crosswise or coaxially irradiated with 16 μm laser radiation. Although super-cooled UF_6 will remain gaseous during its transit through the irradiation chamber if UF_6 is diluted in G at concentrations less than $UF_6/G \sim 0.05$. Such nozzle-cooling in MOLIS is quite similar to Becker's scheme shown in Figure 1 except that jet expansion was carried out to colder downstream temperatures of about 150 K, but before dimer formation would set in. Dimerization spoils the separated and sharpened ν_3 bands of cold $^{235}UF_6$ and $^{238}UF_6$ monomers and was avoided in MOLIS.[24]

A two-step resonant photon excitation of $^{235}UF_6(\nu_3)$ followed by near-instant multistep photon absorption of high-intensity red-shifted laser irradiation was found to give the highest selectivity in MOLIS. In some MPD experiments, UV irradiation followed two-step IR excitations instantaneously to promote selective dissociation.[5,25] Solid $(^{235}UF_5)_m{:}G_n$ particles enriched with $^{235}UF_5$ were caught by riffle plates in the exit stream of the irradiated gas, thus separating enriched solid product from gaseous depleted UF_6 tails.[5,25] In a variant of MOLIS dubbed CHEMLIS, induction of an accelerated chemical reaction was attempted by irradiation of gaseous $UF_6{:}RX$ complexes where RX is a slow reactant, using isotope-selective high-order vibrational laser excitations.[5] In still another CHEMLIS scheme, selective laser excitation and dissociation of metastable $^{235}UF_5X$ with X = Cl or Br was considered.

SILEX and CRISLA

The AVLIS, MOLIS, and CHEMLIS enrichment processes were never industrialized, and between the mid-1980s and mid-1990s, most research on these processes in the US and other countries was terminated. The major "show-stoppers" for commercialization were expensive reprocessing chemistry, materials corrosion, inefficient laser excitation, and problems with low pulse repetition rates of excitation lasers. United States Enrichment Corporation (USEC) continued the successful but expensive AVLIS program until the late 1990s, but halted it in favor of the less expensive SILEX process, briefly partnering with SILEX in Australia in 1999. In 2003, USEC also terminated the SILEX collaboration in favor of demonstrated advanced centrifuge technology, fearing excessive development costs for improving SILEX's pulsed 16 μm laser system.[6] However, GLE has now resumed development of the SILEX process to assess its commercial viability.

The CRISLA process has also had a checkered history. One of us (Eerkens) started investigating the use of lasers for uranium enrichment in 1967, and after a stint on the centrifuge program at AiResearch in Los Angeles, formed the

Table 1. Historic Milestones of Molecular Isotope Separations by Laser-Assisted Selective Condensation Repression in Supersonic Free Jets

PRE-LASER

1955—E.W. Becker, K. Bier, H. Burghoff; U of Marburg, Germany; Publication of Hydrogen + Argon Mixture Separation by Supersonically Cooled Free Jet using a Nozzle and Skimmer (Ref. 8).

1957—J.W. Eerkens, B. Sehgal, L.M. Grossman; UC-Berkeley Publication of Nitrogen/Oxygen Separation by Supersonically Expanded Free Jet using Nozzle and Jet-Skimming Probe (Ref. 10,11).

POST-LASER

1977—Y.T. Lee (Nobel Laureate); and J.A. Sullivan, J.T. Lee Jr, K.C. Kim; UC-Berkeley/Los Alamos National Lab Patent and Patent Application on Isotope-Selective UF6 Dimer Excitation/Separation in Supersonically Cooled Free Jets (Ref. 15,16).

1985—H. VandenBergh, J.M. Zellweiger, J.M. Philippoz, P. Melinon, R. Monot; Institute de Chemie Physique, Ecole Polytechnique, Lausanne, Switzerland; Publication of Measured SF6 Isotope Separation by CO2 Laser Excitation and Selective Dimerization (Ref. 7).

1986—J.W. Eerkens, R. Griot, A. Semet, J. Hardin; Isotope Technologies, Los Angeles, California; Observation of Modest U-235 Enrichments in UF6 after Selective Laser Irradiation of Supersonic Microjets from Chamber Injectors (Ref. 25).

1993—D. Garratt, J. Wang, B. Olson; CRISLA Technologies /CAMECO, Saskatoon, Canada; Observation of slightly U-235- depleted Clusters in Condensed UF6 after Selective IR Laser Irradiation (Private Communication).

1993—M. Goldsworthy, H. Struve; SILEX Systems, St Lucas Heights, Australia; Observation of UF6 Enrichments using 16-micron Raman-converted CO2 Laser Irradiation of Supersonically Cooled Free Jets (Ref. 6).

2009—T.G. Orr; GLE (subsidiary of GE/Hitachi/CAMECO), Wilmington, N. Carolina; Announced U-235 Enrichment Pilot Plant Program using Licensed SILEX Process (Ref. 1–4).

Lischem Corporation in 1977. Lischem morphed into IT in 1985 in partnership with R. Griot, owner of Melles-Griot, a major US manufacturer of optics and lasers. IT originally pursued UF_6 enrichment using the CHEMLIS approach, naming its technique CRISLA. CRISLA stood for Chemical Reaction by Isotope Selective Laser Activation, but later (1999) this was changed to Condensation Repression by Isotope Selective Laser Activation after it became clear that prevention of dimer formation was the more practical MLIS game. Some felt CR for Chemical Reaction included reactions with dimers and a redefinition was not needed.

After an initial collaboration and exchange of information in 1989, IT began merger negotiations in 1990 with Australian Nuclear Enterprises, later renamed SILEX, to jointly develop the CRISLA process. However, a dispute about the project's funding caused a last-minute break-off of all negotiations. Griot then formed a partnership with CAMECO in 1991, and CRISLA research was continued under Dennis Garratt, technical director of CRISLA Technologies in Saskatoon, Saskatchewan. The entire CRISLA laboratory was moved from Los Angeles to Canada, while Eerkens became a technical consultant to the program with an office in Pacific Palisades, California. In 1993, after the Berlin wall came down, Russia started selling reactor-grade uranium on the world market at less than half the cost of its production in the West. Also large Russian stockpiles of weapons-grade uranium were delivered to the US to be blended down to reactor-grade fuel. CAMECO then decided to halt further development of CRISLA and became a trader of Russian uranium to fulfill its delivery contracts. Under the IT-CAMECO partnership agreement, all CRISLA laboratory equipment was returned to IT and sent to the University of Missouri (MU), Griot's alma mater. In 1994, Eerkens moved to Missouri to reassemble the CRISLA laboratory and investigate laser enrichment of medical isotopes irradiated in MU's research reactor.

Nuclear Proliferation Potential of Uranium Laser Enrichment

Concerns have been expressed that laser enrichment of uranium might make it more difficult for Nonproliferation Treaty inspectors of the International Atomic Energy Agency to detect possible diversions for weapons use. Although a laser enrichment plant has a smaller foot-print than a centrifuge facility, the size of an enrichment plant should not be the main criterion to determine if it is being used for 99% weapons-grade or 5% reactor-grade enrichments, just like one cannot tell from the size of a bank building if it processes billion- or million-dollar transactions. What needs to be monitored is the amount and rate of uranium hexafluoride feed that is delivered to the enrichment plant and how much leaves as tails and how much as product. Regardless of the enrichment plant size, to produce 10 kg of 99% U-235 enriched uranium takes 1.4 metric tons of natural uranium or 2 tons of uranium hexafluoride feed and 1.97 tons of 0.2% hexafluoride tails, which should be traceable. For reactor-grade uranium enrichments, a 2-ton hexafluoride feed would produce about 0.21 tons (= 210 kg) of 5% enriched uranium hexafluoride and 1.79 tons of depleted (to 0.2% U-235) hexafluoride tails. Thus, to detect different enrichment scenarios one must monitor not only the large quantities of natural uranium feed but also the hexafluoride product quantities (10 kg vs. 210 kg) and their assays (99% vs. 5%). Whether enrichment is achieved by diffusion, centrifuges, or lasers makes no difference. Hexafluoride production quantities and their fate need to be accounted for.

If it is important to know, whether hidden lasers instead of centrifuges are used, one might investigate if a lot of far-infrared laser optics and/or cryogenic gases are purchased by an undeclared enrichment facility. Such special laser materials are essential for laser enrichment but mostly absent from centrifuge plants. Manufacturers of infrared lasers, optics, and laser materials are relatively few and it is not too difficult to trace their products.

Conclusions

Laser-Assisted Selective Condensation Repression (LASCOR) using supersonic free jets can be a powerful new technique for the gaseous separation of isotopomers as well as for the separation of mixtures of molecular species. Its chronological evolution is shown in Table 1. Though details of its application to uranium laser enrichment in the SILEX process have been classified, it is similar in concept to

CRISLA except for laser-type, excitation techniques, and operational parameters. It is possible that in the SILEX-based GLE pilot program,[1] continuous 16:m diode lasers have been substituted for the cumbersome pulsed raman-conversion CO_2 lasers reported in Ref. 6. SILEX promoters have stated that if pilot runs are successful, they can supply reactor-grade fuel for power plants at half the price of that from second-generation centrifuges. As with other laser enrichment processes for uranium (e.g., AVLIS), operational "sweet spots" and precise details of the selective excitation of UF_6 isotopomers in both CRISLA and SILEX are proprietary or classified for security reasons. Although CRISLA and SILEX are most lucrative for enriching tons of UF_6 for power reactors, utilization of the LASCOR concept can also be attractive for separations of desirable medical/industrial isotopes and for separating gaseous mixtures of different molecular species. We believe a wider dissemination of LASCOR physics as discussed above and in the references will benefit the applied separation sciences.

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Manuscript received Jan. 8, 2010, and revision received Jan. 25, 2010.