Laser Isotope Separation Employing Condensation Repression

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Abstract - *Molecular laser isotope separation (MLIS) techniques using condensation repression (CR) harvesting are reviewed and compared with atomic vapor laser isotope separation (AVLIS), gaseous diffusion (DIF), ultracentrifuges (UCF), and electromagnetic separations (EMS). Two different CR-MLIS or CRISLA (Condensation Repression Isotope Separation by Laser Activation) approaches have been under investigation at the University of Missouri (MU), one involving supersonic super-cooled free jets and dimer formation, and the other subsonic cold-wall condensation. Both employ mixtures of an isotopomer (e.g.* ${}^{i}QF_6$*) and a carrier gas, operated at low temperatures and pressures. Present theories of VT relaxation, dimerization, and condensation are found to be unsatisfactory to explain/predict experimental CRISLA results. They were replaced by fundamentally new models that allow ab-initio calculation of isotope enrichments and predictions of condensation parameters for laser-excited and non-excited vapors which are in good agreement with experiment. Because of supersonic speeds, throughputs for free-jet CRISLA are a thousand times higher than cold-wall CRISLA schemes, and thus preferred for large-quantity Uranium enrichments. For small-quantity separations of (radioactive) medical isotopes, the simpler cold-wall CRISLA method may be adequate.*

1. INTRODUCTION.

After the birth of the laser, it soon became apparent that laser excitations might separate some isotopes more economically than techniques using mass-action diffusion (DIF), ultracentrifuges (UCF), and electromagnetic separation (EMS). When sufficiently powerful lasers for isotope-selective excitations became available in the 1970's, a world-wide effort to develop laser isotope separation (LIS) methods ensued.[1] The main advantage of quantum LIS methods over mass-action DIF, UCF, and EMS processes, is that for the latter, all isotopes or isotopomers of a desired element must be energized, while in LIS one only energizes one isotope of interest. For example to enrich U-235 with natural abundance 0.71%, a DIF, UCF, or EMS system must energize 140 times more molecules or atoms than the minimum required in a LIS process. In addition single-stage separations in LIS are generally higher ($\beta > 2$) compared with UCF's ($\beta < \sim 1.25$), allowing smaller footprints and the mounting of compact replaceable LIS chambers inside standard hot-cells. Thus LIS can remove radio-isotopes from "hot" mixtures which are presently difficult to extract since the entire EMS or UCF plant would become radioactive.

Two different LIS approaches have evolved since 1970. One labeled AVLIS (Atomic Vapor LIS), employs atomic vapors and utilizes isotope shifts of electronic excitation frequencies. The other called MLIS (Molecular LIS), uses gaseous molecules and takes advantage of isotope-shifts of vibrational absorption bands. In AVLIS, laser photons in the ultraviolet or visible part of the spectrum are required. After suitable lasers with tunable visible photons were found, the Avco and Livermore AVLIS programs were launched in 1971. Using high-temperature furnaces with electronbeams to evaporate elemental Uranium, AVLIS was demonstrated to enrich uranium in the 1980's. An AVLIS pilot unit was built and tested at Livermore around 1990.

When compared to present MLIS and UCF technologies, AVLIS enrichments of Uranium appear less economic and quite expensive to commercialize. While photon excitation and ionization physics of atoms had been well understood since the 1930's, prompting immediate AVLIS investigations, isotope-selective vibrational excitations of molecules in the infrared were less explored. After powerful infrared lasers were developed in the 1970 to 1990 period, a number of favorable laser/isotopomer spectral matches were found. While the first step of providing selective molecular laser excitation was soon achieved, the second MLIS step of separating or "harvesting" excited isotopic species from unexcited ones, proved more difficult. Early MLIS harvesting involved molecular obliterations (MOLIS) and enhanced chemical reactions (CHEMLIS) with a mixed-in coreactant. In these schemes, aside from selective excitation, laser photons are used to induce dissociations and/or chemical reactions of selected isotopomers with mixed-in coreactants, yielding enriched or depleted products that are chemically different and separable from feed molecules. Though some MOLIS/CHEMLIS schemes utilizing multi-photon absorption (e.g. for $^{i}SiH_3Cl$) were successful, they still required a large number of photons per separated isotopomer, partly negating the basic LIS promise of low energy consumption. Experiments showed further that heavy molecules such as UF_6 formed process-complicating dimers, when cooled to improve the spectral separation of adjacent isotopic absorption bands.

Rather than combating dimerization, subsequent research took advantage of it, leading to the present condensation repression (CR) harvesting techniques. A great advantage of CR-MLIS or CRISLA (Condensation Repression Isotope Separation by Laser Activation) is that feed and product gas streams are chemically the same, so staging is easily implemented if desired. One laser beam for example can serve to irradiate four or more enriching chambers in series. Finally, quantum energies needed to affect CR are compatible with single photon energies of high-power CO_2 and CO infrared lasers. That is, CRISLA is activated by single infrared photons of ~0.1 eV per $^{235}UF_6$ monomer or dimer. In contrast, AVLIS needs about 6.2 eV per atom for Uranium ionization supplied sequentially by three visible photons from three Cu-vapor-pumped dye lasers, while CHEMLIS and MOLIS require 6 to 30 infrared photons to deliver 2 to 4 eV per $^{235}UF_6$ molecule for a laser-induced chemical change.

The throughput of a single free-jet CRISLA device (Fig. 1) is on the order of 0.1 moles/hr, sufficient to be of interest for U-235 enrichments and comparable to a single gas ultracentrifuge unit which handles 0.01 to 0.1 moles/hr. On the other hand, a single cold-wall CRISLA unit (Fig. 2) can only process $\sim 10^{-5}$ moles/hr. This may still be useful for separating small quantities of (radio-)isotopes. Table I lists typical performance parameters and estimated product costs of U-235 enrichment by DIF, UCF, EMS, and LIS, showing CRISLA to be quite competitive. In what follows we outline the basics of free-jet and cold-wall CRISLA schemes researched at the University of Missouri.

2. CONDENSATION REPRESSION HARVESTING IN MLIS.

The two CRISLA schemes presently being investigated at the University of Missouri (MU), employ mixtures of a vapor with isotopomers such as $^{i}QF_6$, $^{i}QF_4$, or $^{i}QXYZ$ (e.g. UF_6, MoF_6, SF_6, SiF_4, $XeOF_4$) with ^{i}Q a desired isotope, diluted in excess carrier gas G (G = H_2, He, N_2, Ar, Xe, SF_6, etc).

Both CRISLA schemes are operated at low temperatures and pressures,[3,4,5] one employing supersonic free jets and suppression of dimer formation, and the other utilizing subsonic cold-wall condensation. In the free-jet method, a self-cooling QF_6/G gas stream expands adiabatically through a nozzle into a low-pressure chamber shown in Figure 1. After traversing the chamber, most of the jet core is intercepted and captured by a skimmer, while rim gases that radially diffuse out of the core are pumped out through a separate evacuation system. A tuned laser beam irradiates the jet coaxially or transversely and excites selected $^iQF_6$ isotopomers. Unexcited $^jQF_6$ molecules dimerize in the jet as it cools down and tend to stay in the jet core longer because of their heavier mass. Excited $^iQF_6^*$ migrate out of the jet core more rapidly, following a brief sub-microsecond existence as a $^iQF_6^*$:G dimer that experiences VT conversion due to predissociation, yielding epithermal $^iQF_6$ and G molecules that recoil off each other. As a result the rim gases are enriched by, and the skimmer gas stream is depleted of $^iQF_6$.[3] The heavier the atomic mass M_G of carrier gas G, the higher the separation factor β_i is. However to insure adequate supersonic jet cooling, the gas coefficient of G must be $\gamma_G = c_p/c_v \geq \sim 1.25$.[3] (For atoms $\gamma_G = 1.66$; for polyatomics $\gamma_G \rightarrow 1$ with increasing mass).

In the cold-wall approach, a coaxial laser beam selectively excites $^iQF_6$ in a QF_6/G gas stream that flows subsonically through a wall-cooled tube, shown in Figure 2. The temperature of the wall must be such that the corresponding equilibrium vapor pressure is below the partial vapor pressure of the incoming QF_6 vapor so that some QF_6 can condense out. The precise value of temperature T is selected to optimize isotope separation. The laser beam radius in the tube should be as close as possible to the inner radius of the cylindrical tube, but not overlap it. Then, if sufficient numbers of excited $^iQF_6^*$ reach the cold wall (i.e. at low total pressures), and provided the vibrational excitation quantum ε_a of $^iQF_6^*$ exceeds the well depth D_α of the surface potential, $^iQF_6$ will desorb from the surface at a higher rate than unexcited $^jQF_6$. This is due to VT conversion and recoil of surface-captured $^iQF_6^*$ molecules, mostly from predissociation effects. The exit gas stream is thereby isotope-enriched and the wall condensate isotope-depleted. However the condition $\varepsilon_a > D_\alpha$ and additional surface orientation/configuration restrictions, eliminate some isotopomers as candidates for a CRISLA cold-wall process.[5]

Free-jet and cold-wall CRISLA are only effective at total gas mix pressures below 0.1 torr.[3,5] However because of supersonic speeds, throughputs in the free-jet scheme are still reasonable. In the subsonic cold-wall scheme, process gases move a thousand times more slowly. Free-jets are therefore preferred for CRISLA enrichment of $^{235}UF_6$. For small-quantity radio-isotope separations however, the simpler cold-wall method is still useful.

In both the supersonic free-jet and subsonic cold-wall case, currently favored theories of dimerization, vibrational relaxation, and cold-wall condensation were found incapable of predicting experimental observations. Calculated optimum pressures were far too high. This greatly hindered earlier validations of CRISLA concepts which appeared fundamentally viable. In-depth studies were therefore undertaken to reexamine dimerization, condensation, and vibrational relaxation physics of QF_6 vapor molecules, with outcomes that can be summarized as follows:

A. Prior Theories.

(1). Dimer formation in gases and vapors takes place by three-body collisions because energy and momentum must be conserved simultaneously.
(2). According to established V,T±V energy conversion theory, vibrational deexcitations of excited molecules in gases occur primarily via specular two-body collisions between molecules from the high-energy tail of the Boltzmann distribution.
(3). Condensation rates on surfaces are calculated from relations based on dimensional analysis and thermodynamics using empirical mass/heat transfer coefficients and heats of vaporization.
(4). Theories of vibrational relaxation rates of excited molecules on surfaces are incomplete; calculations and experiment often don't agree. A consistent theory is lacking.

B. New Theories.

(1). At sub-ambient temperatures, dimers in a gas are mostly formed in two-body collisions by low-energy molecules in the Boltzmann distribution. Kinetic energy and momentum are conserved by quantum transitions in the VanderWaals bond and dimer rotation.[2]
(2). At temperatures $T < \sim 250$ K, vibrational relaxation takes place primarily via three steps: QF_6^*:G dimer formation; rapid VT conversion of ε_a by predissociation of QF_6^*:G; mutual recoil of epithermal QF_6 and G. Dimerizations + sub-microsecond predissociations + recoils, far exceed relaxation rates predicted by standard collisional VT theory.[2,3]
(3). A kinetics-based theory was developed that uses the principle of conservation of event probabilities for one-on-one interactions between an impinging gas molecule and a surface condensate molecule. It agrees well with expriment and allows ab-initio calculations of critical temperatures, vapor pressure curves, condensation rates, and partial adsorption parameters, for excited as well as unexcited molecules condensing or adsorbing/desorbing on a surface.
(4). With the theory in (3), temperature-dependent relative probabilities of vibrational relaxation of surface-captured excited QF_6^* molecules can be calculated, via mechanisms such as:
(a) Direct energy transfer of ε_a to condensate phonons, (b) spontaneous photon emission,
(c) VT deexcitation by a surface-striking energetic gas molecule, and (d) predissociation + VT conversion. Under typical CRISLA operating conditions, (d) is most probable for octahedral QF_6^* molecules. Event (a) has an unexpected low probability because of the phonon cut-off energy and mismatch of phonon quantum energies with energies ε_a.

The possibility of laser-induced isotope separation by dimerization repression in supercooled supersonic free jets was first suggested by Y.T. Lee in 1977,[6] and experimentally verified for SF_6 by H. VandenBergh in 1985.[7] Lee's original proposal assumed laser excitation of already formed dimers, which would thereafter pre-dissociate, whereas our work and VandenBergh's indicate that excitation of $^iQF_6$ monomers followed by dimerization (e.g. $^iQF_6^*$:Xe) and subsequent pre-dissociation of the dimer is more profitable for isotope separations. This is because photon absorption peaks of monomers have much higher cross-sections than those of dimers.[3]

As mentioned, originally the major problem in diagnosing and predicting dimerization in free jets was the lack of a reliable theory. It was believed that dimers could only form in three-body collisions because of the requirement of simultaneous energy and momentum conservation. If so, the high rates of dimer formation observed in cold supersonic free jets, would be theoretically impossible. If the three-body theory were correct, laser-pumped vibrational states of QF_6 molecules at low temperatures should last a relatively long time. Well-established vibrational energy transfer theory then would predict that the probability for vibrational relaxation by VT (Vibration → Translation) conversion in direct two-body collisions approaches near-unity values only at elevated temperatures and/or for low-mass collision partners (e.g. H_2, He). At low temperatures ($T < \sim 200$ K) and for heavy molecules QF_6 and G, laser-excited QF_6^* molecules were predicted to last through some 10^5 collisions before loosing their vibrational energy by collisional VT transfers. Early CRISLA experiments relying on this theory therefore used process gas pressures that were much higher than what was found later to be effective.

An independent examination of dimerization physics shows the three-bodies-only theory for creation of dimer populations to be incorrect.[2] The older theory assumes planet-like motions of point particles but actually dimers of finite-sized molecules can form by much more frequent two-body contact collisions with kinetic energies in the low-energy part of the Boltzmann distribution. Excess energy is shed by exchange with vibrational quanta in the VanderWaals bond and by induction of dimer rotation. Dimer formation rates are essentially the same for laser-excited and unexcited QF_6 molecules, since both migrate with the same thermal molecular speeds. However after a few Lissajous motions of a freshly formed QF_6^*:G dimer, stored vibrational energy ε_a in QF_6^* is converted into kinetic energy by the pre-dissociation process. This VT conversion forces the dimer partners to recoil off each other, which is utilized in CRISLA free-jet isotope separations. The new dimer formation theory[2] shows that the probability for dimer formation increases exponentially with decreasing temperature. Thus vibrational relaxation of excited $^iQF_6^*$ also increases as the temperature drops since it is catalyzed by dimerization. This is opposite to standard collisonal VT theory which decreases exponentially with decreasing T. With the new dimer theory, migrations of dimers, and of thermal and epithermal monomers in a supersonic free jet can be calculated with and without laser irradiation. Optimum pressures and temperatures for isotope enrichment can be predicted, as shown for example in Figure 3.

Aside from a re-examination of dimerization in cold gases, some puzzling results observed in subsonic cold-wall adsorption and condensation experiments, spurred a study of the basic physics in these processes.[4,5] In some early experiments with co-axially laser-irradiated subsonic flows of UF_6/G gas mixtures which passed through wall-cooled alumina or nickel tubes, the exit gas stream was found to be slightly isotope-enriched,[8] but only if the wall was clean and not covered with UF_6 or UF_5X product, i.e. only in initial test runs. This effect can now be explained by an improved theory for condensation and adsorption. It also shows that enrichment of laser-excited $^iUF_6^*$ after VT conversion and recoil from a cold wall covered with UF_6 condensate is impossible because the attractive surface well depth $D_\alpha \approx 1200$ cm^{-1} of a UF_6 condensate layer is larger than energy $\varepsilon_a \approx 628$ cm^{-1} released in VT conversion by a wall-captured $^iUF_6^*$ molecule. However for bare (F_2-passivated) gold, nickel, or alumina surfaces with $D_\alpha(M{:}UF_6) < \sim 400$ cm^{-1}, isotope enrichment of the gas stream is initially possible until the surface is covered with UF_6 or UF_5X product.[5] For $^{33}SF_6$ with $D_\alpha \approx 670$ cm^{-1} and $\varepsilon_a \approx 940$ cm^{-1}, cold-wall enrichment with continuously condensing SF_6 is possible on the other hand with β's shown in Fig. 4.

Experiments in Russia involving cold-wall laser isotope separation of $^iBCl_3$ were first published in 1975 by K.S. Gochelasvili e.a.[9] However attempts at Los Alamos by G.K. Anderson and J.T. Lee to duplicate the Russian results failed and caused abandonment of this concept.[10] The new cold-wall condensation theory may explain why Anderson and Lee's experiment failed and Gochelasvili's data are questionable. For planar BCl_3 molecules studied by Gochelasvili and by Anderson and Lee, the surface potential D_α of BCl_3 condensate probably exceeds the released quantum energy ε_a. In addition, because BCl_3 is planar, the recoil momentum from VT conversion of ε_a, is probably in and along the surface plane and thereby dissipated before surface escape might occur. This is in contrast to SF_6 with $\varepsilon_a > D_\alpha$, which has a three-dimensional octahedral shape, and for which surface escapes by ${}^iSF_6^*$:Wall molecules experiencing VT conversion, is quite probable. CRISLA experiments with CO_2 laser irradiations at Idaho State University (ISU) and at MU have confirmed that small-quantity cold-wall enrichments of ${}^iSF_6$ can take place. Measured values between $\beta = 1.5$ and $\beta = 2$ agree with calculated values.

3. CONCLUSIONS.

We believe that supersonic free-jet CRISLA for the enrichment of U-235 or S-33 are promising processes, and that we have developed the requisite physics with which to model the performance of these processes. Much research with different molecular isotopomers is still needed however to widen the data-base of CRISLA methods, and to further validate the new analytic theories. Because in CRISLA, feed and product gases are physically the same (except for isotopic composition), simple enriching stages can be used in series and be irradiated by a single laser beam to obtain desired overall enrichments. When compared with UCF's, the main advantage of CRISLA is the total energy consumed per separated isotope and the smaller chamber size. Ultimately CRISLA techniques might be used for separation of radioactive isotopes from a "hot" mix of products generated in nuclear reactors. This can be done in hot-cells with infrared transmitting windows through which a laser beam is passed from an outside high-power laser.

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TABLE I. COMPARISON OF ^{235}U ENRICHMENTS FOR (0.71% F) TO (3.5% Y/0.25% W).[1]

	MASS ACTION			LASER		
	DIF (UF_6)	UCF (UF_6)	EMS (U)	AVLIS (U)	MOLIS (UF_5Cl)	CRISLA[2] (UF_6)
β_{stage}[3]	1.0025	1.15	10	7	2.7	2
Cascade Stages[4]	1,069 (650+419)	18 (11 + 7)	1	1	2	3
A-plant Sep Units[5]	154,530	494	1	1	4	12
A-Plant[5] Prod $Y=Y_u$ moles/hr[3]	15	0.1	0.001	0.01	0.008	0.02
Average Power P_u per Sep Unit[3,6]	0.372 kW/Unit	0.6 kW/Unit	30 kW/Unit	20 kW/Unit	4 kW/Unit	1 [7] kW/Unit
C-Plant [8] No Units (Ftprint,m^2)	[10,300] [(30,900)]	4,940 (75,00)	1000 (30,000)	100 (10,000)	500 (8,000)	600 [7] (4,800)
C-Plt Pwr [6] kWhr/moleY (keV/U235)	3,832 (144)	2,964 (116)	30,000 (1128)	2,000 (75)	2,000 (75)	600 [7] (23)
Excitation, eV/U-235	----	----	6.2 (ionization)	6.2 (ionization)	3.0 (dissociat'n)	0.1 (dimer pred)
Operating Cost [9]	\$ 0.80/g	\$ 0.62/g	\$ 9.46/g	\$ 0.63/g	\$ 0.63/g	\$ 0.19/g
Write-off Plant(10y)[9]	\$ 1.60/g	\$ 1.23/g	\$ 18.92/g	\$ 1.27/g	\$ 1.27/g	\$ 0.38/g
Tot Product Cost [9]	\$ 2.40/g	\$ 1.84/g	\$ 28.38/g	\$ 1.89/g	\$ 1.89/g	\$ 0.57/g

[1] F = Feed, Y = Product, W = Tails Stream.

[2] CR-MLIS = CRISLA = Condensation Repression by Isotope Selective Laser Activation (by Free-Jet).

[3] Estimated parameters based on values from the open literature.

[4] Ideal DIF and UCF cascades with number of stages in enriching and stripping sections in parentheses.

[5] A-Plant has single separator unit at top, producing 3.5% U-235 at rate $Y = Y_u$. Number of separator units are minimum for a minimum-size A-Plant with $Y = Y_u$. All separator units in cascades assumed to have same Feed F_u, Product Stream Y_u, and Waste Stream W_u, with $Y_u/F_u = \Theta = (1+\beta_{stage})^{-1}$.

[6] Includes pump-through and gas handling energies. For AVLIS, the e-beam heating energy for U vaporization is included; for MOLIS interstage chemical reconversions are accounted for.

[7] For CRISLA, one 3 KW laser beam is shared by three irradiation chambers (= units).

[8] C-Plant has Y = 1 mole(3.5%)/hr (= 1.15 kg-SWU/hr @ 4.82 SWU); F = 7.06 moles(0.71%)/hr; W = 6.06 moles(0.25%)/hr. UCF units mounted vertically. DIF values are fictitious for Y = 1 mole/hr.

[9] Rough cost estimates for C-plants: Electricity @ \$0.025/kwhr; Operating/Electric cost ratio $f_{oe} = 2$ for DIF, UCF; for others $f_{oe} = 3$. Capital/Operating cost ratio assumed to be $f_{co} = 2$ for all methods.

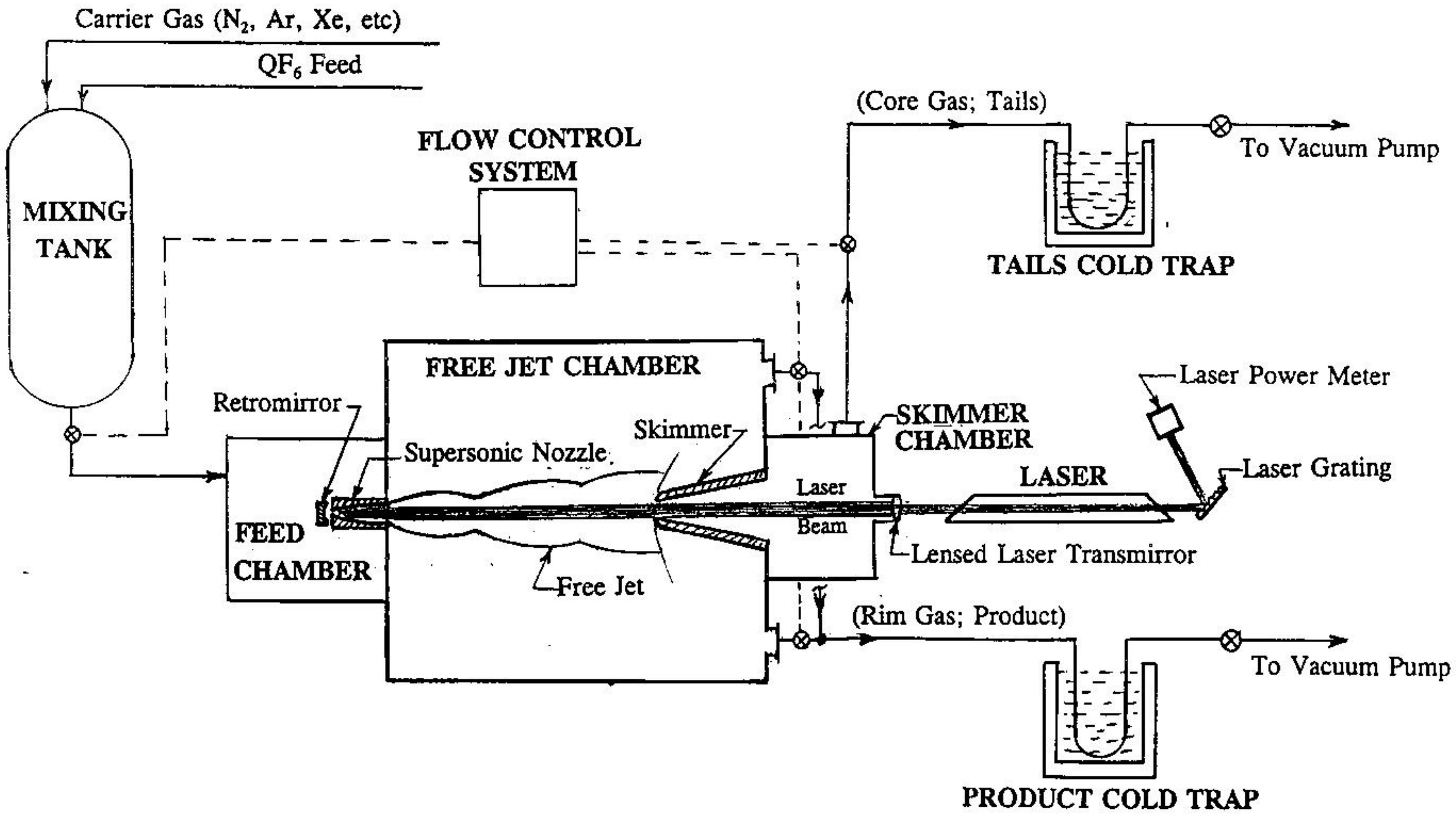

FIG. 1 SCHEMATIC OF FREE-JET LASER ISOTOPE SEPARATION EQUIPMENT

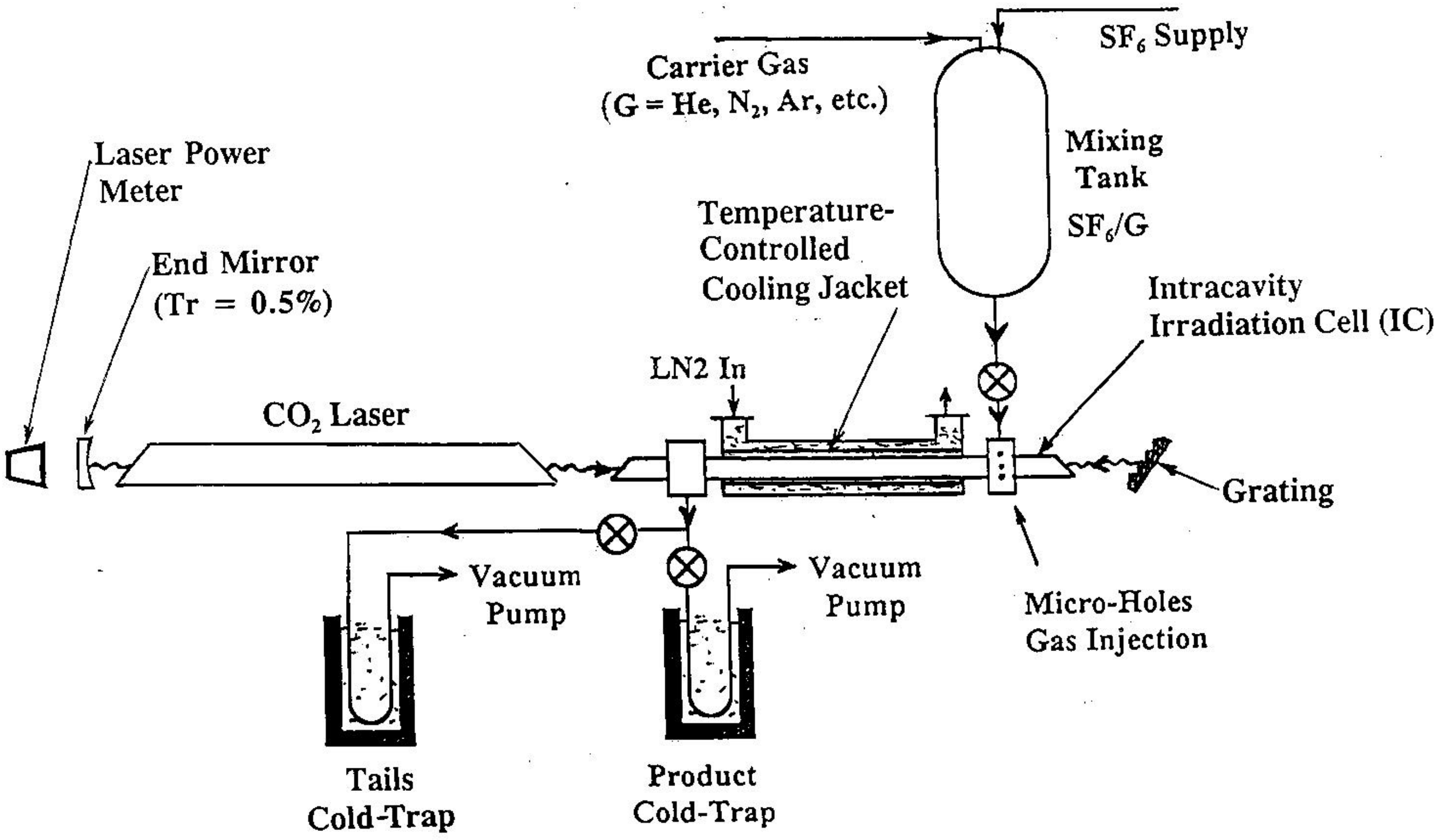

FIG. 2 SCHEMATIC OF COLD-WALL CONDENSATION REPRESSION LASER ISOTOPE SEPARATION EQUIPMENT.

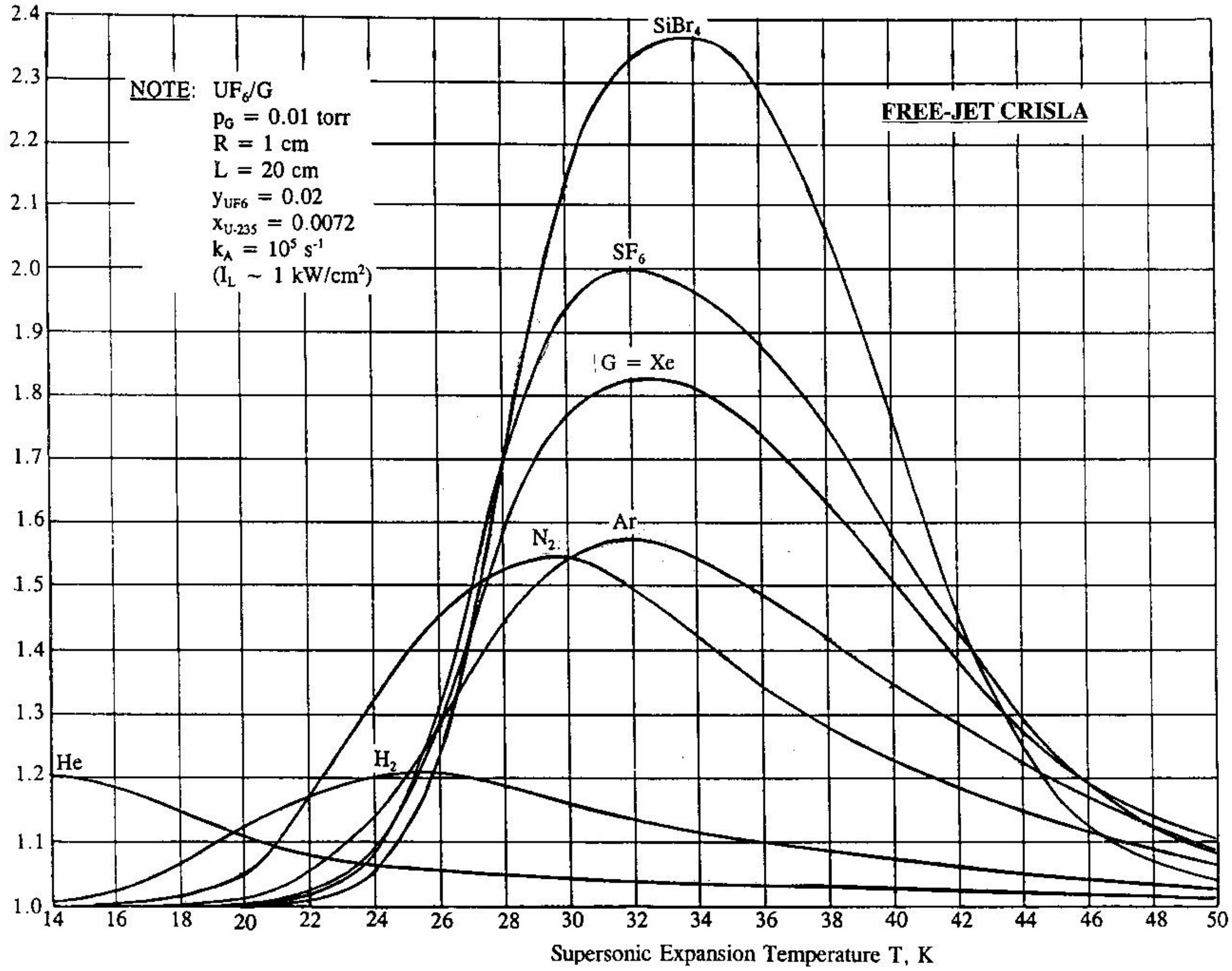

FIG. 3 ENRICHMENT FACTORS β_m(T) FOR UF$_6$(ν_3) MONOMER EXCITATION AT FIXED p_G.

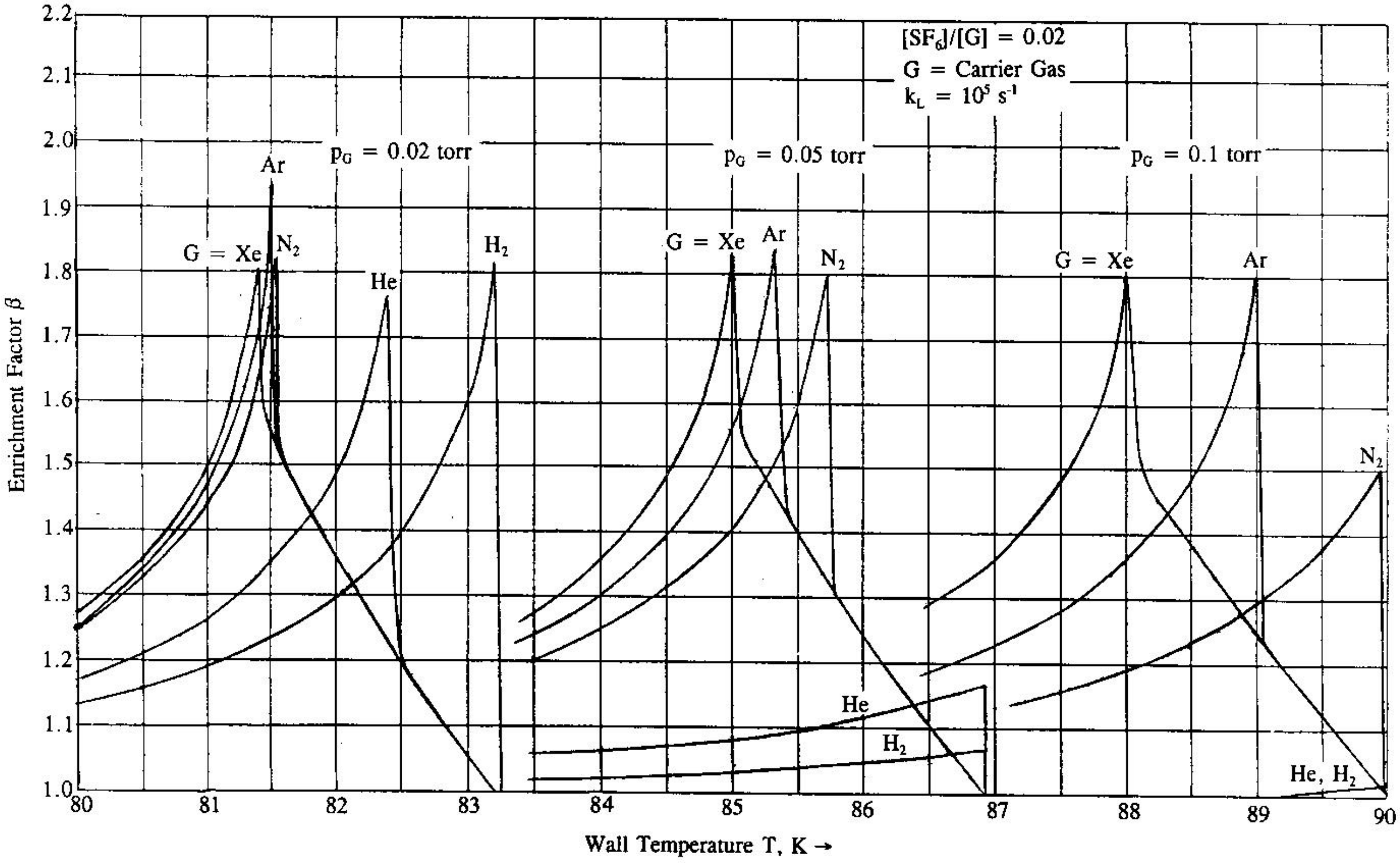

FIG. 4 CALCULATED ENRICHMENT FACTORS FOR $^{i}SF_6$ IN COLD-WALL CRISLA .