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(54) Title: IMPROVED ISOTOPE SEPARATION PROCESS

NOTE: COLLECTORS 'A' ARE USED WHILE MATERIAL IN TANKS 'B' ARE TRANSFERRED TO STORAGE AND VICE-VERSA
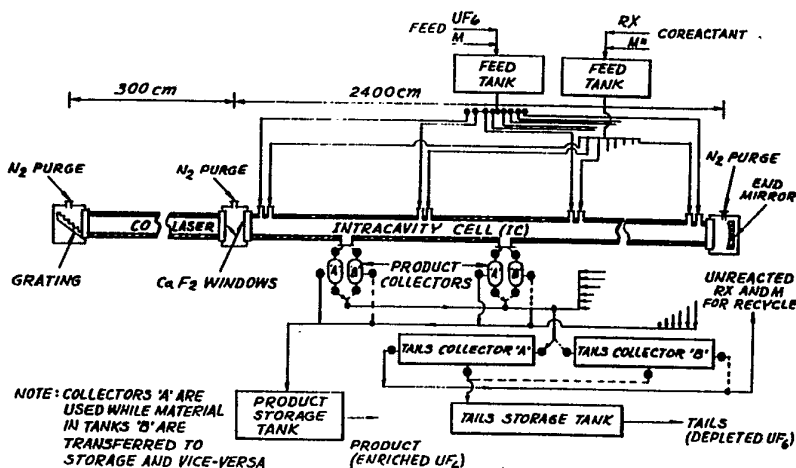
(57) Abstract

Selection criteria are disclosed for choosing a coreactant RX that will improve the isotope separation in laser-activated chemical reactions which may proceed by the steps: $^1MY + h\bar{V}_L \rightarrow {}^1MY^*$ (Laser Activation of Isotopic Materials), $RX + h\bar{V}_L \rightarrow RX^*$ (Laser Activation of Coreactant), $^1MY^* + RX^{(*)} \rightarrow ({}^1MY^*{:}RX^{(*)})^\dagger \rightarrow {}^1MX + RY$ (Chemical Exchange Reaction). The step of coreactant activation can be important in some exchange reactions but unnecessary in others. That is for some laser-activated chemical reactions, the second step may be absent. The selection criteria are based on the relative magnitudes of the bond-energies and therefore vibrational frequencies in the molecules ^1MY and RX, and the requirements for forming a Vanderwaals-like attachment complex. Also, the upper and lower limit of tolerable thermal (non-laser) reaction speeds are defined. It is shown further that it is necessary to restrict suitable RX candidates to those species which yield ^1MX product that does not participate in subsequent chemical reactions which cause isotope scrambling. The employment of a second auxiliary coreactant is recommended in certain cases if its interaction with the complex $({}^1MY^*{:}RX^{(*)})^\dagger$ will increase the latter's reaction rate and/or if it can scavenge the product ^1MX, thereby negating any subsequent isotope scrambling reactions of ^1MX. The auxiliary coreactant should not react, or only slowly react, with the reactants ^1MY or RX. By application of the selection criteria to UF_6, a small group of suitable chemical coreactants are identified which give improved Uranium isotope separations.

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IMPROVED ISOTOPE SEPARATION PROCESS

TECHNICAL FIELD

This invention relates to an improvement in isotope separation processes that employ a selective photon-induced energy level transition of an isotopic molecule containing the isotope to 5 be separated and a chemical reaction with a chemically reactive agent to provide a chemical compound containing atoms of the desired isotope. The invention discloses certain molecular attributes which if possessed by a chemically reactive agent used in the aforementioned process, make it more effective and the 10 isotope separation more economical.

BACKGROUND ART

The application of lasers for isotope separation has been the subject of many studies and development programs in the last 15 two decades. In particular, the separation of U-235 and U-238, needed for nuclear reactor fuel, has received considerable attention and has led to three distinct approaches. These approaches use lasers to cause isotope-specific ionization (AVLIS), dissociation (MOLIS), or activation of a chemical reaction 20 (CRISLA).

In the AVLIS approach, which is an abbreviation for Atomic Vapor Laser Isotope Separation, isotopic metal is vaporized (usually by means of electron guns) and the vapor is irradiated by two ultraviolet or three visible superimposed laser beams at two

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or three different wavelengths. In one AVLIS scheme applied to the
separation of Uranium and developed by the U.S. DOE at the Lawrence
Livermore Laboratory, a copper vapor laser is used as the primary
source of (green) laser photons. Dyes are used to convert these
5 photons to certain visible frequencies required for efficient
three-step selective excitation and ionization of U-235 atoms. The
selectively ionized U-235 ions are next removed from the U-238/
U-235 vapor by electromagnetic fields. This process is discussed
in "Laser Spectroscopy and its Applications," edited by L.J.
10 Radziemski, R.W. Solarz, and J.A. Paisner; Marcel Dekker, Inc. N.Y.
(1987), at pages 235, et seq., hereinafter "Laser Spectroscopy."

In the MOLIS technique, which is an acronym for MOlecular
Laser Isotope Separation, gaseous isotopic molecules are employed
instead of metal vapors. For example, in a Uranium enrichment
15 technique developed by the U.S. DOE Los Alamos Laboratory, gaseous
Uranium Hexafluoride (UF_6) is used and irradiated with two or three
successive 16-micron laser photons causing isotope-selective
excitation of $^{235}UF_6$ to the $2\nu_3$ or $3\nu_3$ vibrational level as stated
in Laser Spectroscopy, at pages 459, et seq. The $2\nu_3$ or $3\nu_3$-
20 excited $^{235}UF_6^*$ is next irradiated with an ultraviolet (UV) laser
beam causing it to dissociate to UF_5 + F. Instead of using a UV
laser beam, the isotope-selectively excited $^{235}UF_6^*$ can be
dissociated by a second high-energy 16-micron infrared (IR) laser
pulse which causes multi-photon absorption and dissociation. Thus,
25 some MOLIS schemes use two or three isotope-selective 16-micron IR
laser pulses followed by a UV laser pulse, while others use two or

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three isotope-selective 16-micron IR laser pulses followed by a high-energy second (red-shifted) 16-micron pulse that causes dissociation by multi-photon absorption.

In CRISLA, which stands for Chemical Reaction by Isotope
5 Selective Laser Activation, one laser beam is used which irradiates a gaseous mixture of the isotopic molecule to be separated (e.g., UF_6) and a coreactant RX. In the case of UF_6, for example, as described in U.S. Patent No. 4,082,633, a mixture of UF_6 and a suitable coreactant RX is isotope-selectively irradiated by 5.3
10 micron CO laser photons in an intracavity reaction cell. In this process, $^{235}UF_6$ is preferentially excited over $^{238}UF_6$ to the $3\nu_3$ vibrational excitation level. The excited $^{235}UF_6{}^*$ molecules react much more rapidly with the coreactant RX than unexcited UF_6, resulting in a Uranium-bearing reaction product that is enriched
15 in ^{235}U.

Both MOLIS and CRISLA depend upon vibrational molecular isotope shifts of hot-banded absorption contours. The overlap of the isotopic bands is generally smaller, the colder the irradiated gas is. This means that higher separation factors are obtained at
20 lower temperatures. However, UF_6 has a very low vapor pressure at the desired lower temperatures, causing throughputs to be very low. To overcome this problem in the MOLIS process, a mixture of UF_6 and a carrier gas such as Helium, Argon, Nitrogen, Hydrogen, or Methane, is usually used and supercooled in an expanding supersonic
25 jet. the jet is then intercepted by a 16-micron laser beam at a point where the UF_6 is still gaseous but far below its normal

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condensation temperature. Although supersonic jet-cooling could also be used in CRISLA, because of the higher isotope shift at = 5.3 micron used in CRISLA, arrangements that require only static or limited adiabatic-expansion cooling are usually adequate.

5 In Uranium enrichment by the CRISLA technique, the preferred wavelength is 5.3 micron at which the isotope-shift between the $^{235}UF_6$ and $^{238}UF_6$ absorption bands is three times larger than at 16 micron. On the otherhand, the UF_6 absorption cross-section at 5.3 micron is 10,000 times less than at 16 micron.

10   The lasers used in the AVLIS and MOLIS Uranium enrichment schemes are pulsed so that different frequencies are absorbed at different times with time frames and intervals that range from nanoseconds to milliseconds. In Uranium enrichment with CRISLA, on the otherhand, only one (or two) continuous-wave (CW) laser 15 beam(s) is (are) employed and no time-gating is required. The result is that the laser systems used in CRISLA are much simpler and less costly than those used in AVLIS and MOLIS. On the otherhand, CRISLA requires the use of a suitable chemical reaction which adds cost and complexity to the subsequent physical 20 separation of product and unreacted UF_6. The proper choice of an effective coreactant in CRISLA is, therefore, desired so that a more efficient process is obtained.

In CRISLA, chemical energy is used for most of the separation work, whereas in AVLIS and MOLIS, all the energy 25 provided for separation is photonic. The attractiveness of CRISLA over AVLIS and MOLIS is in part due to the fact that chemical

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energy is generally less expensive than laser photon energy. The techniques of photon-induced ionization and dissociation used in AVLIS and MOLIS rely on straight-forward extrapolations of earlier developed scientific knowledge. For this reason, investigations

5 of these laser isotope enrichment processes were completed earlier than CRISLA.

The desired coreactant in the CRISLA process is a coreactant RX which in its complexed state with a Uranium-bearing laser-excited molecule UY^*, that is in the molecular complex UY^*:RX,

10 shows a high reaction sensitivity to the vibrational excitation of the bond U-Y. In certain particular cases, the photon energy $E_L = hV_L$ pumped into UY^* is insufficient to overcome the reaction barrier energy E_a, that is $E_L < E_a$. However, if in this case $E_L < E_a < 2E_L$, it is essential that the coreactant RX also absorb a

15 laser photon $E_L = h\dot{V}_L$ so that the total pumped energy in the complex UY^*:RX^* is doubled to $2E_L$ and reaction is promoted. In addition to reaction sensitivity, it is important that the isotope-carrying product formed in a CRISLA reaction does not engage in subsequent chemical scrambling. Therefore, it has long been desired to define

20 certain essential molecular properties and selection criteria for RX that will ensure efficient isotope-selective laser-induced reactions of the complex UF_6^*:RX or UF_6^*:RX^* and the formation of UF_5X products that undergo little or no subsequent chemical scrambling. Application of these selection criteria to all

25 reactable RX molecules, greatly restricts the number of RX molecules that are useful in particular applications of the CRISLA

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process. Thus, by employing coreactants from this limited predefined group, considerable improvements in the CRISLA process result. The selection criteria can be equally applied to the CRISLA enrichment of isotopes other than Uranium.

5

DISCLOSURE OF INVENTION

Accordingly, it is an object of the present invention to provide improvements in the application of the CRISLA laser isotope separation process.

10   It is another object of the present invention to provide a process for the selection of chemical coreactants RX that will lead to an improved CRISLA isotope separation process when used with an isotopic molecule ^{i}MY.

Illustrations are provided for the application of the RX

15 selection criteria to the isotope separation of $^{235}UF_6/^{238}UF_6$ (that is for ^{i}M-Y = ^{i}UF$_5$-F) and specific molecules RX are identified which yield improved CRISLA enrichments of Uranium. However, the criteria are general and can be applied equally well to the separation of other isotopic molecules such as ^{i}ZrF$_4$, ^{i}ZrCl$_4$, ^{i}ZrBr$_4$,

20 ^{i}WF$_6$, and many other volatile halides. As utilized herein, the pre-superscript "i" is used on an atom to indicate that different isotopes exist which one wishes to separate.

As discussed below in greater detail, there are seven criteria which must all be satisfied by a coreactant RX in order

25 to achieve an improved CRISLA process utilizing the steps:

−7−

1
$$^{1}MY + h\nu_{L} \rightarrow {}^{1}MY^{*}(h\nu_{L}) \tag{I}$$

2
$$RX + h\nu_{L} \rightarrow RX^{*}(h\nu_{L}) \tag{II}$$

3
$$^{1}MY^{*}(h\nu_{L}) + RX^{(*)} \rightarrow ({}^{1}MY^{*}:RX^{(*)})^{\dagger} \rightarrow {}^{1}MX\downarrow + RY \tag{III}$$
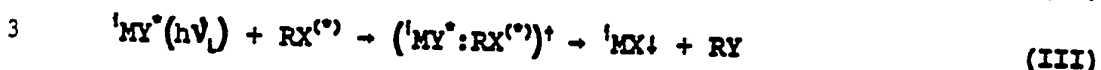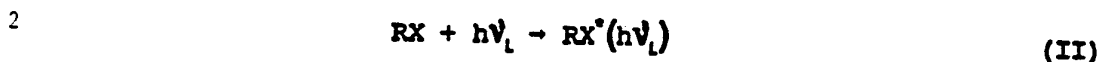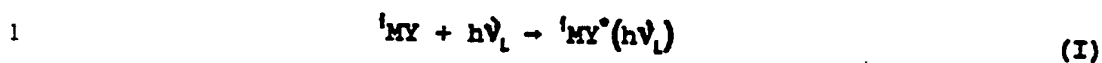
Here $h\nu_{L}$ represents the laser photon and photon energy with frequency ν_{L}. As explained heretofore, Step (II) may not be required and RX need not be excited in the complex $({}^{1}MY^{*}:RX^{(*)})^{\dagger}$ to cause significant reaction except for certain particular cases. It is clear that the coreactant RX must perform efficiently as indicated by the overall reaction (III), or else the resulting isotope separation will be poor. For example, if the reaction is too slow or if other reactions dominate, the resulting isotope effects will be uninteresting. For an improved CRISLA process it is therefore desirable to choose an efficient coreactant RX.

The first four criteria for choosing a suitable RX molecule are defined in U.S. Patent No. 4,082,633 and constitute a preselection process. The remaining three criteria are applied after the preselection process of the first four steps.

As indicated in step (A) of Figure 8, in choosing RX one must begin with the group of chemicals that do react with ^{1}MY. For example, for $^{1}MY = {}^{1}UF_{6}$, molecules such as N_{2}, O_{2}, CO_{2}, etc. do not react and can be left out in the first RX population selection. A more severe restriction is criterion (B), which eliminates all molecules RX from population "A" that strongly absorb photons at the laser wavelength to be used for the CRISLA process. However,

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according to the principles of the present invention, in some applications a mild absorption by RX may sometimes be advantageous.

Step (C) rejects species RX that are totally solid, having vapor pressures well below 10^{-3} torr at room temperature.

5 This selection step is necessary since the substitution reaction (II) must take place in the gas-phase to be effective. Step (D) eliminates RX molecules that could react with ^1MY but would require an amount of energy injection for the activated complex $(^1MY:RX)^\dagger$ which exceeds the energy E_L pumped into the ^1MY molecule alone or

10 $2E_L$ pumped by the laser into ^1MY and RX both. Laser-induced gas-phase reactions of $^1MY^*$ with RX must, of course, obey the law of energy conservation. At the end of step (D), one still has a very large class of possible coreactants RX, a few of which are listed in Table 1.

15 <u>TABLE 1 SOME STEP "D" (FIG. 8) REACTANTS RX FOR REACTION WITH UF$_6$</u>

$TiCl_4$	$SiBr_4$	$SiCl_4$	$GeCl_4$	GeH_4
BCl_3	$SiBr_aF_{4-a}$	$SiCl_aF_{4-a}$	HBr	AsH_3
$NOCl$	$AsCl_3$	CrO_2Cl_2	HCl	CH_4
$NOBr$	$SnCl_4$	SO_2Cl_2	SiH_4	H_2

20 The elimination of inefficient species RX from Step "D" reactants such as those shown in Table 1, is one of the objects of the present invention.

It has been found that reactants whose thermal rates of reaction k_T exceed the value given by equation (24) below, are poor

25 candidates for an efficient CRISLA enrichment process. Typical

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values of $(k_T)_{max}$ for the case of $^iUF_6$ isotope enrichment with a CO laser are $(k_T)_{max} \approx 1$ sec^{-1} per UF_6 molecule. The rate constant k_T should not be too small either or the production rate of enriched product becomes unattractively small. For the CRISLA enrichment

5 of $^iUF_6$ with a CO laser this lower limit on k_T is typically $(k_T)_{min} \approx 10^{-3}$ sec^{-1}. Thus as applied to the CRISLA enrichment of $^iUF_6$ with a CO laser, Step (E) in Figure 8 states that $10^{-3} \lesssim k_T \lesssim 1s^{-1}$. This criterion eliminates the first column and the species H_2 and CH_4 in the last column of coreactants listed in Table 1 because k_T

10 is larger than 1 s^{-1} for species in the first column and k_T is less than 10^{-3} s^{-1} for coreactants in the last column with desirable coreactant partial pressures of $p_{RX} \lesssim 1$ torr. The thermal reaction rates k_T of AsH_3 and GeH_4 in the last column of Table 1 as well as SiH_4 are usually also less than 10^{-3} s^{-1}. However, these reactants

15 may be laser-excited by reaction (II) causing their effective rate of reaction with UF_6 to be increased to an acceptable level.

The upper value of $k_T \approx 1$ s^{-1} for the CRISLA enrichment of UF_6 is only an example and depends on the laser power and $^iUF_6$ absorption cross-section as indicated by equation (24). For higher

20 laser powers and absorption cross-sections (attainable at lower temperatures), the maximum allowable value for k_T may be as much as 10^3 s^{-1} or higher. Figure 4 illustrates the boundaries of allowable thermal reaction rates of suitable CRISLA coreactants to be used for the enrichment of UF_6. For the CRISLA enrichment of

25 other isotopes ^iMY, other upper and lower limits for k_T apply of

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course as determined by equations (24) through (26) set forth below.

Even with a value of the rate constant k_7 that falls in the right range defined by Step "E," many coreactants still within Step "E" fail to provide isotope-selective reactions. The usual reason is that these coreactants fail to satisfy Step "F" of Figure 8, namely that the vibrations of the bonds to be broken are in excess of the laser-excited largest bond vibration of ^iMY. As mentioned most H-bonds have high dissociation energies and vibrational frequencies $\tilde{v}_{RX} \geq 2000$ cm^{-1} which are more than three times larger than $\tilde{v}_{UF6} = 625$ cm^{-1}. For that reason, the molecules RX = HBr and HCl in Table 1 are poor contenders for use in a $^iUF_6$ + RX CRISLA enrichment process.

Of the remaining molecules also satisfying Step "F," it is found that their employment in a CRISLA reaction does generate an isotope effect, but in the case of $^iUF_6$ the primary product $^iUF_5X$ in reaction (III) often exchanges efficiently with the depleted UF6 molecules:

$$^iUF_5X + UF_6 \rightarrow {}^iUF_6 + UF_5X \tag{IV}$$

This is particularly true if X = Cl in reactions (III) and (IV). Thus the isotope separation produced in (III) is quickly undone in (IV) unless one can remove $^iUF_5X$ (but not UF_6) from the UF_6/RX/UF_5X/RF mixture more rapidly than reaction (IV). It has been found that in some cases, the problem arising from (IV) is less severe if X = Br in (III) and (IV) since the product $^iUF_5Br$ is

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unstable and decomposes quickly to $^1UF_5$ and Br_2 with retention of most of the isotope specificity. Thus the last Step "G" of Figure 8 requires an investigation of the product ^1MX whose result reflects itself in the selection of the compound RX.

5   In addition to isotope scrambling exchange reactions such as (IV), other chemical reaction mechanisms can be at work that promote isotope scrambling. For example, investigations of the reactant $SiBr_4$ reveals that products of this coreactant can initiate chemical scrambling of isotopes through the steps:

10 $$^1UF_6(h\nu_L)^* + SiBr_4 \xrightarrow{k_1} [^1UF_6^*:SiBr_4]^\dagger \rightarrow {}^1UF_5Br^{(*)} + SiBr_3F^{(*)} \qquad (V)$$

11 $$UF6 + SiBr_3F^{(*)} \xrightarrow{k_2} [UF_6:SiBr_3F^{(*)}]^\dagger \rightarrow UF_5Br^{(*)} + SiBr_2F_2^{(*)} \qquad (VI)$$

12 $$UF_6 + SiBr_2F_2^{(*)} \xrightarrow{k_3} [UF_6:SiBr_2F_2^{(*)}]^\dagger \rightarrow UF_5Br^{(*)} + SiBrF_3^{(*)} \qquad (VII)$$

13 $$UF_6 + SiBrF_3^{(*)} \xrightarrow{k_4} [UF_6:SiBrF_3^{(*)}]^\dagger \rightarrow UF_5Br^{(*)} + SiF_4^{(*)} \qquad (VIII)$$
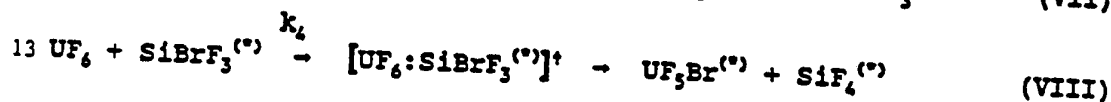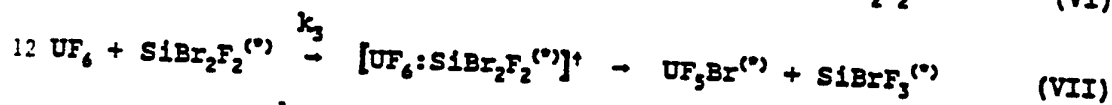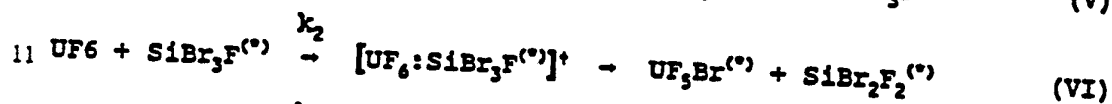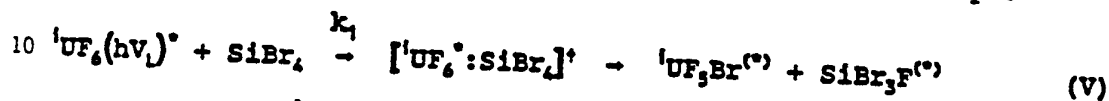
It has been found that $k_1 \ll k_2, k_3, k_4$ so that for each isotope-
15 selective laser-excited $^1UF_6^*$ in (V), three non-isotope-selective products UF_5Br are produced in Steps (VI) through (VIII). For this reason, $SiBrF_3$ is a better coreactant for Uranium enrichment than $SiBr_4$, since only one product UF_5Br can be formed in the laser-controlled reaction:

20   $$^1UF_6(h\nu_L)^* + SiBrF_3 \rightarrow [UF_6^*:SiBrF_3]^\dagger \rightarrow UF_5Br + SiF_4 \qquad (IX)$$
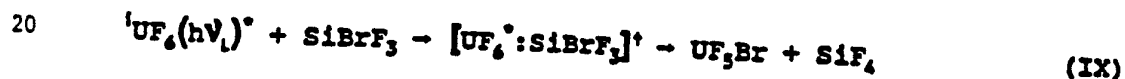
In conclusion, it is necessary in the final selection Step "G" to consider all subsequent chemical isotope scrambling effects of both

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the products ^{i}MX and RY. In the example of the pre-selected UF$_6$ +
SiBr$_a$F$_{4-a}$ reactions, this leads to SiBrF$_3$ as the final preferred
coreactant choice.

In some applications, an even more efficient separation

5　process may be achieved, according to the principles of the present
invention, by utilizing an auxiliary reactant. Step "B" in Figure
8 illustrates the criteria of such an auxiliary reactant. Briefly,
the auxiliary reactant GL is selected as one which complies with
Steps "B" and "C" of Figure 8, as described above, and which:

10　　　　　(a) Rapidly scavenges and stabilizes the product ^{i}MX;
and/or

　　　　　(b) Catalytically increases the formation rate of
enriched product produced by the primary reactants ^{i}MY and RX via
brief Vanderwaals attachments to either one of them or to the

15　complex [^{i}UF$_6^*$:RX$^{(*)}$] and/or by interactive collisions with
[^{i}UF$_6^*$:RX$^{(*)}$]; and

　　　　　(c) Do not react excessively with ^{i}MY or RX.

　　　　　It will be appreciated that the molecules RX may or may
not be laser-excited depending on the particular parameters and

20　products utilized and the particular application. A high degree
of photon absorption by the reactant RX at the laser frequency ν_L
is not desired (Step "B," Figure 8). However, some absorption by
the reactant RX may be desirable in particular cases.

　　　　　The selection process outlined by Figure 8 and discussed

25　in more details below, greatly diminishes unnecessary and costly
experimentation to find an efficient coreactant RX and, if desired,

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an auxiliary reactant GL, for use in the CRISLA separation of ^{1}MY. The application of criteria (A) through (G) or "A" through "H" to the CRISLA enrichment of ^{1}UF$_6$ has resulted in the selection of several coreactants such as SiBrF$_3$ and the combination SiH$_4$ (primary) + HBr (auxiliary) that make the CRISLA process commercially competitive with other laser-isotope separation processes.

Certain aspects of the CRISLA process particularly and laser-isotope separation characteristics in general have been described in: -

(a) U.S. Patent 4,082,633, "High-Mass Isotope Separation Process and Arrangement," by J.W. Eerkens; April 4, 1978;

(b) "Laser Isotope Enrichment of Uranium by the CRISLA process (Vol. I)," by J.W. Eerkens; Report IT-87-006, Isotope Technologies; Sept. 1987;

(c) "Lifetimes, Populations, and Absorptions of the ν_3 and $3\nu_3$ Vibrations in UF$_6$," by J.W. Eerkens; Report IT-88-010, Isotope Technologies; Aug. 1988;

(d) "Uranium Enrichment using the CRISLA Process," by J.W. Eerkens, Nuclear Engineering International (Great Britain); June 1989 issue, p.48;

(e) "Dimer Formation in Gases and Gas Mixtures," by J.W. Eerkens, Report IT-88-003R, Isotope Technologies; March 1988;

(f) "Laser Spectroscopy and its Applications," edited by L.J. Radziemski, R.W. Solarz, and J.A. Paisner; Marcel Dekker, Inc. N.Y. (1987).

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BEST MODE FOR CARRYING OUT THE INVENTION

1. Introduction

Prior to a description of the preferred embodiments of
the present invention, a discussion is given of the physical and
5 chemical processes associated with the practice of the invention.
Such a discussion provides a more comprehensive understanding of
the techniques associated with the practice of the present
invention so that those skilled in the art may be more fully
apprised thereof.

10   Generally for successful CRISLA isotope separations, a
gas-phase chemical substitution or exchange reaction is desired
which can be written:

13              $^iMY + h\nu_L \rightarrow {}^iMY^*$,
14   (1a)
                                              (Laser Excitation)

15              $^iMY^* + RX \rightarrow ({}^iMY^*:RX)^\dagger \rightarrow {}^iMX + RY$
16   (1b)
                                              (Y/X Exchange Reaction)
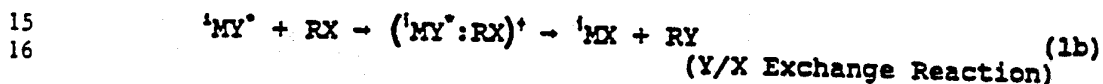
Additionally, as noted above, it may also be advantageous
to have laser photon excitation of the reactant RX. In such
applications, there would also be the reaction defined by the
20 equations:

21              $RX + h\nu_L \rightarrow RX^*$
                                                                    (2a)

22              $^iMY^* + RX^* \rightarrow ({}^iMY^*:RX^*)^\dagger \rightarrow {}^iMX + RY$
                                                                    (2b)
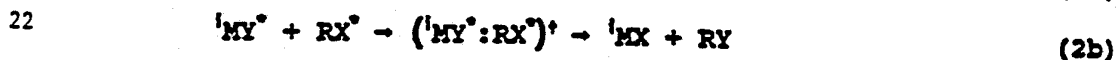
The photon absorption strength of reaction (2a) should not greatly
exceed and preferably be of the same order of magnitude as the
25 absorption strength in reaction (1a) in such applications. In

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these relations ^lM is part of the molecule that contains the isotope to be separated (e.g. $^lM = ^lUF_5$). The activated complex $(^lMY^*:RX^{(*)})^\dagger$ in (1b) or (2b) undergoes an energetically favored exchange of X and Y. The symbol $h\nu_L$ in (1a) and (2a) represents

5 the laser photon energy with frequency ν_L in the customary manner.

The simplest CRISLA reactions are those in which X and Y are two different halogen atoms such as X = Cl or X = Br and Y = F. For example, for UF_6 the following exothermic exchange reactions with RX = QX_3-X can occur:

10 $$^lUF_5 \cdot F^* + QCl_3 \cdot Cl \rightarrow ^lUF_5 \cdot Cl + QCl_3 \cdot F \ , \qquad (3)$$

and:

12 $$^lUF_5 \cdot F^* + QBr_3 \cdot Br \rightarrow ^lUF_5 \cdot Br + QBr_3 \cdot F \qquad (4)$$
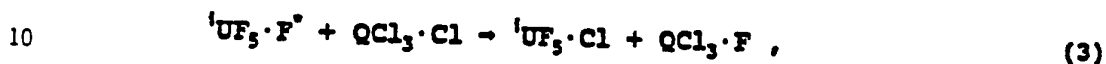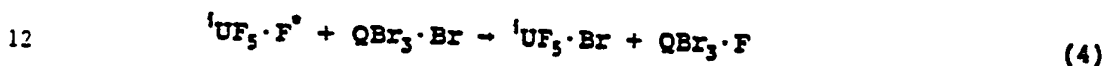
For Q = Si, Ge, or Sn, the reaction speed is moderate while for Q = C, the reaction is endothermic and no reaction occurs at room

15 temperature. For Q = Ti, the reaction is fast. Instead of QX_4, mixed halogenated species are also possible in (3) and (4) like QF_3Cl, QF_2Cl_2, $QFCl_3$, QF_3Br, QF_2Br_2, $QFBr_3$, $QFClBr_2$, $QFBrCl_2$, QF_2ClBr, etc. In addition, the substitution of I for Br in these compounds might constitute a possible coreactant. However, many iodated

20 gaseous molecules are unstable at room temperature and dissociate giving off I_2 or IX.

Other much-studied exothermic reactions as indicated in United States Patent No. 4,082,633 are:

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$$^1UF_6^* + HX \rightarrow UF_5X + HF \quad (X = Br \text{ or } Cl) \tag{5}$$

$$^1UF_6^* + QH_4 \rightarrow UF_5QH_3 + HF \rightarrow {}^1UF_4 + QH_3F + HF \tag{6a}$$

$$^1UF_6^* + QH_4 \rightarrow {}^1UF_5H + QH_3F \rightarrow {}^1UF_4{:}HF + QH_3F \tag{6b}$$
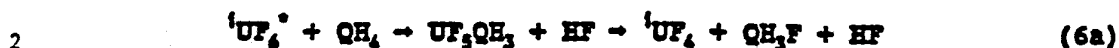
In equations (6a) and (6b), Q is Si or Ge. Additional halogen-exchanging reactions with UF_6 exist involving coreactants such as QO_2X_2 and QOX_2. Some of these will be discussed later. Instead of halogens, in other CRISLA schemes, Y and X might represent -H, -CO (carbonyls), $-BH_4$, $-NH_2$, $-SiH_3$, -SiOH, $-CH_3$, -COH (ketones) or other moieties in addition or in place of the halogens.

Aside from X/Y substitutions reactions (1b) or (2b), other possible gas-phase reactions are:

$$^1MY^* + R \rightarrow ({}^1MY^*{:}R)^\dagger \rightarrow {}^1M + RY \quad \text{(Y-stripping reaction)} \tag{7}$$

$$^1MY^* + RZ \rightarrow ({}^1MY^*{:}RZ)^\dagger \rightarrow {}^1MYR + Z \quad \text{(R-stripping reaction)} \tag{8}$$

$$^1MY^* + RZ \rightarrow ({}^1MY^*{:}RZ)^\dagger \rightarrow {}^1MYRZ^* \tag{9}$$
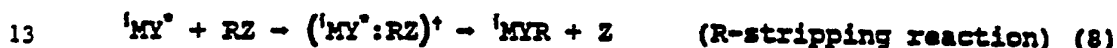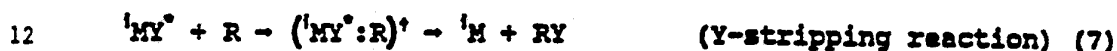
(Permanent Attachment/Rearrangement Reaction)

Examples of reactions (7) through (9) with $^1MY = UF_6$ are:

$$UF_6 + NO \rightarrow UF_5 + NOF \tag{10}$$

$$UF_6 + SF_4 \rightarrow UF_4 + SF_6 \tag{11a}$$

$$UF_6 + AsF_3 \rightarrow UF_4 + AsF_5 \tag{11b}$$

$$UF_6 + NOF \rightarrow NOUF_7 \tag{12a}$$

$$UF_6 + NOCl \rightarrow NOUF_6 + \tfrac{1}{2}Cl_2 \tag{12b}$$
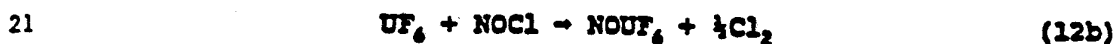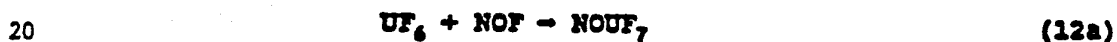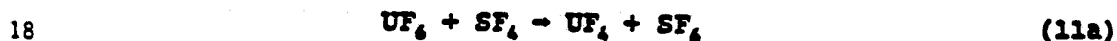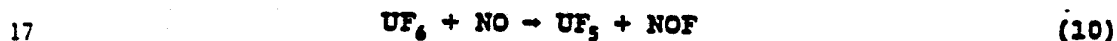
Experiments with reactions (10) through (12) showed reactions (11a) and (11b) to be too slow and (10), (12a), and (12b) to be too fast. As explained later, because of this, such

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reactions are usually not suitable in CRISLA applications of UF_6 enrichment that use (preferred) 5.3 micron CO lasers. The criteria for selection of attractive coreactants RX in a UF_6 CRISLA process developed below apply therefore primarily to exchange reactions
5 (1b) or (2b). For purposes of illustration, the description herein shows the application of the invention to Uranium isotope separation of $^i UF_6$. However, it should be understood that the RX selection criteria can be readily extended to the CRISLA separation of other natural or radioactive isotopes such as $^i Pu$, $^i Zr$, and $^i I$,
10 using suitable volatile molecules $^i MY$ or $^i MX_a Y_n$ where X and/or Y are halogens (F, Cl, Br, I), -H, -CO (carbonyls), $-BH_4$, $-NH_2$, $-CH_3$, -COH (aldehydes), -SiOH (siloxanes), or any other suitable atom or group of atoms.

To determine the type of coreactant RX which will lead
15 to a commercially attractive CRISLA process, it is necessary to examine CRISLA physics in some detail. As described below, the upper and lower limits for the thermal reaction rate of RX + UF_6 are established by an analysis of the expression for the enrichment factor α. This greatly limits the class of gaseous molecules RX
20 that react with gaseous UF_6. Of the group of gaseous RX molecules that fall within the reaction speed limits, there are only certain ones whose reaction rates are speeded up when they encounter, for example, CO-laser excited $UF_6^*(3\nu_3)$ molecules. The attributes of RX molecules that fall in this set are discussed in Section 3. In
25 Section 4, additional restrictions on suitable coreactants are discussed which are due to subsequent chemical scrambling of

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enriched product molecules. Section 5 below describes the
selection process for the auxiliary reactant GL. Finally, in
Section 6, a summary is given of all the requirements that make a
RX coreactant be an attractive candidate for a commercially viable
5 CRISLA·process.

2. CRISLA Enrichment Factor and Reaction Speed Restrictions.

For a clearer understanding of the important CRISLA
operational parameters, Figure 1 shows one possible arrangement of
10 a UF_6 CRISLA process. A carbon monoxide (CO) laser is used to
illuminate an intracavity reaction cell (IC) filled with gaseous
Uranium Hexafluoride (UF_6), a coreactant RX, and possibly an inert
carrier gas (A) such as Ar, N_2, He, Ne, Kr, Xe, or other suitable
gas. The UF_6 (+ A) and the coreactant RX (+ A') are injected
15 separately into the IC through two different nozzle or orifice
banks as shown, and flow at a pre-selected speed through the IC
while being irradiated by CO laser photons. These photons induce
isotope-selective reactions as described above causing the
production of enriched product UF_5X which has different
20 physicochemical properties than UF_6. The UF_5X product is removed
from the $\left(UF_6 + RX + A\right)$ gas stream by precipitation on the IC walls
and in the product collectors labeled A or B in Figure 1. The
depleted UF_6 together with remaining RX, A, and RY is next passed
on to the tails collectors 'A' or 'B' where the depleted UF_6 is
25 separated from the coreactant RX, the carrier gas A, and the
product RY. The gaseous components RX, RY, and A are next

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separated from each other and reconditioned for reuse in the CRISLA process as described further in United States Patent 4,082,633. In the case of RY, the chemical is first reformed back to RX for reuse.

5   The laser excitation of UF_6 by reaction (1) is made isotope-selective in the CRISLA process by operating, for example, the CO laser on one of its strong lines at 1876.3 cm^{-1}. UF_6 has a tertiary $3\nu_3$ absorption band around this frequency as shown in Figure 2. The $^{235}UF_6$ and $^{238}UF_6$ bands of $3\nu_3$ are isotope-shifted by 10 1.85 cm^{-1}. On the Q-slopes of these bands, $^{235}UF_6$ absorbs more strongly than $^{238}UF_6$. At 1876.3 cm^{-1}, the absorption cross-section ratio differs by a factor of 2 to 5 depending on temperature. In general, the colder the gas, the higher the cross-section ratio is. Figure 3 shows the calculated variation of $\zeta_{58} = \sigma\left(^{235}UF_6\right)/\sigma\left(^{238}UF_6\right)$, 15 as a function of temperature using a lumped-lower-vibration (LLV) band model that was fitted to experimental measurements. This calculated value of ζ_{58} is based on smoothed absorption band contours. The real value of ζ_{58} may be higher, particularly at the lower temperatures, due to sharp holes in the actual band spectra 20 and the fact that the IC exerts fine-filtering action. As described in United States Patent 4,082,633, this can force lasing action to breakout at those frequencies of the many allowed ultra-monochromatic resonator lines of the CO laser where $^{238}UF_6$ absorption peaks are avoided and where $^{235}UF_6$ spectral holes exist.

25   The laser photon of frequency $\nu_L = 3\nu_3 = 1876.3$ cm^{-1} is stored in the asymmetric stretch vibration of $F-UF_5$ which is the

-20-

bond to be broken in the rearrangement process of the activated complex in reaction (2), (3), or (4). For many coreactants the stored $3h\nu_3$ energy is insufficient to promote significant enhancement of the reaction. However, for certain special

5 compounds of the RX to be selected and identified below, the $3\nu_3$ vibrational excitation is efficiently redistributed in the activated complex and drives it over the reaction barrier.

Provided that the laser-absorbed energy can cause barrier penetration, it is shown in Section 3 below that the reaction rate

10 $k_R(\text{sec}^{-1}$ per UF_6 molecule) of laser-excited UF_6^* is enhanced over the reaction rate k_T of an average non-laser-excited UF_6 by the factor:

12 $$\theta_L = k_R/k_T = \frac{Z_a}{\rho_a} \exp(h\nu_L/kT) \approx \frac{1}{\rho_a} \exp(2700/T) \qquad (13)$$

Here ρ_a is a factor which depends on the reaction activities of the ν_1, ν_2, and ν_3 vibrations of UF_6 in the associated complex $UF_6^*:RX^*$.

15 This factor equals $\rho_a = 3$ under favorable circumstances and $\rho_a = 56$ in the worst case. The parameter Z_a is the partition function of the reaction-active vibrations which equals $Z_a \approx 1$. At $T = 225°K$ one obtains $\theta_L \approx 1.6 \times 10^5/\rho_a$. In the most favorable case for which $\rho_a = 3$, θ_L has the value 5.4×10^4 (at $T \approx 225°K$). Equation (13)

20 shows that a very slow thermal reaction rate will also cause a relatively slow reaction rate for laser-excited UF_6^*. The implications of (13) and the conditions under which it applies will be examined further below.

For a fuller understanding of the molecular parameters

25 that dictate the effectiveness of a CRISLA coreactant RX, it is

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necessary first to examine the analytical expression for the isotope separation factor α_0 of the CRISLA process. As we shall see, this factor contains the thermal reaction rate k_T, that is the reaction rate of the coreactant RX with non-laser-excited UF_6. The

5 higher the value of α_0 is, the better the isotope separation will be.

The basic separation factor α_0 of a Uranium enrichment process is generally defined as $\alpha_0 = [^5U/^8U]_{Product}/[^5U/^8U]_{Tails}$ in the limit that the product cut $\theta =$ Product/Feed $\rightarrow$ 0. Here and in what

10 follows we shall abbreviate all isotopic superscripts and subscripts 238 and 235 to 8 and 5 for simplicity. The factor α_0 depends on the physics of the molecular separation kinetics. Different separation processes (e.g. Diffusion, Ultracentrifuge, etc.) have quite different α_0's which depend on certain microscopic

15 molecular constants and imposed conditions of operation.

For the CRISLA process, α_0 can be expressed by the relation:

$$\begin{matrix} 18 \\ 19 \\ 20 \end{matrix} \quad \alpha_0 = \frac{\sigma_5 \varphi_L \eta_q + k_T}{\sigma_8 \varphi_L \eta_q + k_T} = \frac{k_{L5} + k_T}{k_{L8} + k_T} = \frac{\zeta_{58} k_L + k_T}{k_L + k_T} = \frac{\zeta_{58} \eta_q k_A + k_T}{\eta_q k_A + k_T} \quad (14)$$

Here σ_5 and σ_8 are the photon absorption cross-sections (cm^2) for $^5UF_6$ and $^8UF_6$ at the laser frequency $\hat{\nu}_L = 1876.3$ cm^{-1} and φ_L is the intracavity bi-directional laser flux (photons cm^{-2} s^{-1}). We already defined the cross-section ratio $\zeta_{58} = \sigma_5/\sigma_8$. The effective laser-

25 induced reaction rate k_L and the molecular laser absorption rate k_A are related by:

-22-

1
$$k_L = \eta_q k_A \quad , s^{-1} \text{ per } UF_6^*,\tag{15}$$

Here k_A can be shown to equal:

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4
5
$$k_A = \varphi_L \sigma_8 = 2.67 \times 10^{19} \frac{P_L \sigma_8}{A_t} \quad , s^{-1} \text{ per } UF_6,\tag{16}$$

in which P_L is the bi-directional CO laser power (Watts) and A_t is the IC tube cross-section (cm^2). Note that in (14), $k_{LS} = \varphi_L \sigma_S$ and $k_{LS} = \varphi_L \sigma_8 = k_L$. That is $k_L = k_{LS}$ is normalized to the $^*UF_6$ population.

10   A very important quantity in the CRISLA process is the quantum efficiency η_q which relates k_L to k_A in equations (14) and (15). It is defined by:

13
14
15
$$\eta_q = \frac{k_R}{k_R + k_V + k_W + k_S + A_t} \approx \frac{k_R}{k_R + k_V + k_S}\tag{17}$$

Here the various rate parameters k_I with $I = R, V, W, S$ are defined by:

18   k_R =   Reaction Rate of Laser-Excited UF_6^*, s^{-1} per UF_6^*.

19   k_V =   Collisional Rate of Deexcitation of $UF_6^*(3v_3) + M \rightarrow$

20           $UF_6^*(2v_3) + M^{(*)}$, s^{-1} per UF_6^*.

21   k_W =   Wall Deexcitation Rate for average UF_6^*, s^{-1} per UF_6^*.

21   k_S =   Scrambling Rate of $^*UF_6^*(3v_3) + UF_6 \rightarrow {}^*UF_6^*(2v_3) +$

23           $UF_6^*(v_3)$, s^{-1} per UF_6^*.

24   A_t =   Spontaneous Emission Rate of $UF_6^*(3v_3) \rightarrow UF_6^*(2v_3) +$

25   hv_3, s^{-1} per UF_6^*.

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Usually λ_R and k_y are negligible compared to k_R, k_y, and k_3 so that the second simpler expression in (17) applies.

Often it is easier to write η_q in terms of collisional interaction probabilities Π_I or numbers of collisions $z_I = (\Pi_I)^{-1}$
5 where $I = R$, V, S. In terms of probabilities, the rates k_R, k_y, and k_3 can be written as the product of collision rate k_c and the probability Π_I. In a reaction mixture with components UF_6, RX, and carrier-gas A, one has:

9 $$k_R = k_c \, \Pi_R/(1 + r_A + r_U) = k_c/\{z_R(1 + r_A + r_U)\} \quad , \quad s^{-1} \tag{18}$$

10 $$k_y = k_c \, \Pi_V = k_c/z_V \quad , \quad s^{-1} \tag{19}$$

11 $$k_3 = k_c \, \Pi_S/(1 + r_U^{-1} + r_A/r_U) = k_c/\{z_S(1 + r_U^{-1} + r_A/r_U)\} \quad , \quad s^{-1} \tag{20}$$

Assuming a typical averaged collision cross-section and reduced mass, and a temperature of $T \approx 225°K$, the collision rate is found to be approximately:

15 $$k_c \approx 5 \times 10^6 \, P_{tot}(torr) \quad , \quad UF_6^* \text{ collisions } s^{-1} \tag{21}$$

In (18) through (21), $P_{tot} = P_A + P_{RX} + P_{UF_6}$ is the total pressure of the CRISLA gas mixture in torr and $r_U = P_{UF_6}/P_{RX}$, $r_A = P_A/P_{RX}$, where it assumed that the mixture is composed of carrier gas A, coreactant RX, and UF_6.

20 Substituting (18) through (20) in equation (17), the latter can be rewritten in the form:

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23
24 $$\eta_q = \left[1 + z_R \left(\frac{1 + r_A + r_U}{z_V} + \frac{1 + r_A + r_U}{z_S(1 + r_U^{-1} + r_A^{-1})}\right)\right]^{-1} \tag{22}$$

-24-

Typically one might have $Z_R = 10^4$ to 10^6 collisions, $Z_V \approx 10^6$ collisions; $Z_S \approx 10^3$ collisions; $r_A \sim 1$; and $r_U \sim 0.1$. Then from (22), $0.003 \lesssim \eta_q \lesssim 0.2$.

Returning to expression (14) for α_e, it is clear from an inspection that the maximum value that α_e can reach is $\alpha_e = \zeta_{SS}$, which is achieved when $k_T \ll k_L = \eta_q k_A$. Also note that the minimum α_e value is $\alpha_e = 1$ which occurs for $k_T \gg k_L$. For typical CO laser powers, $k_A = 1$ to 30 s^{-1}. Then assuming $\eta_q = 0.03$ we have $k_L = 0.03$ to 0.9 s^{-1}. From (14) it is clear then that the thermal rate k_T for a suitable coreactant RX should have a value $k_T < 0.03$ to 0.9 s^{-1}. For stripping and attachment/rearrangement reactions such as (10), (11), and (12), one commonly finds thermal rates of $K_T = 10$ to 10^3 s^{-1} $torr^{-1}$ (RX) per UF_6 molecule, or $k_T = 10^2$ to 10^4 s^{-1} for a typical ten torr of RX. Clearly even with one hundred percent quantum efficiency $(\eta_q = 1)$ which gives $k_L \approx 10$ s^{-1}, the factor α_e would still be close to 1, that is there would be no isotope separation.

The above illustration clearly shows that to achieve useful isotope separation, there is an upper limit on the allowable rate k_T of the thermal reaction of RX + UF_6, namely:

$$(k_T)_{max} - k_L = \eta_q k_A \quad , \quad s^{-1}, \tag{23}$$

where k_A was given by (16). It equals $k_A \approx 3$ s^{-1} for typical values of $P_L = 2000$ Watts and $A_t = 3$ cm^2. Now η_q and k_T are related by equation (13) that is $\eta_q = \eta_q(k_T)$. Solving explicitly for $k_T = (k_T)_{max}$ from (13) and (23) yields:

-25-

1
2
3

$$(k_T)_{max} = k_A - \frac{k_V + k_s}{\theta_L} \quad , \; s^{-1} \tag{24}$$

From equations (23) or (24), it is clear that the laser

5 power and therefore k_A should be high enough so that k_A exceeds $(k_V + k_s)/\theta_L$. As stated, $k_A \sim 3 \; s^{-1}$ typically, while $k_V + k_s \sim 2000$ s^{-1} and $\theta_L \sim 10^4$. This gives $(k_T)_{max} = 2.8 \; s^{-1}$. If k_A is smaller than $0.2 \; s^{-1}$ so that (24) becomes negative, it does not mean that there can be no isotope separation. According to (14), the separation

10 factor α_0 could still be large in this case if f_{58} is large enough. However if (24) is negative, $\alpha_0 - 1$ would be less than half the maximum value at $\alpha_0 = f_{58}$. If one sets the maximum value for k_T equal to k_L as in (23), one makes the assumption (somewhat arbitrarily) that a reduction of $\alpha_0 - 1$ by more than a factor of

15 two from its maximum value of $f_{58} - 1$ is considered to be economically unsatisfactory. An alternative criterion is to consider the thermal reaction rate k_T to be too high when it exceeds the rate k_A. This speed limit $(k_T < k_A)$ and the limit (24) are both illustrated by the dotted lines and arrows in figure 4,

20 which shows a plot of α_0 versus k_T.

A very low thermal reaction rate $k_T \rightarrow 0$ for $RX + UF_6$ might at first appear to be attractive. However because of relation (13) between the thermal reaction rate and the laser-induced reaction rate, k_T cannot be too low since then the isotope production rate

25 would become too low. Equation (17) shows that the quantum efficiency η_q becomes poor if $k_R = \theta_L k_T$ becomes small compared to k_V

-26-

and k_t. For example, if η_q would equal say $\eta_q = 10^{-6}$ and if $k_A \approx 3$ s^{-1} $(P_L = 2$ kW, $A_t = 3$ $cm^2)$, then $k_t = 3 \times 10^{-6}$ $s^{-1} = 0.26$ day^{-1}. This means that it would take 2.7 days to get 50% of the UF$_6$ reacted! If $\eta_q = 10^{-3}$, a 50% reaction would take place in 8.0 minutes instead.

It appears reasonable to take $\eta_q = \eta_{qmin} \sim 0.003$ as the lowest quantum efficiency that still gives a commercially interesting CRISLA process. From (13) and (17) one obtains then for the minimum allowable thermal rate:

$$(k_T)_{min} = \left(\frac{k_V + k_s}{\Theta_L}\right) \cdot \left(\frac{\eta_{qmin}}{1 - \eta_{qmin}}\right) \approx \left(\frac{\eta_{qmin}}{\Theta_L}\right)(k_V + k_s) \; , \; s^{-1} \qquad (25)$$

Thus the value of k_T should be in the range:

$$\eta_{qmin} \cdot q_L \leq \frac{k_T}{k_A} \leq (1 - q_L) \qquad (26a)$$

where the dimensionless parameter q_L equals:

$$q_L = \frac{k_V + k_s}{\Theta_L k_A} = \left(\frac{k_V + k_s}{k_A}\right) \rho_a \cdot \exp\left(\frac{-h\nu_L}{kT}\right) \qquad (26b)$$

Figure 4 illustrates the requirement that the value of k_T be limited more clearly. As shown, if k_T or $\chi_T = k_T/k_A$ becomes too large the separation factor α_e becomes small, while for small values of k_T, the reaction becomes too slow and inefficient. As shown in the insert of figure 4, in terms of the parameter q_L and

-27-

χ_τ, the process factor $\alpha_0 = (\eta_q \, \beta_{58} + \chi_\tau)/(\eta_q + \chi_\tau)$ and $\eta_q = (1 + q_L / \chi_\tau)^{-1}$.

The parameter q_L contains the deexcitation rate $(k_V + k_J)$ of excited $UF_6^*(3V_3)$ which is often not precisely known. Experiments indicate that the relaxation of $UF_6^*(3V_3)$ requires between 100 and 10,000 collisions (depending on the gas mixture), for which q_L has a value between 10 and 0.1 respectively, if $k_A = 10$ sec^{-1} and $P_{tot} = 10$ torr. Figure 4 shows that if $UF_6^*(3V_3)$ relaxation has the most pessimistic value of 100 collisions, one can still achieve good isotope separation by increasing the intracavity laser power from 3 kW to 30 kW thereby increasing k_A from $k_A = 10$ s^{-1} to $k_A = 100$ s^{-1} and lowering q_L by a factor of 10. Intracavity circulating powers of $P_L \sim 30$ kW are achievable with current state-of-the-art laser technology. There is also some uncertainty regarding the parameter ρ_a which can raise or lower the value of q_L. By using q_L in figure 4, the curves for α_0 are general, and can be used whatever the values of ρ_a or $(k_V + k_\tau)$ turn out to be.

Because of the restrictions (26) on k_τ, one finds that most (usually rapid) stripping and rearrangement reactions like (7), (8), and (9) are too fast and that the slower exchange reactions (2) are preferred in CRISLA. Even if CO laser powers were to be increased ten-fold over present state-of-the-art values, that is if $k_A \sim 1000$ s^{-1}, most stripping and attachment reactions

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with typical values of $k_r \gg 10^3$ s^{-1} would still be unsatisfactory for consideration in CRISLA.

3. Consideration of Reaction Physics and the Intermediate Complex

According to reaction rate theories and in agreement with experimental observations, gas-phase chemical exchange reactions such as (1b) or (2b) must have a finite hesitation or atomic rearrangement time during the encounter of the two reactants. This requires the brief existence (many vibrational periods long) of an associated complex of the two reactant molecules. During the existence of this associated complex (also called a Vanderwaals complex), energy is internally transferred to rearrange atoms and to break bonds. The bonding changes occur by the redistribution of electrons that readjust at speeds $10^2 - 10^3$ faster than the motions of the atomic nuclei.

For two reactant molecules to form an associated Vanderwaals complex in a collisional encounter and to remain attached after the encounter, it is necessary that they shed their relative kinetic energy and store this into vibrational energy. Otherwise they bounce off each other and fly apart again in an "elastic collision" as illustrated in Figure 5. The relative kinetic energy of a gaseous molecule at room temperature is on the order of 200 cm^{-1} (~0.025 eV). In the case of UF$_6$ or another heavy polyatomic molecule, such kinetic energy is readily stored into one of several low-energy vibrations by so-called TV (Translation-to-Vibration) transfer collisions. The reverse events (VT transfers)

-29-

occur also with equal frequency. For example, the $v_4 = 186$ cm^{-1}, $v_5 = 200$ cm^{-1}, and $v_6 = 143$ cm^{-1} fundamental vibrations of UF$_6$ are readily excited and deexcited in ten or so collisions. As shown in Reference (e), for a Vanderwaals attachment event, the molecules should have a relative translation energy less than -2 cm^{-1}. The possibility for such an occurrence exists: (a) for a small fraction of the Maxwell-Boltzmann distribution; and (b) during a TV transfer event where $hv_e - kT$.

Intermolecular attractive forces between two gaseous molecules always exist. This can cause molecules to be trapped in the intermolecular potential well if they have little relative kinetic energy or if they loose nearly all of their relative kinetic energy in a TV transition. Unless a reactive molecular rearrangement process occurs, the associated complex usually dissociates again into its original constituents after a few collisions with other molecules.

For a chemical exchange reaction like (1b) or (2b) to proceed during the association ^{1}MY:RX, it is necessary that there be sufficient activation energy in the complex to push it over the reaction barrier. Since activation energies range typically from 0.2 to 1.2eV (~1600 to 10,000 cm^{-1}), it is clear that the average thermal kinetic energy of 0.025 eV (~200 cm^{-1}) is not sufficient to induce a reaction after its storage as vibration in the Vanderwaals attachment. The most probable scenario for an attachment followed by a reaction is a collision in which both reactant molecules are already vibrationally excited (in previous collisions) to a fairly

-30-

high level. In the attachment collision, additional vibrational energy (~200 cm^{-1}) is transferred to the vibration "warehouse" of the complex, but, as stated, this quantity is small and insignificant compared to the vibrational energy that was already
5 present.

The probability of finding reactant molecules with various levels of vibrational excitation is as set forth below. The result also provides the probability that two coreactant molecules which collide and attach have sufficient total
10 vibrational energy E_r to induce a chemical reaction. Thermal (non-laser-induced) reactions such as (1b) are studied first and then reactions with laser-excited molecules will be examined. The main goal is to establish the relationship between the average thermal reaction rate k_T and the reaction rate k_R of laser-excited species
15 which have been pumped to a particular vibrational level.

The probability of finding a polyatomic molecule in the gas which is excited to the v_α-th vibrational level of the α vibration with fundamental frequency V_α is given by:

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21
$$f(v_\alpha, V_\alpha) = \left(\frac{w(v_\alpha)}{Z_{av}}\right) \exp\left(\frac{-v_\alpha \, h V_\alpha}{kT}\right) \tag{27}$$

In equation (27), $w(v_\alpha)$ is the statistical weight of the v_α vibration level and Z_{av} is the vibrational partition function of ^1MY. For brevity $E_\alpha = v_\alpha \, h V_\alpha$ will be written for the energy stored
25 in the α vibration of the first reactant molecule ^1MY, and $E_\beta = v_\beta h V_\beta$

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for that stored in the second molecule RX. The total vibrational energy stored in a molecule ^1MY is then:

$$E_a = \sum_\alpha E_\alpha = h \sum_\alpha (v_\alpha v_\alpha)$$

(28)

Similarly for molecule RX one has:

$$E_b = \sum_\beta E_\beta = h \sum_\beta (v_\beta v_\beta)$$

(29)

Here the v_α and v_β have one of the values 0, 1, 2, 3, ... The total vibrational energy of two reactant molecules that form a complex is of course $E_a + E_b$.

Clearly there are many possible values for E_a and E_b depending on what combinations of v_α and v_β are present. The v_α and v_β of a particular combination of v_α's and v_β's in an encounter of a particularly excited molecule $^1MY^*$ and a particularly excited molecule RX^* are designated by $v_{\alpha j}$ and $v_{\beta j}$. For example for $^1MY = UF_6$ and $RX = SiCl_4$, one might have $v_{1j} = 0$; $v_{2j} = 3$; $v_{3j} = 1$; $v_{4j} = 5$; $v_{5j} = 2$; $v_{6j} = 4$ for the six normal vibrations in UF_6, and $v'_{1j} = v_{7j} = 1$; $v'_{2j} = v_{8j} = 0$; $v'_{3j} = v_{9j} = 1$; $v'_{4j} = v_{10j} = 3$ for the four normal vibrations in $SiCl_4$. Here we relabeled the four vibrations $\bar{v}_1, \bar{v}_2, \bar{v}_3, \bar{v}_4$ in $SiCl_4$ to $\bar{v}_7, \bar{v}_8, \bar{v}_9, \bar{v}_{10}$ to avoid confusion when we examine all ten vibrations in the associated complex $UF_6^*:SiCl_4^*$. The corresponding total energies with these sets of vibrations j are clearly $E_j = E_{aj} + E_{bj} = \sum_{\alpha,\beta} (E_{\alpha j} + E_{\beta j})$. If the vibrational quantum numbers were restricted to say $v_\alpha \leq 5$ and $v_\beta \leq 5$, one would have $(5 + 1)^{10} = 60,466,176$ combinations j for the ten vibrations.

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In the discussion up to this point, there has not been considered the effect of possible degeneracies of the vibrations. It can be expected that reaction of RX with a molecule $UF_6^{\bullet}$ that has vibrational excitation $3\bar{v}_3 = \bar{v}_{3a} + \bar{v}_{3b} + \bar{v}_{3c}$ distributed over the three different axes a, b, c of UF_6, will be different than reaction with $UF_6^{\bullet}$ with $3\bar{v}_3 = 3\bar{v}_{3a}$ in which all of the $\bar{v}_3$ vibrational energy is stored along one axis in UF_6. In accounting for such differences, it is convenient to relabel the degenerate vibrations and enumerate them separately. That is, for the six vibrations of UF_6 and the four vibrations of $SiCl_4$ (of which many are degenerate) the 24 vibrations $[\bar{v}_1, \bar{v}_{2a}, \bar{v}_{2b}, \bar{v}_{3a}, \bar{v}_{3b}, \bar{v}_{3c}, \bar{v}_{4a}, \bar{v}_{4b}, \bar{v}_{4c}, \bar{v}_{5a}, \bar{v}_{5b}, \bar{v}_{5c}, \bar{v}_{6a}, \bar{v}_{6b}, \bar{v}_{6c}]_{UF6}$, and $[\bar{v}_1, \bar{v}_{2a}, \bar{v}_{2b}, \bar{v}_{3a}, \bar{v}_{3b}, \bar{v}_{3c}, \bar{v}_{4a}, \bar{v}_{4b}, \bar{v}_{4c}]_{SiCl4}$ shall be relabeled $\bar{v}_1, \bar{v}_2, \ldots\ldots, \bar{v}_{24}$. Instead of 6^{10} combinations there are $6^{24} = 4.74\times10^{18}$ combinations, if the v_α' are restricted to $v_\alpha' \leq 5$.

By treating all degenerate vibrations as separate vibrations, the probability of finding molecule ^iMY with total vibrational energy E_{aj} and molecule RX with total vibrational energy E_{bj} may be expressed as:

$$f(E_{aj}) = z_{av}^{-1} \exp\left[-\sum_{\alpha}(v_{\alpha j}h\bar{v}_\alpha)/(kT)\right] \tag{30}$$

$$f(E_{bj}) = z_{bv}^{-1} \exp\left[-\sum_{\beta}(v_{\beta j}h\bar{v}_\beta)/(kT)\right] \tag{31}$$

Then the probability $f(E_j)$ of finding total energy $E_j = E_{aj} + E_{bj}$ in the associated complex is:

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$$f(E_j) = f(E_{aj}) \cdot (f(E_{bj}) = z_{av}^{-1} \, z_{bv}^{-1} \, \exp\left[-\sum_{\alpha'}(v_{\alpha'})h\nu_{\alpha'})/(kT)\right], \tag{32}$$

It is assumed that low-energy TV attachment probabilities are unaffected by the internal excited states of the collision partners. Theoretically this is a good first-order assumption. In (32), the summation α' is over all the renumbered vibrations α from ^1MY and β from RX of the combination set j. Degenerate vibrations are counted separately in this sum as discussed in the $UF_6^*:SiCl_4^*$ example. By doing this, the statistical weight $w(v_\alpha)$ of each vibrational level is unity in equation (27), thus permitting the evaluation of simple sums in the exponentials of (30) - (32). The Z_{av} and Z_{bv} in (30) - (32) are the vibrational partition functions of molecules ^1MY and RX.

If all atomic bonding interactions were precisely known in the complex $UF_6^*:SiCl_4^*$, there could be constructed so-called LEPS (=London-Eyring-Polanyi-Sato) potential surfaces as a function of the separation and relative orientation of the atoms in the molecules UF_6 and $SiCl_4$, and the complex $UF_6^*:SiCl_4^*$, for example. Then, in principle, there could be calculated on a computer the outcome of possible Cl/F substitution reactions for various relative kinetic velocities of UF_6 and $SiCl_4$ and different vibrational loadings j in the $UF_6^*:SiCl_4^*$ complex. To date, such computer calculations of a reaction have only been done for one vibrational mode and a total of three atoms (Reactions AB + C → AC + B), using estimated LEPS surfaces. The extension to twelve atoms with (originally) twenty-four non-degenerate vibrational

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modes is far beyond the scope of present computer models, even if
many simplifying assumptions are made.

  If there were some rule which predicted what combinations
j would proceed to reaction and if these were labeled as the
reactive combinations j = r, the total thermal reaction rate of the
substitution reaction $^1MY + RX \rightarrow {}^1MX + RY$ would be given by:

$$k_T = \sum_r f(E_r) \cdot \Pi_{TV}(kT) \cdot (k_c)_{RX} \quad , \quad s^{-1} \quad\quad (33)$$

Here $f(E_r)$ is given by (32) (with j = r) and $(k_c)_{RX}$ is the collisional
encounter rate of ^1MY and RX. For the case that $^1MY = UF_6$, $(k_c)_{RX}$ is
given by (21) with P_{tot} replaced by the RX partial pressure P_{RX}.
$\Pi_{TV}(kT)$ is the attachment probability or TV transfer probability
for storage of the relative kinetic energy kT between the colliding
coreactants into a low-level vibration of UF_6 or $SiCl_4$ as discussed
above. For UF_6:RX reactions, $\Pi_{TV} \approx 0.01 - 0.1$ typically.

  There is one rule which greatly limits the number of
reactable combinations j = r. This is the condition (suggested by
reaction rate measurements and by Eyring's theory) that a certain
minimum activation energy $(E_r)_{min} = E_c$ is required for an associated
complex to pass over the energy barrier and to proceed to an atomic
rearrangement. This means that in the finite sum (33), only terms
with $E_r \gtrsim E_c$ need to be considered, and because of the exponential
dependence of $f(E_r)$ on E_r, only terms with $E_r - E_c$ need to be
retained in the sum.

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There are many sets j with total energy E_j that would meet the condition $E_j - E_c$ but which do not belong to the reactable group j = r. In principle, LEPS-based computations would be able to determine which combinations of j with $E_j - E_c$ can react. For a X/Y substitution reaction (1b) or (2b), it is reasonable to assume that vibrational energy E_a concentrated along the bond ^1M-Y and vibrational energy E_b stored along the bond R-X is most effective. For example for UF_6, the vibration ν_3 with fundamental frequency ν_3 = 625 cm^{-1} provides most energy along one of three possible axes that contain the bond UF_5-F, while for $SiCl_4$ most vibrational energy for possible severance of a Cl atom would be provided by the ν_3 = 619 cm^{-1} fundamental. These bond vibrations are illustrated in figures 6 and 7 for $SiCl_4$ and UF_6, respectively. Thus, if E_c is the measured (or estimated) activation energy for the UF_6 + $SiCl_4$ reaction, the sets j = r with $E_j = h[v_{\alpha j}\nu_\alpha + v_{\beta j}\nu_\beta]$ where α_j = 4, 5, or 6 and β_j = 19, 20, or 21, and for which $E_j - E_c$, are expected to be most effective. Here we used the expanded numbering system in which $\nu_{3a} = \nu_4$, $\nu_{3b} = \nu_5$, $\nu_{3c} = \nu_6$ for UF_6, and $\nu_{3a} = \nu_{19}$, $\nu_{3b} = \nu_{20}$, $\nu_{3c} = \nu_{21}$ for $SiCl_4$.

It is possible that certain wagging and scissoring vibrations like ν_4, ν_5, ν_6 of UF_6 and ν_2, ν_4 of $SiCl_4$ will help (or hinder) the Cl/F exchange reaction in the associated complex in which ν_3 of UF_6 and/or ν_3 of $SiCl_4$ is multiply excited. For temperatures T ≳ 150°K, the low-energy vibrations ($\nu_\epsilon \lesssim 200$ cm^{-1}) in UF_6 and $SiCl_4$ are almost always excited (to 1 ≤ v_ϵ ≤ 5) and their

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effect on the reaction is averaged. (The same comment applies to rotational states.) This holds also for laser-pumped reactions. The possibility does exist that high-level excitations $(v_a, v_\beta \geq 5)$ with $E_j - E_c$ of combinations of v_4, v_5, v_6 in UF_6 and v_2 and v_4 in 5 $SiCl_4$ (with no excitations of v_1, v_2, v_3 in UF_6 and v_1, v_3 in $SiCl_4$) can contribute to the chemical reaction rate, but these contributions are probably small. From V,V±T transfer theory (Ref. 2c), it is found that VV transfer probabilities decrease with increasing numbers of vibrational quantum changes (by factors of 10 10 - 100 for each additional quantum change). Since in a chemical rearrangement of the associated complex, internal VV quantum transfers occur also (together with changes in bond strengths with attendant changes in the vibrational frequency), one can expect that the most efficient reaction-promoting energy loadings are 15 those with the fewest number of vibrational quanta while still satisfying the condition $E_j - E_c$. For the UF_6 + $SiCl_4$ case this means that multi-level excitations of the v_1, v_2, v_3 vibrations of UF_6 and the v_1, v_3 vibrations of $SiCl_4$ will be much more effective than multi-level excitations of v_4, v_5, v_6 in UF_6 and v_2, v_4 in 20 $SiCl_4$.

Because exact LEPS-based reaction calculations for two attached vibrationally-loaded polyatomic molecules are presently impossible, educated approximations will be made based on the above discussions. The combinations j = r are limited to sets of 25 vibrations that contain only the high-energy vibrations. Then the

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thermal reaction rate k_T for a case such as $UF_6 + SiCl_4$ can be estimated from the expression:

$$3 \atop 4 \atop 5 \cdot \quad k_T = k_{ab} \sum_{j=r} \exp\left(\frac{-E_j}{kT}\right) \approx k_{ab} \, \rho_{ab} \, \exp\left(\frac{-E_c}{kT}\right) \tag{34}$$

where:

$$7 \atop 8 \atop 9 \quad k_{ab} = \frac{\prod_{TV}}{z_{aV} \, z_{bV}} \cdot (k_c)_{ux} \quad , \quad s^{-1} \text{ per } {}^1MY \tag{35}$$

10 The parameter ρ_{ab} in (34) is the effective statistical weight of all reactable combinations of excited levels. Approximate expressions for ρ_{ab} under various limiting assumptions are given below.

The activation energy E_c in (34) can usually be obtained experimentally. Theoretically it should equal:

$$16 \quad E_c = E_a + E_b = h[v_{an}\bar{v}_{ar} + v_{bn}\bar{v}_{\beta r}], \tag{36}$$

where v_{an} is the minimum number of quanta of the highest-energy reaction-generating vibration α_r in ${}^1MY$ that yields $hv_{an}\bar{v}_{ar} \approx E_a$. Similarly, $v_{\beta n}$ is the minimum number of quanta in RX such that 20 $hv_{\beta n}\bar{v}_{\beta r} \approx E_b$. If there exist several reaction-promoting vibrations α_r with energies close to each other, then $\bar{v}_{ar}$ in (36) is the averaged value of the fundamental frequencies of these vibrations (e.g. $\bar{v}_1 = 666 \text{ cm}^{-1}$, $\bar{v}_2 = 533 \text{ cm}^{-1}$, $\bar{v}_3 = 626 \text{ cm}^{-1}$ in UF_6 with $\bar{v}_{ar} = 608$ cm^{-1}). Similarly, for RX, an average value $\bar{v}_{\beta r}$ may apply (e.g. 25 $\bar{v}_1 = 424 \text{ cm}^{-1}$, $\bar{v}_3 = 619 \text{ cm}^{-1}$ in $SiCl_4$ with $\bar{v}_{\beta r} = 522 \text{ cm}^{-1}$).

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Experimentally, only $E_t = E_a + E_b$ are usually measured and not E_a and E_b separately. In principle E_a and E_b can be quite different and without additional information, one can have several fits of the sum of their values and of v_{am} and v_{bm} to the measured value for E_t. For example, if it is found that the experimental activation energy $E_t \approx 0.35$ eV ≈ 2800 cm^{-1}, and $\bar{v}_{\alpha r} \approx 600$ cm^{-1}, $\bar{v}_{\beta r} \approx 500$ cm^{-1}, then a possible fit is $v_{am} = 3$, $v_{bm} = 2$. The problem of how to estimate E_a and E_b separately is discussed below.

The statistical weight ρ_{ab} of reactable combinations of vibrational excitations can under one approximation (Case A) be expressed by:

$$\rho_{ab} = \rho_a \cdot \rho_b \approx \left(\frac{(v_{am} + n_{\alpha r} - 1)!}{v_{am}!\,(n_{\alpha r} - 1)!} \right)_a \cdot \left(\frac{(v_{bm} + n_{\beta r} - 1)!}{v_{bm}!\,(n_{\beta r} - 1)!} \right)_b \quad (37)$$

(Case A)

In equation (37), as before, v_{am} and v_{bm} are the minimum number of vibrational quanta in the vibrations α_r and β_r of ^{1}MY and RX that can induce reaction, when present in the associated complex ^{1}MY$^\circ$:RX$^\circ$. The $n_{\alpha r}$ are the total number of high-energy vibrations α_r including degeneracies, that can cause reaction with v_{am} number of quanta. For example, if for UF$_6$ we assume that the $\bar{v}_1$ ($= 666$ cm^{-1}), $\bar{v}_2$ ($= 533$ cm^{-1}), $\bar{v}_3$ ($= 626$ cm^{-1}) vibrations can all contribute to reaction, we have $n_{\alpha r} = 1 + 2 + 3 = 6$ since the $\bar{v}_1$ vibration has degeneracy $d_1 = 1$, $\bar{v}_2$ has $d_2 = 2$, and $\bar{v}_3$ has $d_3 = 3$. That is, under this assumption, vibrational combinations like $\bar{v}_1 + 2\bar{v}_{2a} + \bar{v}_{3b}$; $\bar{v}_{3a} + \bar{v}_{3b} + 2\bar{v}_{3c}$; $3\bar{v}_1 + \bar{v}_{2b}$; $4\bar{v}_{3a}$, etc. have an equal probability of

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inducing reaction if the energy criterion $E_a \approx hv_m\bar{v}_{er}$ requires $v_m = 4$. In this case, ρ_a in (37) would equal $\rho_a = 126$. Thus, ρ_a is the statistical weight or total number of possible different combinations of storing four quanta in the vibrations v_1, v_{2a}, v_{2b}, v_{3a}, v_{3b}, and v_{3c}.

If the UF$_6$ reaction were able to proceed via excitation of a number of quanta $v_{er} = v_3$ of the triple degenerate v_3 vibration only and by no other vibrations, it would be found that $n_{er} = d_3 = 3$, and $\rho_a = (v_3 + d_3 - 1)!/\{(v_3!)(d_3 - 1)!\} = \frac{1}{2}(v_3 + 1)(v_3 + 2)$ which is equal to the usual statistical weight of a triply degenerate vibration excited to level v. If similarly only one particular vibration in RX would be effective for reaction, there would be obtained for the general Case B:

$$\rho_{ab} = \rho_a \cdot \rho_b = \left(\frac{(v_{er} + d_{er} - 1)!}{v_{er}!(d_{er} - 1)!}\right)_a \cdot \left(\frac{(v_{\beta r} + d_{\beta r} - 1)!}{v_{\beta r}!(d_{\beta r} - 1)!}\right)_b , \quad (38)$$

one (degenerate) α_r only
one (degenerate) β_r only

(Case B)

where d_{er} and $d_{\beta r}$ are the degeneracies of the reaction-sensitive vibrations α_r and β_r. For example, if $v_{er} = v_3$ in UF$_6$ and $v_{\beta r} = v_3$ in SiCl$_4$, and if $v_3(UF_6) = 4$, and $v_3(SiCl_4) = 3$ is required for a reaction, one would have $\rho_a = 15$ and $\rho_b = 10$ so that $\rho_{ab} = 150$.

Even more restrictive assumptions may be made than (38) about the reactability of a loaded vibration, such as assuming that only "stacked" quanta in one vibrational axis can be operative.

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That is, it can be postulated that only say $E_a = 3h\tilde{v}_{3a}$ with $v_{3a} = 3$ is effective to cause a reaction, and not say $E_a = h(\tilde{v}_{3a} + \tilde{v}_{3b} + \tilde{v}_{3c})$ with $v_{3a} = 1$, $v_{3b} = 1$, $v_{3c} = 1$ in which each of the three F-U-F axes has one quantum of vibrational energy. If the same restriction of one reaction-active vibration $v_{\beta r}$ in molecule RX is assumed, the weight ρ_{ab} would be, in this case:

$$\rho_{ab} = \rho_a \cdot \rho_b = d_{\alpha r} \cdot d_{\beta r} \quad , \tag{39}$$

stacked vibrations of α_r only
stacked vibrations of β_r only

(Case C)

where $d_{\alpha r}$ and $d_{\beta r}$ are the degeneracies of vibrations α_r and β_r. For example, there could be $\alpha_r = 3a$; $d_{\alpha r} = 3$ in UF_6 and $\beta_r = 1$; $d_1 = 1$ in $SiCl_4$ so that $\rho_{ab} = 3$. In this last case (which shall be called Case C), the statistical weight ρ_{ab} is independent of the vibrational levels $v_{\alpha a}$ and $v_{\beta a}$.

The partition functions Z_a and Z_b to be used in equation (35) depend also on whether Case A, B, or C is applicable in a particular reaction. Since it is assumed in these three cases that low-energy vibrations have little or no effect on reaction, it is necessary that the partition function for the vibrations α_r is used in the presence of any quantum-level combinations of the low-energy vibrations (Reference (e)). In such a situation, for the Cases A, B, and C:

$$Z_a = \prod_{\alpha r}\left(Z_{\alpha r}^{d_{\alpha r}}\right) \quad , \tag{40a}$$

(Case A)

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1
2

$$Z_a = Z_{er}^{d_{er}} \, , \tag{40b}$$

3   (Case B)

4

$$Z_a = Z_{er} \, , \tag{40c}$$

5   (Case C)

with similar expression for Z_b with β substituted for α. The partition function Z_{er} is given by:

8
9
10

$$Z_{er} = \left[1 - \exp\left(- \frac{h\nu_{er}}{kT} \right) \right]^{-1} \tag{41}$$

Since in most cases of interest $h\nu_{er} \gtrsim 3kT$, $Z_{er} \lesssim 1.05 \approx 1$. Thus, as was done in equation (13), $Z_a \approx 1$. Similarly, usually $Z_b \approx 1$.

It is very difficult to determine, in general, which of the above three possible expressions (Cases A, B, or C) for ρ_{ab}
15 applies in a particular reaction. It would appear that Case A is too inclusive, while Case C is probably too restrictive. As shown below, it is very important to know what ρ_a is in a CRISLA reaction. Unless hard data are available, the best that can be done is to calculate ρ_a for the three Cases A, B, and C in order
20 to establish an upper and lower limit. For example, if $v_{rn} = 3$, it would be found for reactant UF_6^* that $\rho_a = 56$ in Case A; $\rho_a = 10$ in Case B; and $\rho_a = 3$ in Case C, assuming that $\nu_{er} = \nu_3$ for Cases B and C. If, instead, $v_{rn} = 4$, it is found that $\rho_a = 126$ for Case A; $\rho_a = 15$ for Case B; and $\rho_a = 3$ for Case C. For $SiCl_4^*$ there is
25 obtained, similarly, (assuming $\nu_1 = 424$ cm^{-1} and $\nu_3 = 619$ cm^{-1} to be reaction-active) $\rho_b = 20$ in Case A, $\rho_b = 10$ in Case B, and $\rho_b = 3$

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in Case C if $v_{AL} = 3$; and $\rho_b = 35$ in Case A, $\rho_b = 15$ in Case B, and $\rho_b = 3$ in Case C if $v_{AL} = 4$. Here we assume that in Cases B and C only the triply degenerate v_3 vibration of $SiCl_4$ is reaction-active.

5   As mentioned above, the low-energy wagging and scissoring vibrations v_4, v_5, v_6 of UF_6 which are almost always excited in an average UF_6 molecule at temperatures above 100°K, probably promote the reaction of an activated complex (with sufficient energy E_r from the high-energy vibrations), by providing bending motions that 10 help the X for Y substitution. Thus, even though the energy quanta in v_4, v_5, v_6 are insufficient to give adequately high (and directed) activation energies, they probably help to increase the possible reaction channels of the activated complex $(UF_6:SiCl_4)^{\dagger}$ by their motions. It will be appreciated that UF_6 and $SiCl_4$ have been 15 utilized for purposes of illustration. Similar considerations would apply for utilization of coreactants other than $SiCl_4$ and/or other isotopic molecules.

      In the case that a laser excites a reactant $^i MY$ (for example, the $3v_3$ excitation of UF_6 with a CO laser), the reaction 20 rate k_r of laser-excited $^i MY^*$ must be known. Assuming that the laser energy $hv_L - E_a$ and that it is placed in a reaction-active vibration (e.g. v_3 of UF_6), this rate can be found from the thermal rate by dividing k_r by the fraction $f(hv_L) = f(v_{er}hv_{er})$ in the thermal population that has energy $hv_L = v_{er}hv_{er}$. One obtains:

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$$k_\mathrm{R} = \frac{k_\mathrm{T}}{f(h\nu_L)} = \left(\frac{z_{ev}\exp(h\nu_L/kT)}{\rho_a(\nu_{aL})}\right)k_\mathrm{T} \approx \left(\frac{\exp(h\nu_L/kT)}{\rho_a(\nu_{aL})}\right)k_\mathrm{T}, \quad \mathrm{s}^{-1} \text{ per } {}^1\mathrm{MY}^*(h\nu_L),$$

$$(42)$$

Laser photons excite optically-active molecular vibrations along only one molecular axis (e.g. $3\nu_3$ in UF_6) and no other (degenerate) vibrations, whereas the rate k_T is based on collision-produced populations that can excite all degenerate vibrations of a reactable one (e.g. $\nu_{3a}\nu_{3a}$, $\nu_{3b}\nu_{3b}$, $\nu_{3c}\nu_{3c}$ in UF_6) as well as other (possibly non-optically-active) reactive vibrations (e.g. $\nu_1\nu_1$, $\nu_{2a}\nu_{2a}$, $\nu_{2b}\nu_{2b}$ in UF_6). With $T = 225°K$, $\rho_a = 10$, and $h\nu_L = 1876$ cm^{-1}, equation (42) yields, for example, $k_\mathrm{R}/k_\mathrm{T} = 1.6 \times 10^4$.

The result (42) which can also be expressed as equation (13), shows that the reaction rate of laser-pumped UF_6 molecules can be increased by several orders of magnitude, provided that the laser-excited vibration is the dominant reaction-active vibration in the activated complex and $E_a \approx h\nu_L$. For fluorine-substitution reactions of UF_6, it is clear from Figure 7, that the ν_3 vibration should be the most reaction-active. This has indeed been borne out by experiments on the reactions $UF_6 + RX \rightarrow UF_5X + RF$ in which the normal vibrational quanta $h\nu_j$ of RX were of the same order of magnitude and not larger than twice the quantum $h\nu_3 = 625$ cm^{-1} of UF_6. For example, the coreactants QX_aF_{4-a} with $Q = Si$, Ge, or Sn and $X = Cl$, Br, H, or I (if stable) which have normal vibrations $\nu_j < 2\nu_e$ ($\nu_e = \nu_3$ for UF_6), show, indeed, laser-enhanced reactions when the ν_3 vibration of UF_6 is multiply excited. In the dimer

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complex, the original monomer vibrational frequencies are shifted due to orbital bonding changes. If (ν_β) dimer - (ν_α) dimer, near-resonant quantum transfers between the α and β vibrations can occur.

If, on the other hand, the R-X bond normal vibration ν_β of RX is much larger than twice the normal vibration $\nu_\alpha = \nu_3$ of UF_6, which is laser-pumped, it is found that (multiple) quantum excitation of the ν_3 vibration in UF_6 does not efficiently promote reaction in the $UF_6:RX^\dagger$ complex. For example, for RX = HCl or HBr, ν_β = 2991 cm^{-1} and 2649 cm^{-1}, respectively, which compares to ν_3 = 625 cm^{-1} of UF_6, which is CO laser-excited to $3\nu_3$ (= ν_L). The thermal reaction UF_6 + HX → UF_5X + HF with X = Cl or Br appears to be controlled by collisionally excited HX^*(v=1) and not by UF_6^*($3\nu_3$ or ν_3). If it is assumed that $E_a - h\nu_3 - h\nu_2 - h\nu_1$ and v_{an} = 1, while $E_b \approx h\nu_\beta$ with v_{bn} = 1, it is found for laser-excited $UF_6^*(\nu_3)$ reactions with HX that:

$$\frac{k_\pi}{k_T} = \frac{\exp(h\nu_3/kT)}{\rho_a} \approx 0.2\ \exp(899/T) \approx 11,\ \text{for}\ T = 225°K \qquad (43)$$

Here it is assumed that Case A applied, (with v_{an} = 1, n_{er} = 6), so that ρ_a = 5 according to equation (37). If, in the UF_6 + HX reaction, a minimum of three high-energy quanta were needed in UF_6 and one in HX, this ratio would instead equal k_π/k_T = (1/56) $\exp(3h\nu_{er}/kT) \approx 707$ at T = 225°K, since for v_{an} = 3, m_{er} = 6, one has ρ_a = 56. Experimental data on UF_6 + HX reactions with X = Br or

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Cl suggest, however, that only one or two high-energy vibrational excitations $(v_1 = v_2 = v_3 = 1$ or $2)$ in UF_6 are sufficient to induce reaction, <u>provided</u> HX in the complex UF_6:HX is once excited $(v_b = 1)$.

5   If (43) applies and if $3\nu_3$ is excited in UF_6 by a CO laser in a UF_6 + HX reaction mixture, the effect on the isotope-specific reaction rate is equivalent to providing only $1\nu_3$ excitation if $V_m = 1$ and $E_a = 1h\nu_3$. Multiple quantum excitations of the ν_3 vibration in one UF_6 will not increase its reaction rate in this

10 case. In fact, each $3\nu_3$ laser-excitation of $^iUF_6$ to $^iUF_6^*(3\nu_3)$ can, in subsequent VV scrambling transfers, produce two non-isotope-selective excited $UF_6^*(\nu_3)$ molecules. That is, each isotope-specific $^iUF_6^*(3\nu_3)$ that decays to $^iUF_6^*(\nu_3)$ and reacts is accompanied by two reacting $UF_6^*(\nu_3)$'s which are not isotope-specific. Thus, not

15 only is η_q very small because of (43), but a parasitic scrambling term $k_s \approx 2 \int_{ss} k_1$ must be added to the denominator and numerator of equation (14). Unless $\int_{ss} \gg 2$, equation (14) shows that in this case $\alpha \to 1$ so that there is no isotope separation.

        It may also be possible in some reactions that $E_a = 4h\nu_e$

20 $= 4h\nu_3$ say, and that $h\nu_L$ falls short of E_a by one quantum $h\nu_e = h\nu_3$. In that case, the reaction rate of $3\nu_3$-laser-excited $^iUF_6^*$ molecules is given by:

$$\begin{matrix}23\\24\\25\end{matrix}\ \frac{k_R}{k_r} = g(\Delta v_e \nu_e; \nu_L) \cdot \frac{\exp(E_a/kT)}{P_a} = g(\Delta v_e \nu_e; \nu_L) \cdot \exp\left(\frac{\Delta v_e h\nu_e}{kT}\right) \cdot \frac{\exp\left(\frac{h\nu_L}{kT}\right)}{P_a} \quad (44)$$

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Here $g(\Delta v_e \vec{v}_e; \vec{v}_L)$ is the fraction of UF_6 molecules in the gas that are resonant to the photon absorption transition $\Delta v_e \vec{v}_e - \vec{v}_L + \Delta v_e \vec{v}_e$, and $E_a = h\vec{v}_L + \Delta v_e h\vec{v}_e$. Often (fortuitously), the factor $g(\Delta v_e \vec{v}_e; \vec{v}_L)$ $\sim \exp(- \Delta v_e \vec{v}_e/kT)$ and in that case one finds that k_R/k_T again reduces
5   to (13).

From the considerations presented above and from experimental data, it appears that the most efficient laser-induced CRISLA reactions occur when vibrational frequencies of the bonds to be broken in R-X do not exceed the normal vibrational
10   frequencies of bonds to be broken in the molecule ^iM-Y by more than a factor of 2. It is known from VV transfer theory that vibrational quantum exchanges inside the activated complex are most efficient in that case because of near-resonance. Since X-for-Y atom exchanges should be enhanced if internal VV transfers are
15   promoted, reaction should also be most efficient then. The pumped laser energy $h\vec{v}_L$ should preferably be deposited in the highest-energy bond-breaking vibration of the reaction complex $(^iMY:RX)^*$ and one should have $h\vec{v}_L \approx E_a$. This means that if one wishes to separate the isotope ^iM via the CRISLA technique, the highest vibration $\vec{v}_e$
20   in ^iM-Y whose bond is to be broken should be of the same order of magnitude (not more than a factor of 2) as the vibration $\vec{v}_\beta$ of the coreactant R-X bond. That is, the more suitable CRISLA partners RX for use with UF_6 have $\vec{v}_\beta - \vec{v}_e (= \vec{v}_3)$ or $E_b - E_a$. This also means that $E_c \leq 2E_a \approx 2h\vec{v}_L$. Then approximately half (or less) of the
25   required activation energy E_c is provided by collisionally-prepared

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RX* and half (or more) by laser-excited $^lUF_6^*(3\overset{\vee}{v}_3)$, if RX does not

absorb any laser photons (see below).

Hydrogen bonds in compounds such as HX (X = Cl, Br) have

vibrations $\overset{\vee}{v}_\beta$ > 2000 cm^{-1}. Therefore, from the rule $\overset{\vee}{v}_\epsilon - \overset{\vee}{v}_\beta$, the

5 simple two-component HX + UF$_6$ reaction with laser-excited UF$_6^*(3\overset{\vee}{v}_3)$

and $\overset{\vee}{v}_\epsilon = \overset{\vee}{v}_3$ = 625 cm^{-1} is not expected to be very efficient, as borne

out by experiment. Of course, one or more hydrogen atoms (e.g. a

-QH$_2$ or -QH$_3$ group with Q = C, Si, Ge) can be present as part of a

larger coreactant molecule. A single Q-H bond then need not be

10 directly involved in the rearrangement reaction with UF$_6$ if bond

changes occur through collective motions and/or in another part of

the coreactant molecule. For such coreactants, the comments about

the inefficiency of H-bond coreactants do not apply.

As mentioned, the most suitable CRISLA coreactant

15 partners RX for UF$_6$ provide half of the activation energy which is

collisionally prepared. Instead, a second laser, or the same CO

laser that prepares isotope-specifically excited UF$_6^*$, could be used

to produce and enhance the desirable excited RX* population for use

in the reaction of the activated complex [UF$_6^*$:RX*]†. This is

20 particularly true if the total activation energy E$_\epsilon$ is closer to

2h$\overset{\vee}{v}_L$ than h$\overset{\vee}{v}_L$. The laser-generated reaction rate k$_R$ and the quantum

efficiency η_q would, in this case, be enhanced and laser

controlled. An interesting example is DBr which does absorb at

several CO laser wavelengths near 1876 cm^{-1}. Two different laser

25 frequencies obtainable from the same CO laser, that is a "two-

-48-

color" CO laser would be needed in this case, since the 1876.3 cm^{-1} line which is best for UF_6 misses the DBr lines. However, the CO laser lines at 1872.3 cm^{-1} and 1880.3 cm^{-1} coincide with the R-3 and R-4 lines of DBr and could be used to prepare a DBr^* (v = 1)
5   background gas. Other examples are SiH_4, $SiBrF_3$, and $SiClF_3$ whose binary bands $(\bar{v}_2 + \bar{v}_4)$, $(\bar{v}_1 + \bar{v}_4)$, and $(\bar{v}_1 + \bar{v}_4)$ respectively absorb the same 1876.3 cm^{-1} CO laser line used to excite $UF_6^*(3\bar{v}_3)$.

The main advantage of co-excitation of the coreactant is that reaction rates can be enhanced which will increase process
10 yield rates. However, we shall show that the isotope separation factor cannot be enhanced and may even be decreased. That is, in certain cases, isotope separation would be suppressed. Also, if one laser and one laser frequency is used to excite both ^1MY and RX, which is the preferred embodiment in coexcitation, the
15 absorption cross-section of RX should not be excessive. It should be less or of the same order of magnitude as the absorption by ^1MY and not exceed it by several orders of magnitude.

The separation factor α_0 (see equation (14)) for reactions with laser-excited RX^* and UF_6^* is:

20
21
22
$$\alpha_0 = \frac{\zeta_{58} + \mu^*}{1 + \mu^*} \tag{45}$$

where:

24
25   $\mu^* = \dfrac{k_T^*}{k_L^*} = \left(\dfrac{1}{k_A}\right) \cdot \left(\dfrac{k_T^*}{\eta_q^*}\right) = \left(\dfrac{k_T^*}{k_R^*}\right) \cdot \left(\dfrac{k_R^* + k_V + k_3}{k_A}\right) = c_L^*/\theta_L^*, \tag{46}$
26

and:

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1

$$c_L^* = (k_R^* + k_V + k_S)/k_A \qquad (47)$$

Here k_T^* is the reaction rate of laser-excited RX^* with non-laser-excited UF_6 and k_R^* is the rate of RX^* with laser-excited UF_6^*. The superscripts * in the above expressions denote conditions with

5 laser-excited RX^* (as well as UF_6^*, of course) and no superscript refers to reactions with RX.

Usually $\theta_L^* = k_R^*/k_T^* \approx \theta_L = k_R/k_T$ (See equation (13)) since both k_T^* and k_R^* will increase by the same factor $\rho_b^{-1} \exp(h\nu_L/kT)$ if the same laser photons $h\nu_L$ can be absorbed by RX and by UF_6, and

10 if $E_a - E_b - E_c/2 - h\nu_L$. However, the factor $c_L^* = (k_R^* + k_V + k_S)/k_A$ in equation (47) could increase undesirably so that $\mu^* > \mu$ if $k_R^* \gg (k_V + k_S)$. For high values of α_0, one wants μ or μ^* to be as small as possible, of course. Thus, unless $k_A(\propto P_L)$ is increased correspondingly or k_R^* is not too large in comparision with $k_V + k_S$,

15 there is no advantage gained by laser-excitation of the coreactant RX <u>if the objective is only to increase α_0</u>.

The assumption that k_T^* and k_R^* increase by the same factor $\rho_b^{-1} \exp(h\nu_L/kT)$ is only correct if the total threshold energy E_c for reaction by the activated complex $[UF_6^*:RX^*]$ satisfies the condition

20 $E_c - 2h\nu_L$ and $E_a - E_b - E_c/2$. It is assumed that the laser photon energy for resonant excitation of RX and UF_6 are the same or of about the same magnitude. If $E_c - h\nu_L$, that is, if the chemical reaction can be promoted equally well by a laser-excited RX^* as by

-50-

a laser-excited UF_6^*, then $\Theta_L^* < \Theta_L$ since a large portion of the laser-induced reactions would no longer be isotope-specific. Particularly if there is more RX than UF_6 in the CRISLA reaction mixture and/or if the laser photon absorption cross-section for RX is much larger than that for UF_6, one can cause $\Theta_L^* \to 1$ if RX is also laser-excited. In conclusion, it is clear that laser-excitation of RX should be avoided if $RX^*(h\tilde{V}_L)$ reacts equally well with unexcited UF_6 as with laser-excited UF_6^*.

In spite of the fact that the value of α_0 cannot be improved by laser-exciting RX, as mentioned there can be process-flow advantages sometimes, provided, of course, that $\Theta_L^* \approx \Theta_L$ and $c_L^* \approx c_L$. If the thermal reaction rate k_T of an otherwise promising coreactant is low and therefore $k_R = \Theta_L k_T$, $\eta_q = k_R/(k_R + k_V + k_J)$, and $k_L = \eta_q k_A$ are also low, one can increase k_R, η_q, and k_L by laser-exciting RX. The reaction cell residence time which is proportional to k_L^{-1}, would then be decreased (by the factor $\rho_b^{-1} \cdot \exp(h\tilde{V}_L/kT)$) and thus the throughput through the cell increased if the coreactant RX is also laser-excited besides UF_6. Although different lasers for exciting RX and UF_6 could be considered, for an industrially attractive CRISLA process, the most advantageous situation in this case (with $\Theta_L^* \approx \Theta_L$ and $c_L^* \approx c_L$) would occur if RX and UF_6 would absorb the same CO laser photons. In this case, one could also use smaller RX/UF_6 ratios, which would mean less circulation (= less cost) of RX. How much less RX is needed and how much the residence flow-through time can be reduced will depend
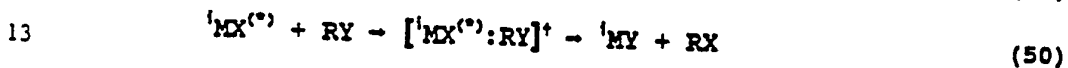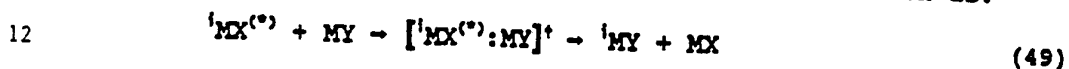
-51-

on the laser-photon absorption cross-section ratio of RX and UF_6.
In general, the macroscopic absorption $\Sigma_a = \sigma_a \cdot n$ for RX and UF_6 in
this case should be of the same order of magnitude for maximum
efficiency and to avoid excessive depression of the intracavity
5 circulating power.

4. Chemical Scrambling Problems

Even with an effective CRISLA coreactant $RX^{(*)}$ reacting
with laser-excited $^iMY^\circ$ by:

9 $$^iMY^\circ + RX^{(*)} \to {}^iMX^{(*)} + RY^{(*)}, \tag{48}$$
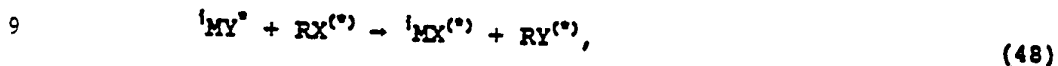
10 the enriched product ^iMX can subsequently undergo isotope-
scrambling reactions and reverse chemical reactions such as:

12 $$^iMX^{(*)} + MY \to [{}^iMX^{(*)}{:}MY]^\dagger \to {}^iMY + MX \tag{49}$$

13 $$^iMX^{(*)} + RY \to [{}^iMX^{(*)}{:}RY]^\dagger \to {}^iMY + RX \tag{50}$$

Reaction (49) would undo the isotope separation that was just
15 achieved by transferring the substitute X atom to non-isotope-
selected MY feed molecules, while reaction (50) reverses the
isotope-selective reaction (48) completely. Because energy is
liberated in the exothermic reaction (48), the product molecules
^iMX and RY in (48) are often vibrationally excited. This is
20 indicated by the superscript $^{(*)}$. The parentheses in the
superscript $^{(*)}$ signify that the molecules may or may not be
excited. Because of this excitation, reactions (49) and (50) can
be promoted if the liberated energy is not quickly relaxed and
dissipated.

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For example, under certain operating conditions the enriched product molecules $^1UF_5X$ (X = Cl, Br, H) can react efficiently in the gas phase with UF_6 by the exchange reaction:

$$^1UF_5X^{(*)} + UF_6 \rightarrow [^1UF_5X:UF_6]^\dagger \rightarrow {}^1UF_6 + UF_5X \qquad (51)$$
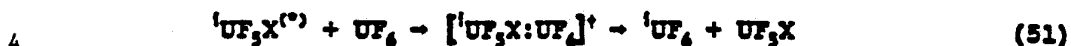
The $^1UF_5X^{(*)}$ in this reaction may not only be excited due to the exothermicity of reaction (48) but also due to absorption of CO laser photons used to excite $3\bar\nu_3$ in UF_6. The $3\bar\nu_2$ vibrational absorption bands of UF_5Cl and UF_5Br appear to partially overlap the $3\bar\nu_3$ band of UF_6, for example.

On UF_5X-covered walls, another chemical scrambling reaction can take place:

$$^1UF_5X^{(*)} + UF_5X:Wall \rightarrow [^1UF_5X:UF_5X:Wall]^\dagger \rightarrow {}^1UF_6 + UF_4:Wall + X_2 \qquad (52)$$
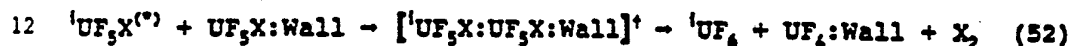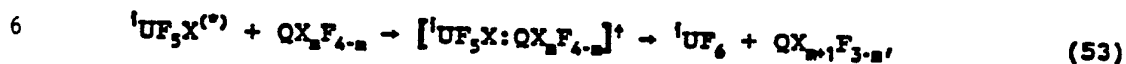
Both reactions (51) and (52) destroy earlier isotope-selective changes and are clearly undesirable. Of the products UF_5Cl, UF_5Br, and UF_5H, it appears that gaseous UF_5Cl is fairly stable in the gas but prone to undergo the wall reaction (52). UF_5Br on the other hand seems to experience both reactions (51) and (52) and the reaction (53) discussed below. UF_5H probably transforms into the strongly-bound complex $UF_4:HF$. It appears to be stable and somewhat volatile, unless or until it breaks up into UF_4 + HF on the wall. The infrared gas-phase spectrum of the product UF_5Cl can be seen for minutes in a UF_6 + RCl reaction, while UF_5Br is observed to "live" only for fractions of seconds after its formation in a UF_6 + RBr reaction. With UF_5H an absorption band centered at 557
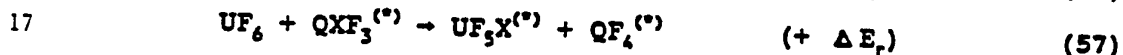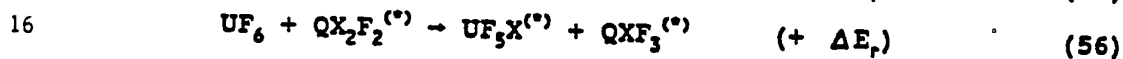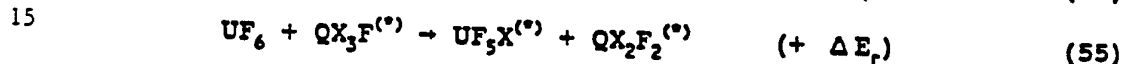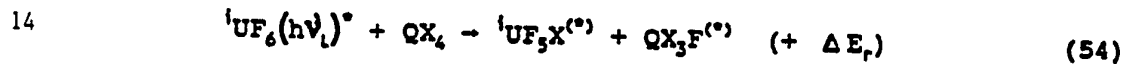
cm^{-1} is seen which is attributed to $UF_4:HF$ and which persists for seconds after the gas-phase formation of $UF_5H \rightarrow UF_4:HF$.

In addition to the undesired $^{235}U/U$ isotope exchange reactions (51) and (52), reverse gas-phase reactions can occur for UF_5X such as:

$$^{235}UF_5X^{(*)} + QX_mF_{4-m} \rightarrow [^{235}UF_5X:QX_mF_{4-m}]^{\dagger} \rightarrow {}^{235}UF_6 + QX_{m+1}F_{3-m},\qquad (53)$$

Reaction (53) is particularly favorable if $^{235}UF_5X$ emerges in an excited state in the exothermic reaction (48) or if $^{235}UF_5X$ absorbs CO laser photons.

Still another problem may be encountered if the chosen coreactant is, for example, QX_4. In this case, several undesirable side-reactions could occur directly after the first (desirable) step:

$$^{235}UF_6(h\nu_L)^* + QX_4 \rightarrow {}^{235}UF_5X^{(*)} + QX_3F^{(*)} \quad (+ \Delta E_r)\qquad (54)$$

$$UF_6 + QX_3F^{(*)} \rightarrow UF_5X^{(*)} + QX_2F_2^{(*)} \quad (+ \Delta E_r)\qquad (55)$$

$$UF_6 + QX_2F_2^{(*)} \rightarrow UF_5X^{(*)} + QXF_3^{(*)} \quad (+ \Delta E_r)\qquad (56)$$

$$UF_6 + QXF_3^{(*)} \rightarrow UF_5X^{(*)} + QF_4^{(*)} \quad (+ \Delta E_r)\qquad (57)$$

Here Q might be Q = Si, Si_2OF_2, CF_2SiO, Ge, Sn, while X = Br, Cl, I, or H. Many I-carrying compounds are very unstable and therefore X = Br, Cl, or H in most practical cases. For Q = Si, and X = Br, the heat of reaction $\Delta E_r \approx 0.8$ eV for example. The rates k_{55}, k_{56}, and k_{57} of reactions (55), (56), and (57) are usually much faster than k_{54} of reaction (54) because the molecules QX_mF_{4-m} are polar while QX_4 is not. The heats of reaction ΔE_r liberated in (54) –

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(57) can also contribute to the rapid secondary reactions (53) and (55) - (57), once reaction (54) is initiated by a laser photon absorption. Since only reaction (54) is isotope-selective and induces (55) - (57) which are not isotope-selective, the isotope separation effect is considerably diminished. In fact, it is not difficult to show that the separation factor α_0 given by equation (14) is changed in this case to (not considering the losses by (51) - (53)):

$$\alpha_0 \approx \frac{(\zeta_{58} + 3f_r) k_L + k_T}{(1 + 3f_r) k_L + k_T} \tag{58}$$

where f_r is the fraction of product molecules $QX_mF_{4-m}^{(*)}$ in reactions (54) - (57) that initiate a secondary reaction. If, for example, $f_r = 1$, $\zeta_{58} = 2$ and $\mu = k_T/k_L = 1$, the value of $\alpha_0 = 1.20$ instead of $\alpha_0 = 1.50$ for the case that $f_r = 0$.

If reactions (55) - (57) do present a problem (i.e. $f_r \neq 0$), one can avoid them by using only QXF_3 as a coreactant and not QX_4. Then only one reaction can take place:

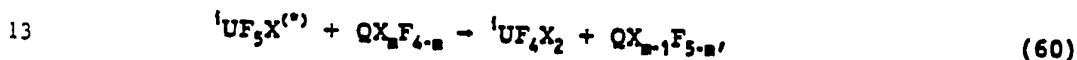$$^iUF_6(h\nu_L)^* + QXF_3 \rightarrow {}^iUF_5X^{(*)} + QF_4^{(*)}, \tag{59}$$

which is isotope-specific. The fully fluorinated product QF_4 can do no further harm.

The above difficulties in the CRISLA isotope separation of $^iUF_6$ can be directly generalized to the CRISLA separations of other isotopic molecules ^iMY of course. Three distinct problems due to secondary chemical scrambling reactions are clearly evident:
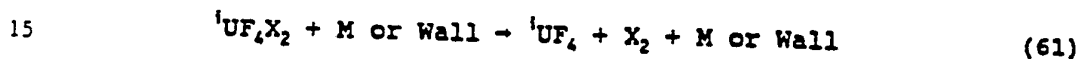
-55-

(1) ^{l}M for M isotopic exchange reactions.

(2) Reverse reactions due to reaction heat and/or laser photon absorption by ^{l}MX.

(3) Laser-driven non-isotope-specific secondary reactions of QX_aF_{4-a} reactant products with ^{l}MY.

As mentioned, Item (3) can be avoided by employing a coreactant that has only one atom X to exchange. The first two scrambling reactions may be unimportant in some cases if the product molecule ^{l}MX quickly undergoes a second different (not reverse) reaction with the coreactant RX. For example, in the case of ^{l}UF$_5$X$^{(*)}$, the latter may in addition to (or instead of) reaction (53) experience the reaction:

$$^l UF_5X^{(*)} + QX_aF_{4-a} \rightarrow\ ^l UF_4X_2 + QX_{a-1}F_{5-a}, \tag{60}$$

followed by:

$$^l UF_4X_2 + M \text{ or Wall} \rightarrow\ ^l UF_4 + X_2 + M \text{ or Wall} \tag{61}$$

Here the unstable molecule UF_4X_2 decays rapidly to ultrastable solid UF_4 and X_2 either in a gaseous collision or on the wall. Unfortunately, reaction (60) is usually not very much faster than reactions (51), (52), or (53). Only if $k_{60} \gg k_{51}, k_{52}, k_{53}$, would the undesirable reactions (51), (52), and (53) be suppressed.

5. Auxiliary Reactants

Instead of relying on the primary coreactant RX or QX_aF_{4-a} to provide satisfactory removal and physical separation of the enriched product ^{l}MX of ^{l}UF$_5$X via reactions (60) and (61), it has been found advantageous to employ a second coreactant such as HBr

-56-

or QBr_4 to speed up the product formation rate and the product scavenging function. Two possible reaction effects can be envisioned by adding a secondary reactant like, for example, HBr. One effect is that (with sufficient HBr) the following reaction is

5 promoted:

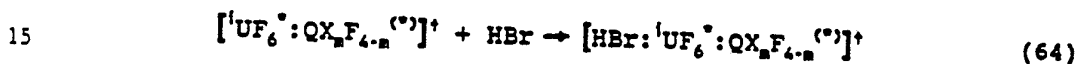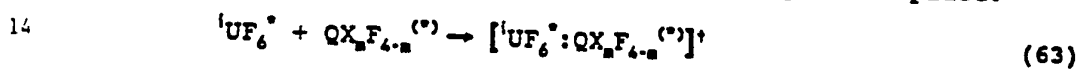6 $HBr + {}^iUF_5X^* \rightarrow [HBr:{}^iUF_5X]^+ \rightarrow HF + {}^iUF_4XBr,$ (62)
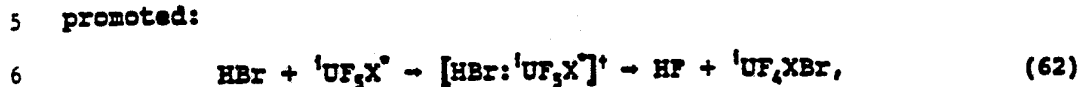
Here ${}^iUF_4XBr$ subsequently decays quickly to solid ${}^iUF_4$ and BrX (X = H, Cl, Br) by (61). Thus, isotope scrambling and other secondary chemical reactions of ${}^iUF_5X^*$ is preempted. For this

10 secondary reactant approach to be successful, it is essential that the secondary reactant can act speedily on UF_5X, but does not react excessively with UF_4. A CRISLA process using UF_5X instead of UF_4 and HBr, in which CO laser photons preferentially excite ${}^iUF_5X$ might also be considered. However, it has been found that UF_5X

15· (generated directly upstream of the IC from UF_4 and TiX_4, for example) quickly reconverts to a large extent to UF_4 because of reaction (52). In addition, as discussed in Section 3, coreactants in which H bonds are to be broken appear not to be very sensitive to the $3\nu_3$ excitation in UF_4. It is possible that this may be

20 different from the $3\nu_2$ excitation in UF_5X. However, exploratory CRISLA experiments with UF_5X + HBr mixtures have shown virtually no isotope-selective effects. In place of HBr, another coreactant such as $QX_{4-a}F_a$ may give better results. Here Q = Si and X = Br, Cl, or H, for example.

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Although HBr reacts moderately fast with UF_6, it is expected to react almost a hundred times faster with $UF_5X^{(\cdot)}$. This is because the fluorine bonds in UF_5X are weaker than in UF_6 and because UF_5X is polar which will enhance the attachment rate.

5 Particularly if $UF_5X = UF_5Br$, the rate k_{62} of reaction (62) appears to exceed the rates k_{51}, k_{52}, and k_{53} of (51), (52), and (53) in the presence of sufficient HBr. Thus, before freshly formed $^lUF_5Br^{\cdot}$ can undergo reactions (51) - (53), HBr will quickly scrub it out by reaction (62).

10 The second effect of a secondary reactant such as HBr is believed to be a speed-up or enhancement of the rate of reaction of the activated complex $[UF_6^{\cdot}:QX_mF_{4-m}^{(\cdot)}]$. That is, it appears that in the case of HBr additive, the following steps take place:

14

$$^lUF_6^{\cdot} + QX_mF_{4-m}^{(\cdot)} \rightarrow [^lUF_6^{\cdot}:QX_mF_{4-m}^{(\cdot)}]^\dagger \qquad (63)$$

15

$$[^lUF_6^{\cdot}:QX_mF_{4-m}^{(\cdot)}]^\dagger + HBr \rightarrow [HBr:^lUF_6^{\cdot}:QX_mF_{4-m}^{(\cdot)}]^\dagger \qquad (64)$$

16
17
18

$$[HBr:^lUF_6^{\cdot}:QX_mF_{4-m}^{(\cdot)}]^\dagger \nearrow \begin{array}{l} UF_5X + QX_{m-1}F_{5-m} + HBr \qquad (65a) \\ UF_4XBr + QX_{m-1}F_{5-m} + HF \qquad (65b) \end{array}$$

In these reactions X = H, Br, or Cl, or some other radical group
20 mentioned above. The strong dipolar field of HBr superimposed in the new complex of (65) speeds the reaction. Because the complex $[^lUF_6^{\cdot}:QX_mF_{4-m}^{(\cdot)}]$ formed in (63) by laser-excited $UF_6^{\cdot}$ and $QX_mF_{4-m}^{(\cdot)}$, lives through some 10 collisions, it is very likely that it will encounter several HBr molecules (if $HBr/UF_6 \gtrsim 1$ to 10) during its
25 lifetime. It then can undergo a Vanderwaals attachment collision

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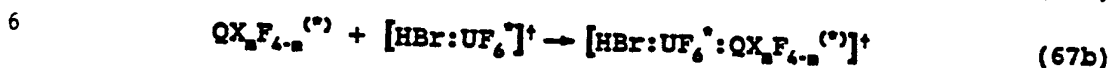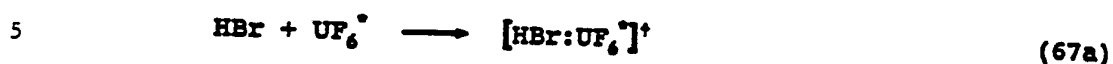such as (64) followed by the decays (65a) or (65b), or it experiences a local electric field excursion during one collisional encounter with HBr resulting in its dissociation by routes (65a) or (65b). Without interaction with the highly polar HBr molecule, the complex $[^i UF_6^*:QX_n F_{4-n}^{(*)}]$ will dissociate by the following possible pathways after about 10 collisions:

$$[^i UF_6^*:QX_n F_{4-n}^{(*)}]^* \longrightarrow \begin{cases} ^i UF_6^{(*)} + QX_n F_{4-n}^{(*)} & \text{(Thermoneutral)} \quad (66a) \\ ^i UF_5 X^{(*)} + QX_{n-1} F_{5-n}^{(*)} & \text{(Exothermic)} \quad (66b) \end{cases}$$
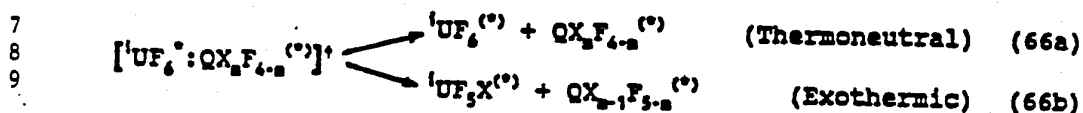
Without HBr, the probability for the desired pathway (66b) may only be on the order of 0.01 to 0.1, while avenue (66a) occurs 90% to 99% of the time. In the presence of HBr on the other hand, the initial complex in (66) may be "kicked" by the HBr electric field pulse into the exothermic reaction (66b) with almost 100% certainty.

The reason why the presence of, for example, HBr is believed to exert the effects described by (64), (65), and by (62), is that both the rate of production of enriched $^i UF_5 X$ (and/or $^i UF_6$) product as well as the degree of isotopic separation are enhanced when some HBr is added to $UF_6^* + QX_n F_{4-n}^{(*)}$ reaction mixtures. If reaction (66b) is efficiently induced by HBr, it is possible that reaction (65a) followed by (62) is not very active. In other words, it is possible that $^i UF_6$ is formed almost directly from the $[UF_6^*:QX_n F_{4-n}^{(*)}:HBr]$ complex by (65b) and decomposition of $UF_6 XBr$ by (61) with $^i UF_6$ and BrX as final products.

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Instead of the secondary attachment of HBr to the activated complex $[UF_6^*:QX_nF_{4-n}^{(*)}]$, it is possible that the following alternate steps leading to the triple complex $[HBr:UF_6^*:QX_nF_{4-n}]^\dagger$ can occur as well:

5    $$HBr + UF_6^* \longrightarrow [HBr:UF_6^*]^\dagger \tag{67a}$$

6    $$QX_nF_{4-n}^{(*)} + [HBr:UF_6^*]^\dagger \rightarrow [HBr:UF_6^*:QX_nF_{4-n}^{(*)}]^\dagger \tag{67b}$$

or

8    $$HBr + QX_nF_{4-n}^{(*)} \longrightarrow [HBr:QX_nF_{4-n}^{(*)}]^\dagger \tag{68a}$$

9    $$UF_6^* + [HBr:QX_nF_{4-n}^{(*)}]^\dagger \rightarrow [HBr:QX_nF_{4-n}^{(*)}:UF_6^*]^\dagger \tag{68b}$$
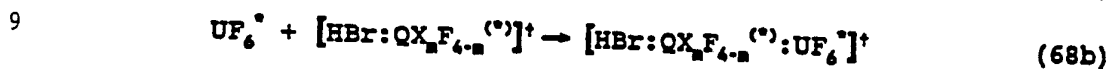
10 Steps (67b) and (68b) yield the same final complex as step (64), and the ensuing decays should be as described by (65a) and (65b). Again it is possible that Steps (67b) and (68b) only occur during the lifetime of one collisional encounter without the formation of a longer-lasting Vanderwaals complex prior to the decays (65a) and 15 (65b).

We have used HBr only as an example. Many other auxiliary reactants GL such as, for example, QBr_4, QBr_nH_{4-n}, QCl_4, QCl_nH_{4-n}, QBr_nF_{4-n}, or QCl_nF_{4-n} with Q = Si, Ge, Sn, may be equally effective.

20   In conclusion, the CRISLA enrichment of ^iMY with a suitable coreactant RX may sometimes be considerably improved if a secondary coreactant GL is added to the CRISLA gas mixture which catalyzes or enhances the rate of formation of isotopically enriched product after an attachment complex is formed or by

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electric field impulse kicks of the complex [^{l}MY*:RX$^{(-)}$] in collisions
with GL and/or which rapidly scrubs out the enriched product
chemical ^{l}MX, before the latter can undergo any undesirable
secondary scrambling reactions. Whereas, the best coreactant RX

5   is selected on the basis of its reactability given in Sections 2
and 3, the secondary reactant GL must be chosen so as to aid the
rate of production and removal of the enriched product ^{l}MX. It
should not significantly react with pure ^{l}MY alone.

        If the scrubbing agent GL only acts to remove product ^{l}MX

10 by reactions like (62) and is not involved in the reaction complex
such as reaction (64), GL may be injected into the outflowing
laser-irradiated CRISLA reactants stream outside the intracavity
irradiation cell (IC), as this gas mixture leaves the IC. In this
way there would be no interference of the action of GL with the

15 laser-induced reaction. Also in this case, instead of adding
gaseous GL to the primary CRISLA reactant mixture, another approach
is to operate at low IC pressures (p_{ic} < 0.1 torr) and to use a
surface agent for scavenging ^{l}MX. That is, back reactions or
chemical scrambling of the product ^{l}MX can be inhibited on the IC

20 walls by use of a specially prepared wall material or surface agent
such as activated Ni, Cu or C which quickly converts ^{l}MX to a more
stable chemical form (e.g. ^{l}UF$_4$). By keeping the IC pressure low,
the product ^{l}MX can diffuse to the wall with little or no
obstruction and is immediately converted there to the more stable

25 chemical form. Like a gaseous auxiliary agent GL, a surface agent

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should, of course, have no or little effect on the feed molecules ^1MY (e.g. UF_6) and primarily act on product molecules ^1MX (e.g. $^1UF_5X$). Instead of collection in the IC, the desired surface action may be effected outside the IC by rapid passage of the irradiated

5 CRISLA gas mixture of ^1MX, MY and RX through a scrubber with plates, tubes, or saddles whose surfaces contain the special agent that quickly reduces ^1MX (e.g. $^1UF_5X$) to a more stable form (e.g. $^1UF_4$ and X_2).

If, on the other hand, the auxiliary agent GL is critical

10 in promoting a reaction like (62), it must be present in the IC and be thoroughly mixed with ^1MY and RX while this mixture is being irradiated. Usually it is desirable to have high throughputs, and, therefore, higher IC operating pressures $(p_{IC} > 0.1 \text{ torr})$. In that case, it is also necessary that the agent GL be gaseous and

15 intimately mixed with ^1MY and RX to effectively suppress reactions like (51) - (53), even if it does not participate in reactions like (64) and (65).

6. Conclusions

Some general conclusions can be drawn that follow from

15 the analytical review of UF_6 CRISLA reactions given above. One important finding is that coreacant molecules HX can be expected to give unsatisfactory $^1UF_6$ enrichments if the CRISLA process is driven by only one laser quantum with energy $3 h\nu_3 = h\nu_L < 1876$ cm^{-1} (CO laser). This is because of the fact that the frequency of

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the hydrogen bond vibration $(\bar{v}_{vib})_{.H} \geq 2000$ cm^{-1}. Consequently, if this bond is to be broken in the activated complex of a rearrangement reaction such as (2), the necessary energy can usually not be quickly and efficiently channeled to it from the $\bar{v}_3 = 625$ cm^{-1} vibrational quanta that are pumped up in UF_6^* through two-quantum (the most probable) internal VV transitions. The minimum number of quantum changes in a VV-transfer is two since at a minimum one quantum is lost by one vibration while a second quantum is gained by another vibration. Only in pure VT or TV transitions is there a one-quantum change in the "warehouse of vibrations." Multi-quantum transfers would be required to feed the $\bar{v}_\beta \geq 2000$ cm^{-1} vibration. Such multi-quantum transfers are less probable by factors of 100-10,000 over two-quantum transitions. Thus, it is found that the slow gas-phase reactions of UF_6 with HX molecules which would appear to be attractive candidates according to equation (24), are not attractive. The slowness of the reaction is due to the requirement that activation energy be provided by once (or higher) thermally excited $HX^*(v_\beta \geq 1)$ species in the gas whose population is approximately equal to the small fraction $\exp(-v_\beta h\bar{v}_\beta/kT)$. Since excited molecules $HX^*(v_\beta \geq 1)$ control the reaction with UF_6, only laser-pumping of HX could cause the reaction to become laser-driven. The laser-pumping of $^iUF_6$ (necessary if one wishes to enrich ^iU) appears rather ineffective in promoting the reaction of $^iUF_6 + HX$. Also, θ_L is probably small for this reaction (see the discussion surrounding equation (43)).

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Many early attempts to promote CRISLA enrichment with UF_6 + RX reactions gave disappointing results.

The rule that emerges is that only if the vibrations in a coreactant molecule RX can easily accept quanta from UF_6^* in the activated complex $['UF_6^*:RX]'$, can laser excitation of $'UF_6$ be effective in promoting a reaction. This is the case when $\nu_\alpha = \nu_3(UF_6) - \nu_\beta(RX)$ or $E_\alpha - E_b - E_c/2$ which means that RX must be a molecule with fairly heavy atoms. This also means that some of such preselected reactants RX may fortuitously have one or more vibrations β_1, β_2, ..., such that one of its binary or tertiary absorption bonds has $(h\nu_{\beta 1} + h\nu_{\beta 2}) - h\nu_L$ or $(h\nu_{\beta 1} + h\nu_{\beta 2} + h\nu_{\beta 3}) - h\nu_L$. Here $h\nu_L = 3h\nu_3 \approx 1876$ cm^{-1}, for example, for the CO-laser driven isotopic excitation of UF_6. Such an accidental coincidence of a weak absorption of $h\nu_L$ by RX occurs, for example, for SiH_4 with $(h\nu_2 + h\nu_4) - 1876$ cm^{-1}. This may be used advantageously to improve the effective reaction rate of SiH_4 by promoting reaction over the complex $[UF_6^*:SiH_4^*]$ during laser irradiation instead of $[UF_6^*:SiH_4]$ as discussed above.

In addition to the desirability that $\nu_\alpha - \nu_\beta$, the complex formation rate which is controlled by the Vanderwaals attachment probability of UF_6/RX collisions should be reasonably high. This condition is usually satisfied automatically since most heavy polyatomic molecules have wagging or scissoring vibrations with frequencies close to room temperature (T = 290°K ≈ 200 cm^{-1}; see

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also Figures 6 and 7). Although the intermolecular potential well depth controls the attachment rate (see Reference e), the frequent loss (~ 10 collisions) of most of kT in TV collisions will enhance the Vanderwaals attachment rate considerably.

Another general conclusion is that coreactants RX suitable for CRISLA enrichment of UF_6 should not react too fast under thermal conditions, but also not be too slow. The criteria of what constitutes a reaction that is "too fast" or "too slow" were defined by equations (24), (25), and (26). Figure 4 illustrated the speed limits.

Finally, it is often found to be beneficial to use a secondary reactant labeled GL. The reactant GL must rapidly remove the enriched product molecules ^1MX by converting ^1MX further to a more stable species before it can back-react or scramble the desired ^1M isotopes by additional chemical exchange reactions. GL should not react excessively with ^1MY or RX, of course. Some highly polar coreactants GL (such as HBr) may also promote and speed up the desired reaction of the attachment complex $[RX^{(*)}:^1MY^*]$ by kicking it during a collision with its strong dipolar or quadrupolar electric field or by superimposing such a strong field in the new transient complex $[GL:RX^{(*)}:^1MY^*]^+$ formed after a collisional encounter. A triple complex may alternatively be produced by a first association of GL with $RX^{(*)}$ to form $[GL:RX^{(*)}]$ followed by the latters attachment to or interaction with UF_6^*.

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The restrictions on RX discussed in the previous sections allows one to narrow the number of economically attractive coreactants to a relatively small group. Figure 8 summarizes the selection process that leads to a commerically suitable coreactant RX. The first four selection steps (A) - (D) shown in Figure 8 are relatively obvious and were discussed earlier in Reference (a). Steps (E) and (F) are newer discoveries which, taken together with Steps (G) and (H), yield an efficient primary CRISLA coreactant and possibly a secondary auxiliary reactant.

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BRIEF DESCRIPTION OF THE DRAWINGS

The above and other embodiments of the present invention may be more fully understood from the following
5   description and the accompanying drawings wherein similar reference characters refer to similar elements throughout and in which:

Fig. 1 is a schematic diagram of the process equipment associated with one embodiment of the present
10 invention;

Fig. 2 is a graphical representation of the photon absorption characteristics associated with the isotopic molecules in one embodiment of the present invention;

Figs. 3A through 3C is an additional graphical
15 representation of the representation of the photon absorption characteristics associated with the isotopic molecules in one embodiment of the present invention;

Fig. 4 is a graphical representation of the isotope separation factor as a function of chemical reaction rate
20 in one embodiment of the present invention;

Fig. 5 is a graphical illustration of the pre-reaction attachment process of coreactant RX with UF6 in one embodiment of the present invention;

Figs. 6A through 6I are graphical representations
25 of the molecular vibration characteristics associated with the isotopic molecules in one embodiment of the present invention;

Figs. 7A through 7F are graphical representations of the molecular vibration characteristics associated with
30 the coreactant molecules in one embodiment of the present invention; and

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FIG. 8 is a schematic diagram illustrating the selection procedure required to obtain effective and suitable coreactants RX auxiliary coreactants GL for use in a commercially attractive CRISLA isotope enrichment process.

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Claims:

1   1.   In a process for separating predetermined isotopic
2   molecules from a mixture of chemically identical but
3   isotopically different molecules, to obtain a
4   concentration of the predetermined isotope wherein the
5   molecules comprising the mixture have a lower
6   rovibrational energy state and a higher rovibrational
7   energy state with photon-inducible transitions between
8   the lower rovibrational energy state and the higher
9   rovibrational energy state, and the photon frequency for
10 the photon-inducible transitions between the lower
11 rovibrational energy state and the higher rovibrational
12 energy state of the predetermined isotopic molecules is
13 different from the photon frequency for the photon-
14 inducible transitions between the lower rovibrational
15 energy state and the higher rovibrational energy state of
16 the other chemically identical but isotopically different
17 molecules in the mixture, the improvement comprising the
18 step of:
19   selectively reacting the predetermined isotopic
20 molecules having a preselected vibrational frequency in a
21 first physicochemical state and at the higher
22 rovibrational energy state with a first chemically-
23 reactive agent to provide a chemical compound at a second
24 physicochemical state different from the first
25 physicochemical state and containing atoms of the
26 predetermined isotope, said step of selectively reacting
27 the predetermined isotopic molecules further comprises
28 the step of selecting said first chemically-reactive
29 agent to have:
30   a first predetermined reaction speed range with
31 said isotopic molecules bounded by a maximum speed of
32 said first chemically-reactive agent which is not greater
33 than $(k_T)_{max}$ where $(k_T)_{max}$ is determined by:

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34

35   $$(k_T)_{min} = \left(\frac{k_V + k_S}{\theta_L}\right) \cdot \left(\frac{\eta_{gain}}{1 - \eta_{gain}}\right) \approx \frac{\eta_{gain}}{\theta_L}(k_V + k_S) \ , \ s^{-1}$$

36

37   ;

38   a minimum reaction speed not less than $(k_T)_{min}$

39 where $(k_T)_{min}$ is determined by:

40

41       $$(k_T)_{max} = k_A - \frac{k_V + k_S}{\theta_L} \ , \ s^{-1}$$

42

43   ; and

      a first predetermined vibrational frequency;

44 and in which said second physicochemical state is

45 substantially free of scrambling reactions of the

46 chemical compound.

1   2. The process defined in Claim 1 wherein said first

2 predetermined vibrational frequency of said first

3 chemically-reactive agent does not exceed, by a factor

4 greater than about 2, the preselected vibrational

5 frequency of said rovibrational energy states with said

6 photon inducible transitions of said predetermined

7 isotopic molecules.

1   3. The process defined in Claim 1 and further

2 comprising the step of:

3   reacting said chemical compound at said

4 second physicochemical state with a second chemically-

5 reactive agent capable of rapidly scavenging said

6 chemical compound at said second physicochemical state.

1   4. The process defined in Claim 3 wherein said second

2 chemically-reactive agent is chosen to be capable of

3 stabilizing said chemical compound at said second

4 physicochemical state.

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1   5. The process defined in Claim 3 wherein said second
2   chemically-reactive agent is chosen to be capable of
3   increasing the formation rate of said chemical compound
4   at said second physicochemical state.

1   6. The process defined in Claim 4 wherein said second
2   chemically-reactive agent is chosen to be capable of
3   increasing the formation rate of said chemical compound
4   at said second physicochemical state.

1   7. The process defined in Claim 4 wherein said second
2   chemically-reactive agent is chosen to be substantially
3   free of excessive reaction with said first chemically
4   reactive agent and substantially free of excessive
5   reactions with said predetermined isotopic molecules at
6   the first physicochemical state.

1   8. The process defined in Claim 5 wherein said second
2   chemically-reactive agent is chosen to be substantially
3   free of excessive reaction with said first chemically
4   reactive agent and substantially free of excessive
5   reactions with said predetermined isotopic molecules at
6   the first physicochemical state.

1   9. The process defined in Claim 6 wherein said second
2   chemically-reactive agent is chosen to be substantially
3   free of excessive reaction with said first chemically
4   reactive agent and substantially free of excessive
5   reactions with said predetermined isotopic molecules at
6   the first physicochemical state.

1   10. A process for separating ^{235}U from a mix of ^{238}UF$_6$
2   and ^{235}UF$_6$, to obtain a chemical compound in which the
3   ratio of ^{235}U to ^{238}U is higher than in the mix, the process
4   comprising the steps of:
5   combining the mix of ^{238}UF$_6$ and ^{235}UF$_6$ with at least

6 one type of reactant molecules which is selected from a
7 group consisting of:
8     $GeCl_4$, GeH_4, $SiBr_4$, $SiCl_4$, SiH_4, $SiOH_3F_3$, and
9 $SiOH_6$, to form a mixture thereof;
10   exposing the mixture to electromagnetic energy of
11 at least one predetermined wave length which is absorbed
12 more strongly by $^{235}UF_6$ than by $^{238}UF_6$, in the presence of
13 at least one type of polar molecule to cause the $^{235}UF_6$ to
14 go from a first physicochemical state to a second
15 physicochemical state where the $^{235}UF_6$ combines with the
16 reactant molecules at a higher rate than does $^{238}UF_6$ to
17 form the chemical compound; and
18   separating the chemical compound from the
19 mixture.

1   11.   The process as defined in Claim 10 including the
2 further step of:
3   fluorinating the separated chemical compound with
4 at least one of a group consisting of:
5   F_2, ClF_3, and IF_7 to produce a mixture of
6 $^{235}UF_6$ and $^{238}UF_6$ at the higher ratio.

1   12.   The process as defined in Claim 10 wherein the at
2 least one type of reactant molecule is SiH_4 and the polar
3 molecule is HBr.

1   13.   The process as defined in Claim 10 wherein the
2 type of polar molecule is chosen from a group consisting
3 of:
4   HBr, HI, HCl, $SiBrH_3$, $SiBrF_3$, $SiClH_3$, and $SiClF_3$
5 which type of polar molecule is present as a catalyst.

1   14.   The process as defined in Claim 10 wherein the
2 type of polar molecule is chosen from a group consisting
3 of:
4   HBr, HI, HCl, $SiBrH_3$, $SiBrF_3$, $SiClH_3$, and $SiClF_3$

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5   which type of polar molecule is present as a scavenger.

1   15. The process as defined in Claim 10 wherein the
2   type of polar molecule is chosen from a group consisting
3   of:
4   HBr, HI, HCl, $SiBrH_3$, $SiBrF_3$, $SiClH_3$, and $SiClF_3$
5   which type of polar molecule is present to prevent back
6   reactions of the chemical compound to UF_6.

1   16. The process as defined in Claim 10 wherein the at
2   least one reactant is SiH_4, wherein HBr is the polar
3   molecule present, and wherein the reaction is:
4        $^{235}UF_6{}^* + SiH_4{}^{(*)} + {}^+HBr^- \rightarrow [{}^{235}UF_6{}^*{:}SiH_4{}^*] + {}^+HBr^- \rightarrow$
5   $[{}^{235}UF_6{}^*{:}SiH_4{}^*] \cdot [{}^-BrH^+] \rightarrow {}^+HBr^- + $ Reaction Products.

1   17. The process as defined in Claim 16 wherein the
2   Reaction Products are:
3        $^{235}UF_5SiH_3{}^{(*)} + HF \rightarrow {}^{235}UF_4{}^{(*)} + SiH_3F^{(*)} + HF.$

1   18. The process as defined in Claim 16 wherein the
2   Reaction Products are:
3        $^{235}UF_5H^{(*)} + SiH_3F^{(*)} \rightarrow {}^{235}UF_4{:}HF^{(*)} + SiH_3F^{(*)}.$

1   19. The process as defined in Claim 10 wherein the
2   electromagnetic energy whose at least one predetermined
3   wave number is about 1876 cm^{-1}.

1   20. The process as defined in Claim 10 wherein the
2   separating step is performed by cooling the chemical
3   compound until it changes phase.

1   21. A process for separating ^{235}U gas from a first
2   gaseous mixture of $^{238}UF_6$ and $^{235}UF_6$, to obtain a desired
3   chemical compound containing ^{235}U, comprising the steps
4   of:
5   mixing the first gaseous mixture of $^{238}UF_6$ and

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6   $^{235}UF_6$ with reactant molecules in gaseous form to form a
7   second gaseous mixture;
8   subjecting the second gaseous mixture to
9   electromagnetic energy of at least one predetermined wave
10 length which is absorbed more strongly by $^{235}UF_6$ than
11 $^{238}UF_6$, said step being performed in the presence of at
12 least one type of polar molecule, the electromagnetic
13 energy causing the $^{235}UF_6$ to go from a first
14 physicochemical state to a second physicochemical state
15 wherein the $^{235}UF_6$ combines at a higher rate than $^{238}UF_6$
16 with the reactant molecules when the polar molecules are
17 present to produce a chemical compound containing atoms
18 of ^{235}U; and
19   separating the chemical compound from the second
20 gaseous mixture.

1   22. The process as defined in Claim 21 including the
2   further step of:
3   fluorinating the separated chemical compound with
4   at least one of a group consisting of:
5   F_2, ClF_3, and IF_7.

1   23. The process as defined in Claim 21 wherein the
2   reactant molecules are SiH_4 which are reacted in the
3   presence of HBr molecules.

1   24. The process as defined in Claim 21 wherein the
2   polar molecules include HBr molecules which are present
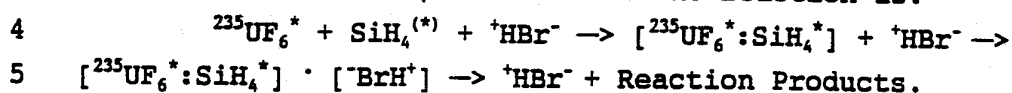3   as a catalyst.

1   25. The process as defined in Claim 21 wherein the
2   polar molecule is chosen from a group consisting of:
3   HBr, HI, HCl, $SiBrH_3$, $SiBrF_3$, $SiClH_3$, and $SiClF_3$.

1   26. The process as defined in Claim 21 wherein the
2   polar molecule is chosen from a group consisting of:

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3   QX_4, QX_mH_{4-m}, and HBr, HCl, and HI, where Q = Si,
4   Ge, or Sn, and X = Br, Cl or F.

1   27.   The process as defined in Claim 21 wherein the
2   reactant molecules are SiH_4, wherein the polar molecules
3   at least include HBr, and wherein the reaction is:
4              $^{235}UF_6^* + SiH_4^{(*)} + {}^+HBr^- \rightarrow [^{235}UF_6^*{:}SiH_4^*] + {}^+HBr^- \rightarrow$
5      $[^{235}UF_6^*{:}SiH_4^*] \cdot [^-BrH^+] \rightarrow {}^+HBr^- +$ Reaction Products.

1   28.   The process as defined in Claim 27 wherein the
2   Reaction Products are:
3              $^{235}UF_5SiH_3^{(*)} + HF \rightarrow {}^{235}UF_4^{(*)} + SiH_3F^{(*)} + HF$.

1   29.   The process as defined in Claim 27 wherein the
2   Reaction Products are:
3              $^{235}UF_5H^{(*)} + SiH_3F^{(*)} \rightarrow {}^{235}UF_4{:}HF^{(*)} + SiH_3F^{(*)}$.
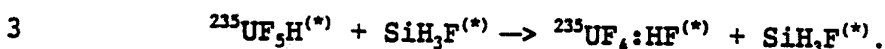
1   30.   The process as defined in Claim 27 wherein the
2   electromagnetic energy whose at least one predetermined
3   wave number is about 1876 cm^{-1}.

1   31.   Uranium product which is enriched with ^{235}U beyond
2   what is available in nature which is obtained by the
3   steps of:
4   reacting uranium with fluorine to produce a first
5   gaseous mixture of $^{238}UF_6$ and $^{235}UF_6$;
6   mixing the first gaseous mixture of $^{238}UF_6$ and
7      $^{235}UF_6$ with reactant molecules in gaseous form to form a
8   second gaseous mixture;
9   subjecting the second gaseous mixture to
10   electromagnetic energy of at least one predetermined wave
11   length which is absorbed more strongly by $^{235}UF_6$ than $^{238}UF_6$
12   in the presence of at least one type of polar molecule,
13   the electromagnetic energy causing the $^{235}UF_6$ to go from a
14   first physicochemical state to a second physicochemical
15   state wherein the $^{235}UF_6$ combines at a higher rate than

16 $^{238}UF_6$ with the reactant molecules when the polar molecules
17 are present to produce a chemical compound containing
18 atoms of ^{235}U;
19   separating the chemical compound from the second
20 gaseous mixture;
21   fluorinating the separated chemical compound; and
22   oxidizing the fluorinated chemical compound to
23 produce said enriched uranium product.

1   32. The uranium product as defined in Claim 31
2 wherein the reactant molecules are SiH_4 which are reacted
3 in the presence of HBr molecules.

1   33. The uranium product as defined in Claim 31
2 wherein the polar molecule is chosen from a group
3 consisting of:
4   HBr, HI, HCl, $SiBrH_3$, $SiBrF_3$, $SiClH_3$, and $SiClF_3$.

1   34. The uranium product as defined in Claim 31
2 wherein the first reactant molecules are SiH_4, wherein the
3 polar molecules at least include HBr, and wherein the
4 reaction is:
5      $^{235}UF_6^* + SiH_4^* + {}^+HBr^- \rightarrow [{}^{235}UF_6^*:SiH_4^*] + {}^+HBr^- \rightarrow$
6 $[{}^{235}UF_6^*:SiH_4^*] \cdot [{}^-BrH^+] \rightarrow {}^+HBr^- +$ Reaction Products.

1   35. A process for separating predetermined isotopic
2 molecules from a mixture of chemically identical but
3 isotopically different molecules, to obtain a
4 concentration of the predetermined isotope wherein the
5 molecules comprising the mixture have a lower
6 rovibrational energy state and a higher rovibrational
7 energy state with photon-inducible transitions between
8 the lower rovibrational energy state and the higher
9 rovibrational energy state, and the photon frequency for
10 the photon-inducible transitions between the lower
11 rovibrational energy state and the higher rovibrational

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12 energy state of the predetermined isotopic molecules is
13 different from the photon frequency for the photon-
14 inducible transitions between the lower rovibrational
15 energy state and the higher rovibrational energy state of
16 the other chemically identical but isotopically different
17 molecules in the mixture, the improvement comprising the
18 step of:

19   selectively reacting the predetermined isotopic
20 molecules having a preselected vibrational frequency in a
21 first physicochemical state and at the higher
22 rovibrational energy state with a first chemically-
23 reactive agent to provide a chemical compound at a second
24 physicochemical state different from the first
25 physicochemical state and containing atoms of the
26 predetermined isotope in the presence of polar molecules,
27 said first chemically-reactive agent having:

28   a first predetermined reaction speed range
29 with said isotopic molecules bounded by a maximum speed
30 of said first chemically-reactive agent which is not
31 greater than $(k_T)_{max}$ where $(k_T)_{max}$ is determined by:

32
33 $$(k_T)_{min} = \left(\frac{k_V + k_S}{\theta_L}\right) \cdot \left(\frac{\eta_{qmin}}{1 - \eta_{qmin}}\right) \approx \frac{\eta_{qmin}}{\theta_L}(k_V + k_S) \ , \ s^{-1}$$
34
                                                              ;

35   a minimum reaction speed not less than
36 $(k_T)_{min}$ where $(k_T)_{min}$ is determined by:

37
38 $$(k_T)_{max} = k_A - \frac{k_V + k_S}{\theta_L} \ , \ s^{-1}$$
39   ; and

40   a first predetermined vibrational frequency in
41 which said second physicochemical state is substantially
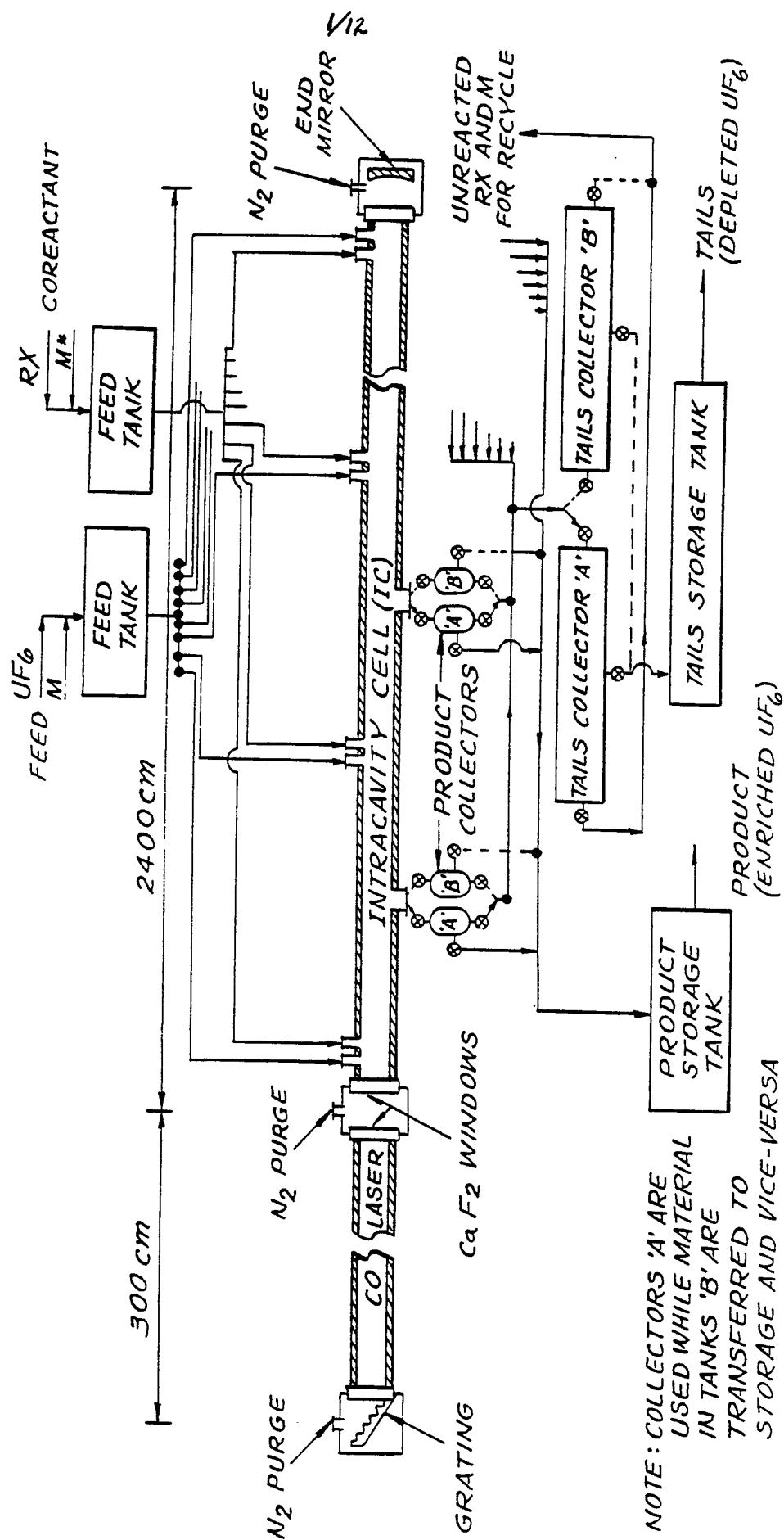42 free of scrambling reactions of the chemical compound.

1   36. The process as defined in Claim 35 wherein the
2 polar molecules are chosen from a group consisting of:

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3   QX_4, QX_mH_{4-m}, and HY, where Q = Si, Ge, or Sn,

4 X = Br, Cl or F, and Y = Br, I, or Cl.

1   37. A process for separating predetermined isotopic

2 molecules from a mixture of chemically identical but

3 isotopically different molecules substantially as
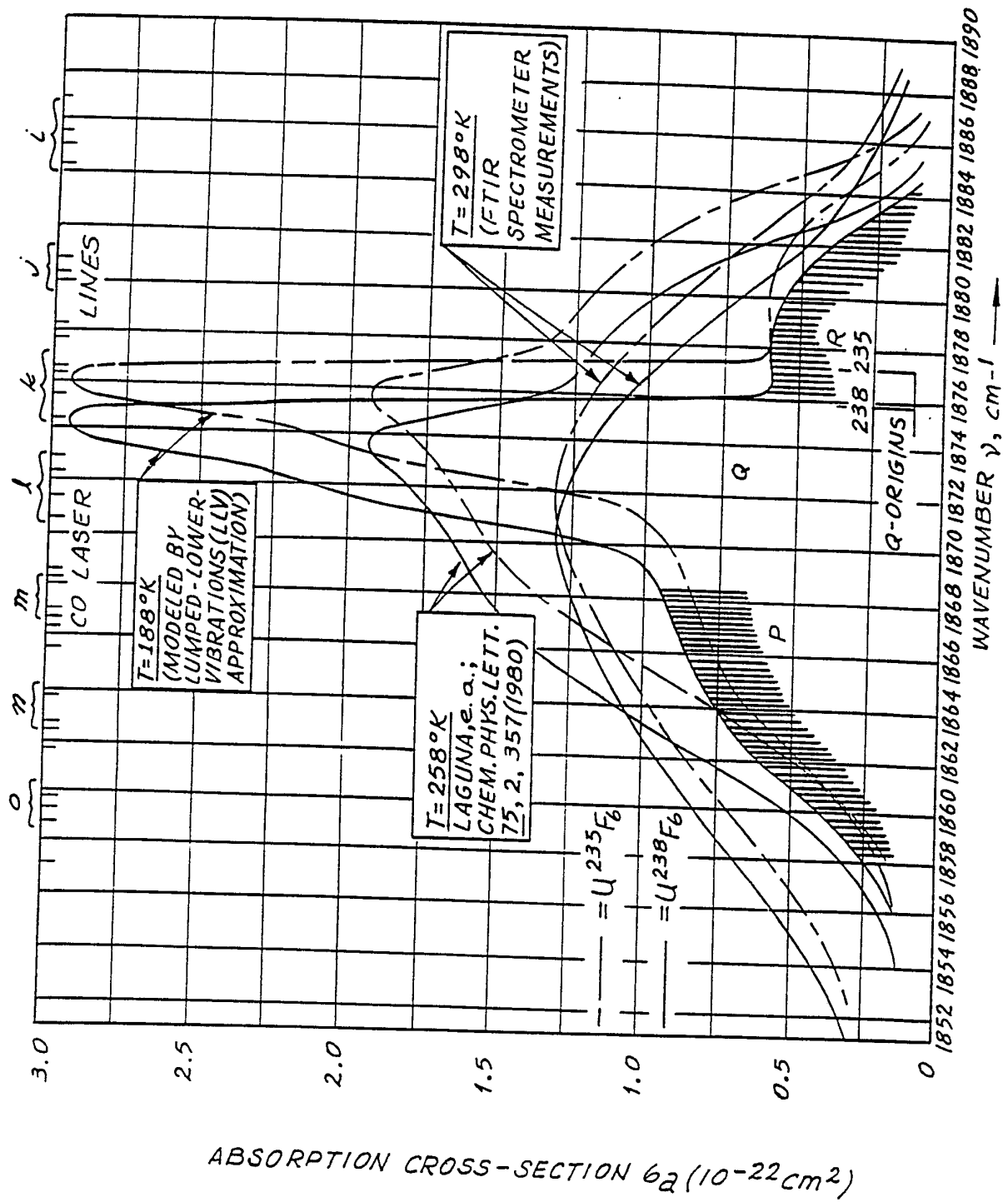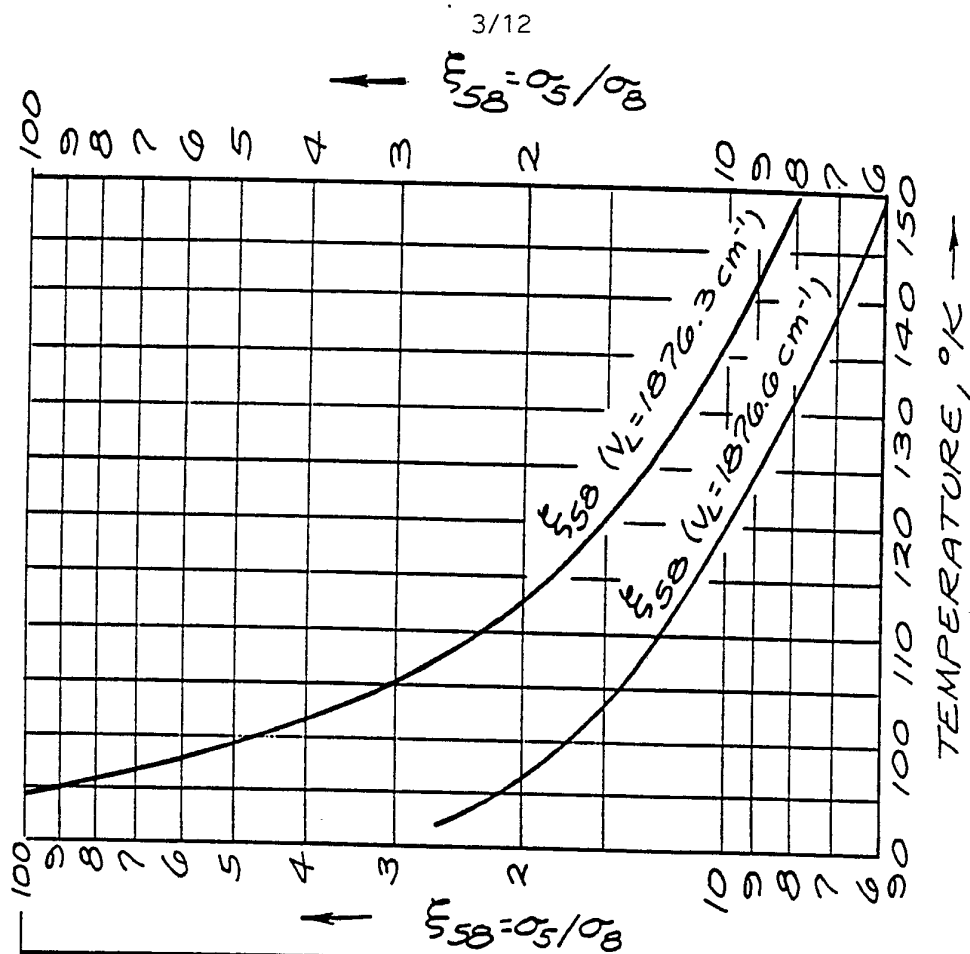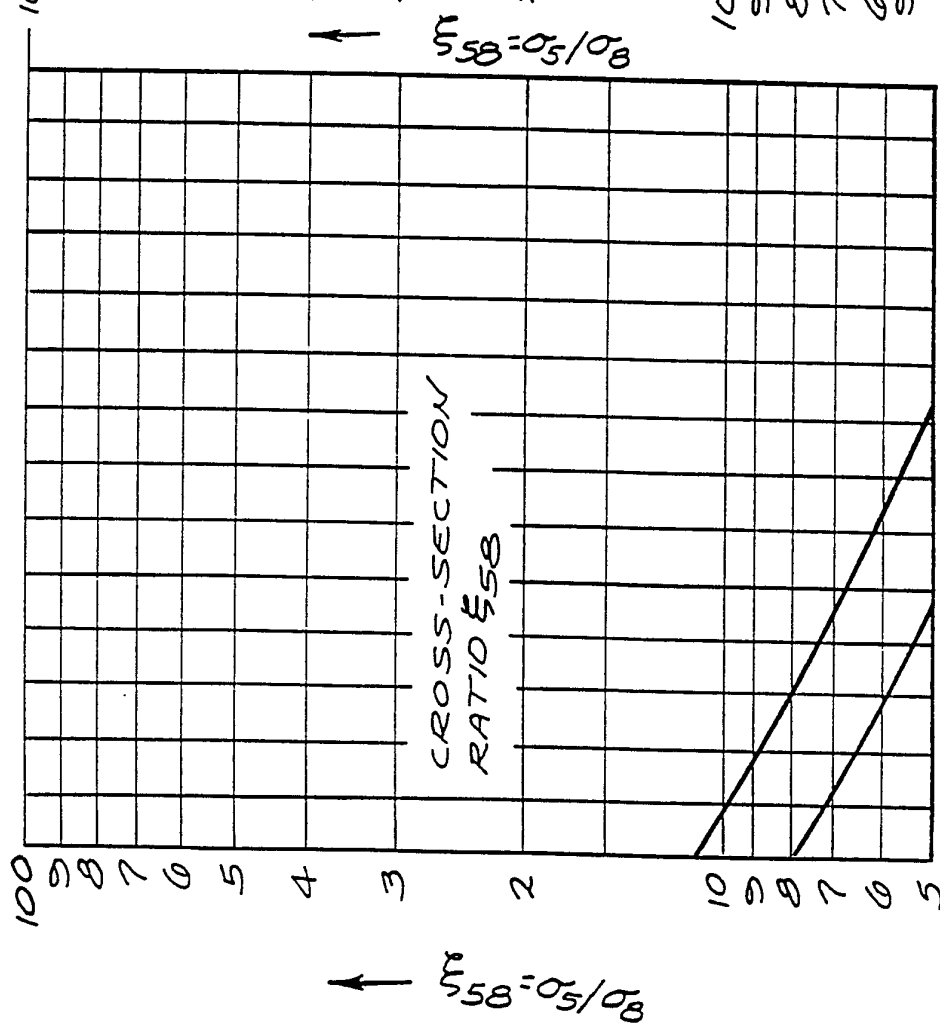
4 hereinbefore described.

FIG. 1

NOTE: COLLECTORS 'A' ARE USED WHILE MATERIAL IN TANKS 'B' ARE TRANSFERRED TO STORAGE AND VICE-VERSA

FIG.2

FIG. 3B

FIG. 3A

FIG. 3C

The table shown in the figure:

$k_C/(k_V + k_S)$ NUMBER OF COLLISIONS	q_L (APPROX. VALUE if $k_A = 10\,s^{-1}$ $P_{tot} = 10$ torr)
100	10
1,000	1.0
10,000	0.1

$$\alpha_{MAX} = \frac{\frac{3}{58} + q_L}{1 + q_L}$$

$$(x_T \to 0)$$

PROCESS IS TOO SLOW $(\tau_L \gtrsim \frac{1}{2}$ MIN, IF $k_A = 10\,s^{-1})$

THERMAL REACTION RATE, k_T, sec^{-1} (if $k_A = 10$ sec^{-1}

FIG. 4A

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NOTES: $\overset{\zeta}{3}_{58} = 2.5$ $(T = 225°K)$

$$\alpha_o = \frac{\eta q \overset{\zeta}{3}_{58} + \chi_T}{\eta q + \chi_T} ; \eta q = \left[1 + \frac{q_L}{\chi_T}\right]^{-1}$$

$q_L = (k_V + k_S)/(\theta_L k_A); \quad \chi_T = k_T/k_A$

$\theta_L = 1.6 \times 10^5/P_a ; \quad 3 \leq P_a \leq 126$

$k_A \approx 3 P_L(kW)A_i^{-1}(cm^2),s^{-1}; \quad k_L = \eta q k_A$

$\tau_L = k_L^{-1} = (\eta q k_A)^{-1}, SEC$

$k_C \sim 5 \times 10^6 P_{tot}(torr), collisions\ sec^{-1}$

ISOTOPE SEPARATION
IS POOR
$(k_A < k_T)$

ISOTOPE SEPARATION IS INEFFICIENT

$$\left(\alpha - 1 < \frac{\overset{\zeta}{3}_{58} - 1}{2}\right)$$

10^{-1} $\chi_T = k_T/k_A \longrightarrow$ 1.0 10

1 10 10^2

THERMAL REACTION RATE, k_T, sec^{-1} (if $k_A = 10\ sec^{-1}$)

FIG.4B

FIG. 5

NOTE: TWO DIFFERENT OUTCOMES OF THE RX-UF₆ ENCOUNTER ARE POSSIBLE:
(A) ELASTIC COLLISION A-B-C
(B) TV/ATTACHMENT A-B-D

RX COLLISION PATH IN RX/UF₆ ENCOUNTER

ELASTIC COLLISION

TV TRANSFER TRANSITION TO LOW-ENERGY VIBRATION V₉ OF RX OR UF₆

K.E.

UF₆ : RX ATTRACTIVE POTENTIAL WELL

RX-UF₆ SEPARATION, S (Å)

TOTAL INTER-MOLECULAR ENERGY

FIG. 6A
V_1
$V_1 = 424\,cm^{-1}$
A_1

FIG. 6B
V_{2a}

FIG. 6C
V_{2b}
E
$V_2 = 150\,cm^{-1}$

FIG. 6D
V_{3a}

FIG. 6E
V_{3b}
F_2

FIG. 6F
V_{3c}
$V_3 = 619\,cm^{-1}$

FIG. 6G
V_{4a}

FIG. 6H
V_{4b}
F_2

FIG. 6I
V_{4c}
$V_4 = 221\,cm^{-1}$

FIG. 7A — $\nu_1 = 666.2\ cm^{-1}$, A_{1g}

FIG. 7B — $\nu_2 = 533.4\ cm^{-1}$, E_g

FIG. 7C — $\nu_3 = 626.0\ cm^{-1}$, F_{1u}

FIG. 7D — $\nu_4 = 186.2\ cm^{-1}$, F_{1u}

FIG. 7E — $\nu_5 = 200.4\ cm^{-1}$, F_{2g}

FIG. 7F — $\nu_6 = 143\ cm^{-1}$, F_{2u}

◉ = U
○ = F

(A)

PRIOR KNOWLEDGE

NEW INSIGHT

SPECIES WITH DESIRABLE PROPERTIES

(B) 1. ALL SPECIES RX THAT DO NOT HAVE A
STRONG ABSORPTION BAND AT THE
CRISLA LASER FREQUENCY V_L .*)

(C) 1. SPECIES RX THAT ARE GASEOUS OR
WHICH FORM VAPORS WITH REASONABLE
VAPOR PRESSURES ($p \gtrsim 10^{-3}$ TORR) AT
REASONABLE TEMPERATURES ($T \leq 600\,^{\circ}K$).

(D) 1. SPECIES RX WHOSE REACTION WITH
^iMY IS EXOTHERMIC, THERMONEUTRAL,
OR ENDOTHERMIC WITH $\Delta H_f \leq h V_L$.

(E) 1. SPECIES RX WHOSE REACTION SPEED
WITH ^iMY FALLS WITHIN THE UPPER AND
LOWER BOUNDS DETERMINED BY
EQ. (24) AND EQ. (25)

(F) 1. SPECIES FOR WHICH THE VIBRATIONAL
FREQUENCY OF THE R-X BOND IS LESS THAN
OR APPROXIMATELY EQUAL TO THE VIBRA-
TIONAL FREQUENCY OF THE ^iM-Y BOND.

(G) 1. SPECIES RX WHICH FORM REACTION
PRODUCTS THAT DO NOT PARTAKE IN
SUBSEQUENT CHEMICAL ISOTOPE
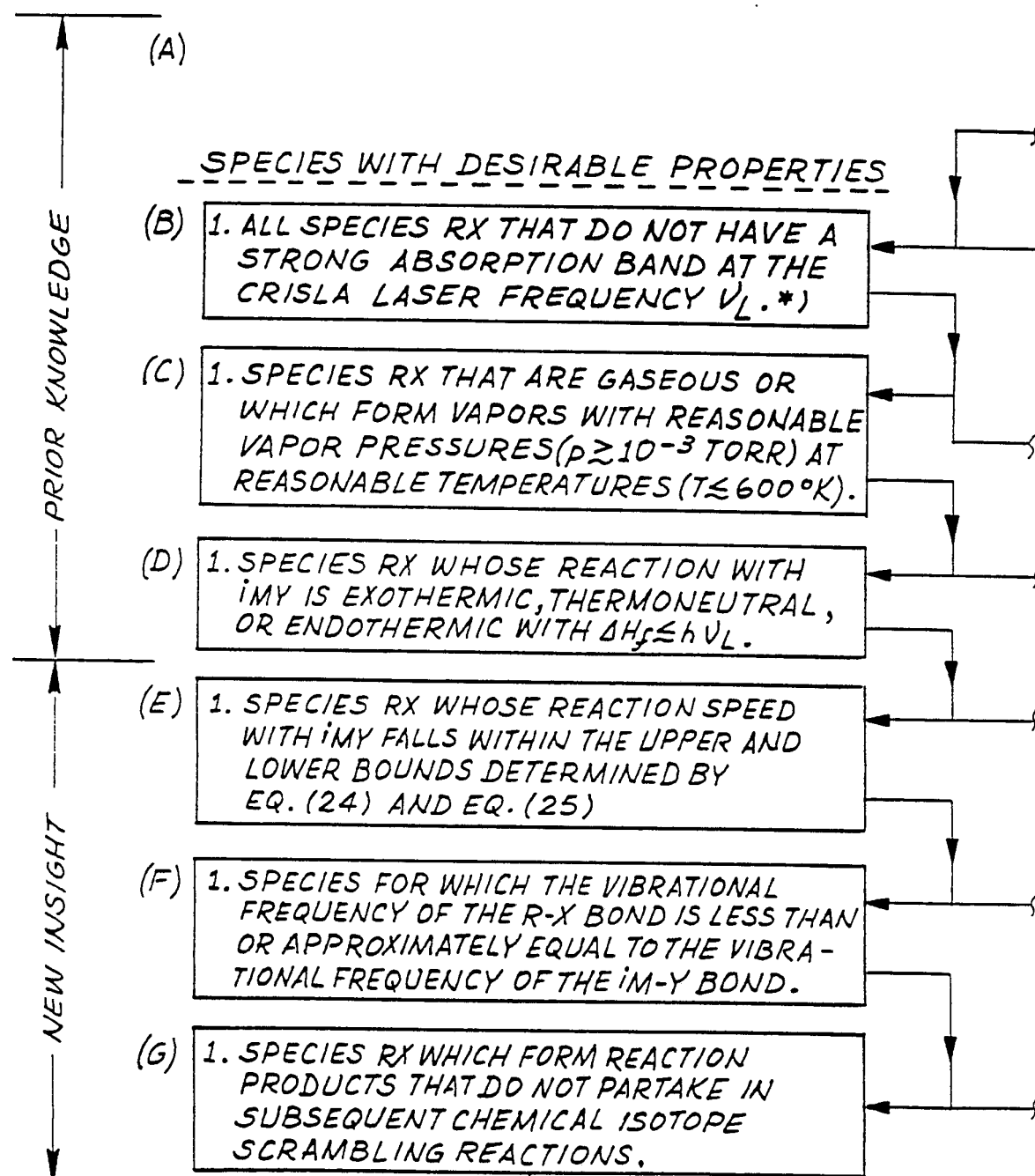SCRAMBLING REACTIONS.

FIG. 8A

ALL SPECIES RX THAT REACT WITH GASEOUS ^iMY (e.g. UF_6) BY
$$RX + {}^iMY \longrightarrow RY + {}^iMX$$

SPECIES WITH UNDESIRABLE PROPERTIES

2. SPECIES RX THAT HAVE STRONG ABSORPTION BANDS AT THE CRISLA LASER FREQUENCY V_L *).

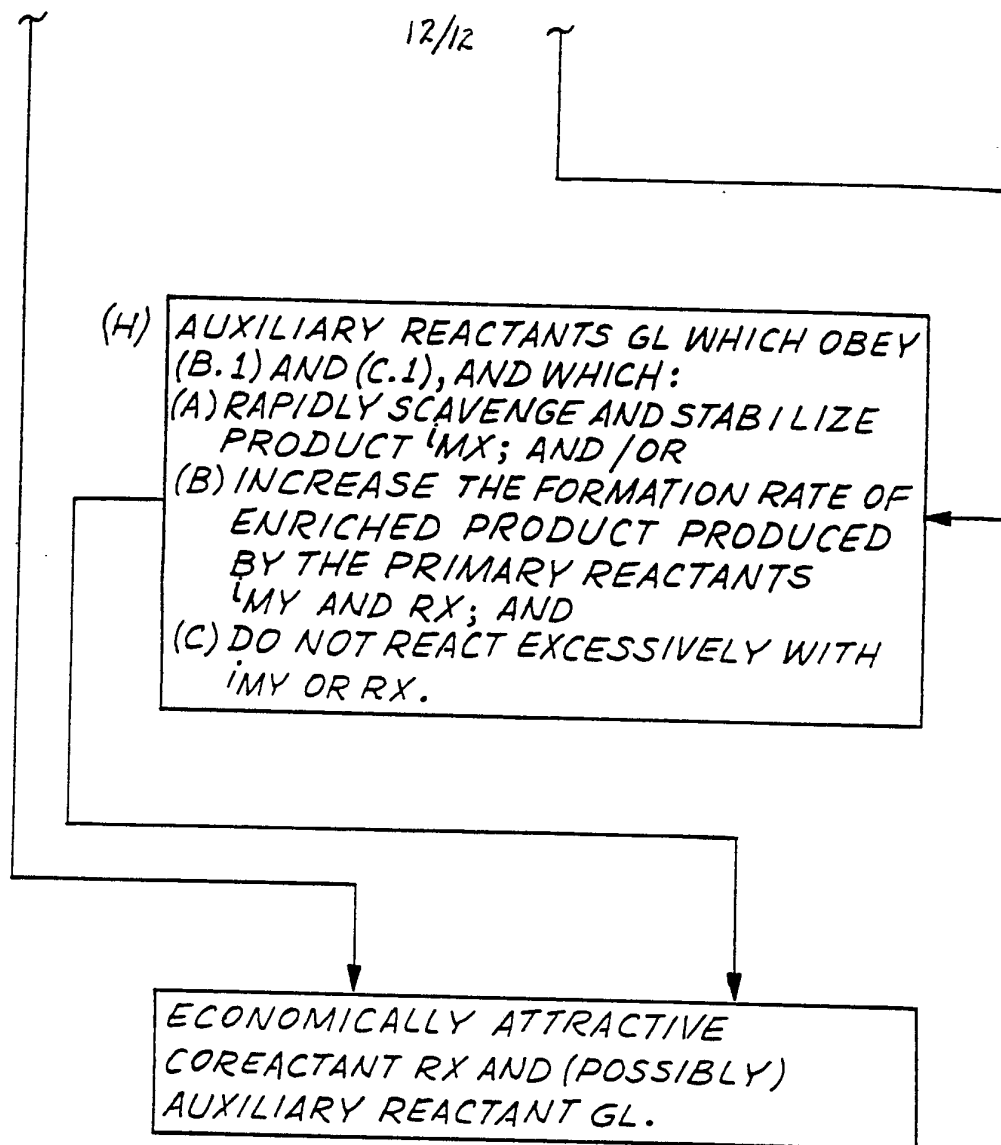2. SPECIES RX THAT ARE SOLID AND ALL OTHER RX THAT DO NOT FALL IN CATEGORY C-1.

2. SPECIES RX WHOSE REACTION WITH ^iMY IS ENDOTHERMIC WITH $\Delta H_f \gtrsim h V_L$.

2. SPECIES RX WHOSE REACTION SPEED WITH ^iMY IS HIGHER THAN THE VALUE DETERMINED BY EQ.(24) OR LOWER THAN THE VALUE DETERMINED BY EQ.(25).

2. SPECIES FOR WHICH THE VIBRATIONAL FREQUENCY OF THE R-X BOND EXCEEDS THE VIBRATIONAL FREQUENCY OF THE ^iM-Y BOND BY A FACTOR OF APPROXIMATELY 1.2 OR MORE.

2. SPECIES RX WHICH FORM REACTION PRODUCTS THAT MAY SUBSEQUENTLY EXPERIENCE CHEMICAL SCRAMBLING REACTIONS WHICH DIMINISH ISOTOPE SEPARATION.
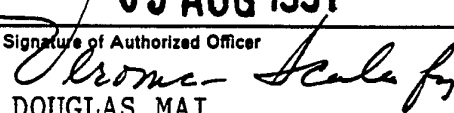
FIG.8B

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(H) AUXILIARY REACTANTS GL WHICH OBEY
(B.1) AND (C.1), AND WHICH:
(A) RAPIDLY SCAVENGE AND STABILIZE
PRODUCT ^iMX; AND /OR
(B) INCREASE THE FORMATION RATE OF
ENRICHED PRODUCT PRODUCED
BY THE PRIMARY REACTANTS
^iMY AND RX; AND
(C) DO NOT REACT EXCESSIVELY WITH
^iMY OR RX.

ECONOMICALLY ATTRACTIVE
COREACTANT RX AND (POSSIBLY)
AUXILIARY REACTANT GL.

* V_L IS THE FREQUENCY AND $E_L = hV_L$
THE ENERGY OF THE LASER PHOTONS
USED IN THE CRISLA PROCESS. MILD
ABSORPTION AT V_L BY RX MAY BE TOLERABLE
OR EVEN BENEFICIAL IN SOME CASES
PROVIDED THAT CONDITION (F) APPLIES
AND LASER-EXCITED RX* DOES NOT REACT
EQUALLY FAST WITH LASER-EXCITED
UF_6 * AS WITH UNEXCITED UF_6.

FIG. 8c

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/01940

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classi::ation (IPC) or to both National Classification and IPC

IPC (5): B01D 5/00   U.S.CL. 204/157.2

II. FIELDS SEARCHED

Minimum Documentation Searched 7	
Classification System	Classification Symbols
U.S. CL.	204/157.2,157.21,157.22

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched 8

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
A	DE, A, 1959767, GURS, 03 June 1971	10-34
A	George Newnes Limit "Separation of Isotope", 1901, H. London et al pages 431-436.	1-36
A	J. Chem. Phys. Vol. 61, No.9, 01 November 1974 "Vibrational Spectrum and Force Field Of Uranium Hexafluoride", McDowell et al, pages 3571-3580.	10-34
A	Applied Physics Letters, vol. 17, No. 12, 15 December 1970, "Isotope Separation with the ew Hydrogen Fluoride laser", S.W. Mayer, pages 516-519.	1-36
A	DE, A, 1284620, GURS 09 August 1972	10-34
A	US, A, 3,951,768, GURS 20 April 1976	10-34
A	US, A, 4,035,270, LYON ET AL 12 July 1977	10-34
A	US, A, 4,096,046, Niemann 20 June 1978	10-34

* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
28 JUNE 1991	05 AUG 1991
International Searching Authority	Signature of Authorized Officer
ISA/US	DOUGLAS MAT

Form PCT/ISA/210 (second sheet) (Rev.11-87)

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers . .... ., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☒ Claim numbers ....37.., because they relate to parts of the international application that do not comply with the prescribed require-ments to such an extent that no meaningful international search can be carried out [13], specifically:

   The phrase "as herein before described" lines 3-4 fails to comply with the prescribed requirement of PCT Rule 6 to such an extent that a meaningful search could not be carried out.

3. ☐ Claim numbers_____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.