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Advances in Laser Isotope Separation

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ABSTRACT

The physical and chemical concepts required to understand laser isotope separation are presented and discussed. The numerous successsful demonstrations of separating isotopes using lasers are reviewed to 1983. Emphasis is placed on the separation of ^{235}U from ^{238}U by multi-step selective ionation of uranium atomic vapor, and on the separation of D and H and of T from D, by pulsed infrared laser multiple-photon dissociation of fluoroform and chloroform, respectively, because they are among the most successful and important examples of laser isotope separation to date.

Introduction

In the past decade isotopes of over two dozen elements have been separated in the laboratory using lasers. The striking successes of laboratory isotope separation, combined with the near-term needs of the nuclear power industry and other applications, has led to an intensive study of practical separation of a few of these isotopes including: uranium, plutonium, deuterium and tritium. Edward Teller has strongly encouraged and supported these studies at the Lawrence Livermore National Laboratory and elsewhere. This chapter describes the remarkable progress in laser isotope separation (LIS), to 1983. The current technology and future trends in the separation of isotopes are discussed, along with an introduction to the scientific basis of the various LIS techniques.

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General Considerations

Laser isotope separation represents, perhaps, the most successful application of laser chemistry and spectroscopy. Typical non-isotopic chemical synthesis and processing consists of several different steps, each controlled by thermal energy and catalysts; the use of lasers to control even a few key steps generally increases production costs because of the relatively high price of laser photons. Conventional methods of isotope separation, however, entail a great many identical energy-intensive enrichment stages. With the proper choice of process and lasers to ensure high isotopic selectivity in absorption and subsequent reaction, ionization or direct physical separation, LIS can produce cheaper isotopes because only one or a few enrichment steps are needed.

The economics of LIS usually limits interest to those processes which remove the minority isotope from the majority species. Depending on the details of the specific case, the products formed after a single LIS stage may be sufficiently enriched to be used directly or else may be inexpensively enriched further by conventional non-laser means. In some instances, the first stage LIS-enriched products may be converted to the initial molecule reactants to be separated again by the same laser method. Naturally, the source and ultimate application of the rare isotopes strongly influence the selection of a separation scheme. Enrichment of uranium from the waste tails of diffusion separation (0.2% $^{235}U/^{238}U$) to light water reactor grade material (3.2%), can be accomplished in a single laser separation stage by multi-step photoionization. The D_2O used in heavy water moderated reactors should have a deuterium content exceeding 99.8%, whereas, normal water (which is the most common deuterium source material for LIS) has a ~140 ppm D/H fraction. After a single isotope separation stage by pulsed infrared laser multiple-photon dissociation (MPD) of a 140 ppm D/H fluoroform mixture, the products are sufficiently deuterated (~1%) to use conventional electrolysis techniques for low-cost final stage enrichment.

A vital requirement of any laser isotope separation process is the isotopically-selective absorption of photons at the wavelength of an efficient laser. A measure of this isotopic selectivity in absorption is provided by S, which is defined as the ratio of the effective absorption cross-section of the (to-be-separated) minority isotope reagent to that of the remaining isotope. Though the products formed immediately after excitation may be highly enriched in the desired isotope for a given physical or chemical LIS process, enrichment can be destroyed by collisions. Chain or simple reactions of laser-

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produced radicals with the undesired isotope reactant or isotope exchange reactions of the separated product can degrade performance in chemical separation LIS, while charge or momentum transfer collisions can deleteriously affect physical separation. The single-step enrichment factor β, defined as the ratio of the isotope fraction in the separated products to that in the reactant feedstream after a single (differential) enrichment cycle, includes all of these factors. (For a given enrichment cycle, this ratio β is sometimes called β_1, while another parameter β_2 is defined as the ratio of feed to tails (waste) assay.) β and S are usually quite sensitive to the exact conditions of the experiment. For example, in a given process these parameters may be promisingly high at lower laser intensities where photoproduct yields are small. However, at the higher laser intensities necessary for large product yields, both β and S may become too small for commercial application. The stripping efficiency, which is the fraction of the isotope in the feed that is photolytically removed and collected as product, and the nonselective pickup, defined as the fraction of the throughput which is collected as product even with the laser turned off, are two other important parameters in the description of a complete LIS process[1].

Application of Isotopes

The lowered cost of laser-separated isotopes is having a dramatic impact on several existing commercial markets, and is expected to open up new markets as well. At present, separated isotopes are in demand in the nuclear power industry, in medicine and in environmental research.

Approximately 11% of U.S. and 8% of world electricity is currently produced by nuclear reactors. This industry is strongly dependent on the use of isotopes as the actual energy source, for neutron moderation and cooling, and for many smaller applications. The nuclear power industry constitutes by far the largest market for isotope separation.

There are two kinds of fission reactors in large scale use today. They are distinguished by both the fuel and the coolant they use. Light water reactors use normal water (H_2O) coolant but require uranium fuel which has been enriched in uranium 235 from the natural isotopic abundance of 0.7% to a value around 3.2%. Heavy water reactors can use natural or, preferably, only slightly enriched uranium, but require heavy water (D_2O) as the moderator and coolant. The natural abundance of deuterium is 0.014%.

Uranium enrichment is a multibillion dollar per year industry. The two methods used to enrich uranium commercially are gaseous diffusion and gas centrifuge separation both which rely on the mass difference between $^{235}UF_6$ and $^{238}UF_6$ for enrichment. Since this mass difference is quite small, the enrichment obtained in one step by classical physical separation is very small and many steps are required to achieve significant enrichment. Using laser techniques the required enrichment can be achieved in a single step, and both the size and cost of an enrichment plant can be significantly reduced. The amortized capital cost for either conventional process is estimated to be ten times that for the atomic vapor laser isotope separation (AVLIS) technology[1]. Annual energy consumption in an AVLIS plant is comparable to that of a centrifuge plant of the same production capacity, and this energy cost is small compared to the centrifuge amortized capital cost. An equivalent gaseous diffusion facility, on the other hand, consumes twenty four times more energy than an AVLIS plant[1] and the cost of operating a diffusion plant is comparable to its amortized capital cost. The current (non-laser) enrichment cost to produce 3.2% ^{235}U (with 0.7% feed and 0.2% tails) is ~\$600/kg product or ~100/SWU (separative work unit[1]). With laser technology the enrichment cost may decrease to ~\$100/kg product[1]. The potential cost savings associated with laser isotope separation for uranium can be several billion dollars per year.

An equally significant cost saving is realized in the reduced quantity of uranium ore required by LIS processes. Conventional separation plants discard over 30% of the ^{235}U in the depleted UF_6. They start with the natural 0.7% fraction of ^{235}U and produce a product stream enriched to 3.2% ^{235}U and a waste stream (or "tails") depleted to only 0.2% ^{235}U. If a conventional plant were required to produce 3.2% ^{235}U with tails of 0.1% ^{235}U, the number of steps and corresponding costs would increase by 40%. Laser enrichment methods extract a much larger fraction of the available ^{235}U than do conventional methods and therefore require less ore input for the same enrichment output. In fact, the enrichment of the inventory of tails from gaseous diffusion plants was an early goal of uranium LIS in the U.S.; however, present efforts are geared to enriching uranium directly from the ore.

Another potential application of laser isotope separation of some significance is the production of plutonium of relatively high isotopic purity required for nuclear weapons. There are programs underway at the Lawrence Livermore National Laboratory (LLNL) and the Los Alamos National Laboratory (LANL) to investigate the applications of laser enrichment methods to plutonium. Needless to say, very little is published on LIS as it applies to the production of weapons grade materials.

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The most important application of deuterium separation is in the production of heavy water for fission reactors. Heavy water reactors have several distinct advantages over light water power plants. Because of the low neutron absorption cross-section of deuterons, heavy water-moderated power reactors can burn uranium with the naturally occurring ^{235}U content (0.7%), and will breed less plutonium than will light water reactors if the ^{235}U content is only slightly enriched to 1.2%[2]. Furthermore, for operation with 0.7–1.2% $^{235}U/^{238}U$, 20–50% less overall U_3O_8 (yellowcake) is required to fuel a once-through fuel cycle heavy water reactor over its lifetime[2]. Heavy water reactors at Savannah River have been used to breed plutonium and tritium for over 25 years. The Canadian version of heavy water power reactors (CANDU), has proven to be safe and has produced electricity at lower costs and more reliably than light water reactors[3]. The D_2O requirement for such power reactors amounts to 800 metric tons per GWatt electrical power capacity, if heavy water is used both as the neutron moderator (which is essential) and the coolant (which is optional, though highly desirable). At the present cost of \$200–300/Kg D_2O, this amounts to about 20–25% of the capital cost of the reactor.

The most promising next-generation fission reactors use heavy water as the moderator and ^{233}U as fuel. Only small amounts of relatively-scarce ^{235}U is required to start the $^{232}Th \rightarrow {}^{233}U$ slow breeder heavy water reactor, with denatured uranium-thorium recycling. Though fusion will not be available for direct power generation until well into the next century, a fusion-fission hybrid in which ^{232}Th is bred to ^{233}U to directly fuel as many as 20 heavy water reactors, may be on-line before the year 2000. Such thorium-based reactors have two impressive features. The world reserves of thorium are quite abundant, being equal to those of ^{238}U (and therefore 140× the ^{235}U world inventory). Furthermore, in contrast to reactors in which plutonium is bred, ^{233}U fuel is easily made proliferation resistant by simply diluting it with ^{238}U to less than 12% ^{233}U[2].

Most of the world's inventory of D_2O is separated from normal water (~140 ppm D/H) by the G-S process. This involves many serial stages of hydrogen sulfide-water dual temperature D/H exchange[4]. The required huge hydrogen sulfide inventories can be extremely dangerous. Other D/H separation methods[5] such as CECE (Combined Electrolysis and Catalytic Exchange) and cryogenic distillation are far more costly. Laser separation of deuterium by pulsed CO_2 laser MPD of CDF_3/CHF_3 appears to be environmentally and even economically superior to the G-S process.

Tritium isotope recovery is useful in removing the slow, but steady build-up of tritiated water in the moderator and coolant inventories of nuclear reactors. Tritium decays via emission of a very weak beta ray ($E_{max}= 18.6$ Kev) and is relatively short-lived (half life = 12.26 years). Any introduction of tritiated water into the human body is a definite health hazard because of the long ~8 day biological half life. Tritium levels in light water reactors are quite low, 10^{-3}–10^{-2} Curie/liter ($\lesssim$1 ppb); while in heavy water reactors concentrations rapidly attain high steady state levels, ~20 Ci/liter (7 ppm T/D), due to the $D + n \rightarrow T + \gamma$ reaction. Though present environmental requirements clearly dictate the need for T/D recovery and not T/H, both may be required for future fusion-fission hybrid and direct fusion electric power reactors. Since tritium itself is quite expensive — with a current market price of about \$1/Ci (\$$10^4$/g T_2), tritium recovery may well pay for itself.

The only presently operating T/D recovery plant is the costly and tightly-licensed Sulzer process, in which water vapor is detritiated by catalyzed vapor phase water-hydrogen exchange, followed by cryogenic distillation of hydrogen[6]. Development of cold and hot wet catalysts, and of electrolysis may improve conventional separation of tritium from deuterium[7,8]. Laser-initiated T/D recovery, exemplified by pulsed 12μ laser multiple-photon dissociation of $CTCl_3/CDCl_3$ mixtures, may well lower the capital and operating costs of tritium cleanup of contaminated heavy water inventories. Another advantage of laser separation vis-a-vis conventional techniques is the small hold-up and safe storage of the highly-concentrated separated tritium using laser processing.

Another potential application of LIS in the nuclear power industry is the enrichment of ^{90}Zr (51.5% natural abundance) — which has an extremely low thermal neutron absorption cross-section, from normal zirconium (^{90}Zr — ^{96}Zr). Thicker fuel claddings would be acceptable if ^{90}Zr rather than normal zirconium were used in construction. This would permit higher temperature operation and higher fuel burn-up. No experimental study of zirconium LIS has been published to date.

With the lowered costs of laser-separated ^{13}C (1.1% abundance) and ^{15}N (0.36%) compared to conventional cryogenic distillation-separated isotopes, new inroads can be made in biological research and medical practice. The combination of the low cost and high safety of stable ^{13}C-labelled tracers (compared to radioactive ^{14}C-labelled compounds) may usher in a new era of inexpensive, routine medical diagnosis of liver, intestinal, general metabolic and other disorders. Use of the stable ^{15}N in diagnosing amino acid and

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Though variations in the measured ^{34}S/^{32}S and ^{18}O/^{16}O ratios in atmospheric and wet/dry deposited sulfur oxides ($SO_4^=$, SO_2 etc.) have been used to track local sources of pollution, the use of natural isotope-labelled tracers to monitor the chemical transformation and long range (1000 Km) transport of these pollutants remains largely unexplored. Only ~100 Kg quantities of laser-separated ^{36}S (140–170 ppm natural abundance) are required to track sulfur dioxide and sulfate transport of ~1000 Km[9]. These amounts of sulfur tracers are environmentally acceptable because they are small compared to normal sulfur releases. One current use of isotopes in long range tracking of atmospheric transport is quite important already — namely, the use of $^{13}CD_4$ in tracing flows 2500 Km from the source[10].

Further discussion of the applications of isotopes, as well as the history of the conventional and non-laser photolytic methods of isotope separation, may be found in several recent reviews of laser isotope separation[11].

Spectroscopic Isotope Shifts

Electronic shifts

In atoms, radiative lifetimes of optical and ultraviolet transitions are generally longer than 3×10^{-9} sec so that natural linewidths are less than 5×10^{7} Hz. Isotope shifts are almost always much larger. For light elements the isotope shift is the result of the different reduced masses of the isotopes[12]. For a hydrogen-like atom

$$E_a = -\mu_a \frac{e^4}{2h^2n^2},$$

where μ_a is the reduced mass of isotope a. Since $\mu_a \sim m_e(1-\frac{m_e}{M_a})$, where m_e is the electron mass and M_a is the nuclear mass, the energy level is displaced toward the continuum for finite nuclear mass. The displacement is larger for the lighter isotope. The difference in transition energy for two isotopes is

$$h\nu_b - h\nu_a = (\mu_b - \mu_a)\frac{e^4}{2h^2}\left(\frac{1}{n_2^2}-\frac{1}{n_1^2}\right) \simeq \frac{M_b - M_a}{M_bM_a}\frac{m_ee^4}{2h^2}\left(\frac{1}{n_2^2}-\frac{1}{n_1^2}\right).$$

From these considerations it is seen that the magnitude of the shift in a hydrogen-like atom is given by $\Delta\nu \sim (m_e/m_p)[(A_b - A_a)/A_aA_b]\nu$, where A is the atomic weight, so that $\Delta\nu \sim 5\times10^{-4}\nu/A^2$. This so called "normal mass effect" is characterized by a smaller transition frequency in the lighter isotopes ($\mu_b > \mu_a \rightarrow \nu_b > \nu_a$) and an isotope shift which is inversely proportional to the square of the atomic weight.

For atoms which have more than one electron outside of a closed shell, the mass dependent isotope shift can become more complicated. Consider, for example, an atom with two electrons. The kinetic energy of the system is

$$\frac{P_n^2}{2M} + \frac{1}{2m_e}(P_1^2 + P_2^2),$$

where M and P_n are the mass and momentum of the nucleus. P_1 and P_2 are the momenta of the two electrons. In the center of mass system, the total momentum is zero so that

$$P_n = -(P_1 + P_2) \text{ and } P_n^2 = P_1^2 + P_2^2 + 2P_1 \cdot P_2.$$

The kinetic energy can then be expressed as

$$\frac{1}{2\mu}(P_1^2 + P_2^2) + \frac{1}{M}P_1 \cdot P_2.$$

The first term gives rise to the "normal mass effect" discussed above while the second term is new. It gives rise to what is referred to as the "specific mass effect". The most apparent property of the specific mass effect is that it can have either sign. For P_1 parallel to P_2 (on the average) it is positive. For opposed motions (on the average) the term has a negative sign. A quantum mechanical treatment of the problem[13] shows that the positive sign applies to singlet terms and the negative sign to triplet terms. Another quantum mechanical result is that the specific mass effect is non-zero only for electron pairs with azimuthal quantum numbers l differing by one. The fractional shift in an energy level is again on the order of the electron-proton mass ratio and the isotope shift is also inversely proportional to the square of the atomic weight, so these mass effects are small in heavy elements ($A \geq 140$)[14].

For heavy atoms, the dominant effect in the isotope shift arises from the change in nuclear charge distribution, which is due primarily to the change in the volume of charge in the nucleus on addition of a neutron to that nucleus. This effect is important only when the optical transition involves

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an s electron, since only an s electron has a non-negligible wavefunction at the nucleus. (An s electron can also cause an isotope shift even if it does not itself change energy levels. It does so through a change in its electrostatic shielding of another electron which absorbs or emits.) Inside the nucleus an s electron no longer sees a r^{-1} potential. Assuming a uniform charge distribution inside a spherical nucleus, $\phi = (Ze/r_0)(-3/2 + 0.5r^2/r_0^2)$, where r_0 is the nuclear radius.

The smaller nucleus has the larger potential and the electron is more strongly bound by it since it is closer to the r^{-1} potential of a point charge. The difference in potential is given by

$$\delta\phi = -\frac{3}{2}\frac{Ze}{r_0^2}\delta r_0\left(1 - \frac{r^2}{r_0^2}\right)$$

where δr_0 is the difference in nuclear radius.

The difference in energy of an s electron in a pair of isotopes is

$$\delta E = \int_0^{r_0} \rho_e \delta\phi dV,$$

where

$$\rho_e = -e\,|\,\psi_s(0)\,|^2 \sim -\frac{e}{\pi a_0^3}\frac{Z}{n^3}$$

(a_0 being the Bohr radius)[15]. Then,

$$\begin{aligned} \delta E &\sim \frac{3}{2}\frac{Z^2e^2}{\pi a_0^3 n^3}\frac{\delta r_0}{r_0^2}\int_0^{r_0}\left(1 - \frac{r^2}{r_0^2}\right)4\pi r^2 dr \\ &\sim \frac{8}{15}\frac{Z^2}{n^3}\frac{r_0^2}{a_0^2}\frac{\delta A}{A}R_H \end{aligned}$$

where R_H is the rydberg.

Thus the isotope shift due to the change in nuclear volume decreases inversely with atomic weight but the heavy isotope always lies higher in energy (closer to the continuum). Therefore, an electron transition from a p orbital to a lower s orbital will be less energetic for the heavier isotope. Conversely, a transition from an s orbital to a lower p orbital will be less energetic for the lighter isotope.

The assumption of a spherical nucleus which merely increases in radius when a neutron is added ($r_0 \propto A^{1/3}$) ignores the change in nuclear shape when neutrons are added. Only near the magic neutron numbers 50, 82, and 126 is the nucleus nearly spherical (except for Sn which has a magic number of protons). An isotope shift results from a change in nuclear shape as well as from a change in nuclear volume[16]. Volume effects still contribute in a manner similar to that discussed in the preceding paragraph, but changes in shape must also be included. The potential inside an ellipsoidal nucleus is smaller than that in a spherical nucleus of the same volume. Thus an increase in nuclear deformation has an effect similar to an increase in volume at constant charge, while a decrease in nuclear deformation has the opposite effect. In certain isotope pairs, such as ^{86}Sr-^{88}Sr (ref. 17) and ^{136}Ba-^{137}Ba (ref. 18) the shift resulting from a *decrease* in nuclear deformation with the addition of one neutron is so pronounced as to cancel the shift due to the increase in nuclear volume.

The foregoing discussion is intended to give a conceptual understanding of isotope shifts in atoms[19]. For light atoms ($A \lesssim 140$) the normal mass shift ($\Delta\nu \sim 5 \times 10^{-4}\nu/A^2\ Hz$) is large with respect to the natural linewidth for visible transitions ($\Delta\nu \sim 2 \times 10^7 Hz$). At the upper end of this range, the two become comparable. For example, the natural linewidth in barium on the 5536 Å resonance is $\Delta\nu \sim 1.9 \times 10^7$Hz, while the normal mass shift from ^{136}Ba to ^{138}Ba is 3.2×10^7Hz[18]. On the other hand, the increase in nuclear volume, though partially cancelled by a decrease in nuclear deformation, produces a net shift (^{136}Ba–^{138}Ba) of over six times the natural linewidth on the 5536 Å transition[18,19]. In uranium, the heaviest naturally occurring element, volume and deformation effects combine to produce typical isotope shifts in excess of 3×10^9Hz for most lines in its extremely complex visible spectrum[20]. It is rare that various effects sum to less than the natural linewidth. Even if the isotope shifts on a given transition are small with respect to its natural linewidth, it is generally the case that another line can be found where one of the effects changes magnitude or sign with respect to the others and the resulting isotope shift becomes large. In addition to these isotope shifts, isotopic differences in nuclear spin affect atomic electric quadruple and magnetic dipole coupling with electrons. Isotope shifts in the electronic spectra of molecules are further complicated by, and are usually dominated by, very large vibrational and rotational isotope shifts.

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Vibrational shifts

Upon isotopic substitution vibrational band frequencies shift. Also the relative individual rotational line positions in vibrational transitions, as well as the rotational band envelopes, change due to isotopic shifts in the rotational constants. In diatomic molecules the isotope shifts are trivial to determine, as vibrational frequencies vary as $1/\sqrt{\mu}$ and rotational constants as $1/\mu$, where μ is the reduced mass. When *cw* or low intensity pulsed lasers interact with small polyatomic molecules, isotopic shifts of individual vibrational-rotational lines will control the isotopic selectivity in absorption. However, in large molecules and more generally at higher molecular energies (where Doppler profiles of adjacent lines overlap) or upon irradiation by high intensity pulsed infrared lasers, isotopic selectivity is effectively determined by the overall rotational band structure. Another type of vibrational isotope "shift" occurs when one isotope is replaced in molecules that symmetrically contain at least two of this same element. The molecular symmetry will then be lower and, consequently, some previously forbidden vibrational absorption transitions then become formally allowed, though they are usually quite weak.

Isotope shifts may be estimated to first order by modelling a polyatomic as a quasi-diatomic molecule, with atomic masses M_1 and M_2, with the former shifted by ΔM_1. The frequency shift $\Delta\nu$ is on the order of:

$$\Delta\nu \simeq -\frac{\nu}{2}\left(\frac{1}{1+\frac{M_1}{M_2}}\right)\frac{\Delta M_1}{M_1}$$

Consequently, vibrational isotope shifts are largest for light atoms, and particularly so when the other atoms strongly active in the same eigenmode are much heavier. Hydrogen isotope shifts are huge, with C-H, D, T stretching frequencies typically 3050, 2250, 1950 cm^{-1} respectively and C-H, D, T bends characteristically at 1220, 910, 830 cm^{-1} (as in chloroform)[21]. These shifts are much larger than the typical rotational line profile width which is on the order of ~ 25 cm^{-1}. (Because of their much larger absorption cross-sections the C-H bends are more favorably exploited for LIS than are C-H stretches.) ^{13}C/^{12}C shifts, though much smaller, can be as large as $\sim$35 cm^{-1}, leading to very selective LIS. Vibrational isotope shifts are quite small in molecules with heavy Visotopic elements of interest such as the heavy hexafluorides (SeF_6, MoF_6, UF_6, for example), and are typically on the order of 1 cm^{-1}

per mass number change, because M_1 is large and $M_1 > M_2$.

When isotopic variants of a given molecule are readily available, these shifts are easily measured[22]. In other instances, isotope shifts may be determined by straightforward calculation[22,23]. To an excellent approximation, the interatomic force fields — as well as the bond distances and angles — of isotopic variants of the same molecule are identical. Consequently, once the force field of a molecule is obtained from its own vibrational spectrum (and other spectroscopic information), the vibrational frequencies of the isotopically-substituted molecule can then be calculated using the Wilson F-G matrix method[23]. This transfer of force field parameters assumes that the available spectroscopic data, perhaps from several isotopes, yields a unique force field, and that the symmetry of the examined isotopic molecule is no lower than those used to derive the force field. Force fields based on the molecular symmetry coordinates (general harmonic force fields) produce much more accurate normal mode frequencies than do Urey-Bradley type fields — in which individual diatom bond stretching constants, triatom angle bending constants, etc. are transferred from similar molecules.

One important application of this technique has been the accurate general harmonic force field calculation[21,24] of the vibrational frequencies in tritiated halomethanes (CTF_3, $CTCl_3$, etc.) of use in T/D and T/H separation, before those molecules were first synthesized. The observed $^{12}CD^{35}Cl_3$ ν_4 and ν_5 absorption peaks are known to occur at 914.5 and 747 cm^{-1}, respectively. Absorption between these features is extremely weak ($\lesssim 8\times10^{-6}$/cm-torr from 815–842 cm^{-1}), as there are no fundamentals or significant hot bands, overtones or combination bands in this region. These calculations suggested that in $^{12}CT^{35}Cl_3$ ν_4 would shift to 837.1 cm^{-1}, with only a further $+1.6$ cm^{-1} shift for $^{12}CT^{37}Cl_3$. In synthesized $CTCl_3$, the ν_4 peak was observed at 835.3 cm^{-1}. As expected, the low fluence optical selectivity at this frequency as found to be extremely high, $\gtrsim 12,000$[25]. Figure 1 depicts the infrared spectrum of a $CTCl_3/CDCl_3$ gas mixture[25].

Several relations among vibrational frequencies of isotopic molecules have been derived assuming the transfer of force fields between isotopes. Perhaps the most useful is the Teller-Redlich product rule[26,27] that relates the products of harmonic frequencies (ω_i) within a symmetry type of each isotope to

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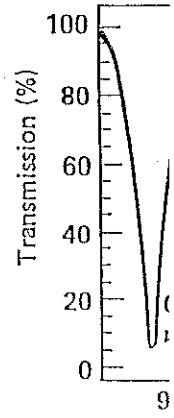

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Methods of Laser I

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Photodeflection

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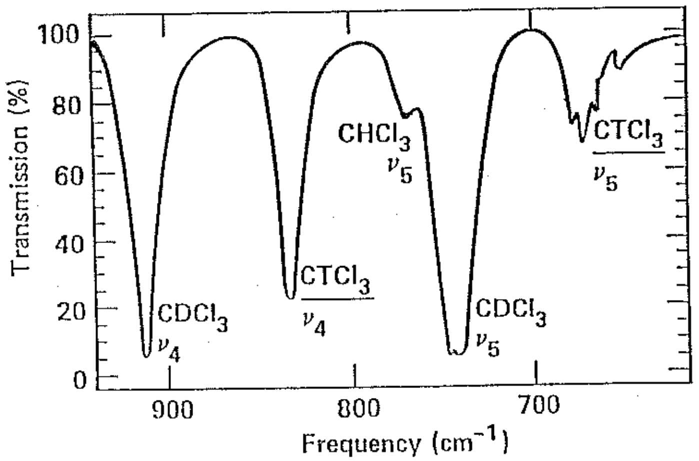

Figure 1. The infrared absorption spectrum of a gaseous mixture of $CTCl_3/CDCl_3$ (adapted from Ref. 25). $CTCl_3$ selectively absorbs 12μ radiation in the ν_4 vibrational ladder.

the molecular structure and atomic masses. Specifically, for isotopes a and b:

$$\prod_{i=1}^{f} \frac{\omega_i^a}{\omega_i^b} = \sqrt{\prod_j \left(\frac{m_j^b}{m_j^a}\right)^{p_j} \left(\frac{M^a}{M^b}\right)^{t} \left(\frac{I_x^a}{I_x^b}\right)^{r_x} \left(\frac{I_y^a}{I_y^b}\right)^{r_y} \left(\frac{I_z^a}{I_z^b}\right)^{r_z}}$$

where m_j are the atomic masses of each set of identical nuclei, with p_j the associated number of modes contributing to the symmetry species; M is the molecular mass and t is the number of translations belonging to the species; I_k is the respective moment of inertia about the k axis and r_k is 1 or 0 depending on whether or not rotation about the k axis belongs to the symmetry species[22].

Useful estimates of isotopic changes in spectroscopic anharmonic constants may be obtained from the empirical Dennison's rule, which states that $X_{ij}/\omega_i\omega_j$ is invariant to isotopic changes; X_{ij} are the first-order anharmonic constants[28].

Methods of Laser Isotope Separation

Physical separation methods

Photodeflection

One of the earliest demonstrations of laser isotope separation relied on momentum transfer from a directed monochromatic light source to one isotopic component of an atomic beam of barium[19,29,30]. When an atom absorbs a photon of energy $h\nu$ it acquires a momentum $h\nu/c$ in the direction of the photon propagation. If the atom decays spontaneously, it gives up momentum $h\nu/c$ to the departing photon in the direction of its propagation. Since an atom is as likely to spontaneously radiate in a given direction as in the opposite direction, the average momentum transfer from N emission events is zero (with scatter about the value of $h\nu/c\sqrt{N}$), whereas contributions from the absorption process with a directed light source sum. Therefore, the rate of momentum transfer is just the spontaneous emission rate times $h\nu/c$[31].

The Doppler width of the atomic beam must be small compared to either the laser linewidth, the natural linewidth, or both. Otherwise, an atom can only be deflected by a fraction of the atomic beam divergence angle, and then separation of a large fraction of the desired isotopic component of the beam is impossible. It is best if the Doppler and laser linewidth are both small compared to the natural linewidth because then every atom in the atomic beam sees the full laser intensity, although it then makes little difference whether the Doppler linewidth or the laser linewidth is the larger. When the laser linewidth is greater than the natural linewidth only a fraction, $\sim \Delta\nu_{\text{natural}}/\Delta\nu_{\text{laser}}$, of the laser radiation falls within the absorption range of the atom. The Doppler width must also be small compared to the isotope shift, otherwise several isotopic components will be deflected.

The principle limitation on the number of absorption-spontaneous emission events per atom is unwanted spontaneous emission to a metastable energy level between the optically excited state and the ground state. Since lifetimes of such states are many orders of magnitude longer than the lifetime of the pumped resonance state, the metastable atom can no longer absorb laser photons and therefore cannot be further deflected. If there are only one or two low-lying metastable states — as in barium but not uranium where there are many — other lasers can be conveniently used to continuously pump the metastables to other levels that rapidly radiatively decay to the ground state[30].

This limitation can be avoided if the atom is deflected before it spontaneously decays. Consider an atomic beam irradiated by two counter-propagating laser beams tuned to the atomic resonance. The atom now has the opportunity to absorb from one beam and to emit into the other beam to produce a cumulative momentum transfer, known as "coherent deflection"[32,33]. For an atom traversing a resonant standing wave, the atomic momentum changes by $h\nu/c$ in a time given by $1/\Omega$ where Ω is the Rabi frequency ($\Omega = \mu \cdot E/\hbar$, where μ is the atomic dipole moment, E is the optical

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electric field amplitude and $\hbar$ is Planck's constant). This rate is generally much faster than the spontaneous emission rate even at moderate laser intensities. Physically, this can be regarded as the high-order diffraction of an atomic wave, of wavelength $\lambda_a = \hbar/mv$, (m=mass, v=velocity) by a phase grating whose periodicity equals the wavelength of the light in the standing wave[34,35].

Although the deflection momentum initially increases linearly with time, this growth is limited. The kinetic energy represented by the accumulated momentum transfer cannot greatly exceed the atom-field interaction $\hbar\Omega$. Dynamic calculations[36] show that the deflection increases to this limit and then reverses direction. Over a long interaction time the deflection momentum becomes distributed over the range limited by the values $|p| \leq (2M\hbar\Omega)^{1/2}$. The effects of non-zero initial transverse momentum, and of frequency detuning and spontaneous emission on coherent deflection have also being studied[36–38].

Experimental studies of coherent photodeflection are currently in progress[39]. Coherent deflection can be used to separate isotopes, provided only that the isotope shift is large compared to the atom-field interaction $\hbar\Omega$[40]. As a practical matter, coherent photodeflection has definite advantages over incoherent photodeflection, though losses in the standing wave mirrors may critically limit the photon efficiency of isotope separation using this process.

Photoionization

Perhaps the most universal and useful isotope separation method for metals and heavy atoms is photoionization[41,42]. Differences in electronic absorption frequency among isotopes are exploited using a narrow bandwidth laser to excite one isotope while leaving others in the ground state. This selective excitation is followed by one or more additional excitation steps which ionize the excited atoms but do not affect the unexcited atoms, which do not absorb any of the incident lasers, as depicted in Figure 2.

The two step ionization process[43–46] is the most general photoionization scheme though it is also the least interesting. Since in most atoms, the absorption of a visible photon provides less than half the energy required for ionization, the second step usually requires a blue or ultraviolet photon which is harder to generate than a visible photon. Furthermore, the ionization cross section is much smaller than the ground-state absorption cross section, the ionizing laser must have very much higher power than the exciting laser for the ionization rate to be comparable to the excitation rate (both of which

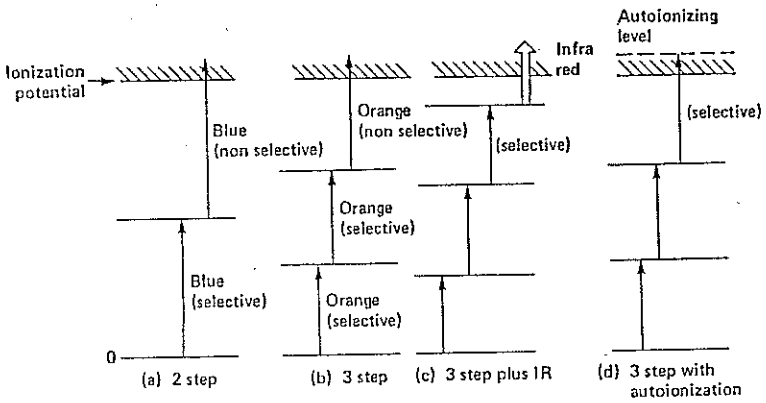

Figure 2. Schematic of several atomic photoionization methods: (a) two-step photoionization, where only the first step is isotopically-selective; (b) three-step ionization to the continuum, where the first two steps are selective; (c) three-step selective excitation to a high-lying Rydberg state, followed by infrared laser excitation to the continuum; and (d) three-step excitation to an autoionizing state, in which all three steps are isotopically-selective.

must be faster than the spontaneous emission rate from the intermediate level). Furthermore, in two step ionization only the first step is isotopically selective.

In multi-step ionization, in contrast, there may be several bound-bound steps which are isotopically selective so that even if a fraction of the wrong isotope is excited in the first step, subsequent excitation ignores this unwanted isotope (Figure 2). The overall isotopic discrimination is the product of the discriminations of the sequential steps. Another advantage of the multi-step scheme is the use of visible excitation in each step. It is best to select the various transitions to have nearly equal absorption cross-sections to optimize photon utilization in multi-step ionization.

In uranium, ionization schemes are more complex due to the presence of an electronic state only 620 cm^{-1} above the ground state. Approximately one-third of the uranium atoms occupy this level at temperatures required to vaporize uranium. Thus additional laser frequencies are required to ionize these atoms.

There are several ways to address the problem of low ionization cross-section in laser photoionization. If the atom is excited to just below the continuum it can be ionized with either a CO_2 laser[47], an electric field[48,49] or electrons[43]. Perhaps the best method is visible laser excitation to an autoionizing level in the continuum[45,50,51] (Figure 2).

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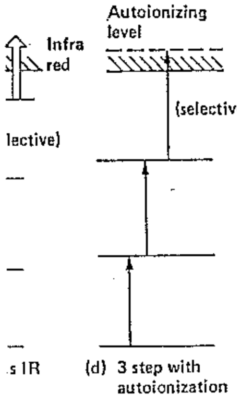

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Use of a CO_2 laser to ionize instead of a visible laser is attractive because CO_2 lasers are both powerful and inexpensive. Furthermore, the ionization cross-section from a given bound state tends to fall off as the cube of the frequency of the ionizing laser[52], and the CO_2 laser wavelength of 10.6μ is fifteen times that of a dye laser operating in the red. This last advantage is mitigated by the fact that the cross-section falls approximately as the fifth power of the principal quantum number, n, of the bound state and ionization with a CO_2 laser photon is possible only from relatively high n. The resulting cross-section[42] of perhaps 10^{-16}cm^2 for uranium, while high, is still over two orders of magnitude smaller than bound-bound cross-sections in uranium[53–55].

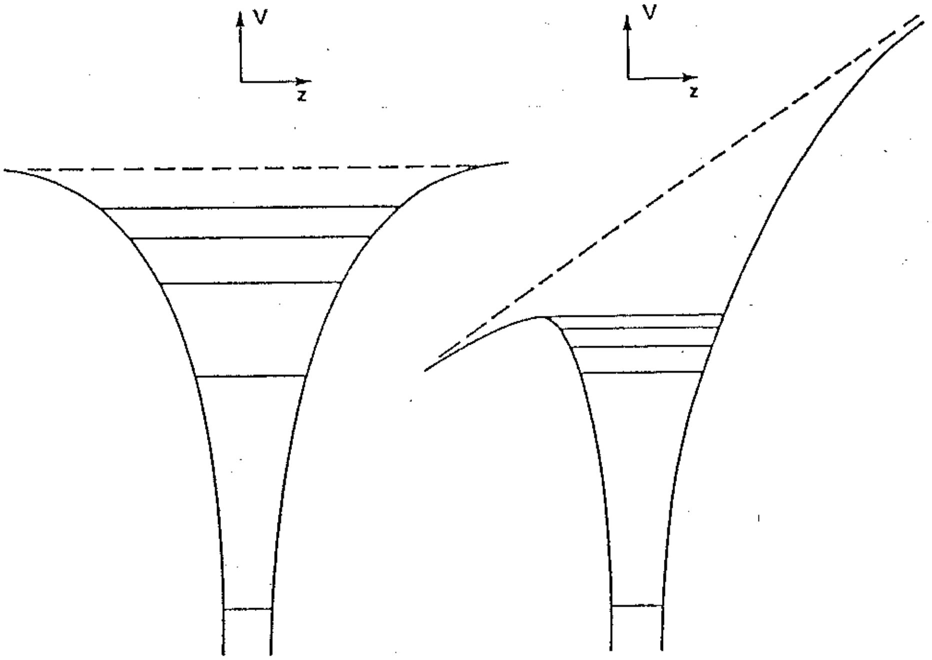
Electric field ionization occurs because a highly excited electron is only weakly bound to the atom, and an electric field of sufficient magnitude can lower the local potential and pull the electron free. The potential energy of a highly excited electron in an electric field is given by

$$V(r) = \frac{e^2}{r} - eEz,$$

as depicted in Figure 3. consequently, it is clear that electrons with energy greater than $-2e^{3/2}E^{1/2}$ can ionize, though it is also possible for such electrons to remain bound to the atom if their orbital motion tends to be confined to very small values of z. From a practical point of view, field ionization is unlarge because high fields (>1 kV/cm) are required, and because plasma shielding can reduce the local field strength. Also, at high vapor densities the primary electrons produced by these fields are accelerated to energies sufficient to excite and ionize atoms of the wrong isotope.

In electron impact ionization near-by free electrons can strip highly excited electrons from atoms in much the same manner as can externally applied large electric field. If the energy of the free electrons can be kept relatively low, only highly excited atoms will be ionized. This process still works at high vapor densities[56]; however, it still has pitfalls. One potential problem with electron impact ionization derives from electron collisions that can deexcite the desired isotope as well as ionize it.

The autoionization process is, in principle, the best of all possible worlds because excitation cross-sections can approach bound state cross-sections. An autoionizing state is essentially a bound state whose energy exceeds the



(a) Without electric field (b) With electric field

Figure 3. Application of a static electric field can change the potential energy curve for an atomic electron, causing ionization of electrons in certgain states with large principal quantum number.

ionization potential. Such a state is readily understood by considering helium, in which both ls electrons are excited to the 2p level. The energy of two 2p electrons far exceeds the ionization energy but the electrons are still bound. Careful analysis[52], reveals that some coupling does exist between the bound state with two excited electrons and a continuum level of the same energy in which one electron is ionized and the other falls back to the ground state. The larger this coupling, the more rapidly the excited atom ionizes. When the ionization rate approaches the spontaneous emission rate the absorption line broadens and its peak absorption cross-section diminishes. For efficient isotope separation the probability for ionization should be very large compared to spontaneous emission. Fortunately, this condition is satisfied even for linewidths on the same order as the Doppler width of

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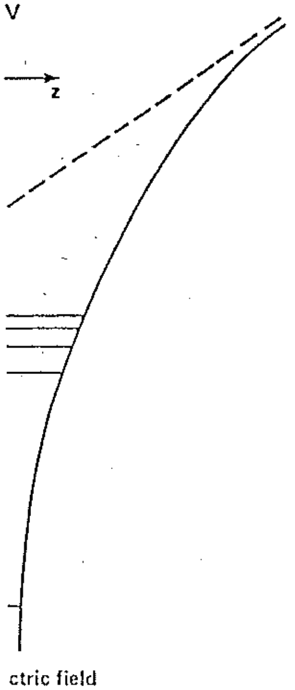

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In practical multi-step ionization process there are additional complications. For instance, laser intensities must be sufficiently high for efficient ionization, and optical path lengths must be long enough for efficient use of laser photons; otherwise laser isotope separation would be very expensive indeed. These two constraints require understanding the interaction of atoms in very intense local laser fields, as well as the evolution of the electromagnetic field as it traverses many optical depths of atoms. This is briefly discussed below.

The interaction of two level atom with an intense, resonant radiation field is well understood[57]. For low intensity fields, the laser field may be treated as a perturbation on the atom. In this regime, the emission of an excited atom is not stimulated by the presence of the field but instead occurs spontaneously. At high intensities, on the other hand, the atom is driven rapidly by the field from one state to the other at a frequency given by

$$\omega_R = \sqrt{(\Delta\omega)^2 + (\mu E/\hbar)^2}$$

where $\Delta\omega$ is the difference between the atomic excitation frequency and the radiation field frequency, and μE is the interaction energy of the atom with the field.

In the strong field case, it is helpful to define "dressed" stationary states of the atom-field system. At low field intensities ($\mu E << |\hbar\Delta\omega|$), one such stationary state corresponds to an excited atom with a certain number of photons in the radiation field, while the other stationary state corresponds to a ground state atom with an additional photon in the field. At high intensities ($\mu E >> |\hbar\Delta\omega|$), each stationary state has almost equal admixtures of ground and excited atomic states. This stationary state description of the atom-field system may be used to understand several features of isotopically-selective coherent excitation.

Ground state atoms exposed to an electromagnetic field which gradually increases in intensity begin to oscillate from ground to excited state and back in phase, at the frequency ω_R. Under similar conditions different ground state

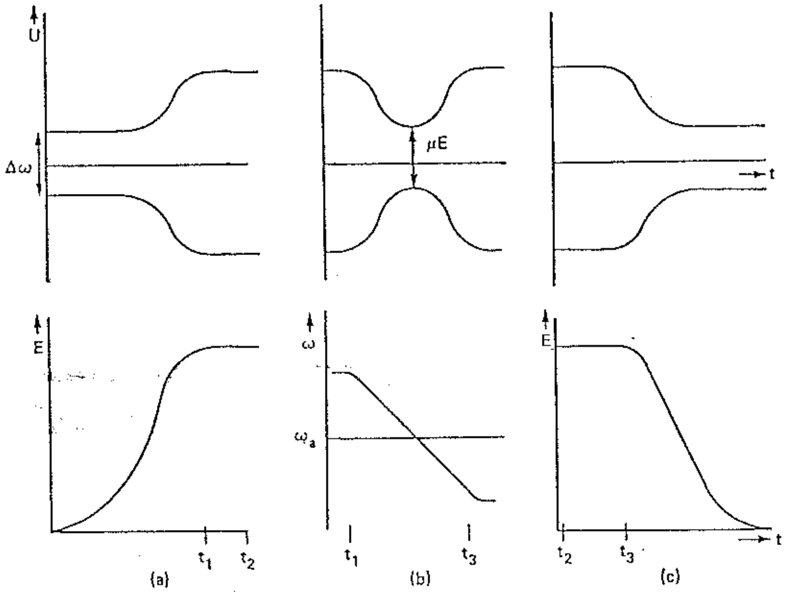

Figure 4. Coherent excitation of an atom by a pulse of light via the process of adiabatic rapid passage. The lower set of graphs indicate the behaviour of the pulse in time (t); first growing in electric filed amplitude (E) at fixed frequency (ω which in this case is initially greater than the atomic transition frequency, ω_a) in (a), then changing frequency at fixed amplitude in (b), and finally diminishing in amplitude at fixed frequency in (c). The corresponding behavior of the potential energy (U) of the atom-field stationary states is indicated in the upper set of curves.

isotopes with different excitation frequencies oscillate at different frequencies. It is therefore possible to expose an isotopic mixture of ground state atoms to a pulse of radiation whose duration, amplitude and frequency are such that one isotope is completely inverted while the other ends up back in the ground state[58]. This demonstrates an important property of coherent excitation processes, namely that all the atoms of a given isotope can be excited. In an incoherent excitation process, populations of ground and excited states are merely equilibrated; for equal degeneracies of ground and excited states, at most half the atoms of a given isotope can then be excited by a pulse of radiation[59].

A second method of completely inverting the atomic population is called adiabatic rapid passage[57]. For $\Delta\omega > 0$, that is when the atomic excitation frequency, ω_a, is greater than the field frequency, ω, the lower energy stationary state of the system corresponds to ground state atoms in the weak field limit. Thus if a ground state atom is exposed to a pulse of radiation which

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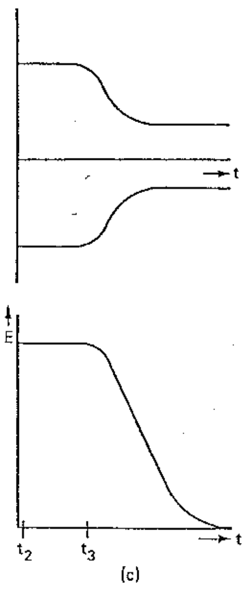

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begins at low intensity with $\Delta\omega > 0$, it remains in the lower energy stationary state as the field intensity increase. Suppose now that the field frequency gradually (adiabatically) increases to $\omega > \omega_a$, as shown in Figure 4, so that the sign of $\Delta\omega$ changes. In this process the states never cross, since their separation, ω_R, is always greater than μE. When the field intensity is again slowly reduced, all the atoms will end up in the excited state since the lower energy stationary state clearly corresponds to having an excited atom rather than an additional photon and a ground state atom. Population inversion by adiabatic rapid passage can be isotopically selective if the full frequency chirp of the pulse, $\sim 2\,|\,\Delta\omega\,|$, is less than the isotope shift[60].

For atoms with more than two levels interacting with the field, the coherent excitation process is certainly far more complex. Teller was one of the first to point out that the hyperfine structure in ^{235}U may severely reduce the fraction of atoms which can be excited in adiabatic rapid passage or other coherent excitation processes[61]. The nuclear spin of ^{235}U is 7/2 and the total electronic angular momentum, J, of the ground electronic state is 6 so that there are 8 hyperfine sublevels in the ground electronic state. For an allowed absorption, J changes by ± 1 or 0 so that there is a similar hyperfine degeneracy in the excited state and about three times that number of transitions (corresponding to $\Delta F = \pm 1, 0$) for a given polarization of the light. Each transition has a slightly different frequency and more than a slightly different transition strength[62–64]. Coherent excitation of complex atoms, has been studied numerically. In particular, these complications do appreciably affect intense-field coherent excitation and ionization rates in ^{235}U (ref. 65).

Coherent effects are important in the propagation of an intense field through many optical depths of uranium vapor because the field interacts primarily with ^{238}U, which has zero nuclear spin and no hyperfine structure. In a natural mixture the density of ^{238}U exceeds that of ^{235}U by a factor of 140, and in the waste from a conventional enrichment plant the ratio is closer to 500. Thus, to a first approximation, the medium can be considered to be composed of ^{238}U, plus a distributed loss due to absorption by ^{235}U.

When a pulse of near resonant radiation enters a two level medium, it slows down, as it would on entering any high index medium. Then, if the pulse is energetic enough, it breaks up into a number of smaller pulses ("2π pulses") each of which tends to propagate without further change[57,58]. Each pulse has amplitude and duration such that atoms execute exactly one Rabi cycle as the pulse passes. This effect, known as self-induced transparency, has been observed in ^{238}U (ref. 66).

The discussion of the preceeding paragraph applies to a quasi monochromatic field. In a practical uranium isotope separation process the frequency spectrum of the field must encompass the Doppler width of the uranium vapor. Even at low intensities, dispersion will alter the shape of a pulse which contains a spectrum of frequencies. If the intrinsic laser linewidth is narrow but this frequency is modulated to achieve the desired spectral coverage, this frequency modulation will become amplitude modulation as the pulse propagates. At high intensities, the temporal evolution of a pulse is more complex and has been modeled numerically[67].

The pulse evolves spatially as well as temporally. Inhomogeneities in the atomic vapor cause refraction of the light while inhomogeneities in the optical wavefront lead to self-focusing via non-linear intensity interactions. This spatial and temporal evolution of the propagating pulse can deleteriously affect the efficiency of the isotope separation process, particularly because in multi-step ionization the medium is actually exposed to several pulses, each with a different frequency, corresponding to a different excitation step in the ionization process. The pulse which excites ground state atoms will be slowed down, broken up, bent and focused far more than the pulse which excites atoms from the 620 cm^{-1} level and this pulse, in turn, will be transformed more than any of the pulses which further excite and ionize the ^{235}U. Thus the various laser pulses will tend to separate in both space and time as they propagate through the atomic vapor.

In laser isotope separation by atomic vapor ionization, problems can also arise due to high vapor densities. Again for economic reasons, it is desirable to keep the size of the hardware as small as possible, which means that the operating vapor density should be as high as possible. Some problems encountered at high densities are collisional excitation exchange, charge exchange, and electrostatic shielding of the plasma from the extraction field[56].

In collisional excitation transfer, an excited atom of the desired isotope collides with a ground state atom of the majority isotope; if the impact parameter is sufficiently small, the excitation can be transferred to the undesired isotope. Fortunately, this process does not severely reduce isotopic ionization selectivity since rapid ionization reduces the probability that a laser-pumped specie will suffer a collision, and furthermore, isotopic selectivity in subsequent excitation steps in the multi-step process lessens the likelihood of ionization of the wrong isotope.

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Charge transfer is, in fact, a more serious problem because an ion of the desired isotope is neutralized while an atom of the wrong isotope is automatically ionized and separated. Unfortunately, typical charge exchange cross-sections are large, several hundred square angstroms. One way to minimize the charge exchange problem (if the momentum transfer cross-section is small) is to pulse the extraction field[68]. When the field is on, the ionized atoms are accelerated for a brief period, following which they simply drift toward the collector plates. If charge exchange occurs during the drift period, the neutralized ^{235}U atom will nevertheless continue to drift and be collected while the newly ionized ^{238}U atom will never see an accelerating potential and will not be collected.

Finally, the ultimate plasma density is limited because the extraction field can be excluded from parts of a dense plasma by electrostatic shielding. This has been observed to limit the density of ions in a simple extractor in which a voltage is applied across parallel plates between which the gas flows[69]. An extractor in which a magnetic field is applied perpendicular to the electric field may alleviate this problem since both the electrons and ions tend to move in the direction $\vec{H} \times \vec{E}$, rather than moving in opposite directions as is the case in the simple E field extractor[42,68].

^{235}U/^{238}U separation by multi-step ionization of uranium vapor is being intensively developed at present by the LLNL AVLIS program. Efficient, high repetition rate copper vapor lasers (5106 and 5782 Å, 5 kHz, 30 nsec pulses) pump three red dye lasers tuned to different wavelengths, to selectively pump ground state ^{235}U in three steps to an autoionizing level. A more complete description of the overall process, including a discussion of the dependence of the cost of AVLIS-enriched uranium on the process parameters, may be found in Ref. 1. Though many of the details of this process have not been publically released, it appears that multi-step ionization cost-effectively, separates ^{235}U/^{238}U (ref. 1). Selective ionization has also been used to separate isotopes of calcium and mercury[70], and has been considered for the LIS of several other elements[42].

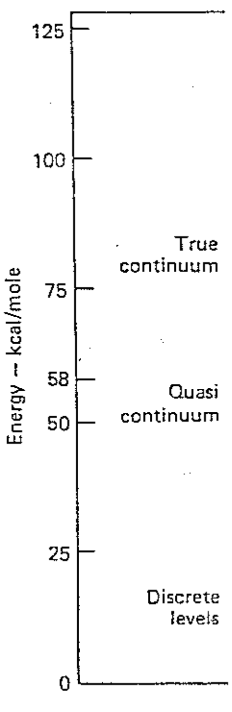
Chemical separation methods

Unimolecular reactions

All laser isotope separation research has proceeded on the frontiers of research in laser chemistry, chemical dynamics and spectroscopy. However, the study of infrared laser multiple-photon dissociation is perhaps unique in the close symbiotic relationship between MPD fundamental research and application to isotope separation. Since the discovery of isotopically-selective MPD in the pulsed CO_2 laser photolysis of SF_6 [71,72] and BCl_3 [73,74], research in this field has been vigorous. The multiple-photon absorption (MPA) process that leads to unimolecular dissociation or isomerization in polyatomic molecules is now qualitatively understood on the basis of the high density of vibrational-rotational transitions. Still much remains to be learned about the MPA interaction. It still seems remarkable that despite severe molecular anharmonicity and broad rotational profiles, a molecule can absorb 30 or more quanta without the aid of collisions. "Collision-free" conditions are typified by pressure < 0.1 torr with irradiation by 100 nsec FWHM laser pulses.

The dynamics of isotope separation by MPD[75,76] can be understood by reference to Figure 5, in which the vibrational levels of a typical polyatomic molecule (CDF_3) are conceptually divided into three energy regions. Region 1 (discrete levels) consists of $v=0$ to ~ 3 of the pumped mode in which absorption occurs between discrete, uncoupled states. Laser intensity effects that influence the resonance condition (AC Stark Shifts) may be important here. The pumped mode is usually a fundamental transition, though if laser power is sufficiently high it can be an overtone or combination band. Isotopically-selective dissociation is determined by the combined effects of the isotopic vibrational shifts of each of the absorption transitions in Region I. Region II (quasicontinuum) extends from $v \sim 4$ to the reaction activation energy. In this regime the core vibrational levels are strongly coupled to background vibrational states. Absorption within this so-called quasicontinuum is spectrally broader and usually red-shifted vis-a-vis ground state absorption. It is in Region II that laser fluence effects dominate and where absorption of over 80% of the photons occurs. There is a true absorption continuum above the dissociation barrier (Region III). Absorption of infrared photons continues until the laser pulse ends or until the reaction rate competes with the absorption rate; clearly, the laser intensity heavily influences MPA in this continuum[75]. In this region and probably in most of Region II, internal energy is apparently pooled among all vibrational modes. Consequently, unimolecular reaction rates of the various available reaction pathways are thought to be well described by RRKM (Rice-Ramsperger-Kassel-Marcus) theory.

In RRKM analysis the rate of unimolecular reaction is statistically obtained from the decay of the activated complex along the reaction



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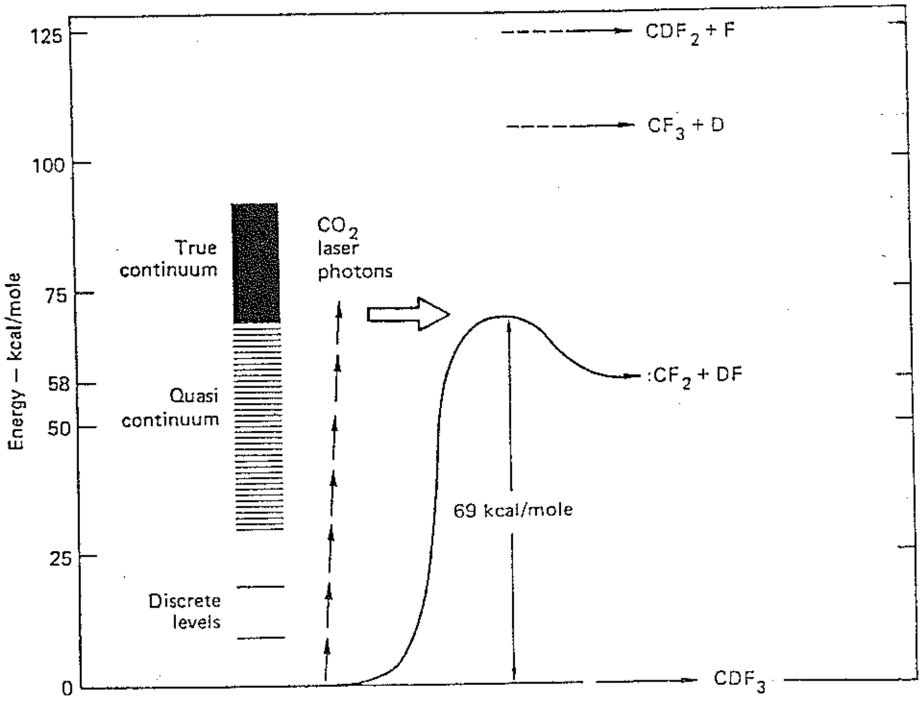


Figure 5. Schematic of the multiple-photon absorption and dissociation processes in the representative example of CDF_3. Absorption begins between discrete levels (Region I), then continues in the "quasicontinuum" (Region II) up to the reaction energy barrier, and then concludes in the true continuum (Region III), where unimolecular reaction occurs. In reality, many more CO_2 laser photons are absorbed before dissociation (about 30 quanta at 10.3μ), than is depicted here. Whereas, in CDF_3 only the lowest energy reaction channel is accessed (decomposition to $:CF_2 + DF$), in other molecules there is sometimes competition between several low-lying dissociation pathways.

coordinate[77]. Dissociation is predicted to be exponential in time, with the reaction rate constant increasing rapidly as molecular energy increases above the critical energy. Experimentally, RRKM theory has proven to be valid in all but a few rare cases; these exceptions involve rapid decomposition ($< 10^{-12}$sec) of non-statistically prepared (chemically activated) molecules[78].

Some characteristic features of MPA and MPD are of particular importance in LIS and therefore are worthy of note here. The frequency profile of MPD induced by a single laser frequency is typically red-shifted by $\sim 10\ cm^{-1}$ from the ground state absorption profile due to a convolution of the effects of ground state absorption and anharmonicity. The dynamics of this aspect of

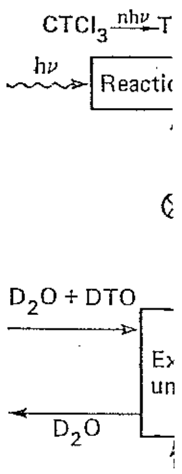
MPD have been well studied in single and two-frequency MPD experiments[79].

When fluence, and not laser intensity, dominates the description of MPA (as is often the case), the experimentally-measured absorption cross-section of the resonantly-pumped species decreases as $1/(\text{fluence})^{1/3}$ (ref. 80). This effective absorption coefficient decreases with fluence because of competing absorption and stimulated emission, the excited state anharmonicity-induced red shift and the diluted oscillator strength due to mixing of the pumped vibrational ladder with other vibrational levels. One consequence of this decreased excited state absorption is that the isotopic absorption selectivity, S, typically decreases by an order of magnitude from its low fluence value (as measured in an infrared spectrometer) to its value at fluences high enough to decompose essentially all local molecules, the saturation fluence[80,81]. There is some evidence for a fluence-independent absorption cross-section in some molecules at very high fluences near the saturation fluence[82].

Despite the apparent lack of absorption resonance conditions for most thermally-populated rotational states, a large fraction of irradiated molecules do, in fact, undergo MPA and MPD. Though this fraction often approaches unity, in some cases it can be significantly smaller as demonstrated by Raman probing experiments[83,84] and by the increased MPA or MPD with added buffer gas[85,86]. In LIS by infrared laser multiple-photon dissociation, the only benefits of collisions are to increase the fraction of molecules participating in MPA, as with rotational hole filling when a buffer gas is added. Otherwise, collisions decrease the yield and isotopic selectivity by removing molecular energy, destroying coherent effects, and by promoting inter-isotope energy transfer and post-MPD isotopic scrambling.

The laser separation of hydrogen isotopes, entailing D/H, T/D and T/H separation, represents a scientifically successful, as well as commercially promising, application of MPD. The extremely high single-step enrichment factors $\beta > 10^3$–10^4 and high fluence optical absorption selectivities $S > 10^3$ observed in hydrogen isotope separation, strikingly exemplify the goals of laser separation of isotopes.

The block diagram in Figure 6 shows the fundamental process units of commercial hydrogen isotope separation by MPD, as applied to tritium-from-deuterium recovery. First rapid, catalyzed hydrogen exchange occurs between water (the rare isotope source) and the working molecule, in this case chloroform. Then, the dried working molecules are isotopically-selectively decomposed in the laser photochemical reactor. After the enriched products are removed, the minority isotope-depleted working molecule (with a small



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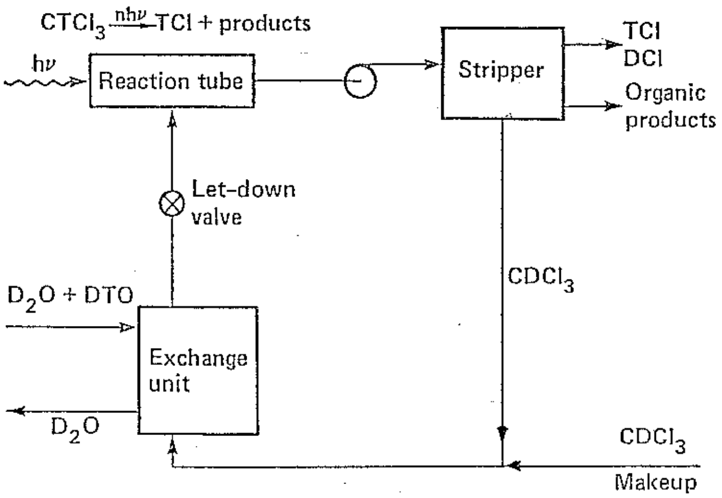


Figure 6. Overall process flow block diagram of laser separation of hydrogen isotopes, as applied to tritium-from-deuterium recovery using 12μ MPD of chloroform. Economically-efficient transfer of the desired isotope to the working molecule, and effective removal of the highly-enriched product and other by-products from the main feedstream are as important to the commercial viability of isotope separation as is the production of the highly-enriched product with minimal photon utilization in the photochemical reactor.

amount of added make-up) is ready to be isotopically replenished again for yet another cycle.

In an early promising D/H separation scheme using MPD, D/H mixtures of 1,1,1 trifluoro -2,2 dichloroethane (Freon 123) were photolyzed by a pulsed CO_2 laser (10.7μ), leading to a very high enrichment, $\beta = 1400^{87}$. This single-step enrichment factor far exceeds the optical selectivity, S~100 at low fluences^{81}, which is characteristic of the non-linear MPA interaction. β and S are limited by weak combination band absorption in normal Freon-123. Product yields in high pressure operation are small even for rapidly excited molecules (laser pulses with FWHM=2 nsec) because species excited above the reaction barrier decompose slowly in this "large" molecule and are efficiently de-excited by collisions.

In contrast, trifluoromethane appears to be a superior and nearly ideal working molecule for D/H separation^{81,85,88,89}. The CDF_3 ν_5 mode is resonant with the CO_2 laser (10.2–10.3μ) in a spectral region where the nearest CHF_3 absorption feature is the weak $2\nu_6 \leftarrow 0$ at 9.9μ, as shown in Figure 7.

The low fluence isotopic selectivity at 10.3μ is extremely high, 6000:1. There is only one energetically accessible decomposition route (Figure 5) and quite simple overall chemistry[85,88,90].

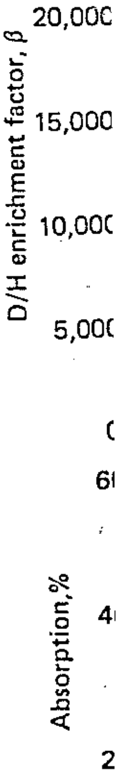
$$CDF_3 + nh\nu \rightarrow :CF_2 + DF \qquad (E_{act} = 69 \text{ Kcal/mole})$$
$$:CF_2 + :CF_2 \rightarrow C_2F_4$$

A fluence of only ~25 J/cm^2 9 delivered in a 100 nsec FWHM pulse is needed to decompose all CDF_3 molecules once the severe rotational absorption bottleneck has been removed by adding a buffer ($\gtrsim$20 torr Ar). Since X_{55} is unusually small (-0.25 cm^{-1}), the single frequency MPD profile is not significantly red-shifted from the ground state absorption spectrum, and, in fact, has the same width as this spectrum[79,91]. However, the two-frequency MPD profile is much broader, and excited state absorption strength at 10.3μ and 10.6μ (where cold CDF_3 is transparent) are nearly equal[79].

As depicted in Figure 7, the single-step D/H enrichment factor in CDF_3/CHF_3 is over 20,000:1 at 10.3μ[88]; still the effects of the tiny contributions of weak CHF_3 MPD on the blue side of CDF_3 ν_5 can be seen in this figure. The optical selectivity at high fluence (~25 J/cm^2) exceeds 1000:1 (10.3μ) when a buffer is added to allow rotational hole-filling[81]. These parameters suggest that in a single stage the D/(H+D) ratio can be enriched from 140 ppm to $\gtrsim$0.6 and, furthermore, that 15% of the absorbed (and efficiently produced) CO_2 laser photons are absorbed by the deuterated species; these results are ideal for practical heavy water production.

Experiments using short-pulse CO_2 lasers (FWHM=2 nsec) have confirmed that high dissociation yields are maintained even at the high total pressures of commercial interest ($\gtrsim$100 torr CDF_3/CHF_3) and that the enrichment factors are still extremely high[81]. In fact, highly deuterated water products have been obtained directly from MPD of normal fluoroform[82]. Detailed studies of short pulse absorption in CDF_3 have been conducted using opto-acoustic and direct absorption techniques[81,82,92].

There are still several important avenues of research that must be travelled before commercial implementation of this technique. In order to separate enough D_2O to satisfy the inventory requirements of one new heavy water reactor every year, very large short pulse CO_2 lasers with ~1 MW average power must be developed. The overall photochemical and economic process trade-offs of providing rotational hole filling by an added buffer ver-



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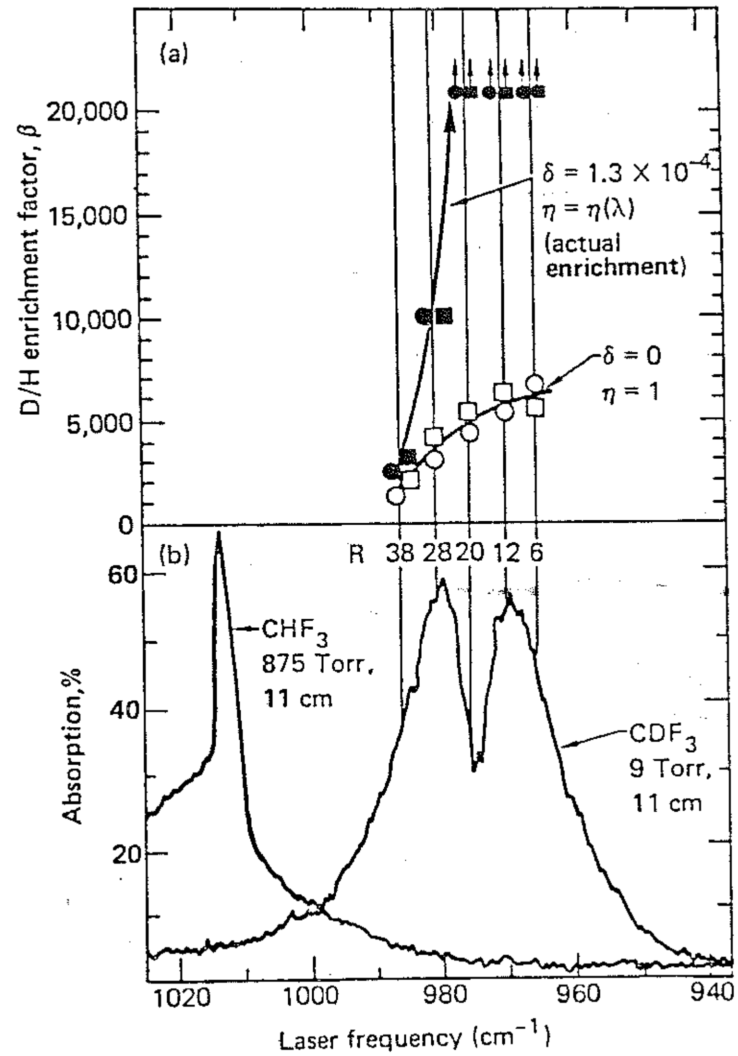

Figure 7. Measured single-step D/H enrichment factor, β, in $^{12}CDF_3/^{13}CHF_3$ mixtures obtained from $^{13}C/^{12}C$ labelling in the products, as a function of laser wavelength (10.4μ R branch) in (a), and the corresponding low-fluence $^{12}CHF_3$ ($2\nu_6 \leftarrow 0$) and $^{12}CDF_3$ ($\nu_5 \leftarrow 0$) absorption profiles in (b). The solid data points in upper half of the figure denote the actual enrichment factor, which exceeds the 20,000:1 measurement limit for photon energies less than 975 cm^{-1}. (The open data points ignore the deuterium content in the employed $^{13}CHF_3$ sample.) Note that the CHF_3 absorption profile is taken at a pressure 100× that of the CDF_3 and that the $^{13}CHF_3$ $2\nu_6 \leftarrow 0$ line shape is shifted to lower energies by ~ 2.2 cm^{-1} relative to the $^{12}CHF_3$ absorption curve portrayed here. (From Ref. 88).

sus naturally-occurring CHF_3 (which can also efficiently quench laser-excited CDF_3) must be examined. Furthermore, at present HDO/CHF_3 exchange is catalyzed by added hydroxide ions and dimethylsulfoxide[93,94]. Process costs could be appreciably lowered if this exchange rate could be accelerated or if simpler catalysis schemes could be developed.

Several other scientifically interesting, though apparently less commercially-attractive, methods of deuterium separation via CO_2 laser MPD of other molecules have been studied, including HDCO[95], $CDCl_3$ [96] and CDF_2Cl [97]. Selective CDF_3 decomposition from ternary $CHF_3/CDF_3/CTF_3$ mixtures has also been investigated [98].

The expertise acquired in deuterium separation has been invaluable in judging working molecules for tritium recovery. In general, halogenated methanes have several spectroscopic and chemical advantages over other classes of hydrogenated compounds as candidates for hydrogen isotope LIS. Because these methanes are relatively small and have few normal modes, there is an accordingly greater probability of locating a spectral region in these molecules where the minority isotope has a strong fundamental transition, with no nearby majority isotope fundamental, overtone, combination or hot band. Since halomethanes have few modes, which tend to have relatively high frequencies, RRKM theory predicts rapid decomposition of these molecules that are pumped above the activation energy barrier. Halomethanes excited $\sim$ 4 vibrational quanta above the dissociation barrier typically decompose in < 1 nsec, which is much faster than the rates of energy removal by collisions even at the high photochemical reactor pressures ($\sim$ 0.5–1 atm) required in commercial separation of isotopes. Another consideration is the location of isotopically-shifted resonances in tritiated halomethanes. Whereas, vibrational eigenfrequencies involving C-D wags and/or C-F stretches are often resonant with the efficient CO_2 laser (9–11μ); those involving C-T and/or C-Cl motions are usually at slightly longer wavelengths, and are resonant with lasers optically-pumped by CO_2 lasers (e.g., NH_3 laser near 12μ) or Raman-shifted CO_2 lasers. The overall photochemical and process constraints in T/D photochemical separation are less severe than in D/H separation despite typically more dilute starting mixtures ($\sim$ 7 ppm T/D vis-a-vis $\sim$ 140 ppm D/H), because of the much greater value of tritium ($\sim$ \$$10^4$/g tritium compared to $\sim$ \$1/g deuterium).

Research in tritium recovery by pulsed infrared laser MPD of halogenated working molecules is quite active. In the first studies of T/D enrichment by MPD, 12.08μ NH_3 laser photolysis of chloroform, was examined and β was

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measured to be $\gtrsim 165$[25]. More recent work has shown that the single step T/D enrichment factor for the chloroform working molecule is, in fact, $>> 1000$[99], as anticipated from the extremely high low-fluence optical selectivity alluded to earlier in this chapter and Figure 1. (S$\gtrsim$12,000 near the 835 cm^{-1} $\nu_4 \leftarrow 0$ absorption peak and S$\gtrsim$6500 near the 828 cm^{-1} single frequency MPD peak). Also, photon utilization is efficient because the high fluence S is still > 400 at 12.08μ[99]. Several factors combine to make this technique perhaps the most attractive process for tritium recovery from contaminated heavy water. The tritium-bearing product (TCl/DCl) is easily stored on a solid support, and only small amounts of this recovered tritium ($\sim$ 1 week inventory) need remain in the separation unit. Only modestly-sized lasers ($\sim$ 3–10 KW at 12μ) are needed to decontaminate a typical heavy water reactor in a reasonably short time ($\sim$ 3 years). The required CO$_2$ lasers are well within the present state of technology, and these 9μ photons can be efficiently converted to 12μ either by optical pumping or Raman shifting in NH$_3$, or by Raman shifting an isotopic CO$_2$ laser (such as ^{13}C^{16}O$_2$) in a hydrogen isotope (such as D$_2$)[100]. Finally, chloroform dissolved in water undergoes sufficiently rapid hydroxide ion-catalyzed tritium exchange to easily satisfy process requirements. A detailed study of the overall process design and cost is in progress[99].

Fluoroform appears to be the best working molecule for T/H separation[24]. Impressively high enrichment factors ($\beta = 580$) have been observed in the CO$_2$ laser (9.3μ) MPD of the CTF$_3$ ν_2 band[101–105]. Large enrichment factors and relatively low saturation fluences ($\sim$ 34 J/cm^2) are observed only after adding an argon buffer to remove the rotational level bottleneck in CTF$_3$ [103], in much the same way as a buffer is needed in D/H separation by MPD of the ν_5 mode in CDF$_3$ [81,85]. In room temperature samples, S decreases from a low fluence value of $\sim$ 700 to, perhaps, $\sim$ 30 at saturation fluences. Significant improvement in S is expected (and is actually seen in β[104]) for cooled samples. High single-step T/H separation ($\beta \gtrsim 500$) has also been measured in the CO$_2$ laser (10.6μ) MPD of C$_2$TF$_5$ without added buffers[106].

^{13}C/^{12}C separation by CO$_2$ laser MPD of several molecules, mostly halomethanes, has been considered thoroughly. The possibility of commercial production of ^{13}C (β = 10–50) by MPD of CF$_3$I has been investigated[107–109]. Even more impressive ^{13}C/^{12}C enrichment ($\beta \simeq 100$) in the C$_2$F$_6$ product has been observed in the MPD of CF$_3$Br and CF$_3$Cl[109]. High pressure, isotopically-selective MPD of these compounds has also been examined using long pulse (100-1000 nsec FWHM) and short pulse (2 nsec FWHM) CO$_2$

lasers[111,112]. The very high single-step enrichment factors approaching 1000 and other superior photochemical parameters, of 9.7μ photolysis of $CHClF_2$ (forming carbon-13 enriched C_2F_4), makes this the $^{13}C/^{12}C$ laser enrichment technology perhaps closest to commercial reality[113]. Smaller, though still significant $^{13}C/^{12}C$ enrichment ($\beta = 5$–40 with large yields) has been observed in infrared laser MPD of other halogenated hydrocarbons: CF_2Cl_2 [114] and C_3F_6 [115] with CO_2 lasers, CCl_4 [116] using an NH_3 laser either alone (12.81μ) or simultaneous with a CO_2 laser (9.29μ), and C_2F_5Cl[117] using two CO_2 laser frequencies. The CO product in 10.76μ photolysis of hexafluoroacetone also shows an impressively large 300-fold $^{13}C/^{12}C$ enrichment factor[118]. Isotopically-selective two frequency MPD studies[119] have also been performed on this molecule.

With the exception of boron and sulfur, MPD separation of isotopes other than hydrogen and carbon has been studied much less intensively. for most of these other elements, serious discussion of practical LIS implementation is ruled out by either the small measured enrichment factors or other less-than-large parameters. The study of $^{10}B/^{11}B$ separation by CO_2 laser MPD of BCl_3 [73,74] represents some of the seminal research in MPD. $^{15}N/^{14}N$ separation has been accomplished by pulsed CO_2 laser dissociation of CH_3NO_2 [120] and isomerization of CH_3NC and CH_3CN[121]. Because of the large 17 cm^{-1} shift between the $U^{16}O_2$ and $U^{16}O^{18}O$ complexes nested in $UO_2(hfacac)_2$-THF, pulsed or cw CO_2 laser photolysis (10.65μ) has produced high enrichment of $^{18}O/^{26}O$ (ref. 122). Selective CO_2 laser excitation of SiF_4 led to measurable, though small, enrichment of the minority isotopes $^{29,30}Si$ by selective depletion of ^{28}Si ($\beta \sim 1.1$)[75]. Separation of $^{32,33,34,36}S$ by single and dual frequency MPD of SF_6 has been extensively studied[71,72], including several investigations of practical implementation[123]. Much of present-day understanding of MPA and MPD has been gained through these studies on SF_6 [76]. In addition, interest in the mechanism of MPA has promoted detailed research into the SF_6 vibrational level structure, and the ground and excited-state absorption[124]. Sulfur isotopes have also been separated by MPD of SF_5Cl, S_2F_{10} and SF_5NF_2 [125,126]. In the aforementioned investigations of carbon isotope separation by MPD of CF_2Cl_2 [114] and CCl_4 [116], small enrichments in $^{37}Cl/^{35}Cl$ were also observed. Using an NH_3 laser (12.8μ) to isotopically selectively excite SeF_6 to the quasi-continuum and a CO_2 laser to non-selectively dissociate excited molecules, the selenium isotopes $^{74-82}Se$ have been separated[127]. Small enrichments in molybdenum isotopes ($^{92-100}Mo$) have been observed by CO_2 laser MPD of a combination band

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in MoF_6 [128]. The effect of two frequency CO_2 laser MPD of OsO_4 on osmium isotope separation ($^{186-192}Os$) has been examined[129]. The products of normal $^{235,238}UF_6$ irradiated simultaneously be a weak CF_4 laser (16.25μ) and a stronger CO_2 laser (9.32μ) have been found to be slightly enriched in ^{235}U ($\beta = 1.049$)[130]. Uranium isotope separation has also been observed in the pulsed and cw CO_2 laser photolysis of $UO_2(hfacac)_2$ THF[122] and $[UO_2(hfacac)_2]_2$ [131], with $^{235}U/^{238}U$ enrichment factors of $\beta \simeq 1.3$.

Two step IR-UV dissociation provided one of the first successful examples of laser isotope separation with the demonstration of $^{15}N/^{14}N$ separation in NH_3 [132]. In two-step processes, a collision-free and often cooled molecule is first isotopically selectively excited by the absorption of one or several infrared photons, from one or more lasers. The vibrationally-excited molecule is then selectively photolyzed using an efficient ultraviolet laser and finally scavenged. The photolytic cross-section of the vibrationally-heated molecules must be very large and, naturally, this cross-section for ground state molecule must be quite small. For successful isotope separation, the selectivity of (isotopic) infrared and (vibrational-energy dependent) ultraviolet absorption must both be maximized. One prospective application of two-step dissociation LIS is in the recovery of deuterium and tritium directly from water[133,134]. Since water is usually the ultimate hydrogen isotope source in many such isotope separation applications, this technique would eliminate the extra step of deuterating or tritiating an LIS working molecule. Unfortunately, this method is unattractive, due to the rapid vibrational exchange in water vapor and the lack of efficient resonant infrared lasers.

In addition to nitrogen isotope separation, two-step dissociation has been used to separate $^{11}B/^{10}B$ (BCl_3; CO_2 laser and UV flashlamp)[135], $^{13}C/^{12}C$ (CF_3I; CO_2 and XeF lasers)[136], $^{81}Br/^{79}Br$ (HBr + NO scavengers; HBr (+ isotopic filter) and doubled dye lasers)[137], and, $^{235}U/^{238}U$ (UF_6)[125]. Uranium isotope separation by two-step dissociation of UF_6 has been studied intensively at the Los Alamos National Laboratory[125]. In this process, the ν_3 mode is selectively excited by one or more 16μ lasers (CF_4 laser or CO_2 laser Raman scattered in H_2), and then an UV excimer laser (XeCl) dissociates those molecules that are sufficiently vibrationally excited. Before excitation, the UF_6 is cooled by expansion in a seeded supersonic jet so essentially all UF_6 is initially in the ground state. After irradiation, ^{235}U-enriched UF_5 forms dimers and then particulates, which are separated from the UF_6 molecular stream. LIS by direct infrared laser MPD has a disadvantage here because it is the lighter isotope — with the higher vibrational frequency —

which is the desired isotope. There is a conflict between isotopically selective dissociation which calls for a blue-shifted irradiation frequency here, and the requirement of large MPD cross-sections which instead demands use of red-shifted radiation.

Two step dissociation of UF_6 (and of other molecules as well) also has some serious shortcomings. The observed single-step yields and enrichment factors may be too small for a practical uranium separation process. Furthermore, as in all IR/UV dissociation schemes, there are diverse and often conflicting requirements in employing both mid-infrared and ultraviolet lasers. For example, efficient photon utilization the absorption cross-section at all (IR and UV) laser frequencies must be very nearly the same; this is usually a quite demanding condition. Though two-step dissociation was once considered an economically promising LIS technique, the associated photochemical requirements are now appearing to be too challenging.

Single photon, ultraviolet laser predissociation of small molecules has led to a rich array of light-atom isotope separation demonstrations. Probably the most notable work has involved isotopically-selective excitation of formaldehyde. At wavelengths longer than 3400Å , H_2CO photolysis yields only the stable products $H_2 + CO$, while at shorter wavelengths undesirable radical production ($H + HCO$) also occurs. Several successful laser separations of isotopes have been performed using tunable dye lasers or fixed-wavelength ion lasers to selectively decompose gas-phase H_2CO: D/H ($\beta = 1110$; dye)[138] $^{12}C/^{13}C$($\beta = 80$; dye)[139], $^{13}C/^{12}C$ ($\beta = 33$, ion)[140], $^{14}C/^{12}C$ ($\beta = 150$, dye)[141], $^{17}O/^{16}O$ ($\beta = 9$; $\beta = 27$ in D_2CO; ion)[140] and $^{18}O/^{16}O$ ($\beta = 9$; 44 in D_2CO; ion[140]. Smaller enrichments were measured in the predissociation of formaldehyde dissolved in cryogenic Xe solutions[142]. Despite the relatively high enrichment factor for deuterium separation, this process is not commercially viable because of the very slow D/H exchange of formaldehyde with standard deuterium sources (H_2O, CH_4, NH_3), the far too low pressure limits < 2 torr) set by collision-broadening overlap of spectral resonances and the formaldehyde vapor pressure, and the lack of suitably-efficient narrow band tunable ultraviolet lasers. In contrast, $^{14}C/^{12}C$ enrichment by selective formaldehyde predissociation may well become a useful laboratory technique to substantially improve the range of radioactive dating[141]. Other examples of isotope separation using ultraviolet laser predissociation include: $^{12,13}C$ and $^{32,34}S$ isotopes (CS_2)[143], and $^{16-18}O$ isotopes (O_2)[76], both using a tuned ArF laser (193 nm), and $^{13}C/^{12}C$ and $^{15}N/^{14}N$ separation by visible dye laser predissociation of both gas-phase[144] and solid-state[145] sym-tetrazine.

Bimolecular reactions

One intriguing method of laser enrichment of isotopes utilizes the typically low barrier, slightly endoergic bimolecular reaction of halogen atoms and halomethanes. These reactions may be selectively accelerated by cw CO_2 laser vibrational pumping of the desired halomethane isotope. The overall mechanism of this halogenation reaction is

$$CHYZ^{\dagger} + X \rightarrow CYZ + HX \quad \text{slow}$$

$$CYZ + X_2 \rightarrow CXYZ + X \quad \text{fast}$$

where CHYZ† is the vibrationally-excited starting material that may be isotopically labelled at either the C,Y or the Z site and X_2 is a halogen molecule. For best results enough buffer gas is added so that the overall V-T quenching rate effectively competes with the rate of inter-isotope V-V exchange[146]. Despite this necessary rapid energy quenching and the several stages of enrichment required to increase the isotope fraction to the desired level (because of the small single-step β, typically 1.5–4.0), the economics of this type of process show some promise because selective excitation occurs by absorption of a single, efficiently-produced cw CO_2 laser photon. Using this technique $^{81}Br/^{79}Br$ (CH_3Br/Cl)[146], D/H ($CH_2D_2/Cl,Br$)[147,148] and $^{13}C/^{12}C$(CH_3F/Br)[149,150] have been separated. Note that in the deuterium separation method CH_2D_2 (natural concentration 10^{-7}) is used, and not the more abundant CH_3D (6×10^{-4}) which is transparent to the CO_2 laser; as such this method is not commercially attractive. However, the possibility of using either CO_2 laser-hot-band-pumped[148] or $N_2(v = 1)$-metastable-collisionally-pumped[151] CO_2 molecules to selectively collisionally excite CH_3D has been examined and looks promising[148]. Since the CH_3F/Br reaction is 15 Kcal/mole endothermic-compared to the 3 Kcal/mole of the single absorbed carbon isotope separation experiments imply that isotope selectivity is retained in the V-V ladder climbing collision that must occur to pump CH_3F to the internal energy needed for a reasonably fast reaction[150].

Another somewhat similar LIS method has been proposed in which normally endoergic hydrogen halide-olefin addition reactions are catalyzed by isotopically-selectively exciting one reagent up the vibrational ladder [152,153]. However, no reaction rate acceleration was observed in a study[154] in which one reactant was excited to a vibrational state ($v_{C-H} = 5, 6$) above the activation energy by direct overtone-pumping. This suggests that both reagents require some internal excitation to induce the addition reaction. This is unsuitable for practical LIS.

There have also been several demonstrations of separation of isotopes using visible-laser catalyzed bimolecular reactions. Most notable are the studies of ^{37}Cl/^{55}Cl separation by narrow-band dye laser, isotopically-selective electronic excitation of ICl followed by addition-type reactions with bromobenzene[155], cis-and trans-1,2 dibromoethylene[156], or acetylene[157]. Chlorine isotopes have also been enriched by selective electronic excitation of either thiophosgene (diethoxyethylene scavenger)[158], Cl_2 (C_2Cl_4) [159] or CIF (SF_4)[160]. Laser isotope separation of oxygen has been observed in the photochemical reduction occurring following selective dye laser excitation of UO_2F_2 in (HF + H_2O) methanol solution[161].

Conclusion

The field of laser isotope separation is presently maturing. This past decade has been highlighted by the demonstration of numerous methods of physical and chemical isotope separation using lasers. Some of these techniques have been studied in detail. Further LIS research and development will be strongly influenced by the state-of-the-art in laser technology and, most certainly, by the near-term market demand.

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