

The Application of Lasers to Isotope Separation

C. Bradley Moore

Department of Chemistry, University of California, Berkeley, California 94720

Received January 29, 1973

The monochromaticity of lasers allows one to excite a single species in an isotopic mixture. A variety of methods have been proposed for utilizing selective laser excitation to separate isotopes,¹⁻⁴ and at least one has been demonstrated experimentally.³ These methods promise high separation factors, high efficiencies and much-reduced costs. A successful laser method of uranium isotope separation could have an important economic impact.^{5,6} For lighter elements dramatic cost reduction could open up new applications of isotopes in research and technology. Some of the possible methods for laser separation of isotopes are discussed below. A proposal, based on the demonstrated separation of formaldehyde isotopes, is described for increasing the sensitivity of ¹⁴C dating by several orders of magnitude.

The essential prerequisites for a scheme of isotope separation by lasers are: (a) an absorption spectrum with a well-resolved isotope shift; (b) a laser sufficiently monochromatic and tunable to excite the absorption of one isotope and not the other; (c) a chemical or physical process which acts on excited molecules and separates them from unexcited ones, but need not have any inherent isotopic selectivity; and (d) a set of photochemical rate constants and physical conditions such that energy transfer from a laser-excited species to an undesired species does not occur before the separation in (c). It is not trivial to supply all four of these conditions for any particular separation method and isotope. The development of optimum separation techniques for specific isotopes will generally require some mixture of new spectroscopic data, of photochemical research, of laser development, and of engineering. Much of this work is not particularly inspiring fundamental research and will need to be motivated by important applications. A major purpose of this Account is to convince the reader that large-scale applications of separated stable isotopes could soon be feasible and are worth serious thought.

Isotope Shifts and Excitation

Changes in nuclear mass can shift electronic, vibrational, and rotational energy levels. When the shift places the absorption of one isotopic species at a frequency at which the others are transparent, it is possible to excite selectively that species with a laser of sufficiently narrow line width.

The electronic energy levels of atoms are shifted

by interactions with the nuclear spins (hyperfine structure) and with the nuclear charge distribution (volume shift), and for light atoms by simple reduced mass change.⁷ For some heavy elements the only experimentally known isotope shifts are for the free atoms. In uranium the 235-238 shift is 1.4 cm⁻¹ for the 4244.4-Å transition.⁷

The rotational and vibrational level spacings of molecules decrease with increasing nuclear mass.⁸ The rotational envelopes of vibrational bands are on the order of 10-100 cm⁻¹ broad. Deuterium substitution will shift vibrational frequencies beyond this envelope. In some cases isotope shifts for elements Li through O may do the same. Usually, the vibration-rotation bands of an isotopically substituted molecule will overlap those of the abundant molecule, and it is necessary to select among interspersed vibration-rotation lines. For this purpose small linear or symmetric-top molecules are to be preferred. Excited electronic states have still more complicated absorption spectra (Figure 1), but offer more possibilities for the subsequent separation.

Isotope shifts are readily observable in solids, particularly when the absorber is dilute in a host or matrix. Usually, rotational motion is frozen out and a single absorption line appears for each vibrational state. Line widths of infrared absorption spectra in matrices are often less than 1 cm⁻¹ and allow isotope shifts of atoms as heavy as Br to be observed.⁹ While electronic spectral line widths are more capricious, sharp spectra can sometimes be observed.¹⁰ An isotope shift has even been resolved for a uranium compound,⁵ UO₂Cl₂·2CsCl, at 4489 Å. It is unfortunate from the process design point of view that, in the liquid phase, rotational levels are generally broadened into a smooth, unnarrowed band contour.

Tunable laser sources in the infrared, visible, and near-ultraviolet¹⁴ have been developing rapidly as

(1) J. Pressman, U. S. Patent 3558887 (1971); A. Ashkin, *Phys. Rev. Lett.*, **25**, 1321 (1970).

(2) R. V. Ambartzumian and V. S. Letokhov, *Appl. Opt.*, **11**, 354 (1972); V. S. Letokhov, *Chem. Phys. Lett.*, **15**, 221 (1972).

(3) E. S. Yeung and C. B. Moore, *Appl. Phys. Lett.*, **21**, 109 (1972).

(4) S. W. Mayer, M. A. Kwok, R. W. F. Gross, and D. J. Spencer, *Appl. Phys. Lett.*, **17**, 516 (1970).

(5) R. L. Farrar, Jr., and D. F. Smith, "Photochemical Isotope Separation as Applied to Uranium," Report K-L-3054, Rev. 1 (March 15, 1972), Union Carbide Corp., Oak Ridge, Tenn.

(6) The most significant development in laser separation of isotopes may be hidden beneath the simple announcement that AVCO and Jersey Nuclear have a joint venture in uranium separation: *Laser Focus*, **8** (4), 18 (1972).

(7) H. G. Kuhn, "Atomic Spectra," 2nd ed, Academic Press, New York, N. Y., 1969, Chapter VI.

(8) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, II, and III, Van Nostrand, Princeton, N. J., 1950, 1945, and 1966.

(9) L. Andrews, *Annu. Rev. Phys. Chem.*, **22**, 109 (1971).

(10) B. Meyer, "Low Temperature Spectroscopy," Elsevier, New York, N. Y., 1971.

C. Bradley Moore was born in Boston in 1939. He received his bachelor's degree from Harvard, went to Berkeley for graduate work with George C. Pimentel, and, after receiving the Ph.D. in 1963, stayed on the faculty, where he is now Professor. His research interests have been in molecular energy transfer and photochemistry. Much of his work has involved the application of lasers in chemistry and *vice versa*. This year he is a Miller Research Professor.

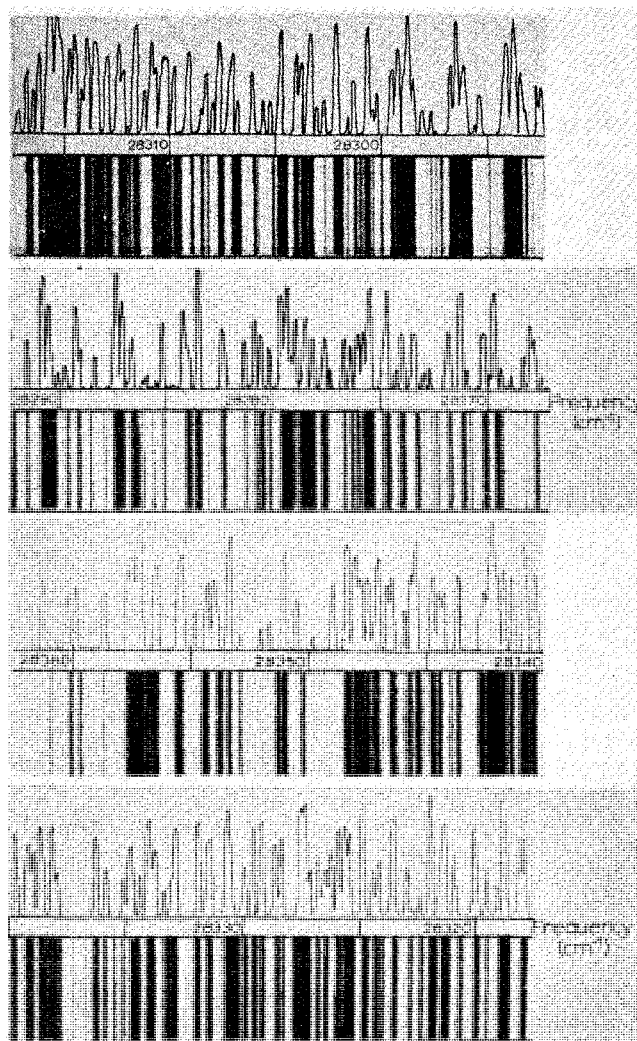


Figure 1. High-resolution spectrum and calculated band contour for the center of the 4_0^1 transition of H_2CO . Note the occasional gaps in this complicated spectrum which allow selective excitation of isotopic molecules such as H_2^{13}CO or H_2^{14}CO . From J. E. Parkin, *J. Mol. Spectrosc.*, 15, 483 (1965), with permission.

tools for research.¹¹⁻¹⁵ Future development can be expected to bring sources in the vacuum ultraviolet, sources with output energies useful for bulk chemical synthesis, and sources which efficiently convert readily available energy into laser photons.

Some orders of magnitude help give a picture of the revolutionary effect that laser separation could have on isotope costs. For example, a process yielding one separated atom for each 3300-Å photon absorbed requires 10^{-1} kWhr of light/mol of product. For a laser efficiency of 10^{-3} , the power cost is about \$3/mol;¹⁶ it is not necessary for either the laser or the separation scheme to be highly efficient. Of course, greater costs will probably be incurred for salary and capital equipment.

Isotope Separation Schemes

There are numerous conceivable methods for real-

(11) R. J. Pressley, "Handbook of Lasers," Chemical Rubber Co., Cleveland, Ohio, 1971.

(12) "Fundamental and Applied Laser Physics: Proceedings of the Esthan Symposium, 1971," M. Feld, N. Kurnit, and A. Javan, Ed., Wiley-Interscience, New York, N. Y., 1973.

(13) M. Bass, T. F. Deutsch, and M. J. Weber, *Lasers*, 3, 269 (1971).

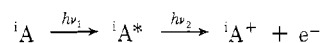
(14) H. R. Schlossberg and P. L. Kelley, *Phys. Today*, 25 (7), 36 (1972).

(15) C. B. Moore, *Annu. Rev. Phys. Chem.*, 22, 387 (1971).

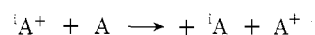
(16) Isotopes Catalogue, Atomic Energy Commission, Mount Laboratory.

izing separation following selective excitation of an atom or molecule. The excited species could spontaneously undergo an irreversible change as in predissociation, preionization, or isomerization. A stable excited state could be ionized, dissociated, or isomerized by absorption of a second photon. A chemical reagent could be used which both reacts with the excited state so rapidly that energy transfer cannot occur and reacts with the ground state so slowly that the reagents can be mixed without reaction. One of the most straightforward approaches is simply to rely on the momentum transferred from photon to absorber. The desired species would be deflected from a molecular beam into a collector.¹ However, it is difficult to imagine that this method would be less costly than the mass spectrometers now used. Of the many conceivable methods for isotope separation using lasers, doubtless most will either be unworkable or too costly. However, from the many alternatives available for each isotope it is certain that major cost reductions for useful isotopes will be achieved.

Selective Two-Step Photoionization. This very general selective excitation scheme has been described by Ambartzumian and Letokhov.² Excited atoms are selectively produced by light at ν_1 and then photoionized by an intense beam at ν_2 (Figure 2a). The authors were able to photoionize Rb vapor



using a tunable dye laser at 7943.6 Å for selective excitation and a doubled ruby at 3471 Å for photoionization. Isotope separation was not attempted. A drawback of the method is that the absorption coefficient at ν_1 is usually seven to ten orders of magnitude greater than that at ν_2 .² Thus the number of photons required may be orders of magnitude larger than the number of isotopic atoms produced. In order to avoid charge exchange



it would be necessary to operate systems at very low pressures or in atomic beams. It should be mentioned that the requirements on ν_2 are only that the frequency be high enough to ionize the excited atom and not so high as to ionize any thermally populated states. The maximum intensity of ν_2 may be limited by nonresonant two-photon ionization. The frequencies ν_1 and ν_2 may be identical, as shown by ν_3 in Figure 2a. This resonant two-photon ionization is currently under study by Berry at Chicago.¹⁷ The method could be used to separate ^{235}U by excitation with a dye laser of a resonance transition of neutral U in an atomic U beam.

Photoionization of molecules is also possible.² If selective excitation is carried out on a high-overtone vibration-rotation transition, the absorption coefficients at ν_1 and ν_2 could be made comparable. Ambartzumian and Letokhov² suggest that mass spectrometer sensitivities might be improved by selective two-step photoionization. Perhaps it will be possible to build a state-selective detector of unit efficiency for neutral atoms and molecules with the full state

(17) R. S. Berry, *Bull. Amer. Phys. Soc.*, 17, 1129 (1972).

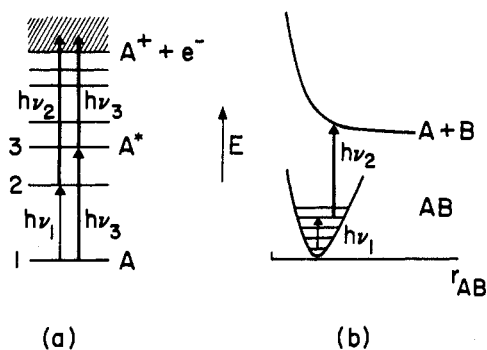


Figure 2. (a) Selective two-step photoionization. Frequency ν_1 is tuned to excite the transition, $1 \rightarrow 2$, of a single isotope. An intense beam at ν_2 ionizes atoms from level 2. A single laser frequency, ν_3 , may be used if it is resonant with a transition $1 \rightarrow 3$ and has sufficient energy to ionize from level 3. (b) Selective two-step photodissociation. Frequency ν_1 excites a vibration-rotation transition in the infrared or a rovibronic transition in the visible or ultraviolet. Frequency ν_2 dissociates the excited molecules. If radical fragments are produced, they must be chemically trapped.

resolution of optical spectroscopy. Such a detector would be of great value in molecular beams and in spectroscopy.

Two-Step Photodissociation. Selective two-step excitation may be used to reach molecular dissociation continua (Figure 2b) as well as ionization con-



tinua.² The selective step, $h\nu_1$, may be either a vibrational or an electronic transition. The level excited must be sufficiently high that its thermal population is negligible and that its absorption coefficient for $h\nu_2$ is substantial while that of thermally populated states is negligible. If the fragments A and B are chemically stable, the isotopically pure ${}^i\text{A}$ (an atom or simple molecule) may be separated simply. If A is reactive, a chemical trapping scheme which does not allow isotopic mixing must be devised. Ambartzumian and Letokhov² excited HCl from $\nu = 0$ to $\nu = 3$ and attempted to detect its dissociation by 2650 Å. NO was added to trap Cl by formation of NOCl. No product was reported—perhaps due to vibrational energy exchange or to inefficient trapping. The dissociation method is not so straightforward nor so general as ionization, but it does offer some important advantages. Dissociation and subsequent chemical trapping and separation may be carried out in bulk gases or even in some solids. The absorption coefficients of ν_1 and ν_2 can be of comparable magnitudes. Finally, the photon energies required will often be more efficiently supplied by available laser systems.

Photopredissociation. A much simpler, though less general, method of isotope separation is photopredissociation.^{2,3} If the excited state of a molecule is sufficiently long-lived, say longer than 10^{-10} sec, it will exhibit sharp, well-resolved absorption spectra. In the simplest case the excited state will decay by spontaneous emission of fluorescence. These radiative lifetimes generally fall within the range of 10^{-8} to 10^{-5} sec. If the molecular excited state is quasi-bound (metastable) with respect to dissociation and if dissociation occurs with a lifetime between 10^{-10} sec and the radiative lifetime, then selective optical

excitation can yield isotopically enriched dissociation products. If these products are stable molecules or if they may be chemically trapped, then an isotope separation has been performed. *The method is simple and efficient.*

Such a separation has been carried out by Yeung and Moore.³ A doubled ruby laser, 3472 Å, was used to photolyze an equimolar mixture of H_2CO and D_2CO . D_2 was produced in a sixfold abundance over H_2 , approximately the same ratio as that of the absorption coefficients of D_2CO and H_2CO at 3472 Å. Five per cent of HD was also formed. Although this experiment neatly demonstrates the simplicity and some of the power of laser photopredissociation, a detailed study of the spectroscopy and photochemistry of formaldehyde is necessary before separations of rare isotopes may be accomplished using formaldehyde.

The spectrum of the first excited singlet state of formaldehyde has been exhaustively studied.¹⁸ Figure 1 shows a typical segment of the vibration-rotation structure near the band origin. The Doppler width of each single line is $\Delta\nu_D = 0.064 \text{ cm}^{-1}$ and the spacings are often as much as 1 cm^{-1} . Vibrational band shifts of some 5 or 10 cm^{-1} for C and O isotopic substitutions allow one to anticipate that strong absorption features of a desired molecule will sometimes lie in a region of weak and sparse absorption of the normal molecule.³ The ruby laser used to separate D_2 from H_2 irradiated just such a region. A clean separation of ${}^{13}\text{C}$, ${}^{14}\text{C}$, ${}^{17}\text{O}$, or ${}^{18}\text{O}$ would best be done by irradiating the center of a single well-chosen line in the spectrum of the isotopic formaldehyde.

The potential of photochemical methods for achieving high separation factors is illustrated by the absorption line profiles¹⁹ shown in Figure 3. The narrow central portion is the Gaussian profile due to Doppler broadening. The broader and much weaker tails are due to the finite lifetime of a molecule in a particular quantum state. In the limit of low pressure, less than 0.1 Torr for H_2CO , this is the predissociation lifetime. At higher pressures collisions cause broadening as well. In Figure 3 the higher pressure curves are calculated with a collision rate equal to the observed quenching rate (larger than the hard-sphere collision rate) of $2 \times 10^7 \text{ sec}^{-1} \text{ Torr}^{-1}$. The Lorentz width, $\Delta\nu_L$, is related to the lifetime of the state by $\Delta\nu_L = 1/(2\pi\tau)$. The intensity of the line in the extreme tails is proportional to $\Delta\nu_L$ and inversely proportional to the square of the displacement from line center. A separation factor of 5×10^6 is predicted at low pressures if two lines of equal strength are spaced by 1 cm^{-1} . Higher pressures are desirable in order to operate with shorter cells and more efficient use of the laser photons. The decrease in line center absorption coefficient and the polymerization of formaldehyde are likely to set a maximum pressure near 100 Torr. The separation factor for 1 cm^{-1} spacing would still be 6×10^3 multiplied by perhaps an order of magnitude for the ratio of line strengths. Of course these rather large

(18) V. A. Job, V. Sethuraman, and K. K. Innes, *J. Mol. Spectrosc.*, **30**, 385 (1969).

(19) A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge University Press, London, pp 97-103.

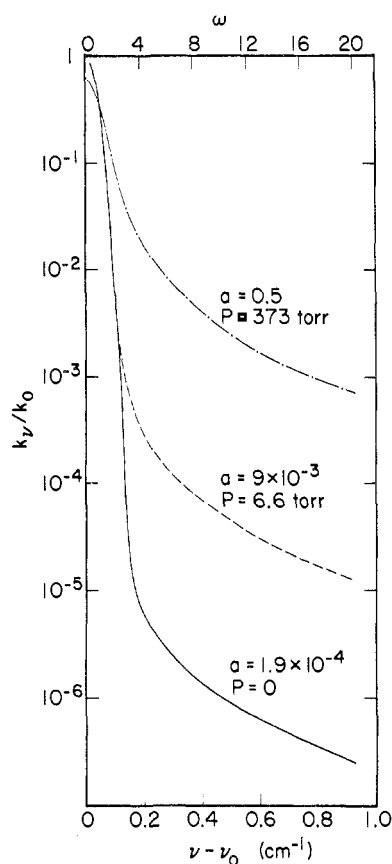


Figure 3. Absorption line profiles showing combined Doppler and Lorentz broadening; k_ν/k_0 is the absorption coefficient divided by the line-center absorption with only Doppler broadening. Pressure and cm^{-1} units are for H_2CO gas near 3500 Å. Dimensionless parameters are $\alpha = (\ln 2)^{1/2} \Delta\nu_L / \Delta\nu_D$ and $\omega = 2(\ln 2)^{1/2} (\nu - \nu_0) / \Delta\nu_D$. For $\omega > 6$, $k_\nu/k_0 = \pi^{-1/2} \alpha \omega^{-2}$. For H_2CO , $\Delta\nu_D = 0.064 \text{ cm}^{-1}$ at room temperature. Laser-excitation selectivity will be limited by the tails of absorptions of unwanted isotopic species at the line-center frequencies of desired species.

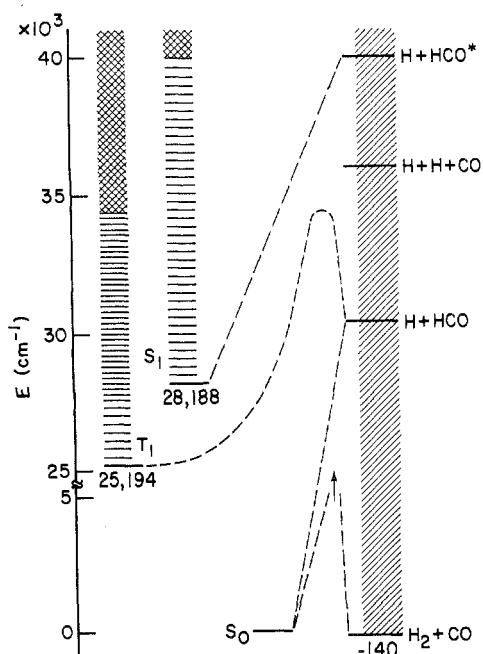
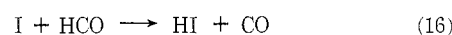
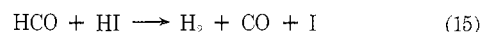
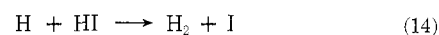
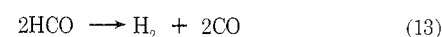
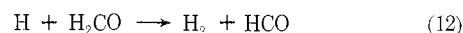
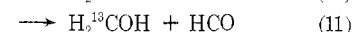
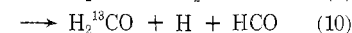
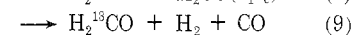
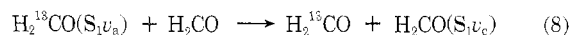
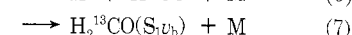
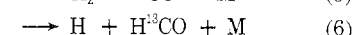
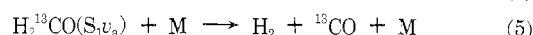
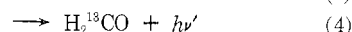
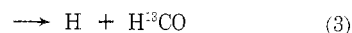
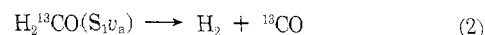
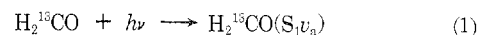


Figure 4. Energy states of formaldehyde, H_2CO . Broken lines indicate asymptotes of potential surfaces and expected barriers on S_0 and T_1 surfaces. Formaldehyde is predissociated by radiationless transitions from S_1 to dissociative levels of S_0 .

separation factors may be limited to much more modest values in practice. Transitions too weak to be seen in normal spectroscopy could be stronger than the tails of prominent features. Absorptions of very high J states, of undesired rare isotopes, and of the triplet state of the abundant isotope are all possible. Laser types will realize the possibility of broadening the transitions by use of too powerful a laser. Finally, the photochemistry itself may degrade the selectivity.

Some of the photochemistry^{20,21} involved in the separation of formaldehyde isotopes is illustrated in eq 1–16 and Figure 4.



The photoexcited molecule in some particular vibrational level of the S_1 electronic state and in the absence of collisions may dissociate to molecular products (eq 2) or to radical products (eq 3) or may fluoresce (eq 4). The $\text{H} + \text{HCO}$ dissociation limit is not well known; however, the best information indicates that the threshold lies above the first few vibrational levels of S_1 (Figure 4). The measured lifetime of 0.3 μsec at the S_1 origin²⁰ is dominated by predissociation since the radiative lifetime is on the order of 5 μsec . At pressures above a few tenths of a Torr, collision processes (eq 5–11) are faster than spontaneous predissociation. The work of McQuigg and Calvert²¹ and of Yeung and Moore^{3,20} shows that in formaldehyde vapor process 5 is the dominant one. The remaining processes occur to an extent less than 10%. Radical products from eq 3 and 6 may be trapped (eq 14–16) by addition of HI or some other substance before chain reactions 12 and 13 produce unlabeled products. The vibrational energy transfer process (7) presents no problems. However, electronic energy transfers (eq 8–10) and the abstraction (eq 11) will produce unlabeled products. Further research is necessary to determine how much less than 10% the contribution of these processes actually is.

(20) E. S. Yeung and C. B. Moore, *J. Chem. Phys.*, **58**, 3988 (1973).

(21) R. D. McQuigg and J. G. Calvert, *J. Amer. Chem. Soc.*, **91**, 1590 (1969).

Electronic transfer places an upper limit on the purity of separated material beyond any limit from the spectroscopic selectivity.

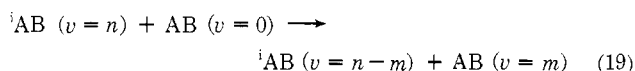
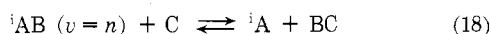
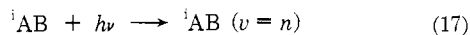
The generality with which isotope separation by photopredissociation may be applied is not known. Formaldehyde is almost unique in terms of the wealth of spectroscopic and photochemical information available. Some other promising candidates might be Br_2 , ICl , Cl_2CO , Cl_2CS , $c\text{-CH}_2\text{N}_2$, and substituted acetylenes. Some molecules exhibit spontaneous predissociations, field-induced predissociations, and collision-induced dissociation. Research directed toward the development of photopredissociation could be quite fruitful.

Photochemical Separation. Mercury,^{5,22} carbon,²³ oxygen,²³ and chlorine²⁴ isotopes have actually been enriched photochemically. A resonance lamp with a ^{202}Hg filling excites primarily ^{202}Hg . The excited atoms are then trapped by reactions with simple molecules such as H_2O , O_2 , or HCl . The laser opens up this separation method for many systems. Even for such an ideal example as mercury, a laser source could be a considerable advantage.

An attempt to separate Br_2 by 6943-Å ruby excitation was foiled by the fact that $\text{Br}_2^* + \text{olefin}$ collisions yielded Br atoms rather than molecular products.²⁵ Under the conditions of the experiment Br atoms initiated isotopic scrambling through free-radical chemistry.

One is tempted to believe that numerous possibilities exist for photochemical separations of atoms and molecules. Since excitation energies are on the order of chemical bond energies, separations should be chemically clean. There is a considerable experimental and theoretical photochemical literature. A cursory examination is sufficient to demonstrate that real photochemical systems are complicated and messy. However, the reward of clean isotope separation in bulk gases at high efficiency is more than ample incentive to dig in.

Vibrational Photochemistry. The chemical reaction rates of vibrationally excited molecules have not yet been thoroughly studied. There is, however, ample evidence that vibrational excitation can reduce the activation energy of a chemical reaction—often by as much as the energy of vibrational excitation itself.^{26,27} Reaction rate increases of many orders of magnitude are to be expected. An idealized isotope separation scheme is shown in eq 17–19.



For separation to occur some rather special condi-

tions must prevail: (1) the rate of the thermal reaction must be much less than the rate of vibrational excitation averaged over the entire time for which the reactants are mixed; (2) the state pumped, ${}^1\text{AB}(v = n)$, must be at least partially depleted by reaction 18 rather than by energy transfer (eq 19); (3) the undesired isotope must not be excited to $v = n$ by energy transfer; (4) the reverse of reaction 18 as well as all other product loss and isotope mixing reactions must be suppressed. The advantages are that vibrational spectra are simpler than electronic, that bulk gases may be used, and that laser energy requirements could be low.

By way of example we might consider a mixture of HCl , Br_2 , and Br . H^{37}Cl may be excited to $v = 2$ by a tunable laser near 1.8μ .²⁸ The reaction $\text{H}^{37}\text{Cl} (v = 2) + \text{Br} \rightarrow \text{HBr} + {}^{37}\text{Cl}$ should proceed rapidly and at a rate 10^{12} times that of the endothermic $v = 0$ reaction. Energy transfer with $n = 2$, $m = 1$ requires 65 HCl-HCl collisions.²⁸ A photolytically produced Br pressure comparable to the HCl pressure should ensure that reaction competes with transfer. Since experimentally observed energy-transfer processes with $m = 1$ require in the range of 1 to 10^3 collisions,²⁹ it is important that (18) be fast and therefore that C be highly reactive. Energy transfer will cause isotope scrambling for $m = n = 2$. This could occur in as few as 100 collisions for HCl , since for $m = n = 1$ only 10 collisions are required in HCl .²⁸ The ${}^{37}\text{Cl}$ atoms produced by (18) would rapidly form ${}^{37}\text{ClBr}$ through reaction with a large excess of Br_2 . The products could then be separated from the depleted HCl .

Separation of H from D has been reported by Mayer, *et al.*⁴ They used an HF laser near 2.7μ to excite the OH stretching vibration of CH_3OH in a mixture made from CH_3OH , CD_3OD , and Br_2 . It was reported that following the laser-induced chemical reaction the remaining alcohol was CD_3OD . The reaction was carried out with about 10^3 photons per molecule of CH_3OH reacted. More experimental data will be needed before the results of this experiment can be fully interpreted.^{4,15}

Enrichment for ^{14}C Dating

The principles, history, and practice of ^{14}C dating have recently been discussed in this journal by Libby.³⁰ It suffices to mention here that the abundance of ^{14}C in living matter is one part in 10^{12} and that its concentration decreases by a factor of two each 5730 years after it ceases to draw CO_2 from the atmosphere. The sensitivity of the ^{14}C dating technique is limited by the noise background of the counters which are used to detect ^{14}C disintegrations from the sample. Isotopic enrichment would allow the ^{14}C from a particular specimen to be concentrated and counted in a very small counter with a much reduced background noise level. For large objects or geologic formations orders of magnitude more ^{14}C could be placed in the counter. Enrichment by four or five orders of magnitude in one step is expected from the formaldehyde photopredissociation method.

(22) B. H. Billings, W. J. Hitchcock, and M. Zelikoff, *J. Chem. Phys.*, **21**, 1762 (1953).

(23) G. Liuti, S. Dondes, and P. Harteck, *J. Chem. Phys.*, **44**, 4052 (1966).

(24) W. Kuhn and H. Martin, *Z. Phys. Chem., Abt. B*, **32**, 93 (1933).

(25) W. B. Tiffany, *J. Chem. Phys.*, **48**, 3019 (1968).

(26) T. J. Odiorne, P. R. Brooks, and J. V. V. Kasper, *J. Chem. Phys.*, **55**, 1980 (1971); L. J. Kirsch and J. C. Polanyi, *ibid.*, **57**, 4498 (1972).

(27) M. I. Buchwald, R. McFarlane, and S. H. Bauer, Laboratory of Plasma Studies, Cornell University, Report No. 104, 1972.

(28) S. R. Leone and C. B. Moore, *Chem. Phys. Lett.*, **19**, 340 (1973).

(29) C. B. Moore, *Advan. Chem. Phys.*, **23**, 41 (1973).

(30) W. F. Libby, *Accounts Chem. Res.*, **5**, 289 (1972).

Further enrichment could be produced by recycling. The increases in sensitivity thus achieved would allow smaller and older samples to be dated.

It has been shown above that a high degree of selectivity should be achieved in the excitation of formaldehyde. Although the greatest enrichment factors could be achieved at pressures below 0.1 Torr, the time and laser energy required to process many moles of sample would be impractical. For a transition with a peak absorption coefficient of $10^{-2} \text{ cm}^{-1} \text{ Torr}^{-1}$ of $^{14}\text{CH}_2\text{O}$ a total energy flux of about 10^{19} photons/cm² or 6 joules/cm² will be required to convert 95% of the $^{14}\text{CH}_2\text{O}$ to ^{14}CO . Since most of the carbon monoxide produced is ^{12}CO we will not be worried by the photochemical complications which may introduce a few per cent of isotopic scrambling. For ^{14}C the enrichment factor will be almost entirely determined by the selectivity of the laser excitation. Cautious but not pessimistic estimates of conditions for separation may be illustrated by two possible sets of conditions. An enrichment of 10^5 at a pressure of 10 Torr could be carried out in a total path length of 10^6 cm using 10 J of laser energy per mole of gas processed. The laser energy is minimal. The 10^6 -cm cell is awkward even with 100 or 200 reflections on 99.5% reflecting dielectric coated mirrors. An enrichment of 10^4 at a pressure of 100 Torr could be achieved with 100 J of laser energy per mole of material and a path of 10^4 cm. The laser and the cell are reaching comparable sizes here. Before optimum conditions for enrichment can be determined, high-resolution spectra of $^{14}\text{CH}_2\text{O}$ will need to be measured and the excitation selectivity determined experimentally. It will also be essential to know what quantities of material and enrichment factors will be useful in dating work.

Conclusion

The subject of laser separation of isotopes has

been a topic of luncheon conversation for several years. Now that a separation has been carried out, the time is ripe for rapid laboratory test and development of practical schemes. Conversation about which elements would be most useful takes on real meaning; there are 60 or so to separate.

The isotope ^{235}U is currently the most important economically. During the next few decades, before large-scale electrical power generation by breeder reactors or fusion reactors, increased use of enriched uranium fuel will help to conserve fossile fuel resources in the face of increasing energy use.³¹ It is anticipated that tens of billions of dollars will be spent during that time in the United States on uranium separation. A substantial decrease in this cost would have a significant effect on electrical power prices. A more far dramatic effect to consider is the availability of fissionable material for bomb construction. The basic concepts of laser separation of isotopes are simple and can neither be hidden nor escaped. The possibility of relatively cheap, simple, small-scale production of ^{235}U is neither great nor wisely ignored. At this point it is not yet clear that ^{235}U separation by lasers will even be practical with highly sophisticated technology and engineering, much less with simple means.

My personal prejudice is that the real excitement and new directions in science and technology will come from the application of the stable isotopes of many elements to problems which we have never been able to tackle before.

I am especially indebted to E. S. Yeung whose work on formaldehyde is the cornerstone of this account. I am also grateful to B. B. McInteer and W. F. Libby for suggestions on ^{14}C dating. The Miller Institute for Basic Research in Science has supported this work through a professorship.

(31) "The Energy Crisis, Part I," *Bull. At. Sci.*, 27 (7) (1971).