Infrared Photochemistry (II): Multiphoton Isotope Separation

Over the last 2 years, scientists have discovered that they can selectively isolate and collect a wide variety of isotopes when they irradiate gaseous samples containing mixtures of isotopes with a powerful infrared laser. They used a carbon dioxide (CO_2) laser that was tuned to one of the absorption frequencies of the gas. Since researchers had suspected that the primary effect of irradiating an object with a high-power laser would be a generalized heating of the area absorbing the light, the discovery has been met with no little surprise.

Several groups in the United States, the Soviet Union, West Germany, Israel, and elsewhere are now busily—and competitively—racing to devise theories and experiments that will help explain what is still an incompletely understood phenomenon. The possibility exists that a new way to selectively synthesize specific compounds by infrared photochemistry will result from such research. But a principal goal right now is to understand the process, called multiple photon infrared photodissociation, well enough to apply it to the problem of separating uranium-235 from uranium-238 in order to produce enriched uranium for nuclear reactor fuel (or for nuclear weapons).

Also of considerable interest would be separation of deuterium from hydrogen for use in heavy water reactors, such as the Canadian CANDU, and separation of uranium-235 and plutonium-239 from spent nuclear fuel as part of a reprocessing cycle. Numerous other isotopes are or could be in demand as radioactive sources for medicine (diagnostic or therapeutic), scientific research, and industry.

In the United States, research on laser isotope separation has become big business, with the Energy Research and Development Administration (ERDA) committed to spend nearly $31 million in fiscal 1977 on all aspects of laser processes for separating uranium isotopes; and at least one company, Jersey Nuclear-Avco Isotopes, Inc., is planning a $15-million experimental test facility for laser enrichment of uranium. The attraction of the multiple photon infrared photodissociation phenomenon is that it seems to require only one laser rather than the two (or one laser and an ultraviolet flash lamp) needed in other available techniques (*Science*, 19 March, p. 1162), hence it is simpler and potentially more economical than any of the latter.

As a laboratory experiment, multiple photon infrared photodissociation is extremely straightforward—so much so that Curt Wittig and C. R. Quick of the University of Southern California are planning an experiment for undergraduates on the dissociation of sulfur hexafluoride (SF_6). One needs a gas-filled reaction cell—SF_6 is the most commonly studied compound—and a pulsed CO_2 laser that emits infrared pulses with energies of the order of 1 joule per pulse and with a variable pulse length of a few nanoseconds to microseconds.

By adjusting the pulse length, focusing the laser light, and tuning the laser to an absorption frequency of molecules containing a particular isotope, researchers can inject up to a few gigawatts per square centimeter into the gas, energy that is absorbed selectively by the target molecules. The absorbing molecules dissociate, and the resulting isotopically selected fragments react with molecules of a residual gas left in the reaction cell or with molecules of a gas specifically added for that purpose (scavenger molecules). The scavenged species can then be separated from the cell contents.

Despite the apparent simplicity of the technique, researchers took some time to grasp the possibilities of high-power infrared irradiation. Absorption of infrared photons is usually thought to cause gas molecules to become vibrationally excited. But collisions between molecules can rapidly cause the vibrational energy to be converted into translational energy. (How rapidly depends on the gas pressure.) Thus, collisional deexcitation by the V-T process, as it is known, simply heats the gas. Since all molecules, even those not absorbing the laser light, are heated, no selectivity results, isotopic or otherwise.

Collision-Free Dissociation

Experiments by Neil Isenor of the University of Waterloo and Martin Richardson of the National Research Council of Canada in Ottawa provided one of the first hints that collisional deexcitation was not always the dominant process. These investigators irradiated certain gaseous compounds with CO_2 laser pulses of 10^8 to 10^9 watts per square centimeter, whereupon they observed visible fluorescence. Several infrared photons are needed to excite a molecule sufficiently to allow it to emit visible fluorescence. Hence, the researchers reasoned, many such photons were either absorbed simultaneously or so rapidly in succession that collisions did not have time to deexcite the molecules before they reached a high state of excitation.

Although the correctness of this logic and the corollary that a collisionless excitation process has the potential of being highly selective now seems well established, it was 3 years after the Canadian discovery before accounts of such an experiment were published.

Separation of boron isotopes (boron-10 and boron-11) by laser irradiation of boron trichloride (BCl_3) was announced nearly simultaneously by two groups in the fall of 1974. In the Soviet Union, researchers led by Vladilen Letokhov and Raphael Ambartsumian of the Institute of Spectroscopy, Moscow, demonstrated isotopic selectivity by monitoring the spectrum of the luminescence emitted by boron oxide when they tuned the CO_2 laser to a particular vibrational mode in boron trichloride. Boron oxide formed when boron from the dissociated molecules reacted with oxygen that was also in the cell. The luminescence shifted in frequency according to whether $^{10}BCl_3$ or $^{11}BCl_3$ was excited. Later on, the same group used infrared spectroscopy to obtain evidence for actual separation of isotopes. They found that the magnitude of the infrared absorption of the $^{10}BCl_3$ or $^{11}BCl_3$ remaining in the reaction cell was reduced according to which molecule was photodissociated.

In the United States, Samuel Freund (now at the Los Alamos Scientific Laboratory in New Mexico) and Joseph Ritter of the National Bureau of Standards, Gaithersburg, Maryland, reported separation of the boron isotopes at about the same time as the Institute of Spectroscopy group. Freund and Ritter used dihydrogen sulfide as a scavenger. Apparently, the boron trichloride was not dissociated by irradiation with the CO_2 laser. Instead, it was excited to a very high vibrational level where reaction with the dihydrogen sulfide was enhanced. Gaseous hydrogen chloride and certain solid products were chemically separated from the boron trichloride reagent, which was found to be enriched in either boron-11 or boron-10, depending on the laser frequency.

Since then the focus of interest has shifted to separation of sulfur-32 from sulfur-34 in SF_6, perhaps because this compound is exceptionally easy to dissociate with a CO_2 laser and because it may bear some resemblance to uranium hexafluoride, the molecule that would be of interest for separating uranium isotopes. According to Paul Robinson at Los Alamos, however, researchers there have set up a working table-top model of a boron separation plant that can collect about 1 gram of boron-10 per day. This isotope is of interest as a neutron absorber for control purposes in reactors. The laser isotope separation project at Los Alamos, headed by Robinson and Reed Jensen, has also become the principal competitor in infrared photodissociation research to the Soviet group.

As of this date, in addition to isotopes of boron and sulfur, researchers at several institutions have demonstrated selective excitation and separation of isotopes of hydrogen, carbon, silicon, chlorine, osmium, and molybdenum contained in various organic and inorganic compounds. The molybdenum experiments are especially interesting because, as compared to that of SF_6, the spectrum of molybdenum hexafluoride, a heavy molecule, is more like that of uranium hexafluoride. Researchers at Los Alamos have obtained about 15 percent enrichment of molybdenum-92 with respect to molybdenum-98.

In the case of SF_6, the Soviet researchers have shown that irradiating with several hundred laser pulses can increase the ratio of sulfur-34 to sulfur-32 in naturally occurring sulfur by several hundredfold. The Los Alamos group has reported lower enrichment ratios, but they also used a different experimental geometry. Exact enrichment ratios depend on such variables as the laser frequency, the pulse energy, the length of the pulse, the number of pulses, and the gas pressure in the reaction cell. The latter factor is especially important because of the increasing probability of collisions as the pressure rises, and the best results for SF_6 are obtained for pressures of 1 torr or less.

Although laser intensities were about 10^9 watts per square centimeter in the original experiments, recently investigators have found that the apparent threshold for laser dissociation of SF_6 could be orders of magnitude smaller. For example, Dennis Keefer and Willis Person of the University of Florida have found a threshold as low as 21×10^6 watts per square centimeter when the pulse length was 200 nanoseconds and 6×10^6 watts per square centimeter when the pulse length was 3 microseconds. The threshold also increased with the gas pressure.

At Moscow's Institute of Spectroscopy, Letokhov, Ambartsumian, and their associates recently reported another and, to many theorists, somewhat puzzling result. Using two lasers, the first having a low power and being tuned to a particular vibrational absorption frequency and the second having a much higher power but not being tuned to any resonant frequency, the investigators were able to obtain even higher separation yields than previously. And the

Speaking of Science

The Petroleum Plant: Perhaps We Can Grow Gasoline

The notion of obtaining fuels and energy from plants grown for that purpose has not yet won many converts among either federal energy officials or industrial scientists. But investigators who believe in the concept have not been deterred; they have kept studying sugar cane, kelp, trees, and other high-yield plants. Now a new candidate, shrubs that produce a hydrocarbon substance very much like gasoline, has been proposed by Nobel laureate Melvin Calvin of the University of California at Berkeley The shrubs, members of the genus *Euphorbia*, produce significant quantities of a milklike sap—called latex—that is actually an emulsion of hydrocarbons in water. These hydrocarbons are similar to those produced by the rubber tree, but are much lower in molecular weight. Their size distribution is similar to that of hydrocarbons in petroleum, Calvin says, and the crude hydrocarbon produced by the plants could probably be used directly in existing refineries after it has been separated from the water.

Calvin told the recent Centennial Meeting of the American Chemical Society that he has high hopes for two species in particular: *Euphorbia lathyrus*, also known as the gopher plant, a small bush that grows wild in northern California; and *Euphorbia tirucalli*, a much larger bush that is used as a hedge in Brazil, but which should grow well in southern California. A major advantage of these plants, he argues, is that they should grow well in dry regions on land that is not suitable for growing food. He estimates that the plants might be capable of producing between 10 and 50 barrels of oil per acre per year.

After the plants reach the proper height, he says, they would simply be cut near the ground and run through a crushing mill in much the same fashion as is done with sugar cane. Hydrocarbons would be obtained from the resultant sap with technology that is already available for separating emulsions of oil and water. The plants themselves would regrow from the stumps, so replanting might be necessary only once every 20 years or so. Calvin optimistically estimates that the cost of crude hydrocarbons obtained in this manner would be somewhere between $3 and $10 ber barrel. The oil, furthermore, would be practically free of sulfur and other contaminants.

As might be guessed from the skepticism with which Calvin's estimates have been met, the concept is still very tentative and there are few hard facts from which to draw any conclusions about its potential viability. More facts will be available in a couple of years, though. Calvin has already begun experimental planting of *E. lathyrus* on his ranch in northern California, and he is negotiating with the University of California at Davis for a test planting of *E. tirucalli* there. He has also discussed this concept with energy and agricultural officials in Brazil, and the Brazilian national petroleum company, Petrobras, is now investigating the shrubs. Calvin's first goals are to obtain information about the plant's requirements for water and care and to determine the potential yields. Only with this information will it be possible to say anything about the feasibility of the project.

Substantial quantities of land might be required to implement Calvin's proposal. He estimates, assuming a yield of 40 barrels per acre, that an area the size of Arizona would be necessary to meet current requirements for gasoline. It would obviously also require a substantial initial investment to get the project going. But the investment might be a sound one. Even if cheaper sources of energy for transportation and heating are eventually found, *Euphorbia* might well turn out to be an enduring and stable source of raw materials for the petrochemical industry. —T.H.M.

threshold at the first laser frequency was reduced to only 50 kilowatts per square centimeter.

Theoretical understanding of the photodissociation phenomenon is not yet far advanced. The essential theoretical problem, and perhaps the one responsible for the slow recognition of the potential of multiphoton photodissociation, is the anharmonic nature of the vibrational states in real molecules. In an idealized picture in which molecular vibrations are modeled by harmonic oscillators, a given vibrational mode has states equally spaced in energy. In real molecules, which are anharmonic oscillators, the spacing between higher-lying states becomes progressively smaller. The question is thus: How can several laser photons of the same energy be sequentially absorbed to drive the oscillator to higher and higher vibrational states until it dissociates?

A phenomenological answer has been given by Letokhov, Ambartsumian, and others at the Institute of Spectroscopy and by David Larsen of MIT's Lincoln Laboratory, Lexington, working with Nicholas Bloembergen of Harvard University. These scientists suggest that the energies in the manifold of rotational states associated with each vibrational state are spaced in such a way that their spread in energy compensates for the unequally spaced states of the anharmonic oscillator.

The dissociation energy of SF_6 is equivalent to about 30 CO_2 laser photons, more than even this compensatory arrangement of energy levels will allow. Thus, scientists have postulated that at sufficiently high levels of vibrational excitation, the vibrational-rotational states of one vibrational mode overlap in energy with those of another mode. The effect is of a "quasi-continuum" of states, one of which is always at the right energy to absorb a photon. Once in the quasi-continuum, the molecule can continue to absorb photons until enough energy is stored to permit dissociation. According to Andrew Kaldor of the Exxon Research and Engineering Company, experiments there indicate the onset of the quasi-continuum is above the fifth or sixth vibrational state.

This somewhat arbitrary division into two classes of quantum states also qualitatively explains the two-laser results from the Institute of Spectroscopy. The low-power laser is the agent which selectively excites molecules containing the isotope of interest. Selectivity occurs because the laser must be tuned to a resonant frequency of the molecule. Once molecules are selectively excited, then the high-power laser drives only these molecules through the quasi-continuum to dissociation. Tuning to a resonant frequency is not needed for this stage.

Several groups of theorists have constructed models for the stages of this process. For example, Larsen and Bloembergen calculated the response of a single anharmonic quantum mechanical oscillator (corresponding to one vibrational mode) to a high-intensity electromagnetic field. Their conclusion was that, in the lower energy states—those below the quasi-continuum—a process called coherent multiphoton absorption was dominant. Multiphoton is taken to mean that two or more photons are absorbed simultaneously. Coherent means that the populations of the lower and upper states in the transition oscillate in time with a characteristic frequency, which increases with the laser intensity and with the strength of the transition between the states.

The transition probability is strongly affected by the energies of states with energies lying between the upper and lower states of the transition. If these energies approximately match those needed for the sequential absorption of single photons, then the multiphoton transition is said to be resonantly enhanced and can become quite large.

Not So Anharmonic After All

If recent molecular structure calculations by Cyrus Cantrell and Harold Galbraith are correct, then the resonant enhancement could be quite large indeed. Highly symmetric molecules, such as SF_6, have degenerate vibrational modes—that is, several vibrational states can have the same energy. Cantrell and Galbraith, who are at Los Alamos, have numerically calculated the energy level structure of SF_6 up to the tenth vibrational state for the ν_3 mode, which is the one normally excited by laser radiation in dissociation experiments and corresponds to an asymmetric stretching motion. Cantrell and Galbraith find that, when the anharmonic character of SF_6 is fully accounted for, the normally degenerate ν_3 states split into several states having different energies. The effect is that of having the evenly spaced states of a harmonic oscillator, and the probability of multiple photon transitions increases concomitantly.

Although the calculations are based on existing knowledge of the molecular structure of SF_6, corroboration of these calculations awaits experimentalists' sorting out the absorption spectrum of this molecule, which is incredibly complex. Researchers have described it as a sea of grass, with each blade corresponding to one line of the spectrum. Only recently have Robin McDowell and his collaborators at Los Alamos succeeded in identifying many of the specific transitions responsible for the spectrum lines.

A different approach to this problem has been taken by Aram Mooradian and Peter Moulton of Lincoln Laboratory in their optical double resonance experiments on SF_6. The investigators first vibrationally excite the molecule with a pulsed CO_2 laser. Then they measure the change in the absorption of light from a tunable semiconductor diode laser due to the vibrational excitation. Rather than hundreds of absorption lines, they find a simple spectrum of only a few lines, which they can identify relatively easily. However, the experiments are still at too early a stage to compare with Cantrell and Galbraith's predictions.

In the model of Larsen and Bloembergen, molecules in the upper state of the multiphoton transition then sequentially absorb additional photons to reach the quasi-continuum and eventually dissociate. To model this process, however, inclusion of vibrational modes other than ν_3 is needed. Such a theoretical model to describe how molecules reach the quasicontinuum and progress through it has been constructed by Myron Goodman, James Stone, and David Dows of the University of Southern California.

The Southern California researchers took account of a phenomenon known as power broadening and the enhanced power broadening associated with degenerate quantum states. As molecules are driven from the lower state to the upper state and back again in the coherent laser field, they necessarily reside in neither state for very long. By the Heisenberg uncertainty principle, a short-lived quantum state has an uncertain energy—that is, its energy level is broadened—and the shorter the lifetime, the more the broadening.

At very high laser intensities, the coherent oscillation between states is very rapid, and the energy broadening of the quantum states can be substantial enough to ensure that transitions that normally would not occur because their energy did not quite match the laser frequency can now take place. The power broadening compensates for the mismatch.

Thus, taking account of power broadening, degeneracy of the vibrational states, and the possibility of energy overlap of states from different modes in the quasi-continuum, the investigators were able to calculate a dissociation threshold for SF_6 of about 17×10^6 watts per square centimeter for a 200-nanosecond pulse. This value compares favorably with that obtained experimentally at

Florida. However, the model does not as yet use a realistic set of vibrational states, and Goodman and his associates are currently using a more realistic set of states in an improved treatment of the selective step of the dissociation.

Other groups that have treated one or more aspects of the photodissociation process theoretically include Joshua Jortner and Shaoul Mukamel of Tel Aviv University, Israel, A. A. Makarov and Letokhov of the Institute of Spectroscopy, and C. James Elliott and Barry Feldman of Los Alamos.

None of these treatments is regarded as definitive at present. In fact, some investigators are even adopting a classical mechanics approach for calculating multiple photon dissociation rates. One motivation for such a sentiment lies in the complexity of even such a simple molecule as SF_6. Few theorists believe that an accurately detailed, fully quantum mechanical model will ever appear because the calculations would not be tractable. Classical calculations would involve much less irrelevant detail than quantum calculations and might be done numerically on a high-performance minicomputer, which makes them financially affordable as well.

Willis Lamb of the University of Arizona, who has been studying the interaction of classical oscillators and coherent driving forces for many years, is one advocate of a classical mechanics approach. Ted Cotter of Los Alamos, who is a visiting scientist at the Project Group for Laser Research (formerly the Max Planck Institute for Plasma Physics), Garching, West Germany, is another.

Cotter is especially enthusiastic about some recent calculations he has completed, which, he says, agree very well with published values of dissociation thresholds, enrichment yields, and other parameters in SF_6 experiments. In Cotter's classical treatment of a single anharmonic quantum oscillator, the effect of the laser is to coherently and simultaneously excite all the states in the dominant vibrational mode, and thus is not like the coherent multiphoton process of Larsen and Bloembergen. Provided that the anharmonicity is not too large (Cotter believes it is small), a smeared region of quasi-continuous states from several vibrational modes is not needed for dissociation to occur. Thus, says Cotter, the simplifications needed to make the quantum calculations possible have tended to obscure the real physics of the dissociation process.

Lamb, however, believes that mixing of different vibrational modes at high energies (the quasi-continuum region) is needed to keep the theoretical dissociation threshold values as low as the experimentally measured ones, but he has not completed calculations to show this. In his work so far, Lamb has shown that at low energies, where the vibrational states are spaced widely apart and where quantum mechanical effects should be most evident, the agreement between the results of classical and quantum calculations is quite close, thus providing support for the classical mechanics approach.

Experimental work on the chemistry that occurs following the dissociation is really just getting under way. In the case of SF_6, the chemistry is not critically important, because residual oxygen in the reaction cell reacts quickly with the dissociation products. For more interesting molecules, however, the choice of the proper scavenger could be crucial to the high rates of production needed for an economically viable process.

New Reaction Channels Possible

At Garching, Karl Kompa, W. E. Schmid, and H. Stafast have begun molecular beam experiments. They irradiate a beam of SF_6 molecules in high vacuum with a high-power CO_2 laser and use a mass spectrometer to determine the identity of the initial dissociation fragments. Preliminary results indicate that SF_6 dissociates into SF_4 and F_2. Researchers at Exxon also have some evidence to support the same conclusion.

This result is a surprising one because the lowest energy, and thus expected, dissociation products are SF_5 and F. The possibility of driving the dissociation into a higher-energy reaction channel carries with it the exciting prospect of new chemical processes in synthetic chemistry, as well as in isotope separation, according to some observers. However, Yuan Lee and his colleagues at the University of California at Berkeley are in fact finding in their molecular beam experiments that SF_5 and F are the primary dissociation products. Obviously there is more work to be done.

At the National Bureau of Standards, Walter Braun and Wing Tsang have been using gas chromatography (GC) to analyze the dissociation products in their experiments with certain alkyl halides. In these nonisotope-selective studies of heavy (as compared to SF_6) organic compounds, the possibility exists that the initial dissociation products are further changed by irradiation with photons from the same laser pulse that caused the dissociation. Thus, analysis of the end products may not be informative as to what the intermediate products are.

To help sort out the situation, the NBS scientists infer from the final products of the dissociation what the intermediates may have been. Then they load their reaction cell with a sample of the putative intermediate and irradiate it. The investigators have placed a GC loop and conventional gas mixing system close to the sample chamber so that products can be analyzed after a few laser pulses and new samples can be injected into the chamber in a very short time. Results so far indicate that the intermediate products are indeed the ones expected thermodynamically.

Of considerable interest for now is the question: How applicable is the technique to uranium separation? The answer is not yet known, in part because the subject is so heavily classified, but some speculations are possible.

For uranium hexafluoride, the wavelengths of the absorption bands corresponding to the ν_3 absorption in SF_6 are near 16 micrometers, as compared to 10.6 micrometers in the lighter molecule. Thus, the CO_2 laser, which emits numerous discrete lines between about 9 and 11 micrometers cannot be used. Instead some yet to be developed 16-micrometer laser is needed to vibrationally excite uranium hexafluoride molecules.

In the so-called two-step molecular dissociation method that has been the principal focus of research at Los Alamos, a second ultraviolet laser would be used to photodissociate the selectively excited molecules. An alternative procedure that might be envisioned, if researchers find that achieving a 16-micrometer laser powerful enough for multiple photon dissociation is too formidable a task, is to replace the ultraviolet laser with a high-power laser that need not emit at 16 micrometers. Infrared multiple photon dissociation from selected, vibrationally excited uranium hexafluoride would replace ultraviolet single photon photodissociation. However, other technical details could prevent straightforward application of such a technique to uranium.

Deciding which of the two processes to use, if any, will in the end be an economic question. A major consideration is the relative efficiencies of the multiple photon dissociation and the ultraviolet single photon dissociation. According to Robinson at Los Alamos, in the case of boron trichloride and the CO_2 laser, the advantage seems to lie with the infrared process. For uranium, the issue is unresolved.—ARTHUR L. ROBINSON

Additional Readings

1. V. S. Letokhov and C. B. Moore, *Sov. J. Quant. Electron.* **6**, 129 (1976); *ibid.*, p. 259.
2. J. P. Aldridge, J. H. Birely, C. D. Cantrell, D. C. Cartwright, *Phys. Quant. Electr.* **4**, 57 (1976).