
Laser chemistry: economical because it is nonlinear

Robert Gallagher refutes the thinking of those who claim industrial applications of laser chemistry will cost too much, and reviews the methods to be used.

The Strategic Defense Initiative is advancing laser technology across a broad front and will produce many technologies applicable in industry. Research into optical biophysics required to develop an understanding of the AIDS virus, and develop a vaccine, will advance our knowledge of photochemical processes far beyond their present primitive level. Nonetheless, despite these demands for advancement in science and technology, there has been considerable debate over the economy of using lasers in industrial chemical processes. Many writers have argued that since the cost of laser photons (units of coherent radiation) is hundreds of times more than the price of most bulk-produced industrial chemicals, laser chemistry processes will not find widespread application in industry because they appear uneconomical. If a process depends on the use of one photon to produce one atom or molecule of product, then it will only be economical if the value of the product is extraordinarily high, such as enriched uranium fuel for nuclear reactors. Therefore, some believe that use of lasers would only be economical in specialty production where even with the use of one photon per molecule or atom of product, photon cost will account for a small fraction of overall cost.

This argument fails on at least two counts. First, it rests on current economic conditions. The operating cost of lasers that will be used in industry in the future (such as free electron lasers), will scale directly with the cost of electricity. Entirely for political reasons, the cost of electricity today (on which the calculations of the cost of laser photons are partially based) is about 10 times greater than it was in 1965. A rational energy policy based on nuclear power would return the cost of electricity to at least 1965 levels and thus reduce the operating cost of lasers by an order of magnitude. Commercial nuclear fusion power would bring the cost of electricity (and

therefore laser radiation) down even more.

Second, and more important, successful laser-assisted chemistry processes are economical because they are based on the selective and nonlinear action of coherent radiation. An example of this is a process developed by J. Wolfrum of the Max Planck Institute for Research in Hydrodynamics (Göttingen, Federal Republic of Germany). Absorption of a single photon of ultraviolet light initiates a chemical chain reaction that produces more than 10,000 molecules of vinyl chloride, a principal feedstock used by the chemical industry for the manufacture of polymers. Photon cost ceases to present a problem because the product yield in molecules per photon absorbed (known as the *quantum yield*) is so high.

Fortunately, many of the synthetic reactions used in the production of industrial bulk chemicals, like vinyl chloride synthesis, involve chain reactions initiated by the production of highly reactive chemical "free radicals" (atoms or groups of atoms possessing an odd number of electrons, such as chlorine), which "link" the chain reaction so that it propagates. In comparison with methods of producing free radicals by heat or flashlamps, laser radiation is more selective. As a result it is possible to increase the lengths of the chemical chain reaction by an order of magnitude or more.

All that is required to make lasers economical in many bulk industrial chemical processes is the identification of the particular wavelength(s) of laser radiation whose absorption will optimize free radical production and maximize chemical chain reaction lengths, product output per photon absorbed, and quantum yield. **Figure 1** shows that with a high enough quantum yield, even cheap chemicals like methyl chloride or ethylene can be produced economically with laser photochemistry. (The figure shows the cost of both photons and chemicals in units of dollars per mole. One mole is equal to

6×10^{23} quanta of a substance. Laser photons cost about \$1-2 per mole, while most industrial chemicals cost only a few pennies to a few mills per mole.)

Degrees of freedom

The contention that laser-assisted processes are uneconomical for production of relatively cheap chemicals, appears to be wrong. Indeed, just as misguided is the reasoning that lasers are economical for the production of materials with high price-tags only because laser radiation costs are, in such cases, low relative to product value. This derives from a misunderstanding of the one laser chemistry process that preoccupied laser chemists over the past decade: laser separation of uranium isotopes for production of nuclear fuel.

In atomic vapor laser isotope separation, the quantum yield is low compared to vinyl chloride synthesis (about 10 for production of commercial enriched uranium fuel and theoretically 0.33 for pure U-235); this is because it takes at least three photons to ionize a single atom of the desired U-235 isotope for extraction from the uranium feed. It thus appears, from an accountant's standpoint, that the photon

economics are poor. This is an improper conclusion.

Enriched uranium is expensive only because the product is more difficult to produce than industrial chemicals. There are *fewer degrees of freedom available* by which laser radiation (or any other kind of physical action, for that matter) can separate uranium isotopes, than accomplish practically any other chemical task. The extreme difficulty of laser isotope separation, and its success in laser uranium enrichment, prove that simpler chemical tasks, that have more degrees of freedom available for photochemical action, and whose products are consequently less expensive, will be economical once the appropriate path of nonlinear least action photochemistry is discovered.

It is the powerful nonlinearity of laser processes that makes them economical. Probably the best presentation of such processes appears in *Nonlinear Laser Chemistry* (Springer-Verlag, 1983) by V.S. Letokhov of the Institute of Spectroscopy of the Soviet Academy of Sciences. Remarkably, this book, finished in 1982, remains "the most complete treatment of nonlinear laser chemistry available," according to a laser chemist who plays a leading role in the U.S. laser isotope separation program. It is unfortunate that U.S. surveys of the field (at least unclassified ones), are less general and less optimistic than Letokhov's.

One application of nonlinear laser chemistry is to selectively excite atomic or molecular species until a desired transformation has occurred that allows production of a finished or semi-finished product. Among the methods of nonlinear laser chemistry discussed by Letokhov and others are:

1) Multi-step selective excitation-transformation of atoms or molecules.

This technique is employed in isotope separation, and other applications; Letokhov has proposed this as one method of selective photochemistry with bio-macromolecules, such as the nucleic acids, DNA, and RNA.

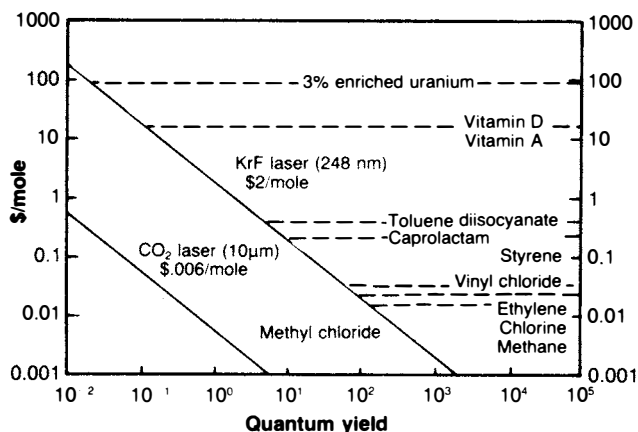
In multi-step excitation, an atom or molecule absorbs a sequence of two or more photons of coherent radiation with wavelengths that are resonant with a sequence of quantum state transitions through which the laser light is said to drive the excited atomic or molecular species. In other words, the photon energies match those of the transitions. (A photon is a quantum of coherent radiation; photons are presently quantified in units of the wavelength of radiation.)

In atomic vapor laser isotope separation, coherent orange light of three distinct wavelengths excites an atom of uranium-235 through three quantum transitions to ionization. The excitation energies of the three transitions total 6.19 electron volts (eV) (Figure 2). (One electron volt is said to equal about 4×10^{-26} calories.)

In accordance with quantum theory, to be excited through multiple steps, an atom or molecule must absorb in sequence, a number of photons equal to the number of transitions and whose photon energies must equal the excitation energies of the sequentially corresponding transitions. If there is a range or band of photon wavelengths that may produce a transition,

FIGURE 1

Laser photochemistry: economics



Photochemical processes with a high quantum yield (the number of product molecules—or atoms—per photon of coherent radiation absorbed) are economical regardless of the cost of photons. The figure shows, on the right, the price per mole of selected products. For comparison, on the left, the hypothetical cost per mole of product, produced with the carbon dioxide and krypton fluoride lasers is plotted for a range of quantum yields (solid lines). The intersection of the dotted line at the height of the cost of a chemical with one of the laser cost lines, indicates the quantum yield at which a laser process becomes economical even in today's economy. For quantum yields greater than 1000, laser production of bulk industrial chemicals becomes economical.

Source: K.V. Reddy, "Ultraviolet Laser-triggered Chemical Chain Reactions," *Applications of Lasers to Industrial Chemistry*, R. Woodin, A. Kaldor, eds., *Proceedings of the SPIE* 458 (1984).

then the exciting photon must fall within this band. Such a resonance between the wavelengths of the orange photons used in atomic vapor laser isotope separation and the quantum states through which they excite uranium-235, is the basis for its high selectivity in separating the fissionable U-235 from the more abundant U-238 whose quantum transitions differ (see *EIR*, May 15, 1985).

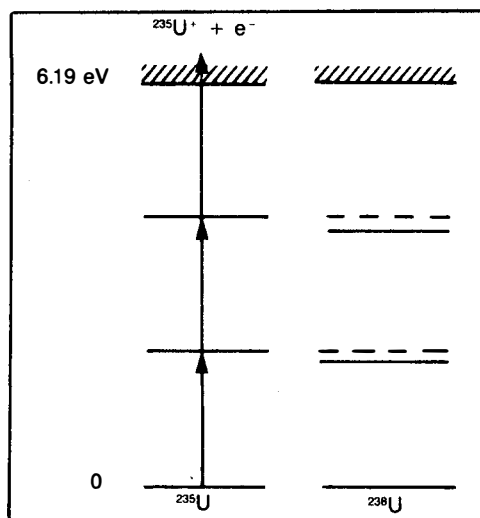
2) Multi-photon excitation of atoms or molecules.

Though in principle this technique appears to violate quantum theory, it has been successfully applied to produce chemical free radicals for the propagation of chain reactions in organic chemical synthesis, to separate isotopes, and to perform many other chemical tasks.

Unlike multi-step excitation, the multi-photon technique does not require absorption of a photon of a wavelength tuned to the absorption band of a quantum transition to excite an atomic or molecular species through it. Absorption of two or more photons none of which are tuned to the transition, and each of whose energy is less than the expected energy of the transition, may produce the transition (**Figure 3a**); or the action of two photons, neither of which is tuned to a transition, may sum to effect the excitation of the atomic or molecular species across two transitions (**Fig. 3b**); or a single photon may accomplish more than one quantum transition, etc.

FIGURE 2

Baseline process



Multi-step excitation of atoms or molecules requires that photons resonate with quantum transitions. Three orange photons that match a sequence of three quantum transitions, excite uranium-235 to ionization in a multi-step process in the atomic vapor laser isotope separation process.

Source: J. Davis and J. Paisner, "Science, Technology, and the Industrialization of Laser-driven Processes," Lawrence Livermore National Lab, May 1985, UCID-20448.

The practical significance of these results, is that they permit use of a wider range of wavelengths of coherent radiation to perform tasks that previously were thought to require a narrow range. They permit a fixed wavelength laser to be adapted to perform tasks to which it was previously thought inapplicable, since the wavelength of its radiation need not fall within a quantum transition's bandwidth. In some cases, product yield and process selectivity can be significantly enhanced.

The U.S. Patent Office issued a patent Feb. 17 to Joshua Zavelovich and Virupaksha Reddy of Amoco Corporation for invention of a process for multi-photon generation of bromine radicals by photochemical dissociation of hydrogen bromide, to initiate chemical chain reactions that produce ethyl bromide from ethylene with a quantum yield greater than 10,000.

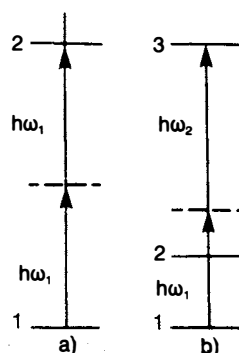
Ethylene is the simplest of the unsaturated hydrocarbons. The unsaturated hydrocarbons, called alkenes or olefins, have less than the maximum quantity of hydrogen in their molecular structure and are characterized by the presence of carbon-carbon double bonds. Zavelovich and Reddy claim that their process will apply to hydrogen bromide reactions with any of the alkenes or olefins, which include propylene, butylene, and other chemicals.

Even if the process is only applicable to ethyl bromide production it will be economically viable. Ethyl bromide is produced from the combination of ethylene with a hydrogen atom and a bromine atom; the reaction sequence is called "hydrobromination." The Zavelovich-Reddy patent (No. 4,643,812) reports: "Ethyl bromide . . . is a commercially significant material which has found use as a refrigerant, as an ethylating agent in organic synthesis, and as a grain and fruit fumigant."

Laser radiation is used in the newly patented process to dissociate hydrogen bromide (HBr) to produce the bromine radical. The single-step electronic transition that produces HBr dissociation has a minimum excitation energy of 3.76 eV, corresponding to absorption of a photon with a wave-

FIGURE 3

Multiple photon excitation



Multiple photon excitation does not require that photon energies match the energies of quantum transitions. In (a), two photons of the same wavelength combine to excite an atom or molecule through a single transition. In (b), two photons of different wavelengths combine to excite an atom or molecule through two transitions.

length of at most 330 billionths of a meter (330 nm). Laser sources are available that produce ultraviolet radiation with photon energy within the bandwidth to dissociate the molecule with a single photon: the xenon chloride laser (193 nm, or 4.03 eV), krypton fluoride (248 nm, or 4.98 eV) and argon fluoride (308 nm, or 6.42 eV), but the radiation of each of these, destructively interacts with the ethyl bromide chain reaction product, dissociating it and reducing the yield. Zavelovich and Reddy discovered, however, that radiation produced by xenon fluoride lasers with a photon wavelength of 351 nm (3.53 eV), if of sufficient intensity, produces HBr dissociation without destructive interaction, even though its radiation is not resonant with hydrogen bromide. Ethyl bromide is transparent to this radiation. The patent states:

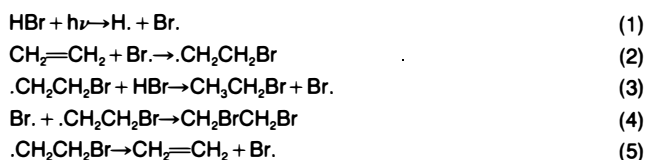
Although the single photon absorption of light by hydrogen bromide is negligible at wavelengths in the range from about 335 to about 500 nm, we have found that coherent light in this range of wavelengths can be utilized to initiate the free radical addition of hydrogen bromide to olefinic double bonds by dissociation of hydrogen bromide into its constituent atoms. The use of photons in this region of the spectrum would not be expected to initiate a free radical hydrobromination process in view of the low absorbance by hydrogen bromide in this region of the spectrum and the fact that these photons have an energy which is less than that which is required to dissociate the hydrogen bromide into its constituent atoms. We have found, however, that at these wavelengths, the very high photon concentrations produced by a laser cause the dissociation of hydrogen bromide by way of an unexpected multiple photon process. . . . Any single photon process is ruled out because light of this wavelength consists of photons having an energy of 3.53 eV, which is less than the hydrogen bromide dissociation energy of 3.76 eV. Only the absorption of two or more photons by hydrogen bromide can lead to its dissociation at 351 nm. There is no state of hydrogen bromide which can be resonant with 351 nm photons. Accordingly, it is believed that the photoinitiation of the hydrobromination of ethylene at this wavelength is by the simultaneous absorption of two photons by a molecule of hydrogen bromide. The sum of the energy of two of the 351 nm photons corresponds to the maximum of a one photon absorption band of hydrogen bromide in the vacuum ultraviolet [7.06 eV].

Laser-initiated free radical chain reactions

The transformation of ethylene to ethyl bromide is a good example of a free-radical initiated chain reaction. In such processes, light or heat produce free radicals by dissociating a molecule that carries a radical, such as bromine. In ethyl bromide production, hydrogen bromide in solution with ethylene, is dissociated into a hydrogen atom and the bromine

TABLE 1

Nonlinear process produces ethyl bromide



Bromine chemical free radical produced by laser dissociation of hydrogen bromide in step 1, initiates but is not consumed by chain reaction of steps 2 and 3. It initiates as many as 10,000 reactions until it is destroyed by collision with the walls of the reactor vessel, or combines with some other reaction product as in step 4.

Source: Zavelovich et al., "Photochemical Process for the Hydrobromination of Olefinic Double Bonds," U.S. Patent 4,643,812, issued Feb. 17, 1987.

radical (Table 1, Equation 1). The bromine atom is highly reactive, because as expressed in chemical theory, like all free radicals, it possesses an electron that is not paired with another of opposite spin. The bromine quickly combines with an ethylene molecule to yield the ethylene-bromine free radical ($\cdot\text{CH}_2\text{CH}_2\text{Br}$, see Table 1, Equation 2), which in turn reacts with a molecule of hydrogen bromide to yield the ethyl bromide product, plus a bromine free radical (Table 1, Equation 3).

The bromine free radical is not consumed in the reactions that produce the ethyl bromide product. It remains available to transform ethylene into ethyl bromide via steps 2 and 3 as shown in Table 1. Production of a single free radical can link the pair of reactions producing the product, into a chain hundreds or thousands of reaction-pairs long. Reaction propagation steps 2 and 3 continue to repeat until the free radical collides with the walls of the reaction vessel (and is neutralized) or is destroyed in a termination reaction (as in Equation 4).

Free radical-initiated chain reactions are widely prevalent in chemical synthesis. Lasers offer several advantages over simple heating or the use of flashlamps for the production of the necessary free radicals.

1) Production of free radicals by thermal means usually requires a higher temperature than that necessary to sustain the chain reaction once it is initiated. These high temperatures may produce undesirable side reactions that reduce selectivity, that is, the proportion of the desired reaction product to all others. The use of lasers to produce the free radicals, eliminates any need for such high temperatures.

2) With heat or flashlamps, the production of the free radicals is not spatially controllable by the chemical engineer. Because of the homogeneous action of heat and the broad divergence of radiation from flashlamps, as many free radicals are produced per unit volume near the walls of the reaction vessel as in the interior. Those produced at the walls

quickly collide with them and are neutralized—reducing the chain reaction length, the number of product molecules per free radical generated. Laser beams on the other hand, can be formed into a column of radiation that only acts on the chemicals well into the interior of the reaction vessel. They also may be pulsed, so that radicals are produced when they are needed, rather than continuously. Free radicals are needed only when neutralization of radicals previously generated, has proceeded so far as to markedly slow process throughput. Use of lasers enables better temporal and spatial control over free radical production.

Lower temperatures are better

Wolfrum's laser-assisted technique for vinyl chloride production confirms this hypothesis. Laser production of chlorine free radicals at the same high temperature as the thermal process (500° C), resulted in a 25% increase in overall yield of reaction products (Table 2). Reducing the temperature to 350° C, brought the yield of the laser process down to that of the high-temperature thermal process, *but increased the selectivity*, the ratio of the desired vinyl chloride to other reaction products, from 6 to 1,000.

The ethyl bromide process discussed above is optimized at lower operating temperatures. Higher temperatures lower the quantum yield. The Zavelovich-Reddy patent states:

The commercial preparation of ethyl bromide by the hydrobromination of ethylene has been carried out photochemically using high-energy ionizing radiation such as gamma radiation from a cobalt-60 radiation source. . . . Although this process has been commercially successful, it requires the use of extensive shielding and the use of a hazardous radiation source. In addition, the use of high-energy ionizing radiation such as gamma radiation is undesirable because each photon carries about 1 million times the amount of

energy actually required to dissociate a molecule of hydrogen bromide into atoms. This excess energy is converted into heat and results in an increase in the temperature of the reaction mixture, which is undesirable since the quantum yield of the reaction decreases as the temperature increases. . . .

The quantum yield for the free radical addition of hydrogen bromide to olefins ordinarily decreases with an increase in temperature. This is believed to be a result of the thermal instability of the intermediate organic free radical which is formed in the hydrobromination reaction. For the case of ethylene, this intermediate free radical is believed to decompose into ethylene and a bromine atom (the reverse of Equation 2) as shown in Equation 5 (see Table 1). As the temperature increases, this decomposition competes more effectively with the propagation steps which are set forth above in Equations 2 and 3. Accordingly, the photochemical hydrobromination reaction of this invention is preferably carried out at relatively low temperatures. For example, the reaction is desirably carried out at a temperature below about 400° C, preferably below about 200° C, and more preferably below about 100° C.

Operating at a lower temperature, the xenon fluoride laser process involves a greater coherence of least action, relative to the gamma-ray process.

Has the economics of such laser processes ever been worked out in detail?

Before a conference of the Society of Photo-optical Instrumentation Engineers in January 1984, Reddy showed that only a few thousand 100-watt excimer laser units were required to produce the entirety of U.S. vinyl chloride and phenol annual output—strongly making the point of the relevance of lasers to industrial chemistry (see Table 3). Given that SDI will bring the capital costs of lasers down tremendously, what are we waiting for?

Nonlinear shifts in absorption spectra

With nonlinear methods, such as multi-photon excitation and efficient production of free radicals, laser chemistry will become quite economical. Within *multi-step* excitation of atoms and molecules, there are also a variety of nonlinear methods available to achieve high selectivities of laser action. Multi-step excitation of molecules displays its own nonlinear features. Selective excitation of infrared radiation produces a transformation in the spectrum of wavelengths of ultraviolet light that are absorbed by the excited molecules, that is, they absorb frequencies of light that they previously had not. This effect provides the basis for separating molecules with atoms of different isotopes from each other, for example, separation of uranium-235 hexafluoride from uranium-238 hexafluoride. Usually there is almost a complete overlap in the ultraviolet absorption spectrum of molecules

TABLE 2
Laser-assisted vinyl chloride production is superior to thermal process

Process type	Product yield*	Selectivity**	Quantum yield
At 500° C			
Thermal	60%	5.7 (85%)	NA
Laser	75%	5.7 (85%)	20,000
At 350° C			
Laser	60%	1,000 (99.9%)	5,000

*Percentage of dichloroethane feed transformed into a reaction product.
**Ratio of vinyl chloride to all other reaction products. In parentheses, this is expressed as vinyl chloride as a percentage of all products.
Source: Figures from A. Kaldor and R. Woodin, "Applications of Lasers to Chemical Processing," *Proceedings of the IEEE*, Vol. 70, No. 6, June 1982.

TABLE 3

Excimer laser power requirements for production of bulk chemicals

Chemical name	Annual volume		Quantum yield	Req. laser power (kW)	# of 100W units
	kg/yr	moles/year			
Vinyl chloride	3.02×10^9	4.90×10^{10}	10,000	110	1,100
Phenol	1.14×10^9	1.21×10^{10}	1,000	190	1,900

Source: K.V. Reddy, "Ultraviolet Laser-triggered Chemical Chain Reactions," *Applications of Lasers to Industrial Chemistry*, R. Woodin, A. Kaldor, eds., *Proceedings of the SPIE* 458 (1984).

with different isotopes. If the initial infrared excitation can be made isotope-specific, the ultraviolet light of the new absorption frequencies can be used to photodissociate the desired molecule and separate the isotope it carries.

In the 1970s, Letokhov and his associates reported that selective excitation of isotopes of ammonia (NH_3) with infrared laser radiation of a wavelength of about 10 microns, produced a dramatic shift in the spectra of ultraviolet light that the ammonia molecules would absorb. The excited molecules displayed high absorption of ultraviolet light at a wavelength of 221 nanometers, at which the unexcited ammonia displayed no or little absorption (see **Figure 4**). By selectively exciting ammonia carrying nitrogen-15 with a specific wavelength of infrared radiation, the shift in the absorption spectra could be induced, so that the isotope-specific molecule could be photodissociated with ultraviolet radiation at the new wavelength that it absorbed, yielding a gas enriched in the nitrogen-15 isotope.

The action of the infrared radiation shifts the absorption spectra of the excited isotope to longer wavelengths relative to the spectra of the unexcited material; the new spectra are called "red-shifted," since in visible light, red light is of the longest wavelength. The red-shift in the absorption spectrum is said to occur because the molecules already excited by absorption of infrared radiation, only require ultraviolet photons of lower energy (and longer wavelength) to be dissociated.

The technique of producing shifts in the absorption spectra of isotopes by irradiation with photons of one wavelength, to prepare them for selective action by photons of other wavelengths, has been employed at Los Alamos National Lab to separate isotopes of uranium, sulphur, and other elements.

In sum, the technique of multi-step molecular excitation is based on selectively transforming the chemical feed material into a state in which its absorption spectra provides opportunities for efficient transformation of the intermediate state of excitation into a product. The model of multi-step excitation refers to excitation through one or more short-lived intermediate states of photon excitation. The two-step photoisomerization of 7-dehydrocholesterol into previtamin-D, illustrates the principle of the technique, even though the pri-

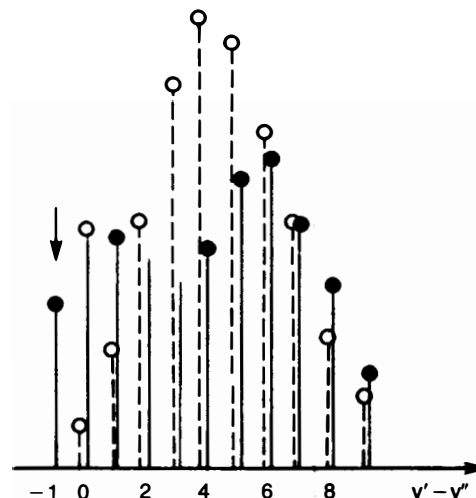
mary intermediate state is not short-lived but is the stable tachysterol isomer.

Vitamin-D regulates bone growth in man, and is produced in the body by the action of sunlight on cholesterol in the skin. Vitamin-D deficiency leads to the disease of rickets. Existing commercial methods of vitamin-D production cannot avoid use of a photochemical stage to convert 7-dihydrocholesterol (7-DHC) to its previtamin-D isomer.

A group of researchers led by Peter Hackett at the National Research Council of Canada, have developed a two-photon, two-step method of photoisomerization (or transformation) of the 7-DHC isomer to the previtamin-D isomer.

An isomer of a molecule has the same elements, though

FIGURE 4
Spectral lines for normal and laser-excited molecules



Infrared laser excitation of molecules shifts their absorption spectra relative to unexcited molecules and presents opportunities for selective action. The figure shows the spectral lines for normal (dashed lines) and laser-excited (solid lines) ammonia.

Source: Adapted from V.S. Letokhov, *Nonlinear Laser Chemistry* (Springer-Verlag, 1983).

arranged in a geometrically different manner. There are several isomers of 7-DHC of which only previtamin-D is biologically active.

Figure 5 shows that the ultraviolet absorption spectra of 7-DHC and its four principal isomers overlap almost entirely, except for the 310 to 370 nanometer absorption band of tachysterol (T_3), which provides the basis for selective action. Under ultraviolet radiation, tachysterol "is smoothly converted . . . into previtamin-D," writes Hackett.

Hackett and his colleagues explored whether the use of two ultraviolet sources operating at different wavelengths, could take advantage of this difference in the absorption spectra of the isomers. Ultimately, they used a krypton-fluoride laser operating at 248 nanometers wavelength, to convert 26% of the 7-DHC input into previtamin-D and 71% of it into tachysterol. They then irradiated this mix of isomers with a nitrogen laser operating at 353 nanometers which selectively acts on the tachysterol to convert it to previtamin-D. They obtained a total two-step conversion of 7-DHC of 99.9% of which previtamin-D constituted 80%.

By contrast, the yield (the percent of 7-DHC converted to reaction products) in the conventional process, is only about 40%, of which only 30% is previtamin-D. Table 4 contrasts the yields and selectivities of the conventional and two-photon processes. The selectivity, the ratio of the desired

TABLE 4

Two-step photochemical production of vitamin-D superior to conventional process

	Product yield*	Selectivity**
Conventional process	40%	0.43 (30%)
Two-photon process	99.9%	4.0 (80%)

*Percentage of 7-dehydrocholesterol feed converted to a reaction product.
 **Ratio of previtamin-D to all other reaction products. The figures in parentheses give previtamin-D as a percentage of all reaction products.
 Source: P.A. Hackett et al., "Viable Commercial Ventures Involving Laser Chemistry Production: Two Medium Scale Processes," *Applications of Lasers to Industrial Chemistry*, Richard L. Woodin and Andrew Kaldor, eds., *Proceedings of the SPIE* 458 (1984).

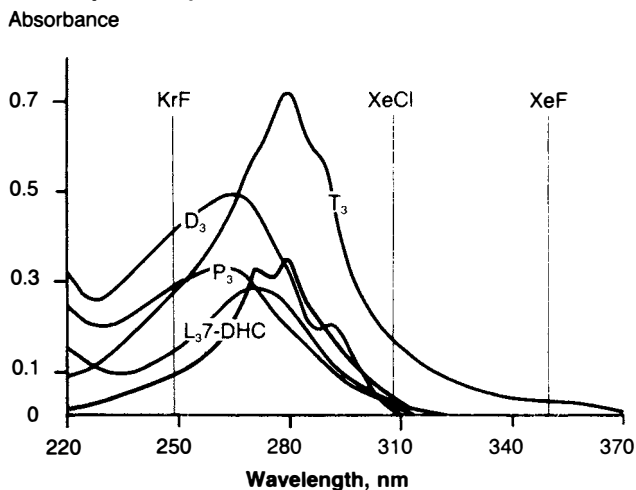
product to all other molecules in the output, is 10 times greater for the two-photon process which makes use of the difference in the absorption spectra of the isomers, than for the conventional process. The yield of the photochemical reaction is more than double. Regarding the industrial feasibility of this process Hackett et al. write:

The immediate implications of this work for industrial production of vitamin-D are straightforward. The KrF photolysis stage can be replaced by the cheap, efficient, reliable, spectrally pure, low pressure mercury lamp at 254 nm. The second stage may be effected by a suitably filtered medium-pressure mercury lamp. Vitamin-D produced by this dual wavelength photolysis route will be sufficiently active . . . for use in animal feed without additional purification. Moreover, existing production facilities could be upgraded simply by adding the second photolysis stage to convert useless tachysterol into potentially active previtamin-D.

Here we have an example of how experimental laser chemistry, can discover new ways to employ existing, less coherent flashlamps.

In some cases of multi-step excitation of isotopes, atoms, or molecules, absorption spectra may overlap so much in the ground state so that there may be no selectivity of action by laser radiation until all chemical feed material has been excited to an intermediate quantum state, from which selective excitation may be achieved. Selectivity may be achievable at the intermediate state as a result of differences in the absorption spectra of the excited isotopes, atoms, or molecules that may occur there, or as a result of differences in the lifetimes of short-lived quantum states excited by absorption of a photon. In the latter case, some species of atoms or molecules may decay from an excited state (produced by absorption of a photon) to the ground or unexcited state, faster than other species. This provides the opportunity for achieving selectivity by exciting both species, and then selectively transforming the species with the longer excited-

FIGURE 5
Absorption spectra of vitamin-D isomers



The shift in the absorption spectra for tachysterol (T_3) versus pre-vitamin-D (P_3) and other 7-dehydrocholesterol (7-DHC) isomers, provides a means of selectively producing the vitamin. Shown here are the ultraviolet absorption spectra for 7-DHC and four of its isomers.

Source: P.A. Hackett et al., "Viable Commercial Ventures Involving Laser Chemistry Production: Two Medium Scale Processes," *Applications of Lasers to Industrial Chemistry*, Richard L. Woodin and Andrew Kaldor, eds., *Proceedings of the SPIE*, Vol. 458 (1984).

state lifetime, after the other species had decayed to the ground state.

Letokhov proposed to apply these methods to develop selective photochemistry and photophysics with DNA and RNA:

All of the nucleic acids [DNA, RNA, etc.] absorb in approximately the same region. However, one can increase the excitation selectivity by exploiting the differences in the lifetimes of the intermediate states, the differences in cross-sections of the transitions from excited states, etc. . . . Nucleic acids which contain five types of bases and deoxyribose-phosphate chains, are one of the most interesting targets of selective processes. Such processes involving DNA and RNA are very important since in this way it is possible to change the genetic structure of living cells and to study the primary structure of DNA and RNA, which is particularly interesting for the development of new physical methods of sequencing the bases of DNA.

Letokhov discusses how, by varying the wavelength of multiple excitation steps and the radiation intensity of ultraviolet laser pulses of trillionths of a second in duration, it is possible to selectively dissociate the five bases from the DNA or RNA macromolecules.

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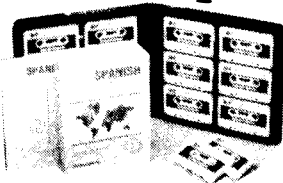
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