these features are almost certainly the result of environmentally stressful conditions that would have excluded contemporary eukaryotes as well as many types of cyanophytes.

This report has shown that geological, geochemical, and paleontological data can be used to interpret the paleoecology of at least some kinds of Proterozoic, fossiliferous deposits. It also demonstrates that microbiotas of Precambrian hypersaline environments, like those of their modern counterparts, have low species diversity, are dominated by prokaryotic organisms, and consequently should not be used for inferring the evolutionary status of the contemporary biosphere or for considerations of evolutionary trends, such as age-related changes in algal diversity and size distribution (*19*). Comparison of the Gillen Member and Loves Creek Member assemblages provides an excellent example of environmental control over the composition of Precambrian biotas. It suggests that the two assemblages, and others of their types, can be useful for local biostratigraphic correlation, for basin analysis, and for environmental interpretation.

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17 April 1979

Isotope Selectivity of Infrared Laser–Driven Unimolecular Dissociation of a Volatile Uranyl Compound

Abstract. *Isotope-selective photodissociation of the volatile complex uranyl hexafluoroacetylacetonate · tetrahydrofuran [UO_2(hfacac)$_2$ · THF] has been achieved with both a continuous-wave and a pulsed carbon dioxide laser. The photodissociation was carried out in a low-density molecular beam under collisionless conditions. Transitions of the laser are in resonance with the asymmetric O-U-O stretch of the uranyl moiety, a vibrational mode whose frequency is sensitive to the masses of the uranium and oxygen isotopes. Unimolecular dissociation is observed mass spectrometrically at an extremely low energy fluence, with no evidence of an energy fluence or intensity threshold. The dissociation yield increases nearly linearly with increasing energy fluence. At constant fluence the dissociation yield is independent of contact time between the radiation field and the molecule, indicating that the decomposition is driven by laser energy fluence and not laser intensity. The oxygen and uranium isotope selectivities measured in these experiments are nearly those predicted by the ratio of the linear absorption cross sections for the respective isotopes. Thus, essentially complete selectivity is observed for oxygen isotopes, while a selectivity of only about 1.25 is measured for the uranium isotopes. A model presented to describe these results is based on rapid intramolecular vibrational energy flow from the pumped mode into a limited number of closely coupled modes.*

We report here the uranium and oxygen isotope selective unimolecular dissociation of a volatile uranium-bearing complex, uranyl hexafluoroacetylacetonate · tetrahydrofuran [UO_2(hfacac)$_2$ · THF], using either a pulsed or a continuous-wave (CW) CO_2 laser. Energy is deposited in this molecule by excitation of the O-U-O asymmetric stretch of the uranyl moiety. This vibrational mode is in resonance with several of the 10.6-μm transitions of the CO_2 laser and is spectroscopically selective for the isotopes of both uranium and oxygen. The absorption spectrum of this vibrational mode for an oxygen-18-enriched sample is indicated in Fig. 1. The 17-cm^{-1} isotope shift between $U^{16}O_2$ and $U^{16}O^{18}O$-bearing species is greater than the width of the absorption band and results in spectrally resolved infrared (IR) bands for the oxygen isotopes. The uranium isotope shift, however, is only 0.7 cm^{-1}, and although either uranium isotope can be preferentially excited depending on the laser transition used, the IR absorption features are not spectrally resolved. Thus we can examine, in the same molecule, the effects of overlapping and nonoverlapping IR absorption bands on the isotope selectivity.

Previously we reported (*1*) the unimolecular decomposition of this molecule with a pulsed CO_2 laser. The results described here also demonstrate that a CW IR laser can induce the unimolecular dissociation of such molecules. Recently the unimolecular decomposition of ions with a CW CO_2 laser was reported (*2*). Multiple photon excitation of uranyl molecules differs from excitation of smaller molecules, for which the anharmonicity barrier is a critical factor. For this molecule the multiple photon process is postulated to be repeated excitation of the 0-1 vibrational transition of the O-U-O asymmetric stretch. This mode relaxes rapidly by an intramolecular vibrational energy transfer into a small subset of strongly coupled modes, leaving the asymmetric stretch in its ground vibrational state so that subsequent photons can be absorbed. The vibrational relaxation time is required to be shorter than 10^{-9} second so that at laser intensities of only a fraction of a megawatt per square centimeter, the few CO_2 laser photons necessary to overcome the barrier to dissociation can be absorbed during the laser contact time with the molecule. This model for multiple photon excitation and the implication for IR laser-induced chemistry in large molecules have been described (*1*). The factors concerning the isotope selectivity of this process are described in this report.

Experimental. The molecule UO_2-

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$(hfacac)_2 \cdot THF$ was synthesized (3) in our laboratory. It is volatile at moderate temperatures (0.5 torr at 100°C) even though typical uranyl derivatives are notoriously involatile (3). As shown in Fig. 2, the UO_2^{2+} moiety is nestled in the center of a planar pentagonal framework, which consists of the four oxygens of the two hfacac groups and the one oxygen of the THF ligand (4). We refer to this framework as the first bonding sphere. The outer boundaries of the molecule consist of "Teflon shock absorbers" in the form of the CF_3 groups of the hfacac ions. These contribute to the isolation of the UO_2^{2+} moiety and to the volatility of the molecule.

Experiments are performed by irradiating a low-density molecular beam of the compound with the CO_2 laser and causing decomposition to occur. This is observed as a decrease of molecular density in the beam. The schematic of the apparatus is shown in Fig. 3. The molecular beam is formed in an effusive oven held at 50° to 100°C; it is crossed by a CO_2 laser about 2 cm downstream from the oven and then traverses a 50-cm path before entering the ionizer of a quadrupole mass spectrometer. The acceptance solid angle of the ionizer is very small, $\sim 10^{-4}$ steradian, and thus photofragments that attain sufficient translational energy to leave the beam are not detected. The ion signal is averaged on a multichannel analyzer triggered by the laser.

A commercial grating-tuned Lumonics 801 CO_2 TEA laser, operating on the TEM_{00} mode, crosses the molecular beam at a right angle. The TEA laser is collimated with a beam diameter of about 1.2 cm and a pulse width of 400 nsec full width at half-maximum (FWHM). The TEA laser fluence is varied between 4 and 500 mJ/cm^2 by attenuation through a propylene-filled gas cell. The laser pulse width determines the mean interaction time between the molecules and the TEA laser.

The CW CO_2 laser is grating-tuned to produce a TEM_{00} output beam of about 4 W on each of a number of P-branch transitions of the 10°0-00°1 band. The laser beam, after traversing the propylene gas-filled attenuator cell, is mechanically chopped at 25 Hz and is brought to focus within the center of the molecular beam apparatus. The confocal parameter of the focused beam is about 6 cm, with a focused spot diameter of 0.06 cm resulting in a peak intensity of about 2 kW/cm^2. The laser beam diameter, which is about twice the molecular beam diameter, determines the mean irradiation time of the molecules. That time is the laser beam diameter divided by the mean molecular beam speed and is 4.6×10^{-6} second. The effective fluence from the CW laser is varied from 10 to 0.25 mJ/cm^2, which corresponds to an intensity range of 2 kW/cm^2 to 50 W/cm^2. Absolute fractional dissociation is measured as a function of laser intensity and laser frequency. Isotope selectivity is calculated from the ratio of the measured dissociation fractions for the isotope species of interest.

TEA laser photodissociation. The spectral dependence of the dissociation yield is shown in Fig. 4 for TEA laser irradiation. At constant TEA laser power, the dissociation yield nearly mimics the small-signal absorption spectrum obtained by optoacoustic spectroscopy, as shown in Fig. 1, provided the laser power is limited to values that produce less than 50 percent dissociation. The redshifted dissociation spectrum reported in the laser-induced unimolecular decomposition of SF_6, as well as most other molecules, is not observed (5). The dissociation yield also has an apparent first-order dependence on laser fluence, except at high dissociation yields. For example, on the $P(10)$ 10.6-μm CO_2 laser transition, the observed depletion at 2 mJ/cm^2 is 1 percent, at 20 mJ/cm^2 about 10 percent, and at 200 mJ/cm^2 nearly 100 percent. Similar results are observed with about the same energy fluence, but higher peak powers, when a 70-nsec CO_2 laser pulse is used, indicating that energy fluence and not peak power is the determining factor for dissociation yield. The high dissociation yield is indicative of a homogeneously broadened absorption line, an interpretation consistent with the observed Lorentzian line shape. As shown in Fig. 5, for laser energy fluences greater than 200 mJ/cm^2 the more strong-

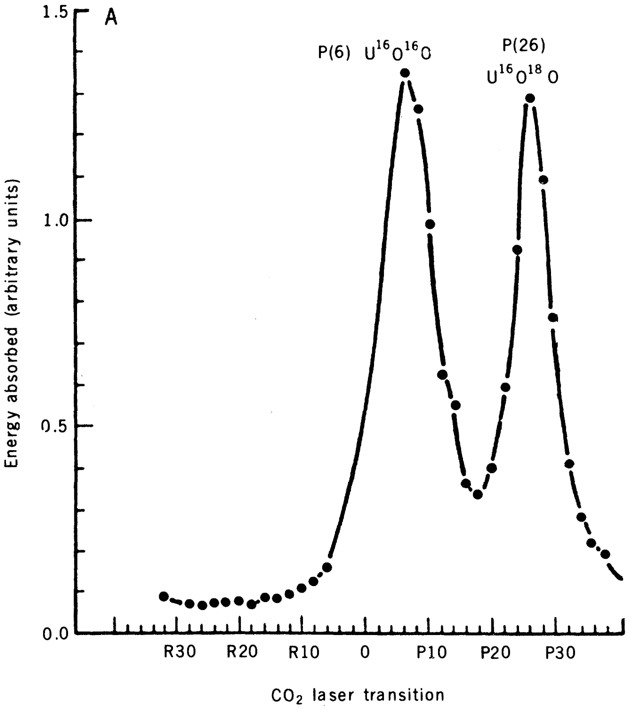


Fig. 1 (left). Infrared absorption spectrum for a mixture of $U^{16}O_2(hfacac)_2 \cdot THF$ and $U^{16}O^{18}O(hfacac)_2 \cdot THF$.

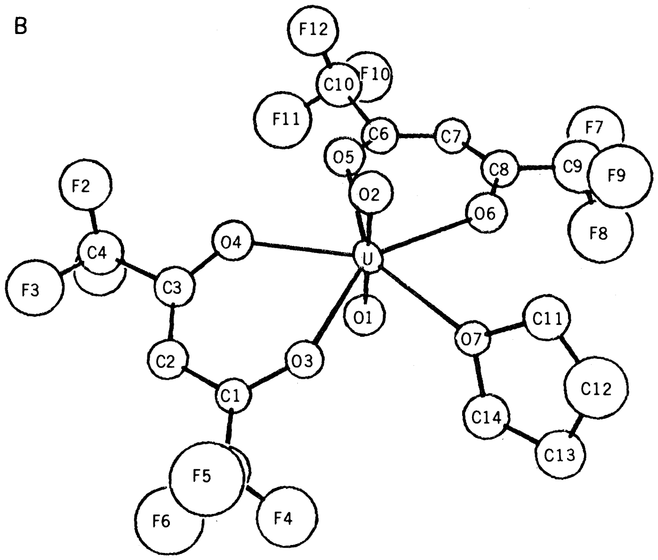


Fig. 2 (right). Structure of the $UO_2(hfacac)_2 \cdot THF$ molecule. The labels refer to the atomic constituents in the molecule.

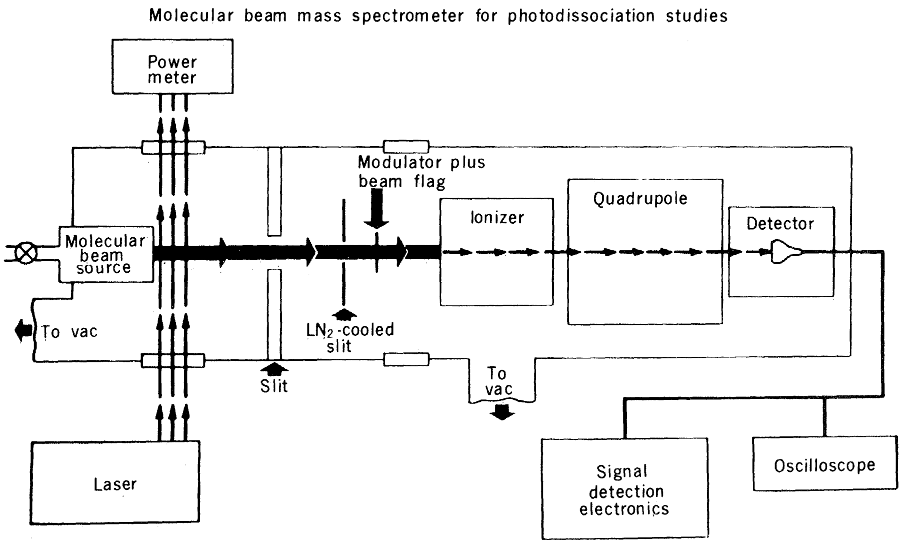


Fig. 3. Schematic of the experimental apparatus.

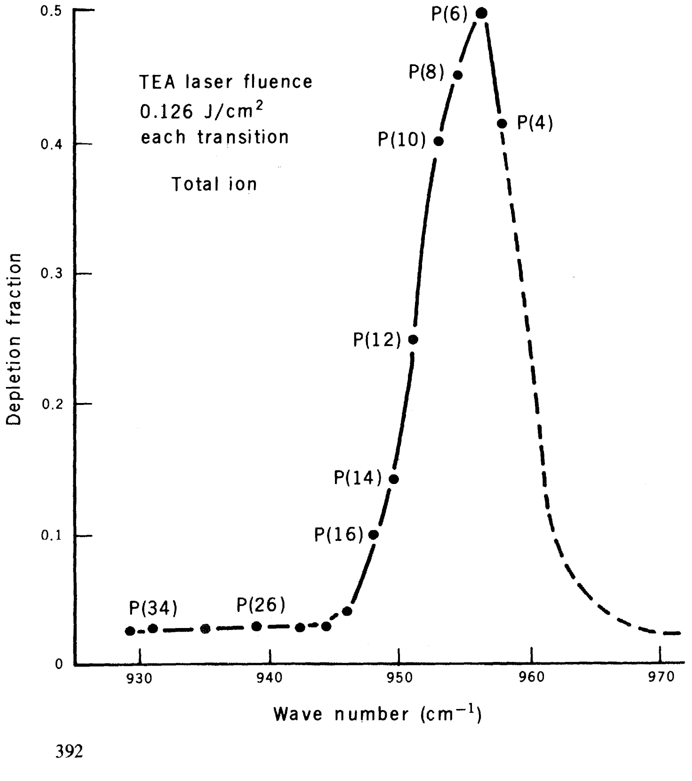
ly absorbed CO_2 laser transitions $P(4)$, $P(6)$, $P(8)$, and $P(10)$ exhibit reduced spectral selectivity, since in each instance nearly 100 percent of the laser-irradiated molecules are decomposed. No energy fluence or intensity threshold for dissociation is observed (6). Below 1 percent depletion TEA laser measurements are limited by instrumental sensitivity. For the data shown in Figs. 4 and 5 the TEA laser pulse width is about 400 nsec.

The dissociation products obtained with the CO_2 laser were identified as $UO_2(hfacac)_2$ and THF (1). Thus the bond pumped, the UO_2 asymmetric stretch, is not the bond broken. Transfer of energy from the pumped mode to the first bonding sphere must be efficient; the weakest bond in this sphere, the U-O bond associated with THF, is the one that breaks.

Continuous-wave CO_2 laser photodissociation. The intensity dependence observed in the TEA laser experiments strongly suggests that the field strength and energy fluence required to drive the process can be attained with CW laser radiation, and that the CW photodissociation can be operated selectively in the collisionless environment of a molecular beam. An important criterion in the description of these results is the contact time between the radiation field and the molecule. This can be related to different parameters for various experimental conditions. In a molecular beam the contact time is d/v, where d is the laser beam diameter ($1/e^2$) and v is the speed of the molecule in the beam. Of course, the contact time must be adequate to deposit sufficient energy to decompose the molecule. In a static or slow-flow cell, the contact time must also be shorter than the gas kinetic collision time because collisions during the excitation process disrupt both excitation and dissociation. In fact, the contact time or the energy deposition time has to be shorter than the unimolecular decomposition time, and both of these times have to be shorter than the inter- and intramolecular energy transfer times.

To test these assumptions, we measured the intensity dependence of the absolute dissociation fraction for the $P(6)$ and $P(10)$ 10.6-μm transitions, using a CW CO_2 laser. The fractional depletion increases nearly linearly in the laser intensity range investigated, 0.16 to 2.4 kW/cm^2 (fluence, 0.7 to 11 mJ/cm^2), for both transitions. A dissociation yield of 1 percent is observed at an intensity of only about 0.6 kW/cm^2 (fluence, 3 mJ/cm^2). The magnitude of the fractional depletion as a function of laser frequency (transition) at constant laser fluence again closely follows the small-signal absorption spectrum.

We previously reported (1) that the unimolecular decomposition time has an upper limit of 10 nsec. This is about two orders of magnitude shorter than the var-



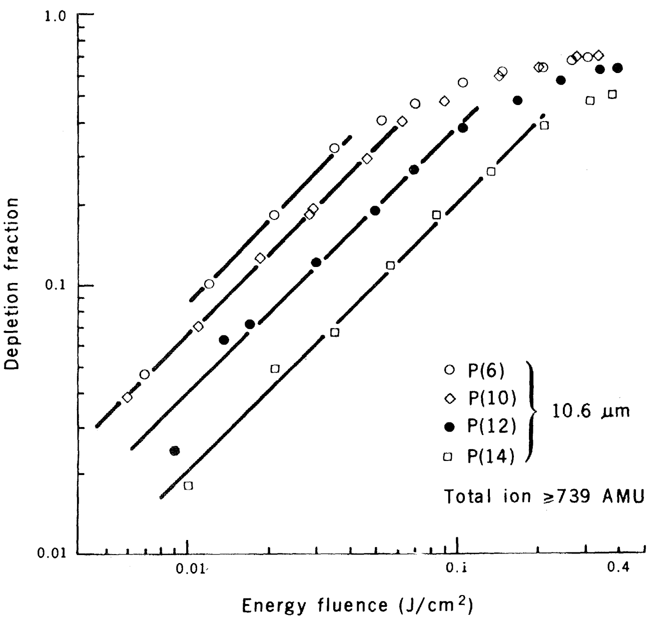


Fig. 4 (left). Frequency dependence of the pulsed TEA laser-induced unimolecular dissociation of $UO_2(hfacac)_2 \cdot THF$. Fig. 5 (right). Intensity dependence of the pulsed TEA laser-induced unimolecular dissociation of $UO_2(hfacac)_2 \cdot THF$.

ious contact times between the laser field and the molecule. The contact time in the pulsed laser-molecular beam experiments is equal to the pulse width, 400 nsec FWHM, and in the CW laser-molecular beam experiments the contact time is about 5 μsec, the mean time necessary for the molecular beam to cross the laser beam diameter. In the static cell experiments (*1*) the contact time is taken to be equal to the time between collisions and is typically about 1 μsec.

Table 1. Isotopes and transitions used in the isotope-selective experiments.

Isotopic species	Abundance (%)	CO_2 TEA laser transition (10.6 μm)
	Oxygen experiments	
(A) $^{238}U^{16}O^{16}O(hfacac)_2 \cdot THF$	48	*P*(6) peak absorption
(B) $^{238}U^{16}O^{18}O(hfacac)_2 \cdot THF$	40	*P*(26) peak absorption
(C) $^{238}U^{18}O^{18}O(hfacac)_2 \cdot THF$	12	
	Uranium experiments	
(D) $^{238}U^{16}O^{16}O(hfacac)_2 \cdot THF$	47	*P*(10) (red side)
(E) $^{235}U^{16}O^{16}O(hfacac)_2 \cdot THF$	53	*P*(4) (blue side)

When the fractional dissociation induced by the CW CO_2 laser and that induced by the CO_2 TEA laser are plotted as a function of energy fluence, as shown in Fig. 6, the two kinds of data agree well. This is not surprising since the contact time for both the pulsed and the CW laser is considerably longer than the decomposition time.

With the CW CO_2 laser, the linear dependence of dissociation yield on laser energy fluence is extended down to 0.25 mJ/cm². Even at this low value no evidence for an energy fluence threshold can be detected in either CW or pulsed laser irradiations. This is a clear indication that the photophysics observed for this molecule is different from that proposed for the multiphoton dissociation of SF_6 (*7, 8*) and similar molecules. These observations are consistent with a model where rapid energy coupling to a group of normal modes occurs during the laser excitation (*1*). Looked at in this manner, the laser is simply equivalent to a vibrational heating device. The unimolecular decomposition rate can then be predicted by unimolecular reaction theory.

The homogeneous character of the absorption (and dissociation) line shape can be viewed as being due to rapid energy and phase relaxation of the pumped mode, and one can assign T_1 and T_2 relaxation times to this process. Details of a model developed to describe the laser-induced unimolecular decomposition of large molecules have been reported (*1*).

Isotope-selective results. The isotope-selective experiments are performed on ^{18}O- and ^{235}U-enriched samples. Table 1 shows the mass spectrometrically determined isotopic abundances of the respective samples and the CO_2 laser transitions used for selective excitation in the TEA laser experiments. For oxygen, the measured and calculated spectroscopic isotope shift between species A and B is about 17 cm^{-1}, the IR absorption line width about 7 cm^{-1} FWHM (Fig. 1). The $U^{18}O^{18}O$ IR absorption band falls outside the easily accessible CO_2 laser transitions and was not examined except by conventional IR absorption spectroscopy. Even at the highest laser fluence used, 500 mJ/cm², complete spectroscopic selectivity between species A, B, and C is reproduced in the observed beam depletion. Only species A shows depletion if the *P*(6) transition is used and only species B is affected by the *P*(26) laser line.

The spectroscopic isotope shift between ^{235}U and ^{238}U samples is 0.7 cm^{-1}, a small fraction of the total IR absorption line width of about 7 cm^{-1}. Thus, the *P*(10) CO_2 laser transition preferentially dissociates D, the ^{238}U-bearing species, but some of E, which contains ^{235}U, is also dissociated. The maximum single-photon spectroscopic selectivity between the ^{238}U and ^{235}U compounds at the *P*(10) transition predicted from low-power CW CO_2 laser absorption measurements with optoacoustic detection is about 1.2. For the TEA laser irradiation experiments, the measured selectivity for dissociating species D is 1.23 ± 0.11 at a fluence of 121 mJ/cm². The ^{235}U species, E, is selectively dissociated by the *P*(4) transition. At a fluence of 87 mJ/cm² a selectivity of 1.12 is found for isotopic depletion of species E in the dissociated molecular beam. When the fluence is increased to 150 mJ/cm² on the *P*(4) transition, no isotope selectivity is observed.

The observation of no isotope selectivity at 150 mJ/cm² for the *P*(4) transition shows that the system can be overdriven, in the sense that both isotopic species are nearly 100 percent dissociated. The selectivities observed for the *P*(10) and *P*(4) transitions are comparable to those expected from the ratio of linear absorption coefficients for species D and E.

In similar experiments with the CW CO_2 laser, complete oxygen selectivity is again observed under the irradiation conditions used. Experiments with the CW CO_2 laser are performed with ^{235}U-enriched samples containing 46 percent ^{238}U and 54 percent ^{235}U. With an isotope shift of only 0.7 cm^{-1}, the IR absorption bands are greatly overlapped. Irradiation on the red side of the absorption band

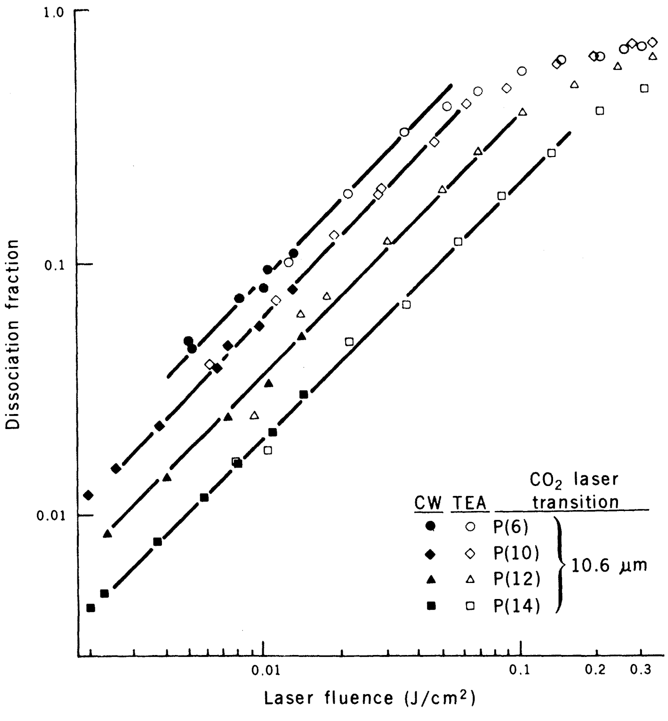


Fig. 6. Intensity dependence of the CW CO_2 laser-induced unimolecular dissociation compared with the pulsed TEA laser-induced dissociation for the *P(6)* 10.6-μm CO_2 laser transition.

with the $P(10)$ 10.6-μm CO_2 laser transition preferentially dissociates the ^{238}U species; the measured selectivity was 1.25 ± 0.08. Irradiation on the blue side of the absorption band with the $P(4)$ 10.6-μm transition similarly results in preferential dissociation of the ^{235}U species with a selectivity of 1.28 ± 0.19. It is interesting that a nearly identical selectivity of 1.23 was obtained in the CO_2 TEA laser experiments with the $P(10)$ 10.6-μm transition. Although most experiments to date have been performed with isotopically enriched starting material, CW CO_2 laser irradiation of uranyl molecules made from unenriched starting material leads to selectivities comparable to those for enriched samples.

Discussion. In the same molecule we compared the effects of both well-resolved and overlapping isotopic spectral features on the photophysics and chemistry of laser-induced dissociation. The uranium photodissociation experiment shows that for a spectrally overlapping system under collisionless conditions it is possible to overdrive the system and lose all the spectral selectivity. This effect is not observed in the spectrally resolved experiments with ^{18}O-enriched samples. A high dissociation yield is observed in these experiments at fluences on the order of 100 mJ/cm^2, indicating unusually efficient photo utilization. We know of no other IR photodissociation process that is as efficient; for example, 15 percent dissociation of UF_6 is achieved only at fluence levels approaching 7 J/cm^2 (*9*). The theoretical model that we developed for this efficient multiple-photon process (*1*) may be generally applicable to all large molecules where fast intramolecular relaxation prevails in the pumping process.

As long as the system is not severely overdriven, either isotopic species may be dissociated with some selectivity. Note that even at the high dissociation fractions achieved with the TEA laser experiments, the isotope selectivity measured in photodissociation experiments is nearly that predicted by the ratio of the IR absorption cross sections for the two isotopic species. At first glance this appears somewhat surprising for a multiple-photon process. On the basis of the model (*1*), it might be expected that the selectivity obtained for the absorption of a single photon (the ratio of the absorption cross sections) would be compounded by the absorption of the second and subsequent photons. One possibility that cannot be dismissed is that the process is, in fact, a single-photon process, at least at low energy fluence. Molecules in the "tail" of the vibrational Boltzmann distribution may already have sufficient thermal energy that the absorption of a single CO_2 laser photon can cause dissociation. If we examine the probability of multiple-photon absorption for irradiation times that are long compared to the time for relaxation out of the driven mode (T_1), then the absorption process may be treated as the occurrence of statistically independent events and the probability that a molecule will absorb a given number of photons can be calculated from the Poisson distribution and the observed absorption cross section. We calculate, for example, that at a fluence of 5 mJ/cm^2, 30 percent of the absorbing molecules absorb more than one photon. At a fluence of 1 mJ/cm^2 this falls to only 6 percent. It could be argued that only the fraction of molecules absorbing more than one photon can dissociate. The results of low fluences must be interpreted with caution because of the large experimental uncertainties. However, the linear dependence of dissociation yield on laser fluence at these levels does suggest a single-photon process. Of course, at higher fluences the dissociation becomes predominantly a multiple-photon process. For example, at 80 mJ/cm^2 the Poisson distribution indicates that 90 percent of the absorbing molecules absorb five or more photons.

No compounding would be expected in a multiple-photon process if the difference between the absorption cross sections for the two isotopic species was negligible for absorption of the second and subsequent photons. However, even if it is assumed that the difference is not negligible, a closer analysis of the isotope selectivity of a multiple-photon process reveals that no significant compounding will occur, except for extremely small dissociation yields.

Consider a set of energy levels representing the total energy of the molecule after absorption of 1, 2, 3, . . . photons, with steadily increasing dissociative decay rates for the higher levels. As the molecules are pumped through those levels by the laser a limiting level is eventually reached for which the dissociation is so fast that all molecules that reach this level dissociate before further excitation can occur. Because of the difference in the rate of absorption of photons between the two isotopic species, significantly different populations of the isotopic species will be pumped up to this limiting level. However, lower levels also decay either during or after the laser pulse. It can be shown that the difference in populations between the two isotopic species at a given energy level falls off very rapidly for levels below the limiting level and eventually becomes zero. The resultant selectivity obtained for the decay of all the dissociative levels will be much less than the selectivity that would be obtained by compounding the single-photon selectivity.

We set up a computational model that represents the multiple-photon absorption and dissociation in a ten-level system, based on the model described above. The Ordinary Master Equation formalism of Stone *et al.* (*8*) was used (that is, rate equations). It was assumed that at least five CO_2 laser photons must be absorbed to overcome the dissociation barrier. Decay rates for the dissociative levels were obtained from the Kassel formula, assuming that the absorbed energy is spread over a critical set of five modes (*1*). The energy levels were equally spaced and the rate of transition between any pair of levels was assumed to be proportional to the observed single-photon cross section for a given isotopic species. The results demonstrate that significant compounding will be observed in a multiple-photon dissociation process only when the yield is small (*10*).

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