

The multiple-photon effect, in which a single polyatomic molecule absorbs many infrared photons, is proving to be a complex and still mysterious phenomenon in laser photochemistry.

MULTIPLE-PHOTON

EXCITATION

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There is no doubt that lasers have revolutionized photochemistry. Initially, the main attraction of lasers was the highly monochromatic nature of the light; many researchers hoped that this feature might serve as the basis for bond-selective photochemistry and for laser-induced isotope separation. However, in the early 1970s another rather surprising feature was discovered involving the interaction of infrared laser light and polyatomic molecules.

This phenomenon, multiple-photon excitation, is the absorption of many infrared photons of the same frequency by a single molecule. Observation of this phenomenon was only possible with the high light intensities typical of lasers. It was a surprising effect because multiple-photon excitation did not fit the established theoretical pictures of how molecules absorb radiation. While considerable experimental and theoretical work has now been directed toward understanding this phenomenon, much remains to be explained.

One can think of multiple-photon excitation or absorption as high-intensity spectroscopy. As such, it is qualitatively different

from normal low-intensity spectroscopy. At low intensities relatively small numbers of photons delicately probe individual energy transitions. Typically, the molecules occupy a known equilibrium distribution of energy states, and, for a given absorption frequency, only a small fraction of these are moved to a single excited state. On the other hand, multiple-photon excitation necessarily affects large fractions of the molecules and drives them through many energy states. In fact, since the absorbed energy becomes vibrational energy, the resulting high degree of vibrational excitation drastically alters the chemical nature of the molecule, even to the point of dissociation. The dissociative reaction led to fulfillment of the early hope for laser isotope separation.

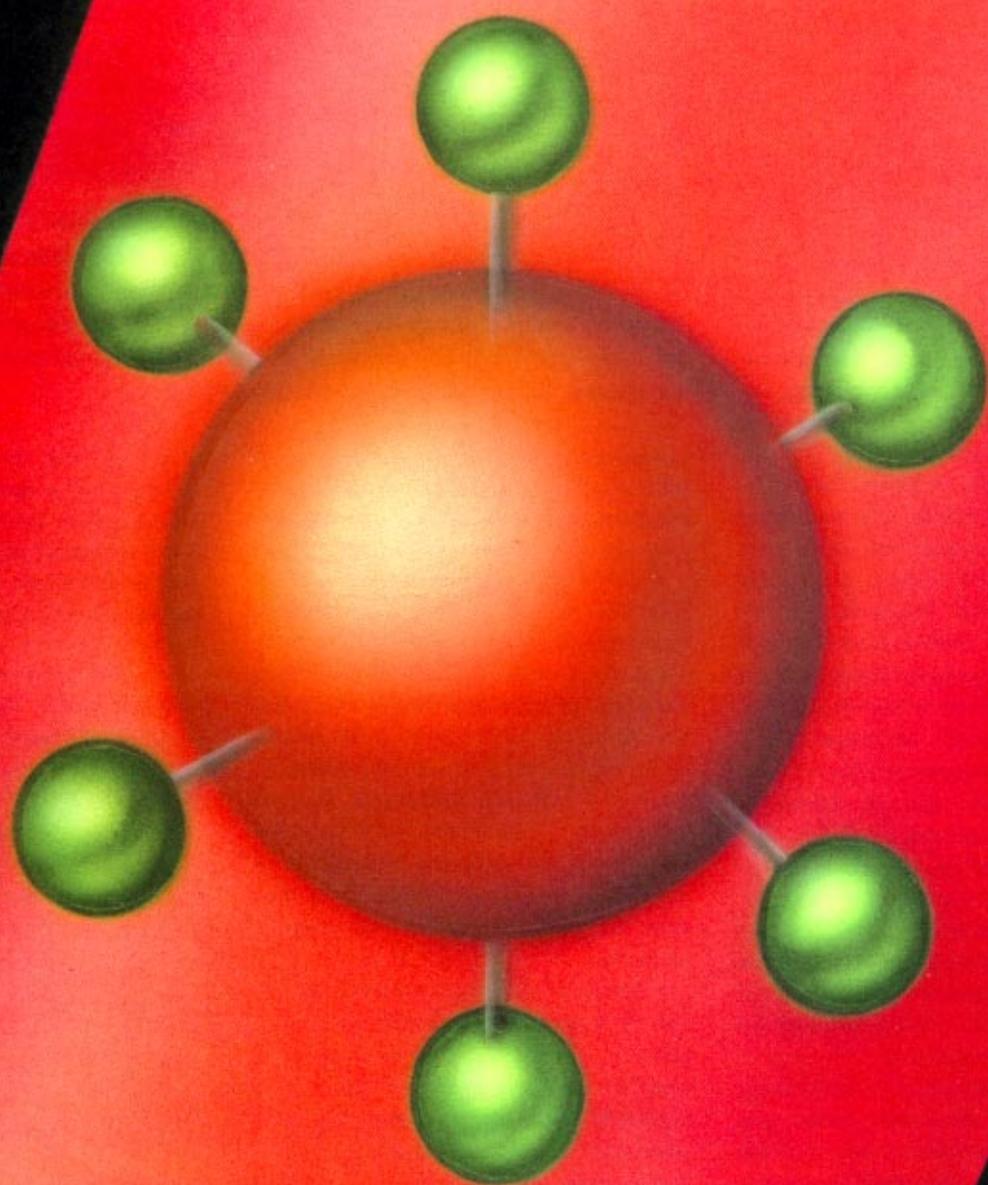
As a result of these differences, the interpretation of data for multiple-photon excitation is much more difficult than for normal absorption spectra; a given absorption feature represents the sum effect of many energy transitions in a collection of molecules driven rapidly into a nonequilibrium distribution. Dissociation data, as well as absorption data, are necessary to characterize that distribution. Also, the theo-

retical picture dealing with the effect is necessarily both statistical and dynamical in nature; it is concerned with the rates at which molecules are driven through the mesh of energy states.

This article will describe the current understanding of multiple-photon excitation and outline both the experimental and theoretical development of this fascinating research area. While the article emphasizes Los Alamos work, we note that scientists in many laboratories have contributed substantially to the understanding of the effect. Multiple-photon excitation is an important phenomenon in laser isotope separation (see "Separating Isotopes With Lasers" in this issue) and is attractive for applications like purification of chemicals, synthesis of new species, and study of chemical reactions. But we have limited our discussion to the phenomenon and its historical development.

The Old Picture

The understanding of the interaction between polyatomic molecules and intense infrared radiation is evolving to give a very different picture from what conventional wis-



dom portrayed ten years ago. In the late sixties only the most naive thought that one could use infrared lasers to induce dissociation (photolysis) of molecules. Those who knew something of infrared spectroscopy and molecular physics used the following logic to discount the possibility of infrared photolysis.

The photon energy of infrared light is substantially less than the energy required to induce most chemical reactions. In fact, photolysis of molecules that are stable at room temperature requires the energy equivalent of 20 to 50 carbon-dioxide (CO₂) laser photons.

A molecule absorbs infrared radiation by interaction of its vibrating electric dipole with the oscillating electric field of the radiation. The radiant energy becomes vibrational energy in the molecule. Because molecular vibrational energy is quantized, this absorption is best treated as a match between the energy of the photon being absorbed and the gap between the energy levels involved in the transition.

An ideal harmonic oscillator, that is, an oscillator with two masses and a restoring force that remains proportional to the separation between those masses, has equally spaced energy levels. However, all real diatomic molecules deviate from this ideal because the restoring force typically drops toward zero as the bond stretches further and further toward breakage. These molecules are vibrationally anharmonic and the spacing between adjacent vibrational energy levels decreases with excitation.

One can think of the vibrational energy levels as rungs in an interatomic-potential-energy ladder (Fig. 1). The rungs get closer as one moves up the ladder. At the top, where the levels are so close as to be, in effect, continuous, the bond breaks and the diatomic molecule dissociates.

Now if the frequency of the photon being absorbed matches the lowest energy gap (between $n = 0$ and $n = 1$ in Fig. 1), it will not match the next gap, which is smaller.

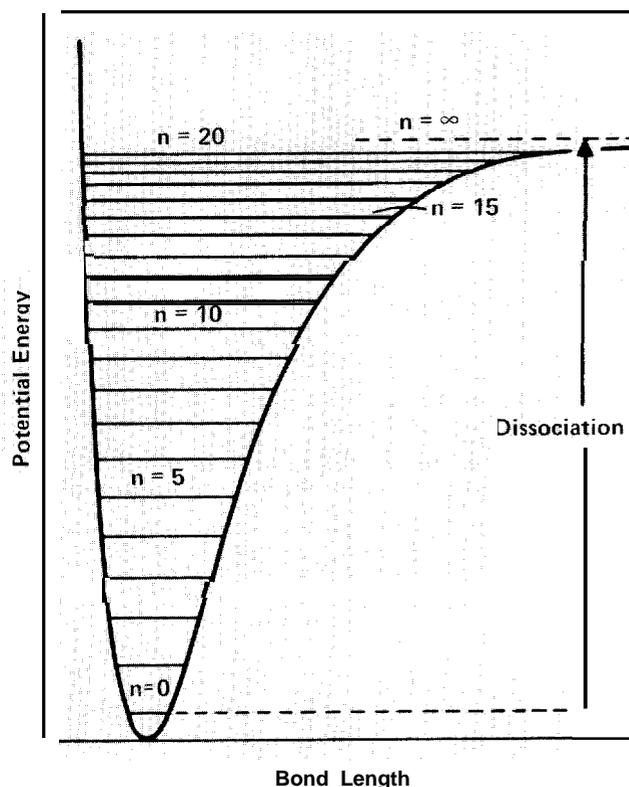


Fig. 1. The potential-energy well of a diatomic molecule. The horizontal lines represent the quantized vibrational energy levels of the molecule with the ground state labeled by $n = 0$. Near the ground state the potential-energy well is approximately harmonic and the energy levels approximately equally spaced. As the molecular bond stretches, the potential-energy curve becomes less steep and the levels merge to a continuum. At $n = \infty$ the molecule will dissociate.

The mismatch becomes progressively larger with increasing vibrational excitation and precludes the possibility that one diatomic molecule will absorb many photons.

Molecular vibrations of polyatomic molecules are somewhat more complex. However, one can resolve a particular vibrational motion into a superposition of several vibrations called normal modes. To a first approximation, each normal mode vibrates independently and maintains the characteristics of a vibrating, anharmonic diatomic molecule. Therefore, vibrational anharmonicity restricts absorption of photons by polyatomic molecules in basically the same way it does for diatomic molecules.

If this were not enough to prevent absorption of large amounts of infrared energy, another severe restriction exists. All molecules in a gas sample do not respond identically to infrared radiation because of differences in rotational and translational energy of the molecules.

In the case of rotational energy, the molecules of a gas sample are distributed among many quantized rotational states. Each rotational state may contribute differently to the total change in internal energy during an absorption, which means that molecules in different rotational states require different infrared frequencies for efficient absorption. The result is the rotational structure discussed in this issue in "The Modern Revolution in Infrared Spectroscopy."

Likewise, the translational energies (or velocities) of the molecules cover a wide thermal distribution. Each velocity component along the path of the light propagation will produce a different Doppler shift in the frequency of the infrared light as viewed by the molecule. Because the optimum frequency for absorption varies with the rotational and translational energy state, the fraction of molecules that can absorb even the first photon for vibrational excitation is greatly reduced.

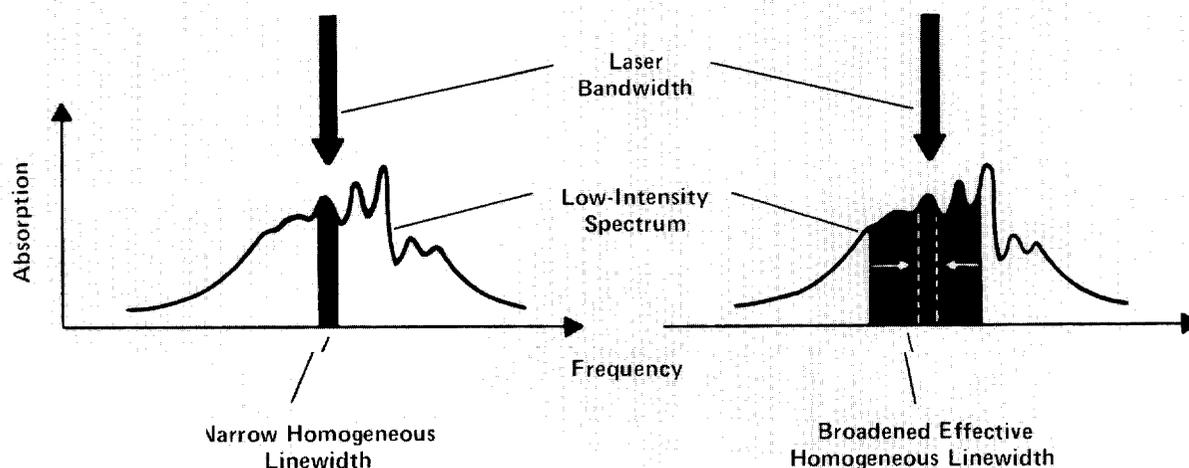


Fig. 2. Homogeneous and effective homogeneous linewidth. The low-intensity spectrum of an absorption band represents the distribution of molecules among various molecular energy states, each state with absorbing transitions at different frequencies. For the absorption on the left, the laser photons interact only with that fraction of the molecules whose states have transition frequencies falling approximately within the laser bandwidth. This fraction of molecules are said to be absorbing homogeneously because they all interact in the same

way with the photons. For this absorption the homogeneous linewidth matches the laser bandwidth. However, certain mechanisms, such as collisions that change energy states or multiphoton absorption, can cause molecules outside the laser bandwidth to absorb photons in a manner identical to those within the homogeneous linewidth. The effective homogeneous linewidth (right) has a larger frequency range that includes this larger fraction of absorbing molecules.

Molecules that all interact in a like manner with the photons are said to absorb homogeneously. Molecules in different states that interact differently with the photons are said to absorb inhomogeneously. Certain mechanisms, such as collisions, can alter the rotational and translational energy states. Thus, during a laser pulse molecules from one homogeneous collection that is not absorbing strongly can be transferred by these mechanisms into another homogeneous collection that *is* absorbing. This increases the fraction of molecules affected in a like manner by the photons. The effective homogeneous linewidth is a measure, in terms of frequency, of the extent of such mechanisms (Fig. 2). However, calculations suggest that many collisions during a pulse from an infrared laser are necessary for even a small fraction of the molecules to absorb the photons needed for dissociation. Those same collisions would tend to distribute the absorbed energy randomly among many molecules in the sample. The net effect of this particular broadening mechanism, then, would be similar to heating the sample by more conventional methods.

Photolysis might be accomplished by multiphoton absorption, which is a single, resonant interaction between several photons and two widely separated states. This effect is

another mechanism broadening the homogeneous absorption linewidth; it requires only that the sum of the photon energies match the gap between the initial and final states, thus bypassing unmatched intermediate states. However, the thirty-photon process that would be necessary for dissociation would have a vanishingly small probability of occurrence.

(Catastrophic dielectric breakdown could lead to dissociation, but this sudden ionization can only be produced in a molecular gas with extremely high-intensity infrared radiation and is quite different from multiphoton dissociation.)

The line of reasoning outlined above led to the conclusion that a single polyatomic molecule could not, in the absence of collisions, absorb sufficient energy from an infrared laser pulse to dissociate. The arguments appeared to have no serious deficiencies; they were based, for the most part, on sound principles of infrared spectroscopy. The conclusion, however, was wrong.

The Historical Development of the Multiple-Photon Effect

In the late sixties people in several laboratories began to induce chemical reactions with the newly developed CO₂ laser. The

experiments tended to fall into two categories. In the first category, absorbed laser energy induced reactions that involved the collision between two molecules. The researchers concluded that a single absorbed photon enhanced the reaction rate. In the second category, the pressure of the sample was high enough to produce rapid collisional scrambling of the absorbed energy. Both types of experiments gave results that fit well into the old picture we portrayed above.

With the advent of high-intensity, pulsed infrared sources, such as a pulsed version of the CO₂ laser, that picture began to show defects.

In 1971 researchers for the National Research Council of Canada showed that when they irradiated low-pressure SiF₄ gas with intense CO₂ laser pulses, the molecules dissociated to give electronically excited SiF fragments. The laser intensity that produced these reactions was close to, but below, the threshold for dielectric breakdown. At these low pressures, the absorption took place under nearly collisionless conditions. This experiment showed that a single, isolated molecule (and its fragments) could absorb well over one hundred photons during a laser pulse.

During the next year experiments at Los Alamos demonstrated that increased pres-

sure, and so increased collisions, impeded, rather than enhanced, the rate of laser-induced dissociation of N_2F_4 to NF_2 . A dissociation reaction that depended on simple conversion of laser energy to thermal energy in the gas would have shown the opposite pressure effect. However, these experiments were still not an unequivocal demonstration of laser-induced dissociation in the complete absence of collisions.

In the period from 1972 to 1974 several experiments gave strong evidence that CO_2 -laser pulses of modest fluence (time-integrated intensity per unit area) could induce chemical reactions producing atomic fragments. At Los Alamos CO_2 -laser pulses were used to initiate explosive reactions in mixtures of H_2 with either the absorber N_2F_4 or SF_6 . These experiments suggested that during the laser pulse the radiant energy fragmented the absorber molecule (N_2F_4 or SF_6) to produce fluorine atoms. These atoms then reacted rapidly with the H_2 to generate energy and more reactive species. This accelerating chain reaction resulted in explosion of the gas mixture. An important finding was the fact that the laser energy absorbed was significantly less than would be required in an equivalent thermally induced reaction.

Experiments at the Institute of Spectroscopy in the Soviet Union demonstrated that the laser-induced reaction of BCl_3 in the presence of oxygen produced electronically excited BO molecules. These reactions were isotopically selective. When the CO_2 -laser frequency was near the vibrational frequency of a particular isotopic form of BCl_3 , the BO fragment favored that boron isotope. About the same time researchers at the National Bureau of Standards demonstrated the laser-induced, isotopically selective reaction of BCl_3 - H_2S mixtures. The isotopic selectivity in the latter two experiments was particularly strong evidence of a nonthermal, infrared photolytic reaction.

But the experiments that demonstrated unequivocally the phenomenon of multi-

photon excitation were performed by the Institute of Spectroscopy in late 1974 and Los Alamos in early 1975. These experiments demonstrated direct photolysis of SF_6 with extremely high isotopic selectivity under conditions where molecular collisions could not have played a major role. Similar demonstrations with other species followed rapidly, as well as a broad range of explanations for the phenomenon.

The Experimental Characterization of Multiple-Photon Excitation

Multiple-photon excitation experiments exhibit many features that are independent of the particular molecular species. These features, which must be included in any successful theory of the process, will be presented below. We will start by giving a qualitative picture of the absorption and dissociation processes and then show how generic properties of the molecules, the laser pulse, and the gas sample influence the phenomenon.

QUALITATIVE FEATURES. Typical laser-induced photolysis experiments examine only the end products of the dissociative reaction. How then can multiple-photon excitation be distinguished from other possible dissociation mechanisms? For example, the dominant process might be laser ionization, rather than vibrational excitation, of the absorbing molecules. In laser ionization the observed products would be generated by ion-molecule reactions rather than single-molecule, or unimolecular, dissociation. But, since experiments have shown that laser pulses produce no ions under conditions of extensive chemical reaction, researchers now feel that the general mechanism most consistent with available data is one in which the polyatomic molecule absorbs the infrared laser energy in the form of vibrational energy. Then, if the molecule absorbs sufficient energy, the molecule may dissociate into fragments.

What type of molecules undergo multiple-photon excitation? Many of the early successful experiments were with highly symmetric molecules like SF_6 and SiF_4 . Is high symmetry an essential feature? Does molecular size play a role? From Table I, which gives a partial list of molecules that dissociate by multiple-photon excitation, we see that it is a general phenomenon. Molecular symmetry is not a restriction. Molecular size is only a partial restriction: diatomic molecules do not dissociate; some triatomic molecules like OCS and O_3 dissociate when irradiated with very intense infrared radiation; and very large molecules like uranyl-bis-hexafluoroacetate and tetrahydrofuran dissociate very easily.

One of the impressive features of multiple-photon excitation is high isotopic selectivity. We define isotopic selectivity as the ratio of dissociation probabilities of two isotopic forms of a molecule. With appropriate laser frequencies and gas pressures one can induce isotopically selective reactions in most polyatomic molecules.

Isotopic selectivity depends strongly on the isotopic shift of absorption features in the infrared spectrum. Basically, the shift is due to a change in the vibrational frequency of the molecule when one of the vibrating atoms has a different isotopic mass. As a result, isotopic selectivities tend to be large for light isotopes, where the relative change in the mass is large, and small for heavy isotopes, where the relative change is small. For example, isotopic selectivities for heavy metals like molybdenum (in MoF_6), osmium (in OsO_4), and uranium [in $U(CH_3O)_6$] fall in the range between 1.0 and 1.1. Selectivities for light isotopes like hydrogen (in CF_3H) may be as high as 20,000. For the well-studied molecule SF_6 , the selectivity for ^{33}S relative to ^{32}S is about eight, and for ^{34}S relative to ^{32}S , it is about fifty. These values are typical for intermediate atomic weight isotopes.

Isotopic selectivity observed in a wide range of molecules gave clear evidence that a

TABLE I
SPECIES DISSOCIATED BY MULTIPLE-PHOTON EXCITATION

OCS	CH ₃ OH	MoF ₆	Benzene
O ₃	CH ₃ CN	UF ₆	Cyclopropane
NH ₃	CH ₃ NC	CF ₃ CHCl ₂	Propylene
H ₂ C=O	C ₂ H ₅ Cl	CF ₃ CH ₃	Hexafluorocyclobutene
BCl ₃	C ₂ H ₅ F	C ₂ H ₅ F	Perfluorocyclobutane
CCl ₄	CF ₂ CH ₂	C ₂ H ₅ NC	Ethylvinylether
CF ₃ HCl	C ₂ H ₄	C ₂ H ₅ OH	Ethyl acetate
CF ₂ Cl ₂	N ₂ F ₄	SF ₅ NF ₂	<i>sec</i> -Butyl acetate
CF ₃ I	SF ₆	CF ₃ COCF ₃	Tetramethyldioxetane
CrO ₂ Cl ₂	SF ₅ Cl	S ₂ F ₁₀	Uranyl-bis-hexafluoroacetyl- acetate.tetrahydrofuran
HCOOH	CH ₃ NH ₂	C ₆ F ₅ H	
O ₂	CH ₃ N ₂ O	U(OCH ₃) ₆	
CHF ₃	SeF ₆	CH ₂ FCH ₂ Cl	

single molecule can absorb many infrared photons with no help from collisional processes and that the resulting vibrational energy is sufficient to induce a unimolecular chemical reaction.

These results suggested that the reactions might be bond selective. That is, if molecules absorbed laser energy under collisionless conditions, perhaps the vibrational energy remained in a single normal mode and cleaved the chemical bond that experienced the highest vibrational amplitude. If this were so, then one could select the point of reaction within the molecule by matching the laser frequency to the frequency of the appropriate normal mode.

Arguments for bond-selective dissociation by multiple-photon excitation rely heavily on many features of the old picture for the absorption of infrared radiation. Because the old picture can't explain multiple-photon excitation in the first place, one should be highly suspicious of the possibility of such a reaction. Many people claimed to have demonstrated bond-selective reactions, or at least some degree of vibrational-energy localization within a polyatomic molecule. However, in all cases that we are aware of, alternate explanations are more plausible.

Researchers at the Berkeley campus of the University of California performed experiments that not only suggested that bond-selective reactions were unlikely, but also demonstrated the collisionless nature of the multiple-photon excitation process. These experiments involved dissociating the molecules in a molecular beam with

C O₂-laser pulses. A molecular beam is a low-density stream of molecules passing through a vacuum. These conditions virtually eliminate collisions between molecules during the time the beam is in the irradiation region. When the molecules dissociate, recoil of the separating fragments frequently causes the reaction products to leave the path of the beam. This altered trajectory permits detection and identification of the fragments.

Reactions of over fifteen species containing from four to eight atoms per molecule were studied. Multiple reaction pathways were available for many of these species. However, all species reacted by the energetically most favorable pathway. This result is consistent with statistical redistribution of the available vibrational energy prior to dissociation. The velocities of the separating molecular fragments were also consistent with a statistical energy distribution.

DENSITY OF VIBRATIONAL STATES. We noted that heavier molecules dissociate more easily than lighter ones. People generally attribute this fact to the increasing density of vibrational states with increasing mass of the molecule. The density of states is simply the number of available vibrational states per unit energy interval of the molecule and is one of the profound differences between a diatomic molecule and a larger polyatomic molecule. ("The Modern Revolution in Infrared Spectroscopy" discusses the origin of this high density of vibrational states for polyatomic molecules.)

From spectroscopic constants one can obtain an adequate estimate of the density of vibrational states. Figure 3 shows how this density depends on vibrational energy for several representative molecules. We see a huge difference in the state density between a small molecule like OCS and a larger one like S₂F₁₀, even at modest energies.

A high state density gives an immense statistical advantage to absorption by large molecules. For example, at an energy near the dissociation threshold of S₂F₁₀ (20,000 cm⁻¹), the densities of vibrational states for S₂F₁₀ and OCS differ by a factor of 10²². This means that if molecules of both species were in equilibrium with some environment (such as a radiation field or a thermal gas), the probability that the S₂F₁₀ molecule is in a vibrational state near 20,000 cm⁻¹ could be as much as 10²² times the same probability for the OCS molecule. Of course, absorption of laser radiation is certainly not an equilibrium process. Moreover, as the energy or temperature of the environment increases and both molecules become distributed throughout a large range of energy levels, the probability ratio will decrease below the 10²² factor. Nevertheless, the huge statistical advantage remains for larger molecules.

Recent dissociation experiments with polyatomic molecules have demonstrated the effect of the density of vibrational states on multiple-photon excitation. To facilitate comparison of these experiments we define two parameters, $\Phi_{1\%}$, the fluence needed to dissociate 1% of the molecules in the laser beam, and $N(10,500)$, the density of vibra-

tional states for each molecule at 10,500 cm^{-1} , which is about half the energy needed to dissociate a typical molecule.

Figure 4 shows the relationship between these two quantities in many different experiments with a wide range of experimental conditions. We see the trend of decreasing $\Phi_{1\%}$ (easier dissociation) with increasing $N(10,500)$ (higher density of vibrational states).

There are, of course, many other variables in these experiments. These include: absorption cross section, chemical bond strength, frequency relative to the infrared absorption band, gas pressure, laser pulse shape, and laser spectral width. To eliminate some of this diversity we report the results of a set of experiments performed under more controlled conditions (Table II). These results all came from the same laboratory (Los Alamos), and the laser pulse shape and gas pressure were nearly the same for all experiments. The species all have the structure SF_nX allowing the laser frequency to be set near the center of a strong infrared absorption band of a sulfur-fluorine stretching vibration for each species. The main parameter that still varies is the strength of the weakest chemical bond: from 50 kilocalories per mole for SF_2NF_2 to 93 kilocalories per mole for SF_6 . However, the most dramatic effect obvious from Table II is the decrease in $\Phi_{1\%}$ with increasing density of states.

The strength of the chemical bond that breaks when the molecule dissociates plays a weaker role in determining $\Phi_{1\%}$. For example, SiF_4 and OsO_4 have similar vibrational-state densities. But SiF_4 has a bond strength of 142 kilocalories per mole and a $\Phi_{1\%}$ of 8.9 joules per square centimeter; OsO_4 has a strength of only 73 kilocalories per mole and a $\Phi_{1\%}$ of 1.1 joules per square centimeter.

The correlation with bond strength is not as strong as the correlation with certain of the other factors. In fact, it is not difficult to find a pair of molecules where the more strongly bound molecule dissociates more

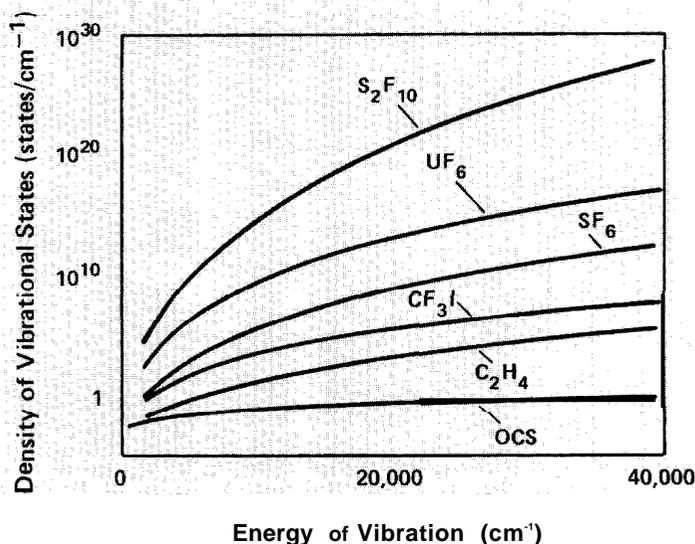


Fig. 3. Density of vibrational states for various molecules as a function of vibrational energy. The density of vibrational states, that is, the number of available states per unit energy interval, increases for all molecules as vibrational excitation increases. However, the large molecules have considerably larger densities than the small molecules at all but the lowest energies. [Here, frequency in wavenumbers is used as an energy unit: 1 reciprocal centimeter (cm^{-1}) = 1.24×10^{-4} electron volt (eV). Also note the logarithmic scale for density of vibrational states.]

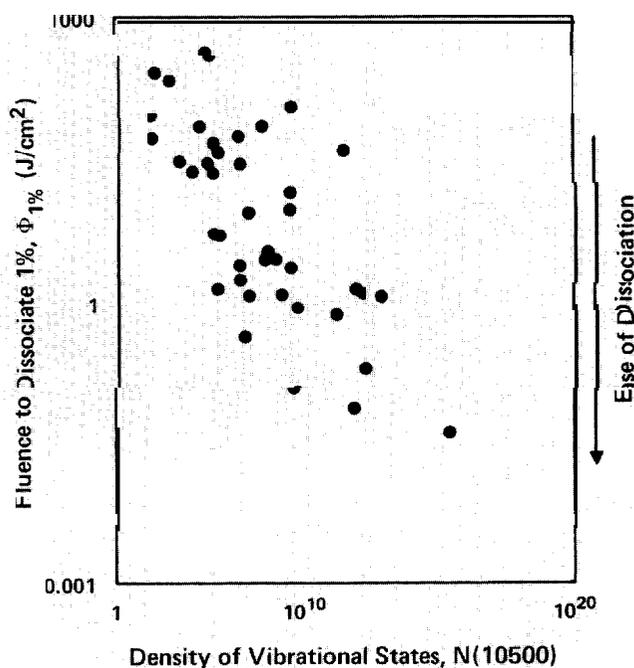


Fig. 4. The dissociation efficiency for various molecules as a function of vibrational state density. The parameter $\Phi_{1\%}$ is the laser fluence (in joules per square centimeter) needed to dissociate 1% of the molecules. Thus, a lower $\Phi_{1\%}$ implies easier dissociation. The overall trend is easier dissociation for larger molecules with higher vibrational state densities (here measured for each molecule at an energy of 10500 cm^{-1}).

TABLE II
COMPARISON OF FLUENCE NECESSARY TO DISSOCIATE 1% OF MOLECULES IN BEAM

Species	N(10500) (l/cm ⁻¹)	Bond Strength (kcal/mole)	$\Phi_{1\%}$ (J/cm ²)
SF ₆	8.5 x 10 ⁸	93	2.8
SF@	2.1 x 10 ⁹	61	0.6
SF ⁵ NF ²	2.6 X 10 ¹²	50	0.05
S ² F ¹⁰	3.1 x 10 ¹⁷	58	0.018

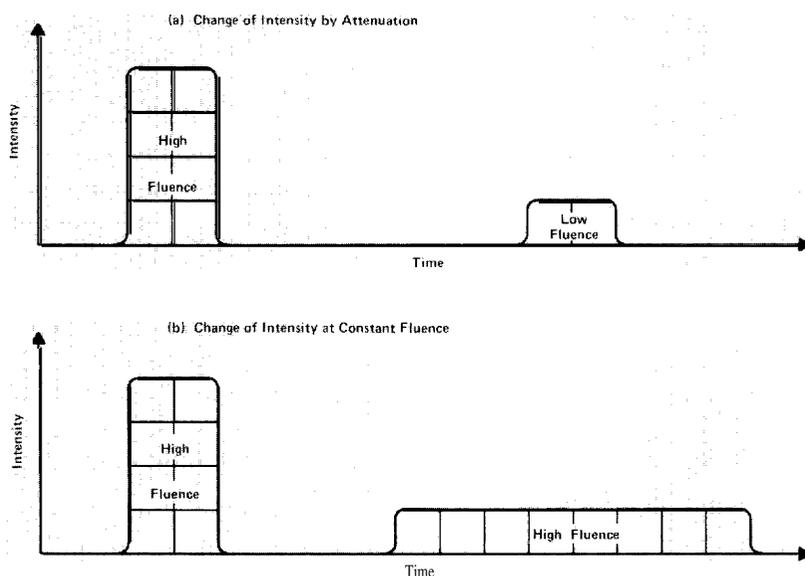


Fig. 5. The intensity-fluence relationship. Laser intensity (power per unit area) is given as a function of time by the height of these idealized laser-pulse curves. The fluence (energy per unit area) is the time-integrated laser intensity, or the area under each curve. (a) If the laser pulse is attenuated (by placing a partial absorber in the beam or by refocusing to a larger area) both the intensity and the fluence are reduced. (b) If the laser pulse is attenuated but, at the same time, the pulse length is increased proportionately, the fluence can be held constant while the intensity is reduced.

easily. Again, from Table II, the density of vibrational states for S₂F₁₀ is larger than for SF₅NF₂, and this fact appears to be more important for ease of dissociation than the weaker bond strength of SF₅NF₂.

FLUENCE EFFECTS. One of the more easily varied parameters in a multiple-photon excitation experiment is the laser fluence. The fluence can be varied by placing attenuators in the beam or by focusing the beam differently in the sample (Fig. 5a). As observed by many researchers, variations in fluence produce profound changes in the dissocia-

tion probability and the absorption cross section.

Figure 6 shows how the laser fluence, Φ , affects the absorption cross section, σ , and dissociation probability of a large molecule (SF₅NF₂). Figure 7 shows the corresponding curves for a somewhat smaller molecule (C₂H₄). Both the differences and similarities between these figures are instructive.

At the threshold for dissociation, the fluence, Φ_{TH} , differs for the two molecules by a factor of about 10³. However, the absorption cross section at threshold, σ_{TH} , also differs by about this factor, only inversely, so

that the product $(\sigma\Phi)_{TH}$ is about the same for both molecules ($\approx 10^{-19}$). The fluence times the cross section is proportional to the energy absorbed per molecule, E_{ab} .

$$E_{ab} \propto \sigma\Phi.$$

Thus both molecules need to absorb approximately the same energy to reach the threshold for dissociation. Furthermore, the observed value of $(E_{ab})_{TH}$ corresponds to about half the energy needed to dissociate either of the molecules. If only a small fraction of the molecules were absorbing the energy, the dissociation reaction would have started at a much lower fluence. These facts suggest that the molecules behave similarly at high levels of excitation and that the absorbed energy must be distributed among many molecules.

For the large molecule (Fig. 6), the cross section remains almost constant from low fluence up to the threshold for dissociation (for both long and short pulses). The drop in cross section at this point is probably due, for the most part, to dissociation of the molecules during the laser pulse. In other words, the probability for absorption of a photon by the molecule remains constant from the low-fluence limit where the molecule's initial state of excitation is low to near the threshold for dissociation where the molecule is highly excited. This behavior contrasts dramatically with the old-picture prediction that the absorption cross section would drop rapidly with excitation due to a growing anharmonic mismatch between photon energy and the gaps in the vibrational energy ladder.

A high absorption cross section over a broad range of fluence suggests that all of the molecules are absorbing laser radiation regardless of their translational or rotational energy states. In terms of linewidth, this means the effective homogeneous linewidth

is on the order of the frequency width of the entire low-intensity absorption band: a broadening mechanism is apparently at work. The high cross section at high fluence suggests that any anharmonic frequency shift with increasing vibrational excitation is less than this effective homogeneous linewidth.

We reach opposite conclusions with the smaller molecule (Fig. 7). The low absorption cross section suggests that at low fluence only a small fraction of the molecules are able to absorb laser radiation. The immediate drop in cross section with increasing fluence suggests that this small fraction is easily depleted. Thus, the homogeneous linewidth for the absorption is much less than the frequency width of the low-intensity absorption band and there is no significant broadening mechanism at low fluence. The low, but finite, cross section at high fluence suggests that the anharmonic frequency shift substantially reduces, but does not eliminate, the probability that an excited molecule absorbs more photons.

Other types of experiments confirm these conclusions. Increasing the pressure (collision rate) increases the absorption cross section for small molecules at high fluence whereas pressure has little effect on the cross section for large molecules. As pointed out earlier, collisions change the energy state of the molecules, bringing more of them into states where absorption is favorable. Similar changes in large molecules are insignificant because the already larger homogeneous linewidth makes absorption somewhat independent of energy state.

In summarizing the above findings for small molecules, we see an intriguing difference between the extremes of low and high fluence. At low fluence only a small fraction of the small molecules absorb photons. This conclusion follows from the large effect pressure has on the effective homogeneous linewidth and the early drop in cross section with increasing fluence. At high fluence a much larger fraction of the small molecules absorb photons. This follows from the facts that, on the average, the molecules absorb

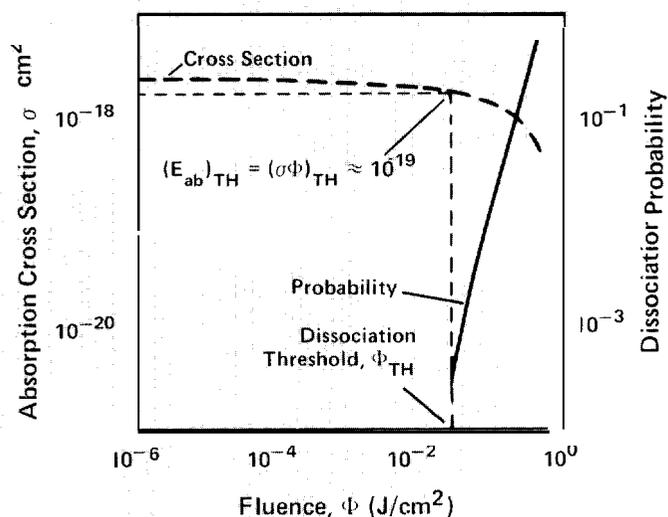


Fig. 6. Absorption cross section (dashed curve) and dissociation probability (solid curve) for SF_5NF_2 . For this large molecule the absorption cross section remains fairly constant with laser fluence out to the threshold fluence, Φ_{TH} , at which dissociation starts. The product of Φ_{TH} and the corresponding threshold absorption cross section is proportional to the average energy absorbed per molecule at threshold conditions; this average is about 10^{19} joule and represents about half the energy needed for a molecule to dissociate. Data are from John L. Lyman, Wayne C. Danen, Alan C. Nilsson, and Andrew V. Nowak, *Journal of Chemical Physics*, 71,12061210 (1979).

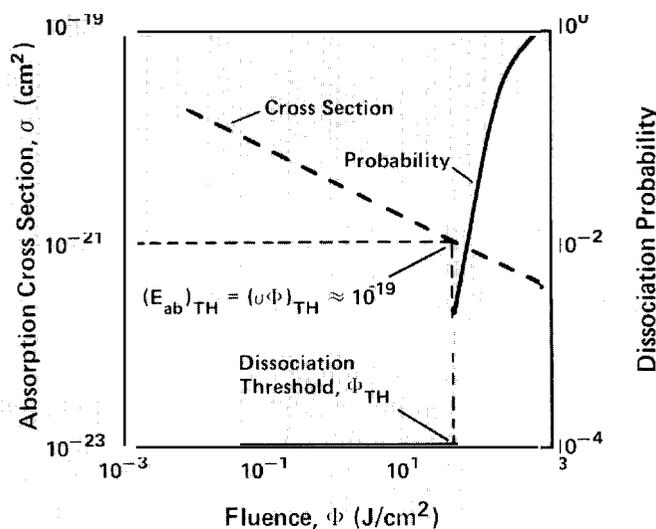


Fig. 7. Absorption cross section (dashed curve) and dissociation probability (solid curve) for C_2H_2 . The absorption cross section for this smaller molecule decreases with increasing fluence long before the threshold fluence for dissociation is reached. Despite large differences in threshold fluence and cross section between this molecule and SF_5NF_2 (Fig. 5), the energy absorbed per molecule at the dissociation threshold is approximately the same. This suggests that both molecules behave similarly at high levels of excitation. The resemblance in the rise of dissociation probability with fluence for both molecules further strengthens this suggestion. Data are from O. N. Avatkov, V. N. Bagratashvili, I. N. Knyazev, Yu. R. Kolomiiskii, V. S. Letokhov, V. V. Lobko, and E. A. Ryabov, *Soviet Journal of Quantum Electronics* 7, 412-417 (1977).

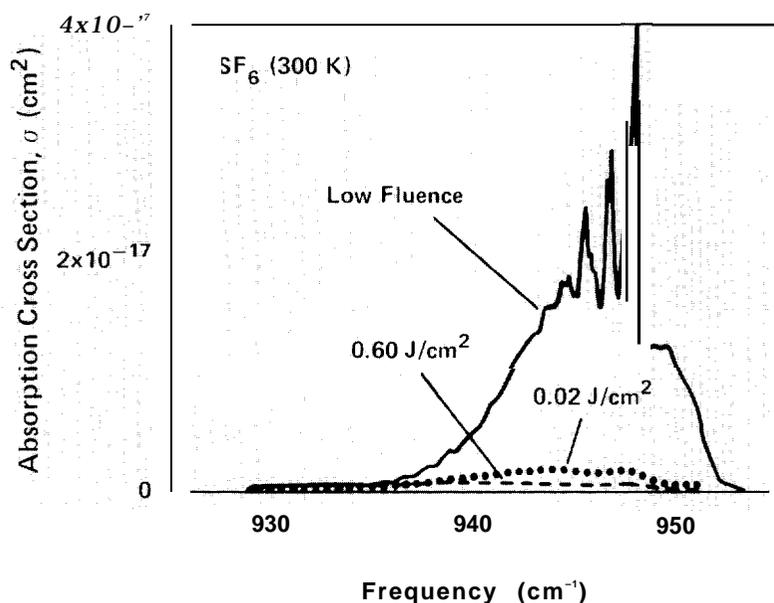


Fig. 8. Fluence dependence of the ν_3 absorption band of SF_6 at 300 kelvin. The low-fluence spectrum was obtained at a fluence typical of conventional spectroscopy, whereas the two high-fluence spectra were obtained with a pulsed CO_2 laser. The most obvious effect of high fluence is a significant drop in the absorption cross section. There is also an indication of a shift to lower frequencies. The high-fluence data are from Wei-shin Tsay, Clyde Riley, and David O. Ham, *Journal of Chemical Physics* 70, 3558-3560 (1979); the low-fluence data are from A. V. Nowak and J. L. Lyman, *Journal of Quantitative Spectroscopy and Radiative Transfer* 15,945 (1975).

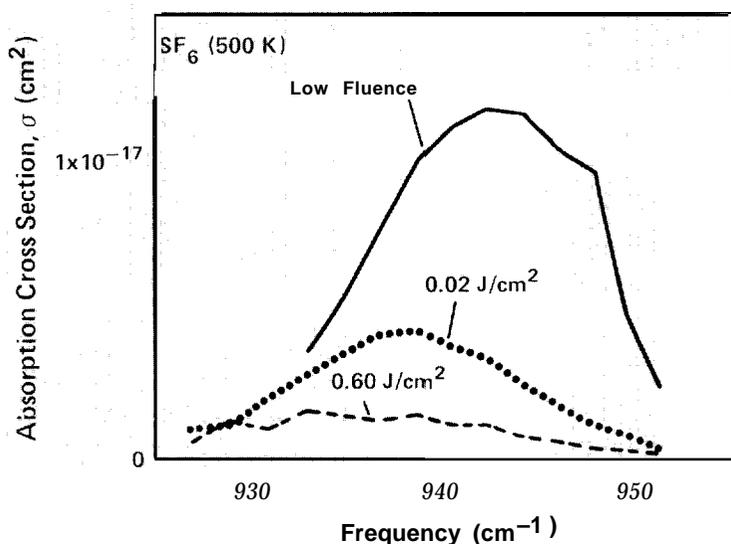


Fig. 9. Fluence dependence of the ν_3 absorption band of SF_6 at 500 kelvin. The increase in temperature @rem 300 kelvin in Fig. 7) eliminates the structure in the low-fluence spectrum. Also, the drop with increasing fluence in the absorption cross section is less precipitous, making obvious the shift to lower frequencies. The data are from the same references cited in Fig. 8.

half the energy needed for dissociation before reaching the threshold, and that thereafter, the reaction probability increases as rapidly as for large molecules.

INTENSITY EFFECTS. When the fluence is varied with attenuators or by focusing the beam differently, the intensity (laser power per unit area) also changes (Fig. 5a). To separate the effects of intensity and fluence, researchers usually vary the intensity while holding the fluence constant. This is a difficult task because it requires changing the temporal shape of the laser pulse while keeping the total pulse energy constant (Fig. 5b). For instance, rapid electro-optical shutters can change the pulse length at the sample. but, at the same time, one must either refocus the beam or change the attenuation to keep the total energy per unit area constant.

The general observation from experiments of this type is that, unlike the effects of fluence, only in special situations does intensity play a major role. One of these situations is for high gas pressures when frequent collisions redistribute the absorbed energy. Thus, the critical effect is the number of these collisions that take place during the laser pulse, rather than the interaction between the laser field and an isolated molecule. As intensity is varied by changing pulse length, the total number of collisions during the pulse will change, altering the ultimate energy distribution.

FREQUENCY DEPENDENCE. Polyatomic molecules absorb low-fluence infrared radiation in frequency bands that correspond to the frequencies of normal-mode vibrations (or some combination of those frequencies). We would expect multiple-photon excitation to have a similar frequency response, but with some modification because of the fact that high-fluence laser pulses severely perturb the absorbing sample. Early experiments verified this approximate relationship between low- and high-fluence spectra.

Figures 8, 9, and 10 compare low- and high-fluence spectra in the region of an

absorption band for SF_6 at two temperatures and for S_2F_{10} at one temperature. In all three examples we see a similarity between the spectra at high and low fluences, but with a shift to lower frequencies at high fluence. This is most certainly related to the anharmonic frequency shift. High-fluence absorption involves excitation up several rungs of the anharmonic ladder with the resonant frequency quickly becoming mismatched. A somewhat lower frequency that matches an intermediate rather than the lowest energy gap is optimum because it averages the mismatch over more levels. Moreover, as suggested earlier, multiphoton absorption necessarily occurs at lower frequencies. As one would expect from our previous discussion, we also see a decrease in absorption cross section at high fluence, and that decrease is most pronounced for the lighter molecules (SF_6) at the lower temperature (300 kelvin).

The effect of temperature on high-fluence spectra is most interesting. For SF_6 the absorption cross section drops quickly with increasing fluence at 300 kelvin but drops much less quickly at 500 kelvin. This could be related to the degree of initial vibrational excitation in the molecule because most SF_6 molecules are not excited at 300 kelvin whereas most are excited at 500 kelvin. For larger molecules, such as S_2F_{10} , even at 300 kelvin there is little loss of cross section with increasing fluence. Again, this could be related to vibrational excitation because these molecules have pliant bending modes with lower energy levels and even at 300 kelvin virtually all molecules have some degree of vibrational excitation. In terms of linewidth, it appears that increased vibrational excitation increases the effective homogeneous linewidth so that a larger fraction of the molecules are able to absorb photons. This trend with vibrational excitation parallels the previously observed trends with density of vibrational states and molecular size. Thus, vibrational excitation may be one, but perhaps not the only, reason for the

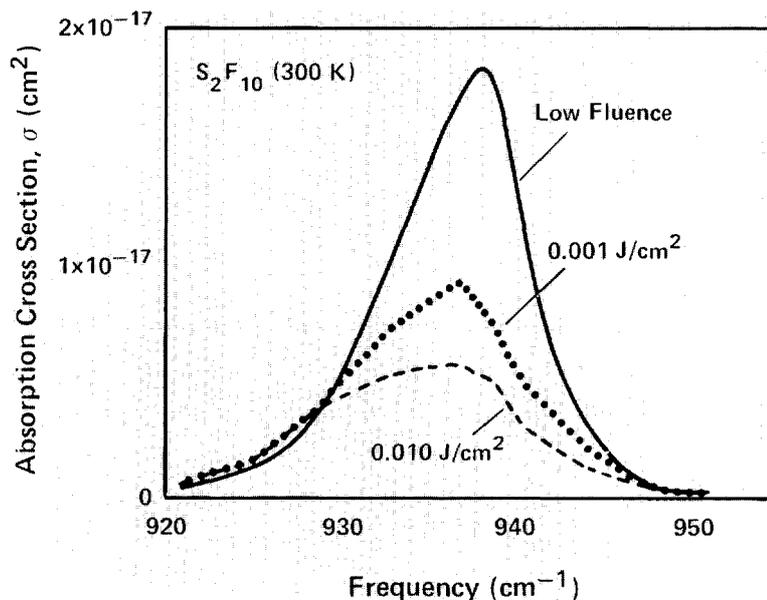


Fig. 10. Fluence dependence of an absorption band of S_2F_{10} at 300 kelvin. Higher fluence here results in a moderate drop in absorption cross section and a shift to lower frequencies. This behavior resembles that of the small SF_6 molecule at high temperature (Fig. 9). Data are from John L. Lyman and Kevin M. Leary, *Journal of Chemical Physics* 69, 1858-1864 (1978).

state-density trend.

EXPERIMENTAL CONCLUSIONS. Clearly, conclusions drawn from the data for multiple-photon excitation experiments do not fit the old picture of the absorption of photons. Most significantly, at high fluence the laser frequencies need not match the absorption features exactly. We suggest four phenomena that contribute to this observation.

1. Absorption in the wings of a spectral line is possible because the cross section does not go to zero, but decreases with the square of the distance from line center.
2. The laser field itself can broaden the absorption lines by a process called Rabi broadening (this will be discussed in more detail later).
3. Multiphoton absorption, which bypasses one or more intermediate states, occurs at frequencies displaced slightly from the single-photon spectrum.
4. Most of the larger molecules have some degree of vibrational excitation *prior* to laser irradiation (because of the higher density of vibrational states), while the smaller molecules do not, and this excita-

tion may play a role similar to collisions in allowing for homogeneous absorption.

The first effect means that there will always be a small amount of off-resonant energy absorbed and that this amount will increase with fluence. The next two effects increase the effective homogeneous linewidth with increasing fluence, and the last effect accounts for differences between large and small molecules at low fluence.

Collisionless Multiple-Photon Excitation Theory

A theory of multiple-photon excitation should be consistent with the experimental observations that we have outlined above. The theory should explain the effect of vibrational-state density. It should give the proper fluence and frequency dependence. It should give an increasing homogeneous linewidth with the degree of vibrational excitation. And it should also suggest additional experiments whereby one could further check the theory.

Early attempts at theories ranged from strict compliance with the old picture to complete rejection of that picture. Enough experimental evidence has accumulated now

to force recognition of two points: multiple-photon excitation is a general, not a peculiar, limited, phenomenon; and theoretical explanation will require an expansion and modification of the old picture in terms of a variety of effects such as absorption line broadening, multiphoton absorption, higher-order interactions among normal-mode states, and intramolecular energy flow between states.

THEORETICAL APPROXIMATIONS. Generally, one bases a theory of light absorption on a quantum-mechanical description of the absorbing medium and either a classical or quantum-electrodynamic description of the light. In the case of multiple-photon excitation, the question is not whether fundamental concepts such as the Schrodinger equation or Maxwell's equations are correct, but rather, what degree of approximation is necessary in the application of the basic theories to this complex problem. In our opinion, the major problem with the old picture was that it used approximations appropriate for spectroscopy problems but not for the multiple-photon problem.

Before we begin to consider the more detailed physical process of multiple-photon absorption in polyatomic molecules, let us review those properties of a molecule that allow it to absorb electromagnetic radiation and point out in this review the various approximations that are needed. First, a molecule consists of some number of atoms bound together by interatomic electromagnetic forces at fixed separation distances and at fixed relative orientations. These positions are obviously not absolutely rigid, but are only relative equilibrium locations for each nucleus.

As a result of the very large mass difference between the electrons and the nuclei, it is valid to treat the electronic and nuclear motions as independent. This approximation, due to Born and Oppenheimer, assumes that the electrons produce a potential in which the nuclei vibrate. For the SF_6 molecule, the

approximation reduces the complexity of the description of vibrational motion from 77 particles (70 electrons and 7 nuclei) to 7 particles.

Because the negative charge of the electrons and the positive charge of the nuclei are spatially separated, it is possible to establish or change an electric dipole moment in the molecule by displacement of any charged particle from its equilibrium position. Typically, it is photons in the infrared whose frequencies match those of the changing dipole moments generated by nuclear displacements (vibrations). The ensuing interaction leads to the absorption of infrared photons.

Displacements of the nuclei from their equilibrium positions can be described by harmonic motions that are referred to as the normal modes of the molecule. The normal-mode approximation allows one to describe the motion as many uncoupled motions. This further reduces the 7-particle problem to a set of 1-particle problems. Furthermore, in conventional infrared spectroscopy one treats interactions between normal modes as minor perturbations on the initial uncoupled motions. This set of approximations gives excellent solutions to infrared-spectroscopy problems when the molecules are in or near the ground vibrational state. This approach is discussed at several levels of perturbation in "The Modern Revolution in Infrared Spectroscopy."

In any octahedral XY_6 molecule there are fifteen normal modes, but, because symmetry leads to mode degeneracies, only six are at different frequencies. Of these only the triply degenerate modes ν_3 and ν_4 generate a changing electric dipole moment and therefore absorb infrared radiation. These normal modes behave initially like harmonic oscillators, but as energy is put into these motions their anharmonic nature becomes more pronounced until dissociation is reached.

In addition to the vibrational motion just discussed, a molecule also undergoes rota-

tional and translational motion. Because translational motion does not affect the internal molecular structure, but leads only to small Doppler broadening of the absorption features, we will neglect it in further discussions. The combined motion of vibration and rotation leads to a greater wealth of possible transitions so that a single vibrational absorption feature actually consists of a broad absorption band containing thousands of individual rotational-vibrational transitions. This rotational broadening is not unlike Doppler broadening in nature, but the effects in frequency dispersion are far greater and must be included here.

So far our discussion has dealt mainly with theory used for conventional spectroscopy, in which only the lowest vibrational excitations are induced by low-intensity light. Do the same assumptions apply when vibrational excitation is high enough to cause dissociation of the molecule? The most well-established theory for the unimolecular dissociation of polyatomic molecules is the so-called RRKM unimolecular reaction-rate theory. Without describing the RRKM theory in detail, we can say that it retains the first approximation of separability of electronic and nuclear motion. However, instead of assuming a very weak coupling among normal modes of vibration, the theory assumes that the interaction among the vibrational states at high vibrational energies is strong enough to continuously maintain a statistical distribution of population among those states. The normal-mode approximation is used in the RRKM theory only to count vibrational states at energies near that needed to dissociate the molecule. This theory explains a large body of data on unimolecular reaction rates for dissociation of molecules with high levels of vibrational energy.

A successful theory of multiple-photon excitation would probably contain elements of both of the previous theories. The initial

absorption of intense infrared radiation produces low vibrational excitation where the normal-mode approximation of the old theory applies. But at excitation energies near the dissociation limit, the molecule is in a state where the approximations of the RRKM theory apply. Also, a theory for multiple-photon excitation can no longer treat the laser radiation simply as a probe because it severely perturbs the absorbing sample.

We will further restrict our theoretical description to the absorption of infrared laser photons by isolated molecules. The introduction of collisions into the theory precludes any first principle description of the problem and, in fact, masks the more interesting phenomena we wish to study here.

A NEW PICTURE. we begin a theoretical explanation of collisionless multiple-photon excitation by sketching a new picture with the three major parts shown in Fig. 11: the region of discrete, low-energy levels described by conventional spectroscopic theory; the region of high-energy levels and high density of states described by RRKM theory; and a region called the molecular quasicontinuum that connects these two extremes. The discrete, low-energy region of Fig. 11 shows resonant absorption at the frequency of the laser, ν_L , in the fundamental of an infrared-active mode, such as ν , for SF_6 . As excitation advances, the anharmonicity necessarily causes a gradual mismatch between the laser frequency and the resonance frequency for excitation to the next higher state.

However, at about the energy level where the mismatch becomes significant, the multiple-photon excitation process merges into the second part of our theoretical picture. In this middle region the excited states of the resonant mode mix with other "background" states (vibrational states at the same energy with different normal mode character.) Briefly, this mixing occurs because the normal mode vibrations are not truly independent, but rather are loosely coupled to each other.

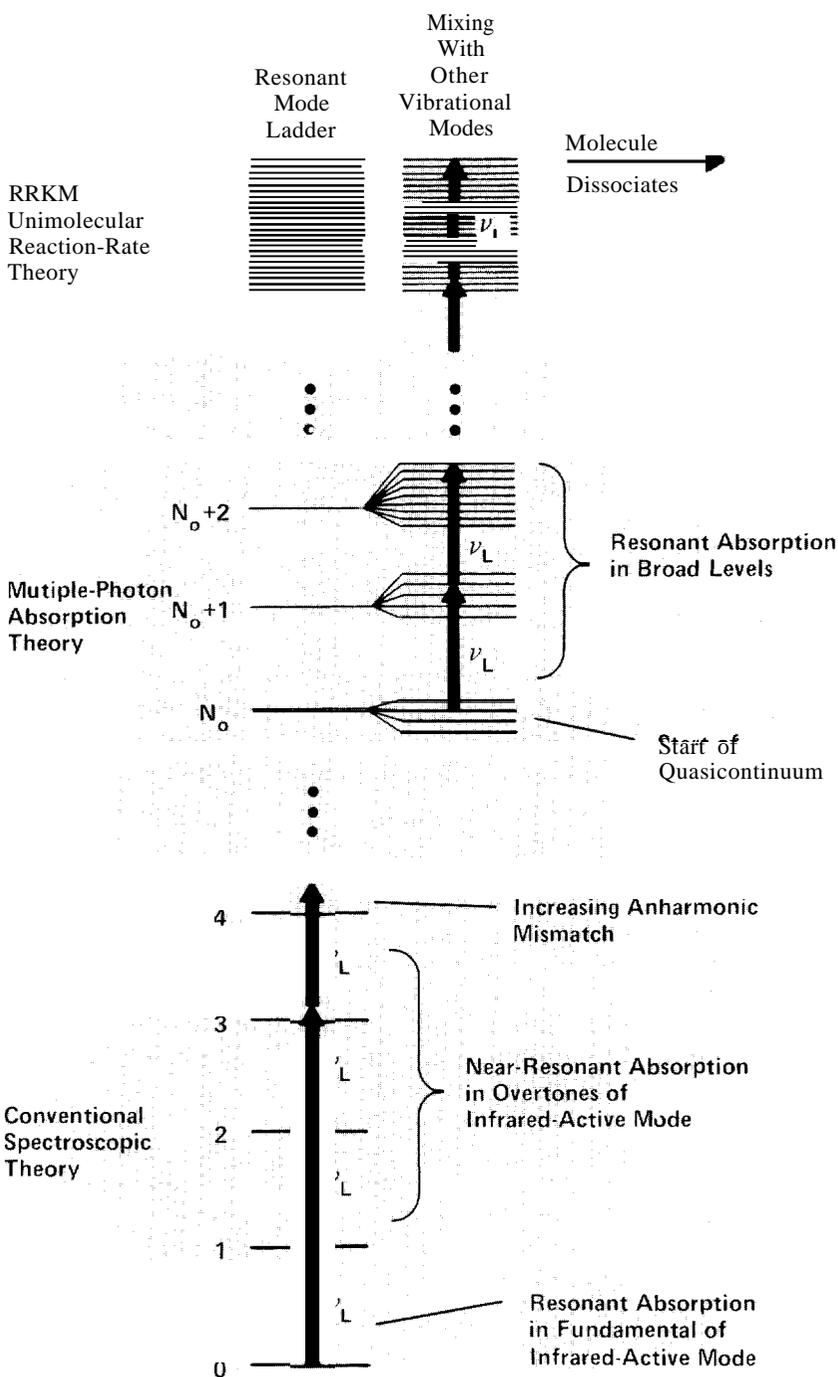


Fig. 11. Theoretical framework of multiple-photon excitation.

Most importantly, this mixing process causes shifts and broadening of the excited states of the molecule. With enough mixing a fine mesh of states, the molecular quasicontinuum, is formed that compensates for the anharmonicities and allows further absorption of laser photons. The mixing allows access to the full density of vibrational states with its huge statistical advantage for absorption. Laser excitation through the

quasicontinuum is resonant, but of a nature different from the simple normal mode excitation that occurs at the low molecular levels: the quasicontinuum states obey quite different dynamics owing to their "strong admixture" character.

Finally, the third part of our theoretical picture in Fig. 11 is reached when enough energy for dissociation has been absorbed. In this region, a statistically random dissociation

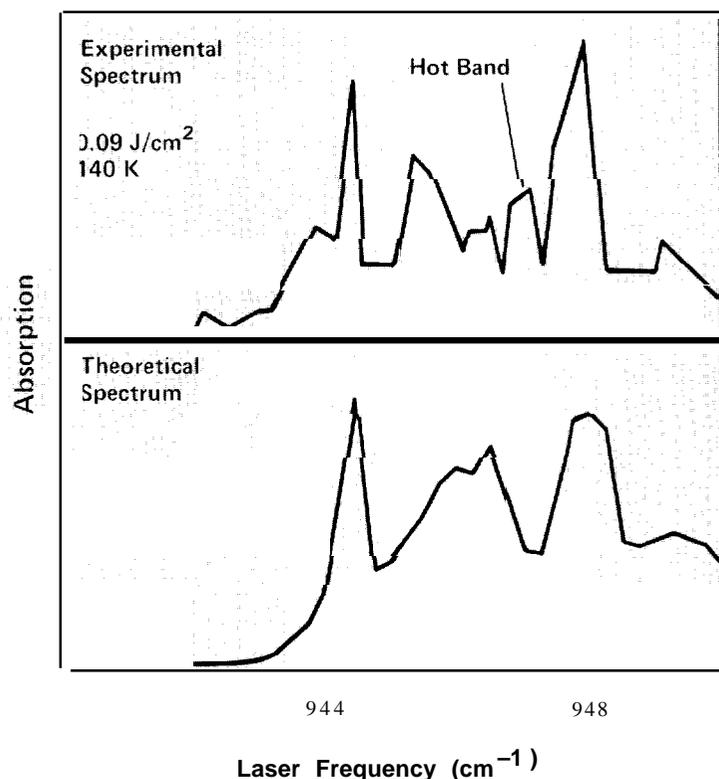


Fig. 12. Experimental and theoretical high-fluence spectra in the region of the ν_3 absorption of SF_6 . The theoretical spectrum was computed for coherent transitions within the three-level system of $0\nu_3$, $1\nu_3$, and $2\nu_3$. Since all molecules were assumed to be initially in the ground state, the theoretical spectrum does not include the hot-band absorption ($\nu_6 \rightarrow \nu_6 + \nu_3$) present in the experimental spectrum. The experimental spectrum is based on data from S. S. Alimpiev, N. V. Karlov, S. M. Kikiforov, A. M. Prokhorov, B. G. Sartakov, E. M. Kohkhlov, and A. L. Shtarkov, *Optics Communications* 31, 309-312 (1979).

tion occurs that can be described by the RRKM unimolecular reaction-rate theory.

Let us now proceed more slowly through the stages of excitation within the framework of a more detailed model constructed by workers at Los Alamos and applied to SF_6 , S_2F_{10} , and UF_6 . All of these molecules have been dissociated with infrared laser photons and, therefore, must proceed through these stages of excitation. A molecule that cannot be dissociated may simply be reaching a bottleneck at the first stage of excitation because the quasicontinuum may not occur low enough in the molecule's vibrational ladder to overcome the anharmonicity.

THE DISCRETE, LOW-ENERGY REGION.

We have obtained very-high-resolution spectra, for both SF_6 and UF_6 , of the ν_3 fundamental band (transitions from the ground state to the first excited state: $0 \rightarrow \nu_3$) and of the second overtone of ν_3 (transitions from

the ground state to the third excited state: $0 \rightarrow 3\nu_3$). By using the spectroscopic data as a basis, a great wealth of information has been obtained about the multiple-photon ladder in the discrete, low-energy region for these molecules.

Two important conclusions follow from this work. First, vibrational splittings that relate to the octahedral symmetry of the SF_6 molecule are a dominant feature of the degenerate energy levels of the ν_3 overtones and may provide levels that compensate for anharmonicity in the discrete, low-energy region. These octahedral splittings are due to interactions between the degenerate components within the ν_3 vibrational ladder. As such, octahedral splittings are not the same as the mixings that generate the molecular quasicontinuum, namely, the mixings between levels with different normal-mode character. Octahedral splittings were anticipated in early work at Los Alamos, but there

was no empirical confirmation until infrared spectra of overtones had been obtained. These splittings are discussed in "The Modern Revolution in Infrared Spectroscopy."

The second conclusion drawn from the spectra is the fact that the quasicontinuum and coupling to other vibrational modes play no role below or even at the $3\nu_3$ level. This is a surprising result because the background vibrational density of states is already $\approx 10^4$ states per cm^{-1} at $3\nu_3$. The data clearly indicate a very weak coupling strength between the $3\nu_3$ overtone levels and this multitude of background states, although the data do not preclude mixing within the background states. The data also show us that simple state counting is not enough for a determination of the energy level that marks the beginning of the quasicontinuum. In fact, a determination of the level and the mechanism for the start of the quasicontinuum with respect to the background state mixing is one of the major outstanding theoretical problems.

These conclusions about the start of the quasicontinuum apply only to molecules that are initially in the ground vibrational state. Excitation in lower vibrational states of other modes prior to laser excitation may substantially alter the quasicontinuum character of the absorber by providing an interaction pathway between the ν_3 mode and states that are not directly coupled to ν_3 -mode states. Because temperature alters the population of the lower vibrational states, absorption features whose transitions originate in these states are usually referred to as hot bands. At 0 kelvin all of the molecules are in the ground state.

The analysis of multiple-photon absorption up the ν_3 ladder begins with the solution of the time-dependent Schrodinger equation for multiple-level systems. The Hamiltonian used is

$$H = H_m - \vec{\mu} \cdot \vec{E}(t).$$

Here H_m describes the energy levels of the

molecule and $-\vec{\mu} \cdot \vec{E}(t)$ describes the interaction between the laser photons and the molecule. The molecular Hamiltonian, H_m , has been developed to second order of perturbation for octahedral molecules, and many of the molecular parameters have been evaluated using the spectra of ν_3 and $3\nu_3$ ("The Modern Revolution in Infrared Spectroscopy"). Typically, H_m contains terms of both scalar and tensor nature that account, respectively, for energy-level shifts and energy-level splittings, including the vibrational octahedral splittings.

The wave function for the total Hamiltonian, H , is expanded in the basis of the first-order molecular energy states so that all operators, except those associated with the octahedral splitting and the photon-molecule interaction, are already diagonal. Ignoring collisions, each rotational state in the ground vibrational state can be chosen to be independent; that is, the absorption for different rotational states is inhomogeneous. Excitation modeling is then done individually for each rotational ground state and the resulting populations are averaged with the appropriate Boltzmann distribution factors at the end of the calculation.

If the number of quanta in the pumped mode is small, simple solutions to the Schrodinger equation can be found by eigenvector techniques using the rotational-state angular momentum as the Hamiltonian matrix index. The multiple-photon spectrum computed for the lowest levels of the ν_3 mode of SF_6 is compared in Fig. 12 with experimental data obtained at the Lebedev Institute in the Soviet Union. Considering that the hot-band peak ($\nu_6 \rightarrow \nu_6 + \nu_3$) at 947 cm^{-1} is not included in our calculation, we find a very good agreement with the measured multiple-photon spectrum. By including the coherent dynamics of the time-dependent Schrodinger equation for the three-level system, the calculated resonances are in better proportion to the experimental spectrum than if one had simply used the population-counting technique typical of conven-

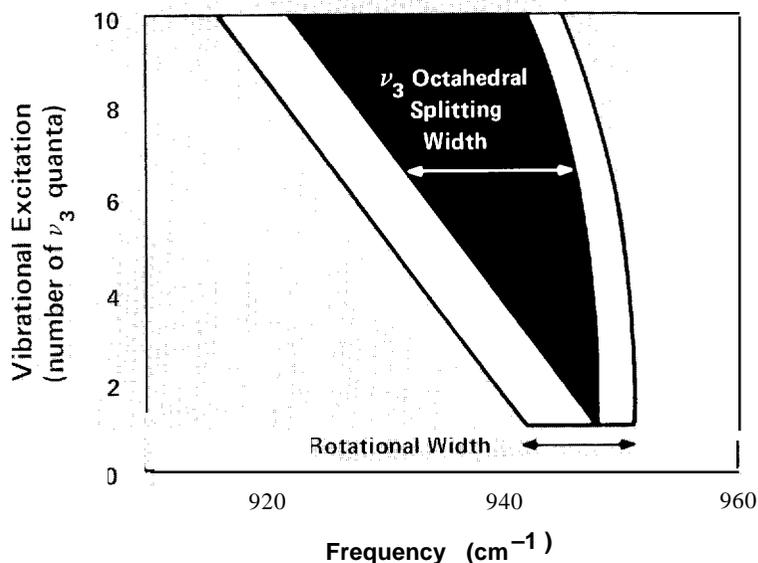


Fig. 13. Range of possible absorption frequencies for the ν_3 mode of SF_6 . The white areas represent the frequency width of the ν_3 absorption band ($0 \rightarrow \nu_3$) due to rotational structure. The black area represents the increase in the range of absorption frequencies that results from the octahedral splitting of ν_3 overtone levels. This latter range increases with vibrational excitation in such a way that it compensates for much of the anharmonic shift up to $10\nu_3$.

tional spectroscopic analysis. This result shows that the anharmonicities of the pumped mode lead naturally to the observed shift to lower frequencies that is characteristic of high-fluence, multiple-photon absorption.

At this fluence (0.09 joule per square centimeter) the average number of photons absorbed per SF_6 molecule is ≈ 0.7 . Since some molecules are not excited, this average implies levels of excitation possibly as high as $4\nu_3$ or $5\nu_3$ for the absorbing molecules. However, above $2\nu_3$, the octahedral splitting operator effectively couples all rotational states, making both the detailed structure unobservable and this method of solution intractable. New methods to cope with this complication are currently being developed. The computed spectrum in Fig. 12, however, reflects the structure of only one and two quanta absorption.

Before leaving the discrete low-energy region of multiple-photon excitation, we need to discuss two important issues: 1) the level N_0 at which resonant normal-mode coupling occurs, that is, the energy level for the start of the quasicontinuum, and 2) the role of "coherence" in the absorption process.

First, consider Fig. 13, which illustrates how the range of possible absorption frequencies in the ν_3 mode of SF_6 changes as

vibrational excitation increases. For example, $n = 1$ on the vertical axis represents the $0 \rightarrow \nu_3$ transition and the horizontal line at $n = 1$ from about 942 cm^{-1} to 951 cm^{-1} represents the width of the ν_3 absorption band resulting from the various rotational-energy transitions. At higher excitation energies this rotational width is shown as the white area split into its traditional low- and high-frequency branches. The black area expanding upward between the rotational-energy branches represents the additional frequency range for absorption that result from the octahedral splitting of ν_3 overtone levels. We note that Fig. 13 is an idealization: many holes are certainly present within the given range where no transitions exist. However, the figure can be used to determine for a given frequency how high in the vibrational energy ladder it may be possible to resonantly excite the ν_3 mode.

As a result of the growing anharmonic mismatch, the center of the frequency range shifts to lower frequencies. However, the increase in frequency range due to the octahedral splitting compensates for the anharmonic shift for many levels of excitation. About eight photons resonant with the center of the ν_3 fundamental band at 948 cm^{-1} can be absorbed before the next excita-

tion is outside the range of possible absorption frequencies. If the laser is tuned to lower frequencies, say around 944 cm^{-1} , about ten photons can be resonantly absorbed up the v_3 ladder of SF_6 . This calculated increase explains, in part, the observed shift of high-fluence absorption spectra to lower frequencies.

Conversely, for the excitation to proceed much above $10v_3$, we *must* have coupling with other normal modes, that is, the start of the quasicontinuum must be below $10v_3$, or SF_6 would never dissociate. By considering an explicit expansion of the molecular vibrational potential in normal coordinates and strong tensor splitting of background states, we have predicted the start of the quasicontinuum in SF_6 to be at $N_0 \approx 8$. Indeed, this most recent work leads to a new counting of all coupled states and shows that the average density of interacting states becomes roughly constant as the molecule is excited to high levels,

The above arguments allow roughly one-quarter of the excitation dynamics to be described by the time-dependent Schrodinger equation in the discrete levels. This description requires the excitation to be coherent, reflecting the fact that the molecule develops a transition dipole moment in phase with the laser. In particular, populations in near-resonant or resonant laser-coupled energy levels are seen to cycle between these levels, that is, to "Rabi oscillate." The absorption and ensuing stimulated emission of energy depends on the product of the magnitudes of the electric field and the transition dipole moment,

When the difference between the laser frequency and the transition resonance frequency is large, that is, for off-resonant states, the populations oscillate rapidly at this detuning frequency, but with very little net transfer of population between states. However, because the Rabi frequency depends on the magnitude of the electric field, increasing the intensity decreases the effect of the detuning; that is, at higher laser

powers an off-resonant state behaves in a resonant manner with population flow between states. This phenomenon is the Rabi broadening mentioned earlier.

An inhomogeneously broadened absorption feature consists of many independent transitions that are separately coherent. For example, the time-dependent Schrodinger equation correctly gives the dynamics of each transition in a typical, rotationally broadened absorption band. However, the excitation that is observed experimentally (as in Fig. 12) is made up of a sum over all these transitions. Because each transition has a slightly different detuning frequency determined by its location in the band, the coherent Rabi oscillation period for each transition is also slightly different. These differences give rise to a dephasing, or loss of coherence, in the dynamics observed for the entire band. In addition, each rotational transition has only a small fraction of the population available to it (determined by the Boltzmann thermal distribution of rotational energy states). Therefore, the overall excitation may not execute simple coherent Rabi oscillation.

The inhomogeneous character of the total absorption process helps explain the observed weak dependence of multiple-photon excitation on laser intensity. Solutions of the Schrodinger equation show strong intensity dependence, especially when multiple-photon resonances are important. However, solutions that are summed over rotational-energy states are a much weaker function of the intensity than the individual terms. Thus, the observed weak intensity dependence in the absorption shows that the excitation does not have the character expressed by a single Schrodinger equation.

Of course, if the laser power is sufficiently great, the middle, or quasicontinuum, region of the molecule also contributes to the excitation. Most models of multiple-photon excitation that incorporate the molecular quasicontinuum ignore coherent effects and use instead a set of population-rate equations for

the dynamics. These rate equations are single-step in nature and do not exhibit Rabi oscillation. They automatically provide for fluence-dependent absorption. The rate equations are derived on the basis of a collisionless, unimolecular damping mechanism whereby energy flows out of the resonant mode into other coupled vibrational background states. However, the fact that the phenomenon can be described as a sum of many different coherent processes shows that the data do not *require* a rate-equation description.

To test these hypotheses experiments are needed that measure the lifetimes of excited states, thereby providing information about damping mechanisms by which energy flows out of one state into others. The Heisenberg uncertainty principle relates the lifetime of a state to frequency linewidths. Thus, measurements are needed of the linewidths of various processes, such as absorption from excited states, double resonance absorption, and fluorescence.

EXCITATION THROUGH THE QUASICONTINUUM. The model for multiple-photon excitation developed at Los Alamos in 1978 is illustrated in Fig. 14. To be definite, we will use as an example the absorption of CO_2 -laser photons by SF_6 . The discrete levels of the v_3 resonant-mode ladder are treated as described above. However, at some level of excitation, N_0 , a coupling occurs from the v_3 overtones (the leftmost column in Fig. 14) to the background subdensity of states (the second column) having (N_0-1) v_3 quanta, but still at the total energy $N_0 v_3$. (Figure 14 is drawn, for simplicity and definiteness, with $N_0 = 3$.) This background subdensity is, in turn, coupled to the subdensity having (N_0-2) v_3 quanta (third column), and so forth. The model is therefore distinguished by the selection rule $\Delta n = \pm 1$, where n is the quantum number for the vibrational excitation of v_3 .

The loss of a single v_3 quantum to another vibrational mode causes the molecule to

drop back one level in its v_3 content. In other words, this construction is convenient since the transition dipole moment is carried by the resonant v_3 mode. Further, the $\Delta n = \pm 1$ selection rule for v_3 is reasonable because v_3 is the highest energy mode in SF_6 and a constant energy change of two or more v_3 quanta would require coupling to many other modes, making such couplings higher order and much less probable.

At a sufficiently large subdensity of states, Fermi's Golden Rule can be used to describe the rate at which the population flows from a given state in the v_3 ladder to the coupled background states with one less v_3 quantum. The Golden Rule rate is proportional to the density of the coupled background states and to the enharmonic coupling strength averaged over the states with one less v_3 quantum. The problem of low-level excitation in the v_3 ladder coupled with leakage into the quasicontinuum is independent of the dynamics of further excitation or energy transfer within the quasicontinuum. This first problem can thus be solved exactly, giving the population at different locations in the quasicontinuum as a function of time.

Heller and Rice have shown that, for molecules in the quasicontinuum, if the signs of the level coupling are random, then sequential population flow is observed to the subdensities having $(N_0 - 2)$, $(N_0 - 3)$, ..., v_3 quanta. This leakage leads to phase interruption and hence loss of coherence. The dynamics can then be determined by population-rate equations provided that the Golden Rule rates exceed the laser upward pumping rates. Our calculations are made self-consistently as follows. We assume the population-rate equations are valid and then obtain the coupling constant and, thus, the Golden Rule rates by fitting the data for absorption versus fluence. We then check to see if these rates do, in fact, exceed the laser pumping rates for the range of intensities considered. Our fit to such absorption data (circles) is shown in Fig. 15. We have also computed the fraction of molecules dissociated using standard RRKM theory

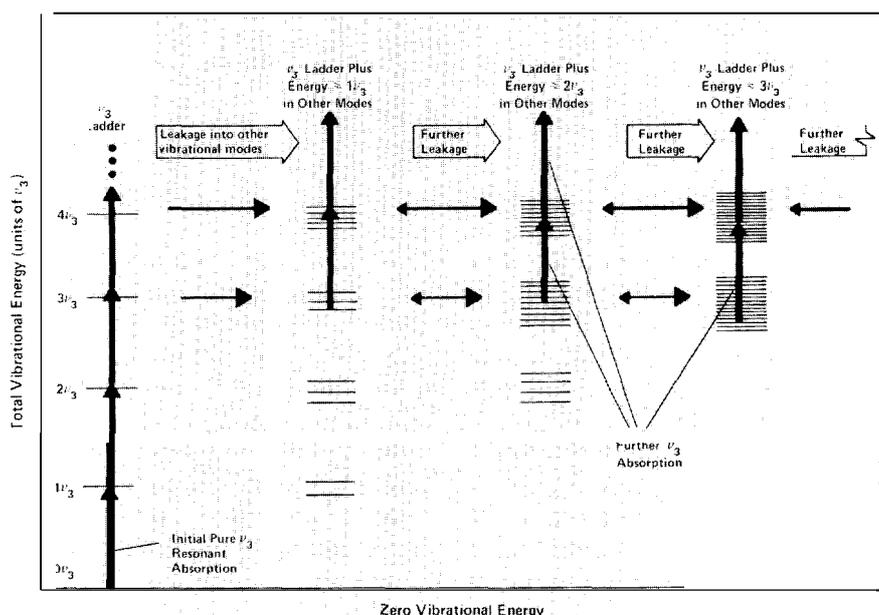


Fig. 14. Transfer of vibrational energy from the resonant, absorbing mode to other vibrational modes. Each column represents a vibrational ladder with the large steps approximately equal to one v_3 quantum of energy. The left column is the ladder for the pure v_3 mode. The next column represents the situation in which one quantum of v_3 energy has leaked into other vibrational modes. This loss of v_3 energy causes the molecule to drop back one level in its v_3 content. Thus a new "ground state" (combination modes with no v_3 content) is fixed at $1v_3$ of total energy. Each further column depicts the same situation with an additional quantum of v_3 energy transferred to other modes and new "ground states" for the v_3 mode at ever increasing levels of total vibrational excitation. Multiple states are drawn at each level to depict the density of modes coupled between ladders. The size of the arrow's and arrowheads between ladders indicates the relative strength of coupling in both directions. The lowest level for which coupling is significant (here depicted for convenience at the $3v_3$ level) is defined as the start of the quasicontinuum.

(black region). The lower edge of the region was defined by using RRKM theory just during the laser pulse, and the upper edge was defined by continuing the calculation after the pulse for all population above the $33v_3$ level. Molecular-beam data (triangles) for SF_6 at 140 kelvin, a temperature at which almost all of the molecules are initially in the ground vibrational state, fit the theoretical curve well. The other data (squares) are included to show a typical range for dissociation data, but are not expected to correspond as well to the calculated curves because of less favorable experimental conditions (a closed cell rather than a molecular beam experiment; a temperature of 300 kelvin and, therefore, higher initial vibrational excitation).

Figure 16 shows the calculated population distributions versus the level of excitation (in terms of CO_2 photons) for various laser energies. Below a laser fluence of 0.5 joule per square centimeter we see a population bottleneck due to the transition from the discrete, low-energy region to the quasicontinuum. Below the bottleneck we see that a fraction of the molecules are unaffected by the laser photons and remain in ground states because of inhomogeneous absorption. We also note that the population distributions are quite broad. The tail of each curve above the $33v_3$ level represents the molecules with enough energy to dissociate.

There is no way to measure these population distributions separately; however, we can compare our results with those predicted

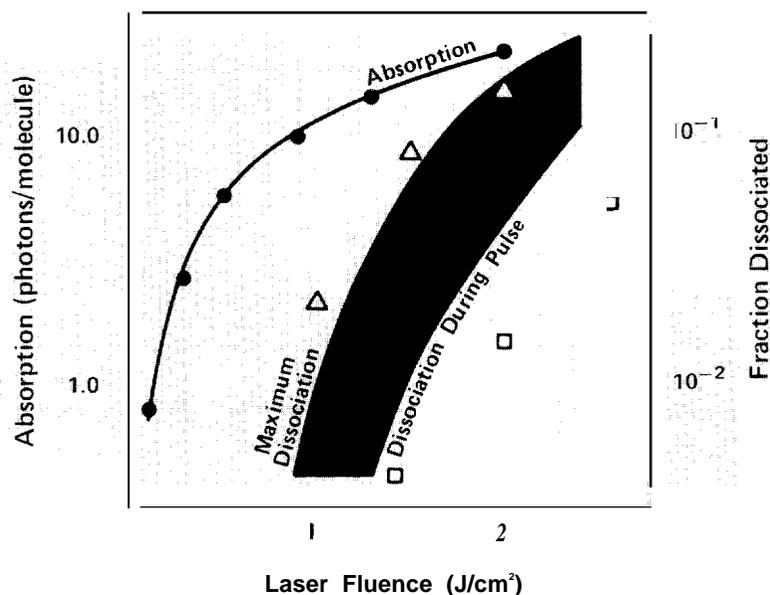


Fig. 15. Theoretical fit for SF_6 of absorption data and the fraction of molecules dissociated as a function of fluence. Absorption data (circles) for SF_6 [T. F. Deutsch, *Optics Letters* 1, 25 (1977)] has been used to evaluate the single coupling constant in the Los Alamos quasicontinuum model for multiple-photon excitation. The fraction of dissociated SF_6 molecules can be calculated when the RRKM unimolecular dissociation theory is combined with the Los Alamos quasicontinuum theory. The curve defining the lower edge of the black region is for the dissociation that occurs during the laser pulse only; the curve defining the upper edge is the result of continuing the rate calculations after the laser pulse for molecules excited above the $33\nu_3$ level. The triangles are molecular-beam data for dissociation of SF_6 at 140 kelvin [F. Brunner and D. Proch, *Journal of Chemical Physics* 68, 4978 (1978)], which agree well with the maximum dissociation curve. The squares are other data [J. G. Black, P. Kolodner, M. J. Shultz, E. Yablonovitch, and N. Bloembergen, *Physical Review A* 19, 704-716 (1979)] taken under conditions less favorable for comparison with theory.

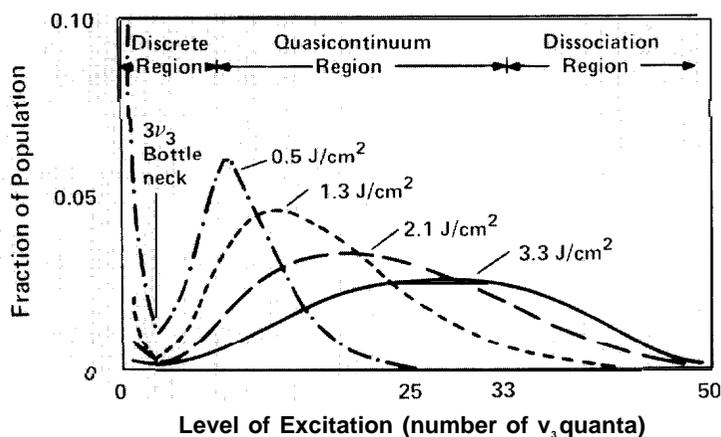


Fig. 16. The distribution of molecules with respect to level of excitation. The distribution curves calculated from the Los Alamos quasicontinuum model become broader with increasing fluence so that more molecules are in the high-energy tail of the dissociation region above $33\nu_3$. The fraction of molecules below the $3\nu_3$ bottleneck represent those molecules that are unaffected by the laser photons because, for instance, they are in rotational-energy states that do not absorb at that frequency.

by a thermal quasicontinuum model. This model is based on the idea that laser excitation leads to a thermal population distribution, that is, a Boltzmann distribution among *all* vibrational modes. A key assumption for the model is constant absorption cross section in the quasicontinuum. This assumption is equivalent to strong coupling between all modes as opposed to our assumption of the $\Delta n = \pm 1$ selection rule for ν_3 that represents weak coupling in the quasicontinuum.

An assumption of constant cross section for all levels from the ground state up leads to a Boltzmann thermal distribution with no $3\nu_3$ bottleneck and a narrow distribution with negligible dissociation (see curve with long dashes in Fig. 17). Surprisingly, however, if the thermal model is solved with a ν_3 energy ladder, that is, discrete energy levels are used for the energy levels below N_0 , the population distribution (short dashes) is almost identical with that calculated from the Los Alamos model (solid line). While the thermal model with the ν_3 ladder does not result in a large inhomogeneous fraction of molecules below $3\nu_3$, the fraction of molecules in the high-energy tail is almost the same.

In summary, the modeling efforts to date on the SF_6-CO_2 laser multiple-photon problem have demonstrated a possible mechanism for this phenomenon. The observed effects of fluence and intensity and the shift to lower frequencies for high-intensity absorption are mostly accounted for by the hot bands and the discrete, low-energy region of the model. The trends in absorption cross section due to temperature and molecular size are accounted for by the vibrational state density of the quasicontinuum. Also, the resonant-mode vibrational ladder has been identified as a critical element of the model in that, without it, the calculated distribution curves are too narrow for significant dissociation to occur.

But there are difficulties. Calculations in the resonant-mode ladder above the first overtone are formidable, and the data appear to be unable to distinguish quasicontinuum

models that originate from opposing hypotheses. It is our belief that new quasicontinuum models must be based upon (if not explicitly derived from) accurate potential-energy surfaces for the molecule. A new model based upon a potential-energy expansion already indicates that the so-called weak coupling model with the $\Delta n = \pm 1$ selection rule for ν_3 overcounts the number of coupled states. The overcounting results from the fact that the selection rule applies only to changes in ν_3 , thus limiting the vibrational coupling of ν_3 with other modes to low order, but not limiting in a similar manner the couplings between all other modes in the quasicontinuum.

There are at least two other important aspects that need eventually to be incorporated into the model for multiple-photon excitation. The first is the effect of initial vibrational excitation. This effect may explain important differences in absorption behavior for different molecules and temperatures by providing alternate pathways for multiple-photon excitation. The second is the effect of collisions, an extremely difficult modeling problem. Nevertheless, many photochemical or laser isotope separation schemes require high molecular concentrations to insure the generation of significant amounts of reaction product. An ade-

quate model for such conditions must necessarily account for collisions.

Concurrently with theoretical advances, experimental techniques need to be developed that reveal more detail about the distribution of vibrational energy, both among the collection of molecules and within given molecules. Presently, dissociation experiments measure the total number of molecules above the dissociation energy, that is, the area under the tip of the high-energy tail of the population distribution curve. Likewise, absorption experiments determine only the average number of photons absorbed per molecule, that is, the mean of the

distribution curve. Experiments need to be designed that map the detailed shape of the curve and so distinguish between alternate models. Also, once photons are absorbed, how is the energy distributed among the vibrational modes of the molecule? Are there pathways of rapid energy flow between certain states, but restricted flow between others?

Much has been learned about the surprising phenomenon of multiple-photon excitation. But there are experimental and theoretical challenges yet to be overcome—many of which undoubtedly harbor further surprises. ■

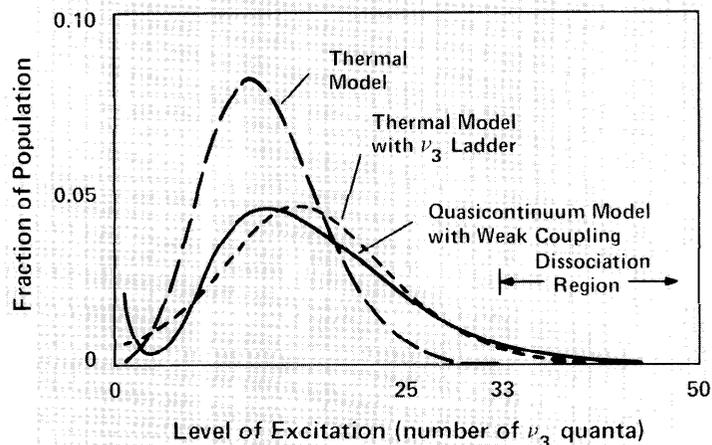


Fig. 17. Distribution curves for thermal and quasicontinuum models. The thermal model (long dashes) results in a Boltzmann thermal distribution with no $3\nu_3$ bottleneck and a narrow overall distribution. The addition of a ν_3 energy ladder to the thermal model broadens the distribution (short dashes). Surprisingly, the high-energy tail nearly matches the tail predicted by the Los Alamos quasicontinuum model (solid curve).

Further Reading

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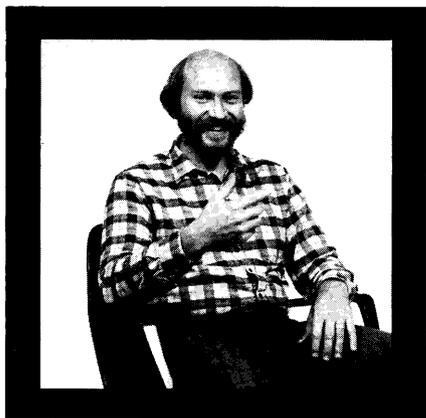
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Harold W. Galbraith earned his Bachelor of Science degree in 1967 at Pennsylvania State University and a Ph.D. in physics from the University of Pennsylvania in 1971. He came to Los Alamos on a postdoctoral appointment in 1973 to work with James D. Louck on group theoretical approaches to the few-nucleon problem. He became interested in molecular spectroscopy in 1974 and began working on problems of interest to the Applied Photochemistry Division. His research interests moved to quantum dynamics in 1976 with the discovery of isotopic selectivity in multiple-infrared-photon dissociation of polyatomic molecules. (Photo by Henry F. Ortega)

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Jay R. Ackerhalt earned his Bachelor of Science (1969) from Hobart College and his Master of Arts (1972) and his Ph.D. (1974) in physics, specializing in quantum optics, from the University of Rochester. Before joining the Laboratory in 1977, he held postdoctoral positions at the Institute for Theoretical Physics of the University of Warsaw, Poland, at the Department of Physics and Astronomy of the University of Rochester, and at the Physics Department of Johns Hopkins University. At Los Alamos he has worked on a theory of multiple-photon excitation in polyatomic molecules, primarily SF_6 and UF_6 , and has shared with Harold Galbraith the Laboratory's Distinguished Service Award for this research and its application to the uranium enrichment program. His present interests include self-focusing effects in polyatomic molecules. (Photo by Henry F. Ortega)



John L. Lyman received his Bachelor of Science and his Ph.D. in chemistry from Brigham Young University in 1968 and 1973, respectively. He performed the research for the Ph.D. degree at Los Alamos under Reed J. Jensen. That research included some of the first experimental studies of infrared-laser-induced reactions of polyatomic molecules. He also worked on HF chemical lasers. After joining the Laboratory in 1973, Lyman, along with Stephen Rockwood, Reed Jensen, C. Paul Robinson, and Jack Aldridge, was active in the early research on multiple-photon excitation. These scientists hold the patent for isotope separation by that process. Lyman has authored over thirty-five papers, including several review articles, on this and related phenomena. He is currently the Assistant Group Leader of the Laser Chemistry Group in the Applied Photochemistry Division. Most of his time is spent working on problems related to the uranium enrichment project. These problems include infrared self-focusing effects in UF_6 gas and the chemical reactions of UF_6 dissociation fragments. (Photo by Henry F. Ortega)

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