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BY MULTIPHOTON INFRARED ABSORPTION

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**Collisionless Dissociation of Polyatomic Molecules
by Multiphoton Infrared Absorption[†]**

N. Bloembergen^{*}, C. D. Cantrell^{} and D. M. Larsen^{***}**

Abstract

The physical theory of dissociation of an isolated molecule of SF₆ by a CO₂ laser pulse is reviewed from both a quantummechanical and classical point of view. The characteristics of the physical process are compared with the experimental data on collisionless dissociation.

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1. Brief Review of Experimental Characteristics

During the past year numerous experimental and theoretical investigations have been carried out on the prompt dissociation of several polyatomic molecules by intense CO_2 laser pulses. The fact that this dissociation process is isotopically selective^{1,2} undoubtedly provided the major impetus for this activity. In this presentation attention will not be focused on the important application of laser isotope separation, but on the physical processes by which a single molecule, without the benefit of collisions, may by exposure to an infrared laser pulse acquire sufficient energy for dissociation to occur.

Historically fluorescence from dissociation products was first detected as a consequence of heating of the gas by absorption of c.w. CO_2 radiation. Gas-kinetic collisions obviously play an important role in this case.³

The discovery by Isenor et al.⁴ of a fast dissociation process occurring during the short duration of a TEA laser pulse with $t_p < 10^{-7}$ sec, provided the first indication of a collisionless mechanism, and these authors already pointed out the importance for dissociation of a quasi-continuum of energy levels for highly excited polyatomic molecules. Since Ambartsumian et al. demonstrated¹ that this fast dissociation process is isotope-selective, a large amount of experimental data has been reported. While the early data were sometimes conflicting and caused some to hold onto the belief that collisions are necessary for dissociation to occur, it is now well established

that collisionless dissociation can take place. The following observations for dissociation of SF_6 molecules are indicative of this fact:

1. The dissociation of SF_6 molecules in a high vacuum molecular beam apparatus has been reported at a recent conference by Cotter.
2. Dissociation rates close to unity occur with pulses of 0.1 joule energy with a duration less than 0.5×10^{-9} sec at pressures less than 10 millitorr.⁵ The gas-kinetic collision time is 50 ns/toir, so that each molecule has a chance of less than 10^{-3} to undergo a collision. Intermolecular V-V transfer can be excluded.
3. The dissociation rate per molecule and isotopic selectivity both decrease monotonically with increasing pressure.⁶

The collisionless dissociation of SF_6 has been studied⁷ as a function of wavelength, power flux density and energy of the CO_2 pulses and as a function of partial pressures of SF_6 and some buffer or scavenging gases (H_2). These data have been reviewed by Ambartsumian,⁸ Letokhov⁹ and Rockwood,¹⁰ and the salient features for our purposes may be summarized as follows,

4. For a pulse duration $t_p \sim 8 \times 10^{-8}$ sec, the dissociation rate has a relatively abrupt threshold at 23×10^6 watts/cm². Above this threshold the dissociation rate increases roughly as the cube of the intensity, but it saturates and reaches unity at power levels of about 0.5×10^9 watts/cm².
5. Above threshold level the dissociation rate as a function of frequency (for S^{32}F_6) shows a maximum at 940 cm^{-1} and is an order of

magnitude smaller at 930 and 950 cm^{-1} . The frequency response is a bell-shaped curve with a width (FWHM) of about 8 cm^{-1} . The dissociate rate for S^{34}F_6 is given by a similar curve displaced 17 cm^{-1} towards lower frequencies.

6. Dissociation may occur at power levels as low as $\sim 10^3$ watts/ cm^2 , provided higher power fluxes are provided at a second frequency, which need not correspond to an absorption band of the SF_6 molecule at room temperature. The radiation at the second frequency may, for example, be provided by a second CO_2 laser in the 9.2 or 9.6 μm band.
7. Dissociation may also occur by single frequency irradiation near combination bands. The effective dissociation rate/molecule appears to be proportional to the dipole matrix element of the combination transition. Again, the frequency response is maximum about 7 cm^{-1} below the Q-branch head of the transition involved.
8. The same process is effective in the dissociation of many other polyatomic molecules. Attempts to dissociate diatomic molecules by this method have always met with failure.

This brief review of experimental findings is concluded with a table of pertinent physical quantities for the SF_6 molecule. The spectroscopy of the SF_6 v-band has been studied extensively,¹¹ and recently high resolution studies at low pressures with semiconductor lasers have been reported.¹² Our primary interest will be in the relative magnitude of the various spectroscopic quantities involved. The electric dipole $[\mu] = 0.1$ Debye for the fundamental transition

$v_3 = 0 \rightarrow 1$ is consistent with an absorption cross-section of $\sigma = 0.5 \times 10^{-17} \text{ cm}^2$ observed¹¹ in the unresolved band at high temperature with a width (FWHM) of 20 cm^{-1} . It is considerably smaller than the value $|\mu| \sim 0.3$ Debye reported by Alimpiev and Karlov.¹³ The strength of the dipole matrix element can be expressed in terms of frequency (cm^{-1}) by introducing the Rabi precession frequency at resonance in a field with an amplitude $|E_{\text{th}}| \sim 1.35 \times 10^5 \text{ volts/cm}$. This field strength corresponds to a power flux density of $23 \times 10^6 \text{ watts/cm}^2$, which is the threshold value for dissociation in the experiments of Ambartsumian.⁸ Thus, the Rabi frequency $\omega_R = \frac{1}{2} \hbar^{-1} |\mu| |E_{\text{th}}| = 0.35 \text{ cm}^{-1}$ has been entered in the table. This value is smaller than the anharmonic defect,² $\Delta W_{\text{anh}} = -2 X_{33} v_3 = -2.88 \text{ cm}^{-1}$. The energy levels of the vibrational levels relative to the ground state $v_3 = 0$ of one anharmonic v_3 -mode are given by

$$W(v_3) = v_3 h v_3 + h v_3 X_{33} v_3 (v_3 - 1) \quad (1)$$

Zero-point energy effects have been suppressed so that $v_3 = 947 \text{ cm}^{-1}$ is the fundamental resonant frequency. The photon energy for an n -photon transition from the ground state to the level $v_3 = n$ is

$$h v_n = h v_3 - (n-1) X_{33} h v_3 \quad (2)$$

The value of the rotational constant $B = 0.0906 \text{ cm}^{-1}$ in the ground state is small, so that at room temperature the statistical distribution over rotational states has a maximum at $J \approx 55$. About

three-quarters of the SF_6 molecules may be found in states with J in the range 30-80.

High resolution data have led to a complete assignment of the complex band structure.¹² The three-fold degeneracy of the ν_3 vibration leads to important Coriolis splittings, which may exceed the rotational spacing. Furthermore, there are many hot bands, because other normal modes may be thermally excited. Coriolis interactions and anharmonic coupling with overtones and nearly degenerate combination states rapidly increase in importance with increasing vibrational energy. Even for $\nu_3 = 1$, the Coriolis interactions have a magnitude of about 0.1 cm^{-1} , while for $\nu_3 = 2$ there appears already a cluster of states separated by a few wave numbers which are a superposition of states belonging to rotational manifolds of several different vibrational states.

The density of vibrational states has been computed by Jackson.¹⁴ The number of vibrational states per cm^{-1} amounts to 30 at a total vibrational excitation of 3000 cm^{-1} , and increases to 10^3 at 5000 cm^{-1} excitational energy. Each of these states has a rotational manifold associated with it.

The quantities at the bottom of the energy scale in the table are the homogeneous linewidths due to finite lifetimes. The uncertainty principle sets a width $\Delta\nu = \hbar/t_p = 1/2\pi \cdot 10^{-2} \text{ cm}^{-1}$ for a pulse duration of $t_p = 5 \times 10^{-8} \text{ sec}$. The infrared radiative lifetime is about $\tau_{\text{IR}} = 10^{-3} \text{ sec}$, corresponding to 10^{-8} cm^{-1} . Since this paper is concerned with collisionless dissociation, the pressure is assumed sufficiently small that even phase-perturbing collisions and rotational interchange are

negligible. Since no phase-interrupting processes take place, the coherence of the excitation of the individual molecule and the radiation field must be taken into account.

2. Quantummechanical Model for Collisionless Dissociation

For dissociation by monochromatic radiation one looks, of course, for a ladder of equally spaced energy levels. It is clear that a harmonic oscillator would readily acquire a level of excitation larger than the dissociation energy. The coupling of the mechanical harmonic oscillator with the coherently excited harmonic oscillator of the radiation field leads to coherent mechanical excitation, a Glauber coherent wave packet,¹⁵ with a Poisson distribution over the energy eigenstates $|n_v\rangle$. The mean excitation energy is equal to that acquired by a classical harmonic oscillator. When the oscillator is in the ground state at $t = 0$, the expectation value for the energy $\langle n_v \rangle h\nu_0$ is determined by,

$$\langle n_v(t) \rangle = \left(\frac{\omega_R}{\omega - \omega_0} \right)^2 \sin^2 \frac{1}{2}(\omega - \omega_0)t \quad (3)$$

The maximum excitation, corresponding to a quantum number $(\omega_R/\omega - \omega_0)^2$ is reached in a time $\pi(\omega - \omega_0)^{-1}$. Exactly at resonance the expectation value for the vibrational quantum number at the end of a laser pulse of duration t_p is given by $\frac{1}{4}(\omega_R t_p)^2$. For a pulse of 8×10^{-8} sec at the threshold value, the data in the table would yield $\langle n_v(t_p) \rangle \sim 3 \times 10^4$, well above the dissociation energy, $\langle n_{diss} \rangle \geq 42$.

The simple equation (3) assumes that the excitation energy of the electromagnetic field oscillator is very large compared to the mechanical

oscillator. The pulse energy in a single EM mode is about 10^{-3} joules, very much larger than the dissociation energy of one molecule, so that Eq. (3) should give an adequate description. Exact solutions of two coupled coherent quantummechanical oscillators are available in the literature,¹⁶ if needed.

It is clear that a harmonic vibrator would be excited to a multiple of the dissociation energy in a small fraction of the pulse duration t_p at field amplitudes considerably below $|E_{th}|$, but it is also evident that in practice the anharmonicity of the vibrator plays a dominant role. This is true even at the lowest levels of excitation, $v_3 = 2$ or 3, if $\hbar \omega_R < X_{33} h \nu_3$.

2.1. Anharmonic Vibrator

The unequal spacing of the energy levels of a nondegenerate slightly anharmonic vibrator is described by Eq. (1). For "weak" infrared radiation fields, $\omega_R \ll 2\pi X_{33} \nu_3$, perturbation theory is applicable. Eq. (2) shows that on the low frequency side of the fundamental resonance, a set of equally spaced multi-photon resonances will occur with a spacing of 1.44 cm^{-1} . The effective matrix element for the two-photon transition in the rotating wave approximation is given by the well-known expression,

$$\hbar \omega_R^{\text{eff}}(2) = \langle 0 | \mu E | 2 \rangle_{\text{eff}} = \frac{\langle 0 | \frac{1}{2} \mu E | 1 \rangle \langle 1 | \frac{1}{2} \mu E | 2 \rangle}{X_{33} h \nu_3} \quad (4)$$

and similarly for the higher order processes. Since $X_{33} \ll 1$, the zero-order wave functions for the harmonic oscillator may be used to

evaluate the matrix element. In this manner one derives an effective Rabi frequency for the n -photon transition, from the ground state to the level $v_3 = n$,

$$\omega_R^{\text{eff}}(n) = \frac{\omega_R^n (n!)^{1/2}}{(\omega_3 X_{33})^{n-1} \prod_{n'=1}^{n-1} n' (n-n')} \quad (5)$$

For a given applied frequency ω , the problem is essentially reduced to a two-level problem, and the probability for the system to be in the state $|v_3 = n\rangle$ at time is given by,

$$p_R(n,t) = \frac{\{\omega_R^{\text{eff}}(n)\}^2}{4\pi^2(\nu - \nu_n)^2 + \{\omega_R^{\text{eff}}(n)\}^2} \sin^2 \frac{1}{2} \left[4\pi^2(\nu - \nu_n)^2 + \{\omega_R^{\text{eff}}(n)\}^2 \right]^{1/2} t \quad (6)$$

where ν_n is given by Eq. (2) and $\omega_R^{\text{eff}}(n)$ by Eq. (5). For $\omega_R^{\text{eff}}(n)t_p \gg 1$ and $\nu = \nu_n$, the system essentially oscillates between the ground state and the state $|v_3 = n\rangle$. The time-averaged probability to be in this state is plotted as a function of frequency for $n = 1, 2, 3, 4$ in Figure 1. The width of each response curve is, of course, proportional to $\omega_R^{\text{eff}}(n)$. This simple perturbation approach is valid if the overlap between the individual two-level resonances is negligible, $\omega_R \ll 2\pi X_{33}\nu_3$.

More complete analyses¹⁷⁻¹⁹ have been made by considering the first $n + 1$ levels together in a $(n + 1) \times (n + 1)$ matrix problem. The coupling by the harmonic field is still between adjacent levels, but $\omega_R \geq 2\pi X_{33}\nu_3$ is now permissible. A numerical solution obtained by Larsen¹⁷ is presented in Figure 2. Note that on the vertical scale

energy is plotted, or $\overline{p_R(n)} \, n h \nu_3$, rather than $\overline{p_R(n)}$ in Figure 1. As expected, the individual n -photon resonances broaden and start to overlap. For $\omega_R \gg X_{33} \nu_3$ the quantummechanical expectation value for the excitation of the anharmonic oscillator clearly approaches the values derived from the classical anharmonic oscillator model.²⁰

Just above the experimental threshold intensity for dissociation, $\omega_R \ll X_{33} \nu_3$, Eq. (5) yields $\omega_R^{\text{eff}}(4) = 3 \times 10^{-4} \text{ cm}^{-1}$ and $\omega_R^{\text{eff}}(5) \approx 10^{-6} \text{ cm}^{-1}$. Thus, for $t_p \sim 8 \times 10^{-8} \text{ sec}$, the level $\nu_3 = 4$ could ideally s. 11 be reached, but the tuning would have to be extremely selective as the width of the four-photon resonance would be $3 \times 10^{-4} \text{ cm}^{-1}$. The levels $\nu_3 \geq 5$ could not be reached at all. Thus, this model needs modification and extensions in order to obtain satisfactory agreement with experiment.

2.2. Rotating Anharmonic Vibrator

Considerable improvement can be obtained by taking into account the rotational band structure. The compensation of anharmonic defects by rotational energy differences has been pointed out by several workers.^{17,21,22} The expression for the effective Rabi frequency for the n -photon transition between the state $|v_3 = 0, J_0\rangle$ and the state $|v_3 = n, J_n\rangle$ is

$$\omega_R^{\text{eff}}(n, J) = \frac{\langle 0, J_0 | \frac{1}{2} \mu E | 1, J_1 \rangle \langle 1, J_1 | \frac{1}{2} \mu E | 2, J_2 \rangle \dots \dots \dots}{h^n (\omega_3 + \Delta \omega_{J_0} - \omega) (2\omega_3 - X_{33} \omega_3 + \Delta \omega_{J_1} - 2\omega) \dots \dots \dots}$$

$$\frac{\langle n-1, J_{n-1} | \frac{1}{2} \mu E | n, J_n \rangle}{\{(n-1)\omega_3 - (n-2)X_{33}\omega_3 + \Delta \omega_{J_{n-2}} - (n-1)\omega\}}$$

(7)

Here ΔJ_1 is the difference in rotational energy of states with J_1 and J_{1+1} . We have, of course, the selection rule $|J_n - J_0| \leq n$. Since the width of the P- and R-branches is much larger than the anharmonic defect, it is possible to reach the vibrational level $v_3 = 3$ with very small energy defects in the intermediate steps. For the P, Q, R sequence $|v_3 = 0, J_0 = 53 \rangle \rightarrow |1, 52 \rangle \rightarrow |2, 52 \rangle \rightarrow |3, 53 \rangle$ one has essentially equally spaced levels. There will be a considerable range of initial J_0 values, where the mismatch in the energy denominators is smaller than the corresponding dipole matrix elements in the numerator. In these cases the perturbation expression Eq. (7) is not valid. If one wishes to avoid extensive numerical calculations for a coupled four-level problem, a crude estimate²³ is obtained by assigning a maximum value of unity to each quotient of dipole matrix element to energy mismatch in Eq. (7). The maximum value of $\omega_R^{\text{eff}}(n)$ is obviously $\omega_R(1)$ for a one-photon transition. It is clear that the state $|v_3 = 3 \rangle$ can be populated with an average probability of one-half for the majority of molecules in the rotational ensemble, even for intensities which are orders of magnitude smaller than the threshold value.

At the threshold field amplitude $|E_{\text{th}}|$, the probability to reach the states $v_3 = 4$, or even 5, during the pulse duration is still considerable for a selected range of values J_0 . Figure 3 illustrates a P P R R sequence to the level $v_3 = 4$, in which one has a small energy mismatch of 1.44 cm^{-1} in only two denominators. Eq. (7) with the cut-off rule for a maximum quotient of unity for successive ratios of $\omega_R^{\text{eff}}(n)/\omega_R^{\text{eff}}(n-1)$ permits an estimate of what fraction of molecules

can reach a certain vibrational state during the laser pulse. One must expect that a considerable fraction of the molecules will reach levels with $v_3 = 4$ if the laser frequency is tuned downward from 947 cm^{-1} to 940 cm^{-1} . A smaller fraction will reach a level $|v_3 = 5\rangle$ via P P Q R R and similar sequences. Perhaps some molecules may even reach the state $|v_3 = 6\rangle$ although $\omega_R^{\text{eff}}(n)$ drops rapidly for $n \geq 5$, because of the increasing anharmonicity. The model of the rotating anharmonic vibrator, which should be a good representation for diatomic molecules, does not permit excitation to the dissociative levels. There is no way to reach levels with $v_3 \sim 10$, let alone $v_3 > 40$. This result is in agreement with the negative attempts to induce collisionless dissociation in diatomic molecules. Our model must be extended to include the effects of anharmonic and Coriolis coupling with other vibrational modes.

2.3. Coupling to the Rotational-Vibrational Quasi-Continuum

The molecule SF_6 has 15 normal modes, the totally symmetric v_1 mode, the two-fold degenerate v_2 mode and four three-fold degenerate modes. Only the v_3 and v_4 modes are IR-active and have dipole matrix elements connecting neighboring oscillator states. So far we have singled out one of the v_3 modes, and we must now consider the coupling of this mode with the other 14 normal modes of vibration. Coupling with the quasi-continuum has been considered by several authors.^{4,17,19,20,24} Here we shall attempt to define the physical mechanisms used in the continuum models. The coupling of the selected v_3 mode with the other two degenerate v_3 modes should be considered first. The vibrational

degeneracy is partially lifted and the Coriolis splittings for lowest vibrational states has been analyzed.¹²

For higher excitations there will be many nearly degenerate vibrational states. The coupling of a selected "zero-order" pure ν_3 state to this quasi-continuum of other vibrational states takes place through a Coriolis term in the Hamiltonian. A typical form of this term is²⁵

$$\mathcal{H}_{C'} = J^2 \sum_{1 \neq 3} C_1 (p_1 q_3 - p_3 q_1) \quad (8)$$

This term will take on values large compared to the spacing between the "zero-order" vibrational levels, and perturbation theory would have to be carried out to very high order. Additional coupling to the quasi-continuum is provided by higher order terms in the anharmonic potential with a representative form,

$$\mathcal{H}_{anh} = V_{anh} f(q_3) F_{1 \neq 3}(q_1 \dots q_i \dots) \quad (9)$$

where f is a polynomial in the "selected" normal coordinate q_3 and F is a polynomial in the other normal coordinates.

It is not possible to carry out detailed quantitative calculations in the quasi-continuum, but obviously some ν_3 character will be admixed to many states in this continuum. Conversely, the higher steps in the ν_3 ladder will acquire a progressively higher admixture of the other states and will eventually become indistinguishable from the continuum. Up to $\nu_3 = 6$, the ν_3 states are still rather well defined, as shown on

the left in Figure .. At this excitation the density of states $\rho_v(v)$ in the quasi-continuum exceeds $10^3/\text{cm}^{-1}$. Since $\rho_v(v) > t_p$, the quasi-continuum becomes a true continuum in the sense of the uncertainty principle.

The effect of the coupling is twofold. The states in the v_3 ladder with an oscillator strength $|\mu(v)|^2 \delta\{v(v_3+1)-v(v_3)\}$ will be displaced in energy. Some states may be pushed up in energy so that the anharmonic defect is partially compensated by Coriolis interaction. Simultaneously, part of the oscillator strength will be distributed over a continuum of frequencies. Suppose that the v_3 admixture by the interactions (8) and (9) is spread out over a frequency interval Δv in the continuum near the zero-order pure v_3 state. Its order of magnitude is given by $h\Delta v \sim |\mathcal{K}_{\text{Cor}}| \sim 10 \text{ cm}^{-1}$. Denote the total amount of admixture to the continuum by $|C_3(v_3)|^2 \Delta v$. A reasonable value for this admixture may lie in the range of 1-10 percent for $v_3 \sim 6$.

In the preceding section it was shown that for a suitably chosen frequency and intensity of the laser pulse, states with $v_3 = 5$ might still be reached, but that the probability to reach the zero-order state $v_3 = 6$ is negligible. For $v_3 \geq 3$, it becomes, however, possible to make a transition to the continuum with the borrowed oscillator strength from the v_3 vibration, while the energy can be conserved by the spread of this oscillator strength over a continuous range. Consider for definiteness the six-photon process, in which for the first five steps the large discrete oscillator strength of the pure "zero-order" v_3 ladder is used, while for the final energy conserving step

the reduced borrowed oscillator strength is used with a density $|C_3(v)|^2 \frac{1}{2} \mu E|^2$. The transition rate to this continuum may be calculated with Fermi's Golden Rule, as coherence effects are washed out by an integration of the Rabi-type probability $p_R(n+1)$ over a distribution of frequencies. The time proportional probability to make an $(n+1)$ -photon transition to the continuum is consequently

$$d \bar{p}_{\text{cont}}(n+1)/dt = \bar{p}_R(n) \hbar^{-2} \left| \frac{1}{2} \mu E \right|^2 |C_3(v)|^2 \quad (10)$$

where $\bar{p}_R$ may be calculated with the aid of Eqs. (6) and (7). The bar denotes not only a time average, but also a statistical average over the initial distribution of rotational states and a summation over possible final rotational states. It is, of course, somewhat artificial to divide the process into two separate factors, one for transitions in the discrete v_3 ladder, and one for the continuum. The advantage of this procedure is that it affords insight as to how the dipole oscillator strength is distributed in the frequency domain. Formally a time proportional transition probability by using Eq. (6) $p(n+1, t)$ with $\omega_R^{\text{eff}}(n+1)$ given by Eq. (7), and summing over all possible final vibrational-rotational states is equivalent. The last integration leads again to a constant transition rate. Eq. (10) shows clearly that even for $|C_3(v)|$ as low as $10^{-2}/\text{cm}^{-1}$ the probability to reach the bottom of the continuum during the early part of the laser pulse is near unity for molecules in the proper range of initial values of J_0 , since even for field strengths well below the threshold field the condition $\left| \frac{1}{2} \mu E \right|^2 |C_3(v)|^2 t_p \gg 1$ can be satisfied.

2.4. Continuum Absorption and Dissociation

The argument may be extended to further absorption of photons by the distributed dipole oscillator strength in the continuum. As the excitation energy increases, all vibrational and rotational degrees of freedom become completely scrambled, and the normal coordinates are no more privileged than the Cartesian coordinates of the individual atoms. The dipole oscillator strength associated at low excitation with the ν_3 and ν_4 normal modes is now perhaps spread into a continuum of several hundred wave numbers. It can best be expressed in terms of an absorption cross-section for the continuum²⁰ $\sigma_{\text{cont}}(\nu)$. Its order of magnitude may be estimated to be about one hundred times smaller than the maximum absorption cross-section in the P-branch of the ν_3 vibration at room temperature, since the oscillator strength is spread out over a hundred times wider frequency range. Thus, $\sigma_{\text{cont}}(\nu) \approx 10^{-19} \text{ cm}^2$ per molecule should be considered an average value. Especially for the lower energy part of the continuum, $\sigma(\nu)$ will display structure.

Several authors have discussed the ergodic nature of the vibrational continuum^{19,26,27,28} in connection with monomolecular reactions. The models are necessarily simplified. Most often harmonic oscillator levels are used with damping and/or anharmonic coupling terms added in an ad hoc fashion. The elaborate numerical calculations cannot be trusted to give realistic results for the complex real situation. It appears, nevertheless, likely that not much intramolecular vibrational energy transfer takes place until dissociation channels open up.

Fortunately, the details of the continuum interactions and the question, whether the damping is of a homogeneous or inhomogeneous origin, are immaterial for our purpose. If the molecule by continuum absorption has acquired sufficient energy to open up one or more dissociation channels, it will dissociate essentially instantaneously on the time scale of t_p . It does not matter how this energy is distributed until the dissociation limit is exceeded.

The amount of energy absorbed by the molecule is obtained by adding the continuum absorption during the later part of the laser pulse to the energy of the photons absorbed in the first few steps on the discrete ladder during the early part of the pulse. Within the accuracy of these calculations, the total amount of energy is well approximated by

$$W_{\text{abs}} = \sigma_{\text{cont}}(\nu) I(\nu) t_p \quad (11)$$

where $I(\nu)$ is the intensity (power flux density) of the laser pulse. When this amount exceeds the dissociation energy W_{diss} by an activation energy ΔW_{act} which is usually small, dissociation will take place. The probability for a molecule to be dissociated is consequently,

$$p_{\text{diss}} \approx \bar{p}_R(n) \quad \text{for } W_{\text{abs}} > W_{\text{diss}} + \Delta W_{\text{act}}$$

$$p_{\text{diss}} \approx \bar{p}_R^0(n) \quad \text{for } W_{\text{abs}} < W_{\text{diss}} + \Delta W_{\text{act}} \quad (12)$$

Here $\bar{p}_R(n)$ is the average probability occurring in Eq. (10) to reach a vibrational level with $v_R = n$, given by Eqs. (6) and (7). The choice for n in the case of SF_6 lies probably in the range 3 to 5.

This simple model leads to an energy threshold per pulse,

$$\sigma_{\text{cont}}(\nu) I_{\text{th}}(\nu) t_p \approx W_{\text{diss}} \quad (13)$$

which is determined by the continuum absorption cross-section.

3. Comparison with Experimental Results and Discussion

The model developed in Section 2 can account for all experimental features enumerated in Section 1, taken up in the same order:

1. Dissociation of isolated polyatomic molecules is clearly theoretically possible. Collisions are not necessary; neither rotational nor vibrational energy needs to be provided.

2. For power densities well above threshold the dissociation rate per molecule will approach unity. At a power level of 10^9 watts/cm² with a pulse duration of 10^{-7} sec, nearly all molecules regardless of initial rotational quantum number J_0 may be excited to a level with $v_3 = 5$, and thence through the continuum to the dissociation level.

3. Collisions with non-excited molecules will lead to a loss of excitation energy and thus to a lowering of the dissociation rate. Collisions are not necessary to reach the dissociation limit. Thus, the dissociation rate per molecule is highest at the lowest pressure. It is assumed that the dissociation products cannot recombine chemically in the interval between pulses. If recombination reactions occur, a scavenger gas at a sufficient partial pressure may be beneficial.

4. The experimental threshold of 23×10^6 watts/cm² for $t_p = 8 \times 10^{-8}$ sec is in agreement with Eq. (13), if $\sigma_{\text{cont}}(\nu)$ is chosen to be 4×10^{-19} cm², which is a reasonable value. No data are available

to verify the prediction that the process has an energy threshold, i.e. the power threshold is inversely proportional to the pulse duration.

Above the threshold the intensity dependence of the dissociation rate is determined by $\bar{p}_R(n)$ given by a suitable average of Eqs. (6) and (7). The experimental dependence of I^3 would appear to point to a three-photon process to the level $n = 3$. It is believed, however, that the intensity dependence is also consistent with transitions to levels $n = 4$ or 5 . The quotients in the perturbation expression Eq. (7) cannot exceed unity. This reduces the power dependence on $|E|$ considerably for the majority of the molecules.

5. The frequency dependence for dissociation rate of SF_6 shows a maximum at 940 cm^{-1} , or 7 cm^{-1} below the fundamental ν_3 transition. With the known value of the anharmonicity, this would point again to four- or five-photon transitions to the levels with $\nu_3 = 4$ or 5 . The width and lack of observed structure in the frequency response is due to the distribution of rotational states and of Coriolis interactions.

6. Continuum absorption is not selective in frequency. Once a molecule is excited to the level $\nu_3 = 5$, it may be dissociated by an intensity exceeding the threshold value at an arbitrary frequency in a relatively wide frequency range, because $\sigma_{\text{cont}}(\nu)$ has no sharp features. The frequency selective absorption in the first stages of the ladder may be provided by radiation at much lower intensities. At power levels as low as 10^6 watts/cm^2 molecules in selected rotational states will still be excited to levels with $\nu_3 = 3$ and 4 by P Q R and P P R R sequences. This feature was not appreciated in early double

resonance experiments.^{29,30} There is a need for more systematic double resonance experiments at low pressures, in which the frequencies and power levels of two simultaneous irradiation fields are varied independently.

7. When the probability $\bar{p}_R(n)$ can still be appreciable at such low power levels, it is also clear from the form of Eq. (7) that it can be appreciable for smaller dipole matrix elements. Thus, irradiation near weak combination bands, e.g. $\nu_2 + \nu_4$, will also lead to dissociation, with the same threshold set by continuum absorption. The dissociation rate per molecule has been reported⁸ to be proportional to the strength of the dipole matrix element $|\mu|$. This would indicate that the molecules in selected range ΔJ of initial values J_0 , with $2BAJ$ proportional to $|\mu||E|$, can be excited in a resonant ladder to the state $3\nu_2 + 3\nu_4$.

8. Since diatomic molecules have no vibrational continuum, they cannot be dissociated by monochromatic infrared radiation. The mechanism should, however, be effective in a variety of polyatomic molecules. Although the general features are similar, the distinct characteristics of individual molecular species will undoubtedly be apparent in detailed parametric studies of the power and frequency dependence for each species. Much further experimental and theoretical work is needed.

As the intensity is increased to high values so that $\hbar\omega_R$ is larger than the anisotropy defect necessary to reach the levels $\nu_3 = 3$ or 4, the quantummechanical model yields results similar to the classical anharmonic oscillator, as shown by comparing the energy of excitation

of the quantummechanical model in Figure 2 with the classical response curve.²⁰ This classical anharmonic oscillator must also be coupled to a continuum to reach the dissociation energy. The dynamics of the continuum can be modeled in a classical manner, as described by Lamb.³¹ The continuum dynamics may be described in terms of Cartesian coordinates of the individual atoms. They are coupled to the IR field via effective charges. They interact with each other via effective induced polarizabilities and short range repulsive forces. The periodic shaking of the classical system will eventually lead to the escape of one or more fluorine atoms from the molecule SF_6 . A type of Monte-Carlo program for different initial conditions is probably within the capabilities of present-day calculating machines. In our opinion no classical program can be used to describe the first steps up the anharmonic ladder for $\hbar \omega_R \ll h\nu_{33}$ where the distinct resonances of Figure 1 occur.

The isotopic selectivity in the collisionless regime is a straightforward consequence of the model. The frequency response $\tilde{\rho}_R(n)$ of the excitation of the first n -steps of the anharmonic ladder is simply displaced in frequency for a second isotopic species, as the resonant frequency is inversely proportional to the square root of the reduced mass of the normal vibration. For S^{34}F_6 the shift is 17 cm^{-1} toward lower frequencies compared to S^{32}F_6 for the ν_3 vibration. Isotopic separation can be obtained with a probability of unity³² for very modest powers of the selective excitation field, provided an off-resonance continuum pumping field is present to satisfy the threshold condition given by Eq. (13).

If the isotopic shift is smaller than the width of the average response function $\bar{p}_R(n)$, which is on the order of the width of the rotational bands, one may still obtain an adequate selectivity factor by operating on the slope of the response curves $\bar{p}_R(n, \omega_A) - \bar{p}_R(n, \omega_B)$ for the two isotopic species A and B.

In practice, requirements of high throughput and efficient use of available infrared power will necessitate operation in a regime of pressures where collisions, even during the short laser pulse, cannot be ignored. Scavenger gas pressures may also be necessary to take away the dissociation products. The problem of collisions with V-V transfer and chemical reactions between excited species of molecules adds a new dimension of complexity to the problem. Many papers have stressed the role played by collisions in chemical dissociation reactions.³² This paper does not deal with these vast, and sometimes bewildering, aspects of laser chemistry. The discussion has been restricted to the physics of one polyatomic molecule in an infrared radiation field. This problem already offers plenty of complexity, but it is believed that the essential features of collisionless dissociation have been identified.

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Table I. Relevant Energies for the Collisionless Dissociation
of SF_6 by Infrared Radiation.

Physical Quantity	Symbol	Energy in cm^{-1}
Dissociation Energy	W_{diss}	40,000
Fundamental Frequency of ν_3 Mode	$h\nu_3$	947
Thermal Energy	kT	200
Rotational Width of P and R Branch	$2B < j >$	5
Coriolis Splitting	-----	0.1-10
Anharmonic Defect	$ 2X_{33}h\nu_3 $	2.88
Electric Dipole Matrix Element	$\hbar \omega_R = \frac{1}{2} \mu E_{\text{ch}} $	0.35
Rotational Constant	B	0.0906
Pulse-Limited Width	$\hbar t_P^{-1}$	10^{-7} 4
Collisional Width at one millitorr	$\hbar \tau_C^{-1}$	10^{-6}
Radiative Width	$\hbar \tau_{\text{IR}}^{-1}$	10^{-8}

Figure Captions

- Figure 1. Time-averaged probability $\bar{p}_R(n)$ to occupy the n^{th} excited level of an isolated anharmonic vibrator by an n -photon process. The horizontal frequency scale is for the ν_3 vibration of SF_6 . Two-level perturbation theory is used with $\hbar \omega_R \sim \frac{1}{4} h\nu_3 X_{33}$.
- Figure 2. Energy of excitation of anharmonic vibrator as a function of frequency for an exact four-level calculation, with $\hbar \omega_R = \frac{1}{2} h\nu_3 X_{33}$ (top) and $\hbar \omega_R = h\nu_3 X_{33}$ (bottom).
- Figure 3. A four-photon process with partial compensation of the anharmonic energy defect with rotational energy differences.
- Figure 4. The ladder of the selected "zero-order" normal mode $|v_3\rangle$ and the quasi-continuum of vibrational states. A possible path of multi-photon dissociation is indicated.

$4\nu_3$ TRANSITION IN SF_6

AVERAGE ENERGY STORED IN 4-LEVEL OSCILLATOR