A QUANTITATIVE COMPARISON OF MULTIPLE-PHOTON
ABSORPTION IN POLYATOMIC MOLECULES*

by

O. P. Judd
University of California
Los Alamos Scientific Laboratory
Los Alamos, NM 87545

NOTICE

This report was prepared by the University of California, Los Alamos, under contract with the United States Government. The United States Government is authorized to reproduce and distribute reprints for government purposes not withstanding any copyright notation that may appear hereon. It is understood that any information disclosed herein is proprietary to the University of California, Los Alamos, and is not to be disclosed or represented in any way as to infringe privately owned rights.

MASTER

*Work performed under the auspices of the U. S. Department of Energy.

ABSTRACT

A quantitative comparison of multiple-photon absorption for a number of polyatomic molecules has been performed. A basis for this comparison has been developed that takes into account the different experimental conditions and molecular parameters, and provides suitable normalization of the fluence and absorption parameters. The normalization, and consequently the generalized interaction process can be specified in terms of the spectroscopic absorption cross section of the molecule $\sigma_0(\nu)$ and the effective fraction of molecules that interact with the radiation field $\langle f \rangle$.

The results of the study indicate that in terms of the normalized absorption variables, multiple-photon absorption is a general phenomena that is qualitatively the same for all molecules; quantitative differences can be related to differences in σ_0 and $\langle f \rangle$. The absorption of all polyatomic molecules can be described in terms of the number of photons absorbed per molecule $\eta(\xi)$ at a fluence ξ . The data indicate that in spectral regions where $\sigma_0(\nu) \gtrsim 0.1 \sigma_0(\text{max})$, $\eta(\xi)$ can be represented by the function ξ^γ where $\gamma = 1$ for $\sigma_0 \xi / \langle f \rangle < 1$ and $\gamma \approx 2/3$ for $\sigma_0 \xi / \langle f \rangle > 1$. Quantitative values of $\langle f \rangle$ and the functional dependence of $\eta(\xi)$ on the experimental parameters such as gas pressure, optical bandwidth, and optical pulse duration are derived and shown to be in good agreement with experimental data for SF_6 . These results are also compared with the anharmonic oscillator model for multiple-photon excitation of polyatomic molecules.

I. INTRODUCTION

Many investigations have been reported related to multiple-photon excitation (MPE) and dissociation of polyatomic molecules. Although detailed studies have been performed for individual molecules, a quantitative comparison of the process in different molecules has so far not been attempted. It is the purpose of this study to effect such a comparison for the absorption process. A similar study related to dissociation will be discussed in a future paper. At first thought, a quantitative comparison appears difficult since; (1) the various molecules differ in symmetry, density of states, and the matrix elements for the transition; (2) the experiments are performed under different conditions of laser beam quality, pulse duration, spectral bandwidth, etc.; and (3) the conditions of the gas such as pressure and material constituents could be different. It is possible, however, to eliminate the major differences in the dependence of these independent variables in the multiphoton absorption (MPA) process through the use of an appropriate normalization of the absorption and fluence variables. Use of these normalized variables eliminates the non-essential aspects of the interaction and provides a universal plot of multiple-photon absorption as a function of fluence for a number of polyatomic molecules that have been discussed in the literature.

The subject of the appropriate normalization parameters is discussed in Section II, a detailed comparison of MPA data is considered in Section III, and the implications of the study and a comparison with theoretical models are discussed in Section IV. The results of the study are summarized in Section V.

II. INTERACTION DYNAMICS AND NORMALIZATION CONCEPTS

1. General Considerations for MPE Processes

The experimental parameters that are usually reported in multiple-photon absorption experiments are the absorption cross section $\sigma(\Phi)$ or

the number of photons absorbed per molecule $n(\phi)$ as a function of the optical fluence ϕ or intensity I . In order to effect a quantitative comparison of absorption data for different molecules, it is necessary to normalize these variables in such a way as to eliminate any additional independent variables of the experiments such as the intrinsic parameters of the molecule, the properties of the optical radiation field, and the thermodynamic conditions of the gas. The problem is then essentially one of specifying a quantitative measure of the strength of the interaction between the molecule and the optical field and the related molecular response to this interaction. In this section we develop the rationale for the normalization procedure and provide an interpretation for the quantities used in the normalization.

As a guide in this development, we consider some fundamental absorption properties of SF_6 . A plot of the fluence-dependent absorption cross section for the Q_2 branch of the ν_3 vibrational mode of SF_6 is shown in Fig. 1 over several decades of the fluence.^(1,2) Two points are evident; (1) the cross section is a smooth function of the fluence; (2) the departure from the limit of linear absorption (small fluence limit) occurs at a very low fluence ($5 \mu\text{J}/\text{cm}^2$). We denote this value by ϕ_t . The fact that the functional dependence of cross section is nearly $\phi^{-1.5}$ from the low fluence limit to almost dissociation of the molecule implies that the threshold for MPE of the molecule may occur at ϕ_t and proceed in a continuous fashion with increasing fluence up to the dissociation limit. In the absence of a MPE process in the molecule, the excitation of the ground state vibrational transition of the ν_3 fundamental mode could be viewed as an "effective" two-level system. For this situation, the cross section $\sigma(\phi)$ would be a constant value σ for increasing fluence until a significant fraction of the ground state population is

transferred to the upper level of the transition. At this fluence value Φ_s , saturation of the transition occurs and $\sigma(\Phi) \propto \Phi^{-1}$ for increasing values of Φ . This behavior is indicated by the dotted curve in Fig. 1. A view of MPE in a first approximation begins with an interaction of the optical field with an isolated two-level system at low fluence. As the fluence increases, population is transferred from the lower level to the upper level of the initial absorbing state(s) where: (1) photon absorption out of the excited-state occurs in the pumped mode; or (2) the population transfers rapidly to other vibrational levels by intramolecular V-V' processes and excited-state photon absorption occurs in combination levels involving the fundamental mode. The onset of MPE would then be associated with the population of the upper level of the initial absorbing state(s), which occurs at a fluence $\Phi_s \sim (2\sigma)^{-1}$ in a non-degenerate two-level system. In a first approximation, $\Phi_t \sim \Phi_s$. Although the presence of rotational levels and strong coupling to other vibrational levels complicates the concept of an isolated two-level interaction, these effects do not qualitatively change the above description and they can be included in a straightforward manner in the formulation of a generalized two-level model.

Observations of $\sigma(\Phi)$ for other molecules such as S_2F_{10} and SF_5NF_2 show qualitatively similar behavior to SF_6 except that the value of Φ_s is different. Unfortunately, most other MPE absorption measurements reported in the literature are obtained at high fluence so that it is difficult to determine if $\sigma(\Phi)$ exhibits the same behavior for these molecules as for SF_6 . In view of these considerations, it would appear that a first step in any comparison study of MPE in different molecules would be to normalize the absorption parameters in a manner similar to that for a generalized two-level system. This normalization is strictly

valid for $\zeta \leq \zeta_s$. For $\zeta > \zeta_s$, the normalization removes the zero-order dependence of the independent variables and allows a comparison of the essential differences of the MFE process in different molecules.

In order to determine a reasonable procedure for including the effects of the numerous independent variables that result in any experiment, it is necessary to develop a generalized quantitative description of the two-level system. After this formulation, the results are interpreted in a conceptual sense that can be generalized to MFE processes and that provide the required normalizations of the dependent and independent variables related to the absorption process. This approach is particularly useful for evaluating the effects of collisions.

Before considering the coupled two-level approximation in detail, a few comments are relevant concerning the method of the analysis and the validity of the related approximations. The description of the interaction is considered in the rate equation approximation rather than a coherent description. This approximation is valid under several conditions. The strength of the optical field can be specified in terms of the Rabi frequency $\Omega = \mu E/\hbar$ where μ is the transition moment and E is the electric field. The rate equation description is valid in the limit that $\Omega \bar{\tau} < 1$, where $\bar{\tau}$ is either the dephasing time T_2 of the pumped levels or the coherence time T_c of the optical source. We also require that the optical pulse duration $\tau_p > \bar{\tau}$. In many MFE absorption experiments the above conditions may be satisfied, either because the gas pressure is sufficiently high to provide a small value for T_2 or because the laser pulse is irregular in temporal character due to self mode locking. In experiments where the pressure is low, such that a collisional time is greater than τ_p , it still may be the case that $T_2 < \tau_p$.

due to rapid collisionless intramolecular V-V' processes resulting from strong anharmonic couplings in the molecule. The primary advantage of the rate equation approximation is that it allows a simplified treatment of the interaction that can be expressed in simple closed-form analytic solutions in limiting cases of interest. The resulting rate equation expressions provide a simple interpretation of the interaction process and a rationale for the choice of the normalized interaction parameters and those parameters related to collisional processes. The motivation for this analysis is to provide, in a first approximation, a basis of comparison of MIA processes for different polyatomic molecules rather than a detailed description of the MPE process itself. Similar results can be obtained by more general methods. A comparison of this analysis with the results of coherent interaction models will be discussed in Section IV.

2. Molecular Absorption in a Coupled Two-level Approximation

The model for a molecular absorber at low fluence can be formulated as follows. A finite bandwidth radiation field interacts with one or several rotational states of a vibrational level of a molecule to promote transitions to an upper vibrational state. This interaction results from the direct spectral overlap of the radiation field and the absorbing transition of the molecule. Other rotational states that are not coupled directly to the radiation field constitute a set of reservoir states that may be indirectly coupled to the interacting rotational levels through collisions. Also included in the reservoir states are other vibrational levels that are coupled to the interacting states either by collisional or collisionless intramodal V-V' transfer processes. In many situations, molecular absorption results from

several overlapping vibrational transitions. The coupled two-level analysis that follows applies to transitions between a pair of vibrational states. These results are easily generalized to accommodate overlapping vibrational transitions; the functional behavior is more complex, however. In most of the quantitative comparisons, we necessarily restrict our attention to absorption features that arise primarily from a single vibrational transition.

A schematic diagram of the model and the related nomenclature are summarized in Fig. 2. This particular formulation of the model is an extension of related work reported in the literature.⁽⁵⁾ The total population density of a given level N is a sum of the population density of the active states n_i and the reservoir states n_R . A prime denotes the upper state of the transition. The populations at time zero are denoted by $n(0)$ or $N(0)$. For the lower level, we take $N(0) \equiv N_0$ as the total population density of the initial state of the absorbing transition. For many applications of interest, $n'(0) = N'(0) = 0$. We also define $f_r = n(0)/N_0$, which is the fraction of population of the total interacting system that can be accessed directly by the radiation field. The fraction of reservoir states is then $1 - f_r = n_R(0)/N_0$. The reservoir states are coupled to the active states by a rate Γ and a reverse rate Γ_r . The rate equations that describe this interacting system are:

$$\frac{dn'}{dt} = -n'\Gamma + n_R' \Gamma_r + \phi\sigma (\delta n - n'); \quad (1)$$

$$\frac{dn}{dt} = -n\Gamma + n_R \Gamma_r - \phi\sigma (\delta n - n'); \quad (2)$$

$$\frac{dn_{r'}}{dt} = n'\Gamma - n_R' \Gamma_{r'}; \quad (3)$$

$$\frac{dn_R}{dt} = n\Gamma - n_R \Gamma_R; \quad (4)$$

where $\sigma(\omega)$ is the average optical absorption cross section for the active states, $\phi(\omega, t)$ is the photon flux at frequency ω , and ξ is the ratio of degeneracies of the upper and lower states. The forward and reverse coupling rates are related by detailed balance, so that

$$\frac{\Gamma_r}{\Gamma} = \frac{f_r}{1 - f_r} \quad (5)$$

At this point we assume that the upper and lower levels of the interacting system are similar to the extent that $f_r \approx f_{r'}$, $\Gamma \approx \Gamma'$, and $\Gamma_R \approx \Gamma_{R'}$. We also define the difference populations for the active states and the total transition as

$$\rho = (\beta n - n') \quad (6)$$

$$\Delta = (\beta n - n') + \xi(n_R - n_{R'}) \quad (7)$$

Equations (1-4) may now be written in the form

$$\frac{d\rho}{dt} = -(1+\beta) \sigma \rho \phi - \frac{(\rho - f_r \Delta)}{\tau}, \quad (8)$$

$$\frac{d\Delta}{dt} = -(1+\beta) \sigma \rho \phi, \quad (9)$$

where $\tau = \bar{\Gamma}_r/f_r$ is the equilibration time between the active and reservoir states. The equation governing the one-dimensional transport of the radiation is

$$\frac{\partial \phi}{\partial t} + c \frac{\partial \phi}{\partial x} = - c \sigma \phi \quad . \quad (10)$$

The optical fluence, ζ , is defined by

$$\zeta = \int_0^\infty \phi(t') dt' \quad . \quad (11)$$

Integration of Eq. (10) over time gives the transport equation in the integral form

$$\frac{d\zeta}{dx} = - \int_0^\infty \sigma \phi(t') \phi(t') dt' \quad . \quad (12)$$

Equations (8), (9), and (12) constitute a closed set of couple equations for the interacting system.

Subject to mildly restrictive conditions, the radiation transport of a nearly collimated optical beam can be described by an equation of the form

$$\frac{d\phi}{dx} = - N_t \sigma(\phi) \phi \quad , \quad (13)$$

where N_t is the total molecular number density and $\sigma(\phi)$ is a phenomenological fluence dependent absorption cross section. By definition the number of photon absorbed per molecule $\eta(\phi)$ is simply $\sigma(\phi) \phi$. Defined in this way $\sigma(\phi)$ and $\eta(\phi)$ are local quantities. Comparison of Eqs. (12) and (13) yields the relation

$$\eta(\phi) = \frac{1}{N_t} \int_0^{\infty} \sigma \rho \phi dt' \quad (14)$$

$$\sigma(\phi) = \eta(\phi) / \phi \quad (15)$$

There are quantities that can be obtained directly from an absorption experiment. Although average values of $\eta(\phi)$ and $\sigma(\phi)$ are obtained in a measurement, good approximations for the local values of these quantities can be related directly to these average values.⁽⁴⁾

The model parameters that govern the interaction are $f_r(\nu)$, $\sigma(\nu)$, and τ . It is necessary, therefore, to carefully relate these model parameters to the corresponding quantities for a given molecule. In the limit of low fluence and for low populations in the upper state of the transition, $\rho \rightarrow \beta f_r N_0$. Since the experimental absorption cross section is referenced to the total molecular density N_t , we define the fraction of population in the initial absorbing state as $f_i \equiv N_0/N_t$. From Eqs. (14) and (15) we then obtain the relation

$$\sigma(o) = f_i f_r \beta \sigma \equiv \sigma_o \quad (16)$$

where $\sigma_o(\nu)$ is the measured spectroscopic absorption cross section.

The value of σ used in the model can be related to fundamental molecular constants by the expression

$$\sigma = \frac{\lambda^2}{8\pi} A g(\nu) \quad (17)$$

where λ is the wavelength of the transition, A is the Einstein A coefficient and $g(\nu)$ is the normalized lineshape factor for a single transition.

The absorption cross section that is measured spectroscopically is referenced to the total molecular density and consequently includes implicitly the population fractions f_r and f_i as indicated in Eq. (10). In order to apply the results of the coupled two-level model to the interpretation of experimental data, it is necessary to evaluate f_i and f_r and to formulate the expressions in terms of the experimental quantities f_i , σ_0 , and $\phi(\phi)$ rather than the fundamental quantities σ and f_r . Consequently, the form of these expressions reflects an explicit dependence on σ_0 , f_i , and f_r rather than a fundamental dependence on σ and f_r . This fact must be taken into account in any evaluation of the fundamental processes involved in the interaction. The interpretation and calculation of f_i and f_r will be considered in more detail after a discussion of the solutions of Eqs. (8), (9), and (11).

In the analysis that follows, the important parameter that governs the fluence dependence of the absorption process and the level populations is

$$\phi_s = \frac{1}{(1+\phi)^2} g(f_r) \quad ,$$

where the function $g(f_r)$ varies over the range $1 \leq g(f_r) \leq 1/f_r$ depending on the coupling to the reservoir states, i.e., τ_p/τ . In a general sense, this parameter can be regarded as the fluence value for which the absorption deviates from linearity or at which a significant fraction of population is depleted from the initial absorbing state of the transition.

3. Analytic Solutions for Limiting Cases

We now derive the functional form of $\sigma(\phi)$ and $\eta(\phi)$ for several limiting cases of importance.

(a) Weak Coupling to the Reservoir States

In this limit, the transition to the collisionless regime is examined. If $\tau \gg \tau_p$, the term containing τ in Eq. (8) can be neglected. The solution of the resulting equations is then straightforward and yields the results

$$\rho = \bar{\rho} n(0) \exp(-t/\tau_s) , \quad (18)$$

where

$$\tau_s = \frac{1}{(1+\beta)\sigma} . \quad (19)$$

Substituting Eq. (18) into Eq. (14) and using Eq. (15) yields the results

$$\sigma(t) = \sigma_0 \left[\frac{1 - \exp(-t/\tau_s)}{t/\tau_s} \right] , \quad (20)$$

$$\eta(t) = \frac{\beta}{1+\beta} f_r f_i (1 - \exp(-t/\tau_s)) , \quad (21)$$

where τ_s can be rewritten in the form

$$\tau_s = \frac{\beta}{1+\beta} \frac{f_r f_i}{\sigma_0} \quad (22)$$

For purposes of later application, it is convenient to combine the factors in Eq.(21) in a form

$$\langle f \rangle = \left(\frac{\beta}{1+\beta} \right) f_r f_i . \quad (23)$$

In terms of $\langle f \rangle$, Eq. (21) can be written in a normalized form

$$\frac{\tau(t)}{\tau_0} = 1 - \exp\left(-\frac{t}{\tau_0}\right) \quad (24)$$

Equation (25) is the desired result for the normalized absorption in the couple two-level model. The normalization parameters that characterize the process are $\tau(t)/\langle f \rangle$ and $\tau_0 t / \langle f \rangle$. The explicit form of Eq. (24) results from the fact that the spectroscopic absorption cross section σ_0 implicitly contains the factor f_r , f_j , and τ .

The population of the active states is obtained from Eq. (18). If we assume that the population in the upper level is zero at $t = 0$, the fraction of population in the lower level of the active state n/N_0 is given by

$$\frac{n(t)}{N_0} = \frac{f_r}{1+\epsilon} \frac{[1 + \epsilon \exp(-t/\tau_s)]}{\tau_s} \quad (25)$$

(b) Strong Coupling Limit (Collisional)

In the limit that $\tau \ll \tau_p$, Eq. (8) may be written in the approximate form

$$(1 + \epsilon) \sigma \phi \tau + \left[\frac{\tau - f_r \tau}{\tau} \right] = 0 \quad (26)$$

Two sublimits of the strong coupling limit can be considered depending on the value of $(1 + \epsilon) \sigma \phi \tau$. This sublimit essentially depends on the optical fluence. In terms of the optical pulse τ_p , this parameter can be written in the approximate form $(1 + \epsilon) \sigma \phi \tau / \tau_p$.

(b-1) Weak Fluence Limit

In this limit the coupling to the reservoir states is strong and the optical flux is weak so that $(1 + \epsilon) \sigma \phi \tau / \tau_p \ll 1$. Combining Eqs. (26), (9), (14), and solving gives the results

$$n(\phi) = n_0 \left[\frac{1 - \exp(-\phi/\phi_s)}{1 + \beta} \right] \quad (27)$$

$$n(\phi) = \langle f \rangle [1 - \exp(-\phi/\phi_s)] \quad (28)$$

$$\phi_s = \frac{1}{(1 + \beta) \langle f \rangle f_r} = \frac{\phi_0}{\langle f \rangle} \quad (29)$$

where

$$\langle f \rangle = \frac{\sum f_j}{1 + \beta} \quad (30)$$

From Eq. (23) we can relate $\langle \bar{f} \rangle$ to $\langle f \rangle$ by $\langle \bar{f} \rangle = \langle f \rangle / f_r$. In the limit of strong reservoir coupling and weak optical flux, all states are effectively coupled to the radiation field during the optical pulse. Consequently $f_r \rightarrow 1$ and $\langle \bar{f} \rangle \rightarrow \langle f \rangle$. In this limit, the effective fraction of states in the molecule that are coupled to the radiation field is simply $\langle \bar{f} \rangle = \langle f \rangle \sim \sum f_j$ which is the maximum value of $\langle f \rangle$ for the transition. Equation (28) can then be written in the normalized form

$$\frac{n(\phi)}{\langle \bar{f} \rangle} = \left[1 - \exp \left(- \frac{\phi/\phi_0}{\langle \bar{f} \rangle} \right) \right] \quad (31)$$

This equation is therefore of the same form as that obtained in the weak coupling limit, Eq. (24).

The fractional population of the active state is given by

$$\frac{n(\phi)}{N_0} = 1 - \frac{\beta}{1 + \beta} [1 - \exp(-\phi/\phi_s)] \quad (32)$$

(b-2) Strong Fluence limit:

In this limit the coupling is large and the fluence is strong so that $(1 + f_r) \tau \gg \tau_p \tau$. Under these conditions, the parameter f_r does not determine the behavior of the system as in the other limits. Instead the optical intensity is sufficiently strong that the rate of depletion of the lower level of the active states by the radiation field is equal to the rate of collisional repopulation of the state by the reservoir. The important parameter that enters in this limit is $f_p \tau_p \tau$, which not only involves τ_p and τ but also the fraction of the molecules that interact with the radiation field.

Combining Eqs. (26), (9), (14) and solving in the limit $(1 + f_r) \tau \gg \tau_p \tau$ yields the results

$$n(t) = \frac{f}{1 + \frac{f}{f_r}} f_i \left[1 - \exp \left(- \frac{f_r \tau_p}{\tau} t \right) \right] \quad (33)$$

$$N = \frac{N_0}{1 + \frac{f}{f_r}} \left[1 + \exp \left(- \frac{f_r \tau_p}{\tau} t \right) \right] \quad (34)$$

The physical origin of f_r in Eqs. (33) and (34) is as follows. Consider an absorber in which the optical field interacts with one state j of a system of k states that are equally populated and are coupled by collisions. If the stimulated rate for population depletion of the absorbing state is larger than the collisional rate for replenishing the state, the absorption process "burns a hole" in the population distribution of the k states. Within one collision time τ , the j level is repopulated by each of the k states in the reservoir contributing $1/k$ of its population. It therefore, requires a time $k\tau$ to significantly deplete the reservoir states. Since all states are equally populated, $f_r = 1/k$. The relevant timescale for the depletion of the manifold of states is consequently τ/f_r rather than τ .

4.0 GENERALIZED CONCEPT OF THE COUPLED TWO LEVEL SYSTEM

The results obtained in the previous section are expressed in a form that emphasizes both the fundamental parameters of the interaction (σ , f_r) and the apparent parameters of the interaction (σ_0 , f_i). A summary of the coupled two level model results for the various limits considered is contained in Table I. For convenience, we have defined $d \equiv \xi/(1 + \xi)$. In view of the physical origin of $\eta(\xi)$ in the high fluence limit, it is reasonable to associate $\langle f \rangle$ with the term

$$\langle f \rangle = d f_i \left[1 - \exp \left(- \frac{f_r}{1 + f_r} \right) \right] \quad (35)$$

We can therefore interpret $\langle f \rangle$ as the effective fraction of the population in a given vibrational transition that is coupled to the radiation field. The value of $\langle f \rangle$ exceeds the low fluence value $f_i f_r$ due to the strong coupling to the reservoir states.

The absorption for the coupled two level system can be written in a general analytic form that is valid in all limits. The results can be expressed as

$$\frac{\eta(\xi)}{\langle f \rangle} = 1 - \exp \left(- \frac{\sigma_0 \xi}{\langle f \rangle} \right) \quad (36)$$

where $\langle f \rangle$ is obtained from the approximate expression

$$\langle f \rangle = d f_i \left\{ 1 - \exp \left(- \frac{f_r}{1 + f_r} \frac{\tau_p}{\tau} \left[1 + \frac{f_r f_i}{\sigma_0 \phi} \frac{\tau_p}{\tau} \right] \right) \right\} \cdot$$

$$[1 - \exp \left(- \frac{\tau_p}{\tau} \right)] + d f_r f_i \exp \left(- \frac{\tau_p}{\tau} \right) \quad (37)$$

The functional form of $\langle f \rangle$ approaches the correct limits summarized in Table I in a smooth and continuous manner as is readily verified by allowing the quantity τ_p^{-1} to vary from zero to infinity. The correction of $(1 - f_r)$ to Eq. (55) as $f_r \rightarrow 1$ is necessary to achieve the value of $\langle f \rangle = f_l$ in this limit. Equations (56) and (57) may be considered to constitute an approximate closed form analytic solution to Eqs. (8), (9), and (12) that is valid for all values of fluence and τ_p^{-1} . Cast in this general form, the optical interaction in a coupled two-level system can apparently be described in terms of two parameters, a fluence parameter $\tau_p^{-1}\langle f \rangle$ and the effective fraction of states that interact with the radiation field $\langle f \rangle$. All effects due to collisions (τ_c), intramolecular $V - V'$ coupling (τ), laser pulse duration (τ_p), gas temperature (f_l , f_r , τ), pressure (τ), and laser spectral bandwidth (f_r) can be regarded in first approximation as affecting the effective fraction of absorber molecules $\langle f \rangle$ that can be coupled to the radiation field. Equations (56) and (57), therefore, constitute a general form for the optical absorption in a coupled two level system in terms of a set of normalized dependent and independent variables.

We now consider the definition and evaluation of f_l and f_r in more detail. The simplest application of the model is to optical absorption from a set of rotational transitions occurring between a pair of vibrational levels that are isolated from the other vibrational levels of the molecule. In this situation, f_l is the fractional population of the lower vibrational level and f_r is the fraction of the rotational population that is coupled directly to the radiation field. For an optical interaction with well defined rotational lines such as occur at low values of J in a $F(J)$ or $R(J)$ branch transition, f_r is less than or

equal to the Boltzmann population factor λ_J for the particular rotational level being accessed. For monochromatic radiation and a homogeneously broadened transition, $f_r = \lambda_J$. If the transition is inhomogeneously broadened, $f_r < \lambda_J$. In many situations, the bandwidth of the optical source Δ is finite. Under these conditions, the value of f_r is obtained by a convolution of the spectral intensity distribution of the source with the absorption features of the molecule.

For a Q branch transition, the absorption results from a number of overlapped rotational transitions. In addition each rotational line may be split into a number of components due to the coriolis interaction in the molecule. The spectral distribution of the Q branch absorption in SF_6 , for example, results from these type splittings. In this situation the spectroscopic absorption cross section $\sigma_o(\nu)$ is directly proportional to the total fraction of population with rotational levels (or split components) being accessed at frequency ν . If the band strength is uniformly distributed in frequency, one can define a spectral population distribution function $f(\nu)$. The value of $f(\nu)$ is normalized such that $\int_{-\infty}^{\infty} f(\nu) d\nu = 1$. In terms of $\sigma_o(\nu)$

$$f(\nu) \approx \frac{\sigma_o(\nu)}{\int \sigma_o(\nu) d\nu} \quad (38)$$

where $\int \sigma_o(\nu) d\nu$ is related to the integrated bandstrength. For ground state transitions in tetrahedral (T_d) XY_4 and Octahedral (O_h) XY_6 molecules, this relation is rigorously correct.⁽⁵⁾ If the bandwidth of the optical source Δ is much less than the width of $f(\nu)$, the value of f_r given directly by $f_r = f(\nu) \Delta$.

The above discussion is valid for a single vibrational transition. If the absorption at a given frequency results from overlapping vibrational transitions, the situation is considerably more complex. The saturation of the absorption depends on the specific values of f_r and f_i for each transition rather than the average values for a given absorption feature. The use of Eq. (58) now results in a value of f_r weighted by f_i and averaged over all overlapped vibrational transitions. Consequently, the use of Eq. (58) for the determination of f_r is subject to numerous uncertainties. The two-level formalism developed previously is only applicable to overlapping vibrational transitions that are uncoupled. From Eq. (56), a partial absorption $\tau_j(\nu)$ can be defined for each transition from which the total absorption $\tau(\nu)$ is given by a sum over all i . If, however, the final state of one transition also serves as an initial state for a second transition, the coupled two level results are not applicable.

If the spectroscopic parameters of the molecule are sufficiently well known, $f(\nu)$ can be calculated from first principles. For most molecules this is not the case and use of Eq. (58) gives a first estimate for f_r subject to the restrictions pointed out previously. The application of Eq. (35) to describe the collisional coupling of rotational levels also implicitly contains the assumption that all values are permitted for the change in rotational angular momentum during a collision.

The reservoir state may also include other vibrational levels of the molecule. Under these circumstances the same formalism applies if the total population density of the absorbing state includes the additional population of coupled vibrational levels. If we define f_v as

the total fractional population of these vibrational states, Eqs. (36) and (37) apply produced f_i and f_r are replaced by

$$f_i' = f_i + f_v \quad (39)$$

$$f_r' = f_r \frac{f_i}{f_i'}, \quad (40)$$

In the limit of strong coupling, the total fraction of the population accessed f_r' can therefore exceed the fraction in the initial absorbing state f_i . Also the fraction of the total population that is directly accessed by the radiation field is smaller than f_r due to the coupling to other vibrational levels in the molecule.

5.0 Generalization to the MPA Processes

In the previous section we developed general expressions for absorption in a coupled two level system, the results of which are summarized by Eqs. (36) and (37). These results should correctly account for molecular absorption at fluence levels for which $\Phi \lesssim \Phi_s$, where $\Phi_s = \langle f \rangle / \sigma_0$. For $\Phi > \Phi_s$, MPE processes become important and the two level approximation breaks down; Eq. (36) predicts that $\eta(\Phi)$ approaches a constant value at high fluence whereas it is observed experimentally that $\eta(\Phi)$ continues to increase in large polyatomic molecules. The model may be modified in a conceptual sense, however, to establish a plausible basis for extension of these results into the MPE regime.

As $\Phi/\Phi_s \rightarrow 1$, a significant fraction of the population in the initial absorbing vibrational state is transferred to the upper vibrational level of the transition by the optical field. In the MPE process we assume that once $\Phi \gtrsim \Phi_s$, successive photon absorption and depletion of population of the upper level occurs on a time scale that is short compared

to the transfer time between the lower level of the active state and the reservoir state. This process may involve a direct absorption out of the upper level of the active state or a strong intermodal coupling of the active state to other vibrational levels and a direct photon absorption out of these final states. The net result is that on the average the upper state population of the transition is always small compared to the lower state population. The dynamics of the interaction is then in a first approximation controlled by the lower vibrational level of the absorbing transition. The coupled two level model considered previously can be reduced to a description of the lower level active and reservoir states by letting $n' = n'_R = 0$ in Eqs. (1-4). The results obtained in the previous section may then be applied directly to this revised model by the formal procedure of taking the limit $\beta \rightarrow \infty$.

In view of the above comments, we consider in a first approximation that the dominant functional behavior of $\eta(\phi)$ is determined by the dynamics of the lower level of the molecular transition that interacts with the radiation field. We therefore consider as an ansatz, a generalization of Eq. (36) which may be written in the normalized functional form

$$\frac{\eta(\phi)}{\langle f \rangle} = G \left(\frac{\sigma_0 \phi}{\langle f \rangle} \right) \quad (41)$$

which is valid for $\sigma_0 \phi / \langle f \rangle > 1$ and approaches the two level result $\bar{G}(x)$ as summarized in Table I for $(\sigma_0 \phi / \langle f \rangle) < 1$. The value of $\langle f \rangle$ is determined from Eq. (37). Experimental absorption data for SF_6 for example, indicates that the $G(x) \rightarrow x^{2/3}$ for $x \gg 1$. In the high fluence regime,

the value of $\langle f \rangle$ as defined in this analysis is independent of fluence. However, the fraction of states that interact with the radiation field may increase with increasing fluence because of power broadening. In typical applications, this effect becomes important for $(\sigma_0 \lambda / \langle f \rangle) > 1$. Consequently, it may also be necessary to also include this contribution to the fraction of molecules that interact with the radiation field. This aspect will be considered in detail in Section III.

III. MPA IN DIFFERENT POLYATOMIC MOLECULES

1. General Comments

In this section the comparison of MPA in different polyatomic molecules is attempted using the normalization procedure developed in Section II. The required absorption parameters are the fluence dependent absorption cross section $\sigma(f)$ or the number of photons absorbed per molecule $\eta(f)$. The quality of such a study is compromised by several factors having to do with the quality of existing data for $\sigma(f)$ or $\eta(f)$. In general, there are only a few molecules that have been studied for which there is detailed data of sufficient quality to incorporate into a study of this type: (a) most quantitative investigations of MPA are limited to a fluence range of less than 10^2 . In order to effect a valid quantitative comparison of different molecules, it is necessary to compare absorption data that extends from the linear absorption range (Beer's law limit) to near dissociation of the molecule; (b) significant differences in both the quantitative value and the functional dependence of the absorption parameters can result from differences in the method of data reduction used in the various experiments; (c) Most MPE experiments use an atmospheric pressure CO_2 laser as an optical

source. Despite the commonality of the source, the source characteristics can vary greatly for different experiments. Of particular importance are the spatial mode quality of the optical beam (single- or multi-mode), the temporal nature of the pulse (gain-switched peak with or without a low-intensity tail), and the effective bandwidth of the laser (self mode locked, single- or multi-longitudinal mode). These differences in the optical source can lead to significant differences in the measured absorption parameters.

In view of these considerations, a detailed quantitative comparison of different MPA data is precluded at the present time. The purpose of the present study is rather to evaluate general trends of the MPA process. Consequently, the results of the study should be regarded as uncertain by at least a factor of two. The particular choice of molecules for this study results primarily from the collection of investigations reported in the literature for which the data is of sufficient quality and has been taken over a sufficient range to make the results useful. In some cases, it was necessary to infer some of the experimental parameters in the analysis.

For purposes of comparison, we will normalize the absorption data in terms of $\eta(\phi)$ in the form derived in Section II.

$$\frac{\eta(\phi)}{\langle f \rangle} = G \frac{\sigma_0 \phi}{\langle f \rangle} \quad (42)$$

where σ_0 is the measured small signal absorption cross section and $\langle f \rangle$ is the effective fraction of the molecular population that interacts with the radiation field. The values of $\eta(\phi)$ in an experiment can be

related to $\sigma(\Phi)$ by $\eta(\Phi) = \sigma(\Phi)\Phi$. At the present time, $\langle f \rangle$ can be calculated directly for only a few molecules. An empirical procedure will be developed to determine the relative value of $\langle f \rangle$ for the different molecules. A value of $\langle f \rangle$ will then be calculated directly for SF_6 to establish a quantitative benchmark for the study. A general evaluation of the derived values of $\langle f \rangle$ will be considered in a concluding section.

2. Absorption Characteristics of Polyatomic Molecules

We consider first a few simple examples to establish the comparison procedure and nomenclature. A summary of the experimental parameters and related references is contained in Table 2. Shown in Fig. (3) are measurements of $\sigma(\Phi)$ for S_2F_{10} at several frequencies corresponding to output lines of the CO_2 laser. Besides increased physical insight, a considerable simplification of these curves results if the data are replotted in terms of the normalized variables $\eta(\Phi)$ and $\sigma_0\Phi$. The results are shown in Fig. (4). The absorbing band in S_2F_{10} is centered at 938 cm^{-1} and is 18 cm^{-1} in width (FWHM). Except for measurements in the extreme wings of the absorption feature, a reasonable fit to the data can be obtained with a single curve. The fit could be made nearly exact by assigning a specific value of $\langle f \rangle$ at each frequency in the absorbing transition to take into account the variation in fractional population accessed by the laser. In the analysis of most molecules the data is not sufficiently extensive to make this refinement warranted. We, therefore, consider $\langle f \rangle$ to be a representative value near the peak of the spectroscopic absorption feature of a particular molecule. It is not surprising that the dependence of $\eta(\Phi)$ in the wings of the absorption band deviates from $\eta(\Phi)$ at the peak. At these frequencies, the absorption cross section can be constant or can increase with fluence.

This effect, which is also observed in other molecules, is uniquely attributable to the MPA process and results when the excited-state absorption strength is comparable to the initial absorbing state in the molecule. As such, $\eta(\omega)$ is strongly dependent on the details of the excited-state interaction dynamics as well as the dynamics of the ground state. The theory developed in Section II should only apply to the latter situation, and consequently the normalization of Eq. (42) would not be expected to be valid in the extreme wings of the absorbing transition.

The general behavior of the absorption curve shows a linear dependence at low values of ω/ω_0 and a departure from this dependence for $\omega/\omega_0 \rightarrow 1$. From Eq. (36), this behavior is typical of a two-level system in which $\langle f \rangle \ll 1$. A similar plot is shown for UF_6 in Fig. (5). The absorbing transition consists of a series of hot bands of the ν_5 vibrational mode centered at 627.1 cm^{-1} with a typical transition bandwidth of 18 cm^{-1} . A comparison of S_2F_{10} and UF_6 indicates that the functional dependence of $\eta(\omega)$ is both qualitatively and quantitatively similar. A plot of $\eta(\omega)$ for several frequencies in SF_6 is shown in Fig. (6). The departure from linear absorption in SF_6 occurs at $\omega/\omega_0 \approx 10^{-5}$. This low value results because $\langle f \rangle$ is considerably smaller for SF_6 than for S_2F_{10} or UF_6 . The specific data points in Figs. (4-6), as well as in the figures in the remainder of the section, are representative of the range of the data and do not necessarily correspond to the actual data points in a given experiment.

A summary of MPA measurements of $\eta(\omega)$ for several molecules is shown in Fig. (7). For purposes of comparison, measurements near the peak of the spectroscopic absorption feature have been selected if

available. This particular form of the data summary indicates the general nature of the MFI process and the fluence range over which these processes are observed. The extent of the range for MFI is only apparent, however, because the fluence variable alone does not constitute a good measure of the interaction of the radiation field with the molecule.

A considerable simplification again results if these absorption data are replotted in terms of $\sigma_0 \Phi$. The results are shown in Fig. (8). With the exception of the triatomic molecules, the fluence behavior of the different molecules can be classified into two types: (1) one in which a deviation from linear absorption begins to occur and (2) one in which $\eta \propto \Phi^\gamma$ where $\gamma \leq 2/3$. The general functional behavior of each molecule is consistent with Eq. (39) depending on whether $\sigma_0 \Phi / \langle f \rangle$ is greater than or less than unity. The factor that has not been taken into account for the different molecules in Fig. (8) is $\langle f \rangle$. If $\langle f \rangle$ could be calculated for each molecule and the absorption data could be replotted in the normalized form of Eq. (39), the curves in Fig. (8) would be expected to merge into a single curve. In practice, $\langle f \rangle$ is difficult to calculate from first principles. Since $\langle f \rangle$ is a divisor in both the dependent and independent variables in Eq. (4.1), we can obtain the ratio of $\langle f \rangle$ for two molecules by simply shifting each plot of $\eta(\Phi)$ vs. $\sigma_0 \Phi$ in Fig. (8) along the linear absorption line until the curves merge. This procedure is tantamount to multiplication or division of the ordinate and abscissa of a given graph by a constant. For convenience, we take the curve for S_2F_{10} as a reference and shift the remaining curves accordingly. The results are shown in Fig. (9); the relative values of $\langle f \rangle$ ($\langle f \rangle_{S_2F_{10}} = 1$) are summarized in Table 2. As expected on physical grounds, all of the data can be fit to a single curve for $\sigma_0 \Phi / \langle f \rangle \lesssim 1$. It is surprising, however, that nearly the same

functional dependence is obtained for all molecules at high fluence. With the exception of SiF_6 , all molecules dissociate at some point on the curve. For the large polyatomic molecules, Cl_3COCl , S_2I_{10} , and Si_5N_{12} , significant dissociation occurs at $\sim 4/f < 1$; i.e., in the range of linear absorption. The absorption in triatomic molecules, on the other hand, shows saturation as in an isolated two-level system and no dissociation occurs over the indicated fluence range. For values of $\sim 4/f > 1$, it appears that most molecules, when excited at a frequency near the peak of the absorbing transition, absorb energy with a fluence dependence of $t^{2/5}$.

3. Calculation of $\langle f \rangle$ for SF_6

It is of interest to establish an absolute calibration for $\langle f \rangle$. To do this we calculate $\langle f \rangle$ for SF_6 using several different methods. We consider the absorption of 947.7 cm^{-1} by the P(16) line of the CO_2 laser. At this frequency, the interaction is primarily with the Q branch of the ground state ν_5 vibrational mode.⁽¹⁷⁾ The absorption by hot bands is less than 15% of that resulting from the ground state transition.⁽¹⁸⁻¹⁹⁾ The spectroscopic structure of the ν_5 -mode ground state Q-branch in SF_6 is now understood in detail as a result of several experimental and theoretical studies.⁽¹⁷⁾ The population at a given frequency, ν , of the transition can therefore be calculated directly to derive a population distribution function $f(\nu)$ as discussed in Section II. The value of f_r is then given by $f_r = f(\nu)\Delta$, where Δ is the approximate bandwidth (FWHM) of the optical source. Alternatively, the value of $f(\nu)$ could be calculated from Eq. (38). Both of these methods give essentially the same result.

At low pressure, $\langle f \rangle$ can then be calculated directly, since $\langle f \rangle = f_i f_r$ where f_i is taken to be the fraction of population in the vibrational

ground state. The value of $f(\nu)$ was obtained numerically⁽²⁰⁾ and is shown in Fig. (10) for two values of temperature. At $\nu = 947.7 \text{ cm}^{-1}$, the value of $f(\nu)$ at 300 K and 140 K are nearly equal. The width of $f(\nu)$ decreases, however, as T decreases. The largest source of uncertainty is the bandwidth $\Delta\nu$ of the CO_2 laser. The absorption measurements taken at 300 K and shown in Fig. (1) were obtained using a TiA laser with a multimode output beam. Under these conditions, $\Delta\nu = 6 \times 10^{-3} \text{ cm}^{-1}$ and $f_p = 8 \times 10^{-5}$. At 300 K, $f_1 = 0.5$. If the interaction of the radiation were primarily with the ground state Q-branch, $\langle f \rangle = 2.4 \times 10^{-5}$. Since some hot band contributors are also involved, $\langle f \rangle \geq 2.4 \times 10^{-5}$.

An independent estimate of $\langle f \rangle$ can be obtained from the functional form of $\eta(\nu)$ for SF_6 . From Fig. (1), the value for which $\eta(\nu)$ decreased to 0.65 of its linear absorption value is taken to be 5 mJ/cm^2 . Since this value corresponds to $\sigma_0 \nu / \langle f \rangle = 1$, $\langle f \rangle$ can be obtained directly. Using this method, $\langle f \rangle = 5 \times 10^{-5}$. This value is within a factor of two of that calculated using $f(\nu)$ and the bandwidth of the laser. We, therefore, adopt the value of $\langle f \rangle = 5 \times 10^{-5}$ for a reference value. The fact the $\langle f \rangle$ is small for SF_6 at 300 K has been pointed by Ambartsunyan, et. al.⁽²¹⁾ The estimate for $\langle f \rangle$ indicated in this work is 0.01-0.1.

Absorption data for SF_6 at 140 K were obtained using a CO_2 laser with a single-longitudinal mode optical output with a pulse duration of 150 ns. From the limitations imposed by the bandwidth of the laser and the finite pulse duration, the value of $\Delta\nu$ can be limited to the range $2 \times 10^{-4} \leq \Delta\nu \leq 3 \times 10^{-3} \text{ cm}^{-1}$. Since $f_1 = 0.89$ and $f(\nu) = 1.1/\text{cm}^{-1}$ at $T = 140 \text{ K}$, the value of $\langle f \rangle_{140}$ is within the range $1.9 \times 10^{-4} \leq \langle f \rangle_{140} \leq 2.9 \times 10^{-3}$. From Table 2 the relative values for $\langle f \rangle$ at 300 K and 140 K is

50. This ratio is consistent with the above estimates if $\langle f \rangle_{140}$ is taken to be 2.5×10^{-4} . The value of f_g at 140 K is estimated to be 10^{-7} J/cm². The calculated value of $\langle f \rangle$ from this value is 5×10^{-4} .

The results of these estimates for SF_6 are summarized in Table 5. Considering factor of two uncertainties in the various quantities, the values of $\langle f \rangle$ computed from $f(f_g)/f_g$ are in good agreement with those estimated from f_g . From the values in the table it appears that the scales for $\sigma f/\langle f \rangle$ and $\gamma(f)/\langle f \rangle$ in Fig. (9) are nearly absolute. This is not surprising since theoretical considerations would indicate a departure from linear absorption at $\sigma f/\langle f \rangle \sim 1$.

4. Discussion

In the previous section, it was established that $\langle f \rangle$ for SF_6 at 500 K is typically 5×10^{-5} , which indicates that the values of $\langle f \rangle$ in Table 2 can be considered to be absolute within the accuracy of the study. Inspection of these results indicates that $\langle f \rangle$ for the large polyatomics (greater than 7 atoms) SF_5NH_2 , Sec Butyl Acetate, CF_3COF_3 , and perhaps S_2F_{10} exceeds unity. As was pointed out previously, these particular molecules also dissociate in the fluence range for linear absorption. One explanation for this behavior is the following: Because of the large number of degrees of freedom in the molecule, several vibrational modes can resonantly interact with the radiation field. Also, once a given vibrational mode is excited, the anharmonic coupling ground state to other vibrational modes is sufficiently strong and the density of states sufficiently great that other vibrational modes are indirectly excited by the radiation field by intramodal V-V' coupling. The net result is that a condition of statistical equilibrium may be established on a rapid time scale and the fraction of molecular population that interacts with the radiation field approaches unity. The fact

that $\langle f \rangle$ exceeds unity may indicate that many successive interactions occur between the vibrational modes of the molecule and the radiation field, which is analogous to the absorption of several photons by a single molecule. The fact that the large polyatomics dissociate in the linear absorption range may also be indicative that many vibrational modes of the molecule are strongly excited in this fluence range.

The coupled two-level model and the general functional form of the MPA measurements shown in Fig. 9 leads to a number of implications that can be evaluated directly. In particular, it is of interest to explore the functional relationships of gas pressure P , bandwidth of the optical source Δ , temporal pulse shape τ_p , and the dependence on optical flux. In order to gain physical insight into those processes, we consider limiting parameter regimes; an evaluation for arbitrary experimental parameters is possible, however, by using the complete expressions for $\langle f \rangle$ as given by Eq. (57).

In the fluence range that $\sigma_0 \phi / \langle f \rangle \gg 1$, the trends in Fig. (9) indicate that $\eta(\phi)$ can be written in the functional form

$$\eta(\phi) \propto \langle f \rangle^{1/3} (\sigma_0 \phi)^{2/3} \quad (43)$$

The MPA process can therefore be completely parameterized in terms of σ_0 and $\langle f \rangle$. The value of σ_0 is determined primarily by the properties of the particular molecule. The effects of most other experimental parameters are manifest in $\langle f \rangle$. From Eq. (40), $\eta(\phi) \propto \langle f \rangle^{1/3}$. This proportionality provides the dominant functional relationship for the dependence of $\eta(\phi)$ on τ_p , P , and Δ . In order to investigate the validity of Eq. (43), we consider several quantitative comparisons with experimental measurements in SF_6 .

The value of $\langle f \rangle$ depends on the value of f_r , the fraction of molecules that interact directly with the radiation field. At low fluence the value of f_r is determined by the bandwidth of the optical source. In the limit that $L \ll 1$ and $f_r \ll 1$, $\langle f \rangle \propto f_r$; consequently $\eta(\Phi) \propto L^{1/5}$. Absorption experiments in Si_6 have been carried out that compare directly the effects of irradiation with a single and multimode laser output.⁽²⁾ The results of the experiment are shown in Fig. (1). The absorption in Si_6 using the multimode output (unsmoothed pulse) was typically a factor of two higher than for a single mode pulse (smoothed) for the same fluence over a fluence range of $10^{-5} \leq \Phi \leq 10^{-1} \text{ J/cm}^2$. From Table 3, the values of L for the two lasers are 5×10^{-4} and $6 \times 10^{-5} \text{ cm}^{-1}$. The calculated cross section ratio at constant fluence is therefore $(60/5)^{1/5} = 2.3$. This value is in good agreement with that measured experimentally.

The pressure dependence of $\eta(\Phi)$ can also be calculated. In the high fluence limit where $\sigma_0 \Phi / \langle f \rangle \gg 1$, and $\tau_p / \tau \ll 1$, Eq. (57) simplifies to the form (c.f. Table 1)

$$\langle f \rangle = f_1 \left\{ 1 - \exp \left[- \frac{f_r}{1 - f_r} \frac{\tau_p}{\tau} \right] \right\} \quad (44)$$

The dominant effect of the collision process is to determine the effective number of molecules that interact with the radiation field during the duration of the optical pulse. As was pointed out previously, this effect depends on f_r as well as τ_p / τ . From Eqs. (43) and (44) one obtains the result

$$\eta(\Phi) \propto \left[1 - \exp \left(- \frac{f_r}{1 - f_r} \frac{\tau_p}{\tau} \right) \right] (\sigma_0 \Phi)^{2/5} \quad (45)$$

If the gas pressure is sufficiently low that $f_r \tau_p/\tau \ll 1$, $\eta(\Phi) \propto P^{1/3} \Phi^{2/5}$. The validity of these results are subject to the condition that $\tau_p/\tau \gtrsim 1$. In the general case, the pressure dependence is obtained directly from $\langle f \rangle^{1/3}$ where $\langle f \rangle$ is calculated from Eq. (37).

It is instructive to compare this result with pressure dependent MPA measurements in SF_6 . Quigley⁽²²⁾ has reported measurements of $\eta(\Phi)$ as a function of Φ and the pressure of xenon buffer gas for the P(16) and P(20) lines of the CO_2 laser. The most direct quantitative comparison can be effected for the P(16) line since f_r has been calculated for the Q branch of the ν_3 vibrational mode (c.f. Table 3) and the effects of hot-band contribution are minimal. The rotational equilibration time for SF_6 -Xe collisions has not been measured. As a first approximation, we consider it be approximately the same as the SF_6 - SF_6 collision time of 100 ns torr. At 0.5 torr and a laser pulse duration of 150 ns, $\tau_p/\tau \ll 1$. The value of f_r relevant to the experiment is $f_r = 5 \times 10^{-5}$. Consequently, at a fluence $\Phi > 10^{-2} \text{ mJ/cm}^2$, the conditions for the validity of Eq. (44) are satisfied and a comparison of this expression with the SF_6 measurements is justified. The comparison is also direct since the buffer gas number density rather than the SF_6 number density is being varied. The value of $f_r \frac{\tau_p}{\tau}$ is much less than unity for pressures less than 10 torr. Consequently at Xenon pressures lower than 10 torr, $\eta(\Phi) \propto (P)^{1/3}$ at constant fluence.

The experimental data in the original reference was in a form that could not be conveniently compared with Eq. (43). The original data has been replotted in Figs. (11) and (12) in a form that displays the functional dependence on fluence and xenon gas pressure. The partial pressure of SF_6 was 0.1 torr, so that the contribution of SF_6 to the collisional processes is relatively ineffective for Xenon pressures exceeding

0.5 torr. The measured data in Fig. (11) indicates that $\eta(\dagger)$ is proportional to $\tau_p^{2/5}$ for $0.1 \leq P \leq 10$ torr. In the pressure range $10 \leq P \leq 100$ torr, there is a small departure from the $\tau_p^{2/5}$ dependence. The $P^{1/5}$ dependence for $\eta(\dagger)$ is clearly evident in Fig. (12) for $P = 10$ torr. Using the values for τ_p , τ , and f_r discussed previously, the value of $\eta f_p^{1/5}$ as given by Eq. (42) was obtained as a function of P . The results is shown as the solid curves in Fig. (11). The measured and calculated values of $\eta(\dagger)$ are taken to be approximately equal at 10 torr for each value of fluence. As indicated in the figure, the use of Eq. (45) provides an excellent quantitative fit to the measurements.

Experiments in SF_6 have also been reported in which the dissociation probability and $\eta(\dagger)$ have been determined as a function of τ_p at constant fluence.^(23,24) It was observed that the dissociation probability or $\eta(\dagger)$ was approximately constant for a factor of 10^2 variation in τ_p . Although several mechanisms can be proposed to explain these important results, the fact that $\eta(\dagger)$ is independent of τ_p in the experiments of Akhmanov, et. al.⁽²⁴⁾ can also be explained in terms of Eq. (45) and the parameter $f_r \tau_p / \tau$. In this experiment, the absorption of SF_6 at a constant pressure of 0.25 torr was determined at a frequency of 944.19 cm^{-1} and at fluences of 0.8 mJ/cm^2 and 25 mJ/cm^2 . The duration of the optical pulse was varied by removing a portion of a $1.5 \mu\text{s}$ pulse by an optical breakdown technique. Data was obtained at $\tau_p = 15, 75, 400, \text{ and } 1500 \text{ ns}$. Under these conditions, the bandwidth of the optical pulse should approach the fourier transform limit of the pulse duration. Consequently $\Delta \propto \tau_p^{-1}$. As discussed previously, the effects of rotational relaxation ($\tau \approx 640 \text{ ns}$), are related to other experimental quantities by the factor $f_r \tau_p / \tau$. Since $f_r \propto \Delta \propto \tau_p^{-1}$ and τ was held constant

during the measurement, the value of $f_r \tau_p / \tau$ was also constant. Since $\eta(\Phi)$ is only a function of this parameter at constant fluence, $\eta(\Phi)$ should be constant with variations in τ_p as was observed experimentally. In view of this possibility, the conclusion reached by these investigators that rotational relaxation does not contribute significantly to the absorption of intense ir radiation may not be valid.

The comparisons of experimental data in terms Eqs. (43) and (44) have produced good quantitative agreement under the assumption that the interaction process is related to the rotational levels and that the fraction of interacting states f_r is determined only by the bandwidth of the laser. This appears to be a valid assumption for SF_6 up to fluence levels of 50 mJ/cm^2 . This result is surprising considering the Rabi frequency Ω at this fluence $\tau_p \approx 100 \text{ ns}$ is $2 \times 10^{10} \text{ s}^{-1}$ and $\Omega/2\pi \approx 0.1 \text{ cm}^{-1}$. This value exceeds the laser bandwidth of $6 \times 10^{-5} \text{ cm}^{-1}$ by a factor of 20. Since the interacting levels in polyatomic molecules are degenerate, both with respect to energy and angular momentum along a fixed space axis, the Rabi frequency is proportional to M_{J_0} for Q-branch transitions and $(J^2 - M^2)^{1/2} \mu_{J_0}$ for P- and R-branch transitions. Consequently, the system is characterized by a distribution of Rabi frequencies, of which the maximum value is $\mu_{J_0} E / \hbar$. The net effect of the M or spatial degeneracy is to decrease the effective value of Ω . Although some of the bandwidth discrepancy can be accounted for by these considerations, a more detailed treatment of these effects is necessary to completely account for the observed behavior.

IV. COMPARISON WITH THEORETICAL MPE MODELS

A remarkable feature of the curves shown in Fig. (9) is that near the peak of the absorption feature, MPA processes in most polyatomic molecules exhibit the same general behavior. For $(\sigma_0 \Phi / \langle f \rangle) <$

1, a linear absorption occurs while in the opposite fluence limit the value of $\eta(\Phi) \propto \Phi^{2/3}$ where $\gamma = 2/3$. The apparent differences in different molecules as indicated in Fig. (7) are due in part to the differences in the spectroscopic parameters of the molecule which can be eliminated by an appropriate normalization of the dependent and independent absorption variables. The theory based on the coupled two level model that was outlined in Section II provides a phenomenological structure for understanding the MFA process near threshold fluence and for comparison of experimental data, but was not intended to represent a model for MPE. This model is based on a rate equation formulation, which neglects the coherence aspects of the interaction of the radiation field with the molecule. Effects such as powerbroadening, phase coherence, coupling to other vibrational states by perturbative interactions with the field, etc., have not been taken into account. It is of interest to determine if the form of Eq. (42) and the curve in Fig. (9) can be derived using a more fundamental basis. In particular, it is important to determine if the $\gamma = 2/3$ fluence dependence is a necessary consequence, in a fundamental sense, of a particular theoretical model. Since most current theoretical models for MPE are in a stage of preliminary development, few results have been reported that give a detailed prediction for the functional form of $\eta(\Phi)$. We will discuss one MPE model that has been proposed for which this comparison is possible - that of the anharmonic oscillator. Since $\eta(\Phi)$ is probably not a very sensitive test of any MPE model, we proceed with this comparison with the precautionary comment that the agreement of a theoretical model with experimental data is certainly a necessary condition but by no means a sufficient condition for its validity.

Several models for MPE have been discussed that are based on the anharmonic oscillator.⁽²⁵⁻²⁹⁾ These formulations involve both quantum mechanical and classical descriptions. A detailed model for MPE in terms of a classical anharmonic oscillator has been described by Cotter.⁽²⁷⁾ The results show that the average excitation energy of the oscillator can be expressed in terms of a convolution integral of a frequency-dependent excitation function $\epsilon(\nu, \xi)$ with the frequency distribution function of interacting states in the molecule, $f'(\nu)$. The parameter ξ is a function of the Rabi frequency $\Omega = \mu F/\hbar$ which is characterized by a fluence dependence of $\xi^{1/2}$. In terms of these parameters

$$\eta(\xi) \propto \int_0^{\infty} \epsilon\left(\frac{\nu - \omega_L}{\xi}\right) f'(\nu) d\nu \quad (46)$$

where ω_L is the laser frequency and $\xi \propto \Omega$. If $f'(\nu)$ is narrow compared with the width of $\epsilon(\nu, \xi)$ in the vicinity of $\nu = \omega_L$, the integral can be written in the approximate form

$$\eta(\xi) \propto \epsilon_{\max}(\xi) f'(\nu) \Delta_{\epsilon}(\xi) \quad (47)$$

where the excitation function has been approximated by a maximum value $\epsilon_{\max}(\xi)$ and a frequency width $\Delta_{\epsilon}(\xi)$. These conditions are approximately satisfied for example for excitation of the Q-branch of the ν_3 vibrational mode in SF_6 by the P(16) line of the CO_2 laser. To good approximation, $\epsilon_{\max} \propto \xi^{2/3}$ and $\Delta_{\epsilon} \propto \xi^{2/3}$. Consequently Eq. (47) can be written in the explicit form

$$\frac{\eta(\frac{1}{2})}{f'(\frac{1}{2})} \propto [\sigma_0 \frac{1}{2} / \langle f \rangle]^2 \frac{1}{2} \quad (48)$$

The 2/5 power dependence is a natural consequence of the theory and results from the anharmonicity of the oscillator. The result is valid for a monochromatic field.

In order to compare this result with the coupled two-level model, we consider the collisionless limit for which $\langle f \rangle = f_i f_r$ and $\sigma_0 = \sigma f_i f_r$. From Eq. (16), $\sigma \propto \mu^2$, where μ is the dipole matrix element for the transition. For an optical source with a finite bandwidth Δ we can identify $f_r = f'(\nu)$. The parameter $\sigma_0 \frac{1}{2} / \langle f \rangle$ is therefore proportional to $\mu^2 \frac{1}{2}$. Equation (48) may therefore be rewritten in the form

$$\frac{\eta(\frac{1}{2})}{\langle f \rangle} \propto \left[\frac{\sigma_0 \frac{1}{2}}{\langle f \rangle} \right]^{2/5} \quad (49)$$

The functional form of this equation in terms of the normalized dependent and independent variables is identical to that derived for the coupled two-level model and that used to normalize the MPA data. More important, however, is that the anharmonic oscillator model correctly predicts the observed fluence dependence in MPA experiments for $\sigma_0 \frac{1}{2} / \langle f \rangle > 1$. The use of the general form given in Eq. (40) also accounts for the observed fluence dependence of $\eta(\frac{1}{2})$ at irradiation frequencies in the extreme wings of the absorption features of SF_6 .⁽⁵⁰⁾

V. CONCLUSIONS

A quantitative comparison of multiple photon absorption in several polyatomic molecules has been performed. A basis for this comparison

has been developed that involves a suitable normalization of the fluence and absorption parameters. The normalization, and consequently the generalized interaction process, can be specified in terms of the spectroscopic absorption cross section of the molecule σ_0 and the effective fraction of molecules that interact with the radiation field $\langle f \rangle$.

Experimental variables such as the thermodynamic condition of the gas, the fundamental constants of the molecule, and the properties of the optical source are taken into account in the determination of σ_0 and $\langle f \rangle$.

The appropriate normalizations have been derived from a phenomenological coupled two-level model for the interaction of the radiation field with the molecule. This simplified model provides physical insight into the effects of the various experimental variables such as the bandwidth of the optical field, the laser pulse duration and the gas pressure.

The results of the comparison of experimental data for several polyatomic molecules in terms of the normalized variables indicates that MPA for almost all polyatomic molecules can be described by a single function of fluence. It appears from this comparison that multiple-photon absorption in polyatomic molecules is a general phenomena that is qualitatively the same for all molecules; quantitative differences can be related to differences in σ_0 and $\langle f \rangle$.

The results of this study indicate that the general functional behavior of the number of photons absorbed per molecule $n(\phi)$ can be represented by a functional form ϕ^γ where $\gamma = 1$ for $\sigma_0 \phi / \langle f \rangle < 1$ and $\gamma = 2/3$ for $\sigma_0 \phi / \langle f \rangle \gg 1$. These results are in agreement with predictions of the

anharmonic oscillator model for multiple-photon absorption. Quantitative values of $\langle f \rangle$ and the functional dependence of $n(t)$ with changes of experimental parameters such as gas pressure, optical bandwidth, and optical pulse duration are derived and shown to be quantitatively consistent with experimental data for SF_6 .

ACKNOWLEDGEMENT

The author wishes to acknowledge many beneficial discussions of this work and related aspects of multiple-photon excitation with Drs. T.P. Cotter, C.P. Robinson, J.L. Lyman, and G.P. Quigley.

REFERENCES

1. J. L. Lyman and K. M. Leary, J. Chem. Phys. 69, 1859 (1978).
2. J. L. Lyman, B. J. Feldman and K. A. Fischer, Opt. Comm. 25, 581 (1978).
3. G. T. Schappert, Appl. Phys. Lett. 23, 519 (1973); V. S. Letokhov and A. A. Makarov, Sov. Phys. JETP 36 1091 (1973); O. P. Judd, "Interaction of Pulsed Optical Radiation with an Inverted Medium," High Power Gas Lasers Techno House 45-57 (1976).
4. A summary of these techniques is contained in Reference 6.
5. K. Fox and W. B. Person, J. Chem. Phys. 64 5218 (1976).
6. The absorption data for SF₆ represent best estimates based on a critical review of results reported in the literature and summarized in the following: J. L. Lyman, G. D. Quigley, and O. P. Judd, "Single-Infrared Frequency Studies Multiple-Photon Excitation and Dissociation of Polyatomic Molecules," C. D. Cantrell, Ed., Springer-Verlag (manuscript in preparation).
7. Ibid.
8. R. A. Lucht, J. S. Beardall, R. C. Kennedy, G. W. Sullivan and J. P. Rink, Opt. Lett. (to be published).
9. J. L. Lyman, J. of Chem. Phys. (to be published).
10. G. P. Quigley, Los Alamos Scientific Laboratory (unpublished data).
11. F. M. Lussier, J. I. Steinfeld and T. F. Deutsch, Chem. Phys. Lett. 58 277 (1978).
12. V. N. Bagratashvili, V. S. Doljikov, V. S. Letokhov, and L. A. Ryabov, (to be published).
13. S. Bittenson and P. L. Houston, J. Chem. Phys., 67, 4819 (1977).
14. P. A. Hackett, M. Gauthier, and C. Willis, J. Chem. Phys., 69, 2924 (1978).
15. W. Fuss, K. L. Kompa, and F. M. G. Tablas, J. Chem. Phys. (to be published).
16. V. N. Bagratashvili, I. N. Knyazev, V. S. Letokhov, and V. V. Lobko, Opt. Comm. 18, 525 (1976).
17. R. S. McDowell, H. W. Galbraith, C. D. Cantrell, N. G. Nereson, and E. D. Hinkley, J. Mol. Spect. 68, 288 (1977).
18. R. S. McDowell, "Laser Diode Spectra of Spherical-Top Molecules," Laser Spectroscopy III - Proceedings of the Third International Conference J. L. Hall and J. L. Carlsten Editors, Springer-Verlag, Berlin 102 (1977).

19. A. V. Nowak and J. L. Lyman, J. Quant. Spectrosc. Radiat. Transfer 15 945 (1975).
20. E. J. Krohn, Los Alamos Scientific Laboratory (private communication).
21. R. V. Ambartsumyan, Y. A. Gorohkov, V. S. Letokhov, and G. N. Makarov, Sov. Phys. EETP 42, 993 (1976).
22. G. P. Quigley, Opt. Lett. 3, 106 (1978).
23. P. Kolodner, G. Winterfeld, and I. Yablonovitch, Optics Comm. 20 119 (1977); J. G. Black, P. Kolodner, M. J. Shultz, I. Yablonovitch, and N. Bloembergen, Phys. Rev. A 19, 704 (1979).
24. A. S. Akhmanov, V. Y. Baranov, V. D. Pismenny, V. N. Bagratashvili, Y. R. Kolomiisky, V. S. Letokhov, and L. A. Ryabov, Optics Comm. 25 357 (1977).
25. N. Bloembergen, Opt. Comm. 15, 416 (1975).
26. D. M. Larsen, Opt. Comm. 19, 404 (1976); D. M. Larsen and N. Bloembergen, Opt. Comm. 17, 254 (1976).
27. T. Cotter, W. Fuss, K. L. Kompa, and H. Stafast, International Conference on Quantum Electronics, Amsterdam, Netherlands 1976; Post deadline paper T-10 Published in Optics Comm. 18 220 (1976).
28. L. M. Narducci, S. S. Mitra, R. A. Shatas, and C. A. Coulter, Phys. Rev. A 16 247 (1977).
29. E. V. Shuryak, Sov. J. Quant. Elect. 81018 (1978); E. V. Shuryak, Sov. Phys. JETP 44 1070 (1976).
30. H. Stafast, W. E. Schmid, and K. L. Kompa, Optics Comm. 21 121 (1977).

TABLE CAPTIONS

1. Summary of the functional dependence of $\gamma(\omega)$ and $\langle f \rangle$ for a coupled two level system.
2. Summary of experimental parameters and derived values of $\langle f \rangle$ for absorption studies of the polyatomic molecules shown in Figs. (7), (8), and (9).
3. Summary of the values of f_r and $\langle f \rangle$ for SH_6 absorption experiments at temperatures of 300 K and 140 K.

TABLE 1

	$\frac{\tau_p}{\tau}$	$\frac{\sigma_0 \phi}{f_r f_i} \frac{\tau}{\tau_p}$	$\eta(\phi)$	$\langle f \rangle$
Weak Coupling (Collisionless)	< 1	> 1	$\langle f \rangle = G\left(\frac{\sigma_0 \phi}{f_r f_i}\right)$	$d = f_r f_i$
Strong Coupling (Collisional)	> 1			
(1) Low flux		< 1	$\langle f \rangle = \bar{G}\left(\frac{\sigma_0 \phi}{f_r f_i}\right)$	$d = f_i$
(2) High Flux		> 1	$\langle f \rangle$	$d = f_i \bar{G}\left(\frac{f_r}{f_i} P\right)$

$$d = \frac{\rho}{1 + \beta}$$

$$\bar{G}(x) = 1 - \exp(-x)$$

TABLE 2

Molecule	Frequency (cm ⁻¹)	σ_0 (10 ⁻¹⁸ cm ²)	Pressure (torr)	τ_p (ns)	$\langle f \rangle$	Reference	Symbol
S ₂ F ₁₀	924-948	17.5-0.4	0.025-0.1	150 ^a	1	1	- - -
SF ₆	944-948		0.025-0.35	150 ^a	5 x 10 ⁻³	6	—
SF ₆ (140)	947.7	83	0.3-1.0	150 ^a	10 ⁻⁴	7	☆
	944.2	4.6			2 x 10 ⁻⁵		△
	951.2	2.5			2 x 10 ⁻⁴		△
UF ₆	620.3-631.4	9.6-4.5	0.2-1.0	50	0.5	8	▲
SF ₅ NF ₂	908-958	2.8-1.5		150 ^a	10	9	□
SBA ^b	1033.5	0.5		150 ^a	2	10	■
C ₂ H ₃ Cl (V.C.) ^c	933.0	0.07	1.0	45	2.5 x 10 ⁻⁵	11	⊕
	942.4	0.31		180	10 ⁻²		⊕
	942.4	0.31		45	10 ⁻⁵		⊙
	933.0	0.07		180	10 ⁻⁵		○
CF ₃ I ^d	1076.0	7.15	0.5	60 ^a	0.2	12, 15	●
CF ₃ COCF ₃	970.6	1.34	0-1	---	50	14, 15	▽
C ₂ H ₄ ^e	952.9, 938.7	0.03	0.7	85 ^a	2.5 x 10 ⁻⁵	16	▼
D ₂ O ^e	1079.8	0.022	0.7	120	0.66	16	+
OCS ^e	1045.0	0.0054	1.0	120	0.5	16	×

a - Pulse includes a nominal 1 μs tail

b - SBA ↔ Sec Butyl Acetate

c - The exact placement of these data

d - The curve has been oriented slightly from the original reference

e - The absolute values of either $\eta(\Phi)$ or Φ at low values of Φ appear to be inconsistent (by a factor of 10) with measured spectroscopic values of σ_0 . The values of τ_p in the table are those derived from the data presented in the reference.

TABLE 5

Temperature	f_i	$f(v)$ (cm)	$\Delta v(\text{cm}^{-1})$	f_r	$\langle f \rangle$	
					Calculated From $f(v)/\Delta$	Estimated From S_g
300 K	0.3	1.3	6×10^{-5}	8×10^{-5}	2.5×10^{-5}	5×10^{-5}
140 K	0.89	1.1				5×10^{-4}
Upperbound			3.0×10^{-5}	3.3×10^{-5}	2.9×10^{-5}	
Lowerbound			2×10^{-4}	2.2×10^{-4}	1.9×10^{-4}	
Best Estimate			5×10^{-4}	5.5×10^{-4}	5×10^{-4}	

Parameter Evaluation for SE_6

TABLE 2

Molecule	Frequency (cm ⁻¹)	σ_0 (10 ⁻¹⁸ cm ²)	Pressure (torr)	τ_P (ns)	<f>	Reference	Symbol
S ₂ F ₁₀	924-948	17.5-0.4	0.025-0.1	150 ^a	1	1	- - -
SF ₆	944-948		0.025-0.35	150 ^a	5 x 10 ⁻³	6	—
SF ₆ (140)	947.7	83	0.3-1.0	150 ^a	10 ⁻⁴	7	⊗
	944.2	4.6			2 x 10 ⁻⁵		△
	951.2	2.5			2 x 10 ⁻⁴		△
UF ₆	620.3-631.4	9.6-4.5	0.2-1.0	50	0.5	8	▲
SF ₅ NF ₂	908-958	2.8-1.5		150 ^a	10	9	□
SBA ^b	1033.5	0.3		150 ^a	2	10	■
C ₂ H ₃ Cl(V.C.) ^c	933.0	0.07	1.0	45	2.5 x 10 ⁻³	11	⊖
	942.4	0.31		180	10 ⁻²		⊕
	942.4	0.31		45	10 ⁻³		⊙
	933.0	0.07		180	10 ⁻³		○
CF ₃ I ^d	1076.0	7.13	0.5	60 ^a	0.2	12, 13	●
CF ₃ COCF ₃	970.6	1.34	0-1	---	30	14, 15	▽
C ₂ H ₄ ^e	952.9, 938.7	0.03	0.7	85 ^a	2.5 x 10 ⁻³	16	▼
D ₂ O ^e	1079.8	0.022	0.7	120	0.66	16	+
OCS ^e	1045.0	0.0034	1.0	120	0.3	16	×

a - Pulse includes a nominal 1 μs tail

b - SBA ↔ Sec Butyl Acetate

c - The exact placement of these data

d - The curve has been oriented slightly from the original reference

e - The absolute values of either $\eta(\phi)$ or ϕ at low values of ϕ appear to be inconsistent (by a factor of 10) with measured spectroscopic values of σ_0 . The values of σ_0 in the table are those derived from the data presented in the reference.

TABLE 5

Temperature	f_i	$f(\nu)$ (cm)	$\Delta\nu(\text{cm}^{-1})$	f_r	$\langle f \rangle$	
					Calculated From $f(\nu)\Delta$	Estimated From b_s
300 K	0.5	1.5	6×10^{-5}	8×10^{-5}	2.5×10^{-5}	5×10^{-5}
140 K	0.89	1.1				5×10^{-4}
Upperbound			3.0×10^{-5}	3.5×10^{-5}	2.9×10^{-5}	
Lowerbound			2×10^{-4}	2.2×10^{-4}	1.9×10^{-4}	
Best Estimate			5×10^{-4}	5.5×10^{-4}	5×10^{-4}	

Parameter Evaluation for SF_6

FIGURE CAPTIONS

1. Fluence dependent absorption cross section at 947.7 cm^{-1} for SF_6 . The dashed curve is the prediction of the coupled two-level model with $\phi = 5 \text{ } \mu\text{J}/\text{cm}^2$. The smoothed and unsmoothed curves were obtained respectively with and without a low pressure gain cell in the CO_2 laser resonator. Ref. 1
2. Coupled two-level model for molecular absorption.
3. Fluence dependent absorption cross sections for several output frequencies of the CO_2 laser. Ref. 2
4. Average number of photons absorbed per molecule $\bar{n}(\phi)$ for SbI_3 as a function of fluence normalized by the spectroscopic cross section $\sigma_0(\nu)$.
5. Average number of photons absorbed per molecule $\bar{n}(\phi)$ for UO_2 as a function of $\sigma_0\phi$. The data were obtained at several frequencies using an optical parametric oscillator with a nominal bandwidth of 0.3 cm^{-1} . Ref. 8
6. Average number of photons absorbed per molecule for SF_6 as a function of $\sigma_0\phi$ obtained at several irradiation frequencies.
7. Summary of fluence dependent absorption data for a number of polyatomic molecules. For most molecules, the frequencies correspond to irradiation near the peak of the spectroscopic absorption feature. The units of ν are cm^{-1} ; SBA = Sec Butyl Acetate; V.C. = Vinyl Chloride; see note in Table 2 concerning D_2O , OCS , and C_2H_4 .
8. Summary of fluence dependent absorption data for a number of polyatomic molecules plotted as a function of the normalized fluence $\sigma_0\phi$.
9. Plot of the multiphoton absorption for a number of polyatomic molecules in terms of the normalized variables $\bar{n}(\phi)/\langle f \rangle$ and $\sigma_0\phi/\langle f \rangle$. For $\sigma_0\phi/\langle f \rangle > 1$, the slope of the absorption curve is nominally $2/3$.
10. Normalized population distribution function $f(\nu)$ calculated for the ground state Q branch ν_3 absorption feature of SF_6 . The detailed structure of the absorption feature has been averaged to give the smooth curve shown in the figure.
11. Functional dependence of $\bar{n}(\phi)$ with fluence for SF_6 at several pressures of xenon buffer gas. The pressure of SF_6 is 0.1 torr. The irradiation frequency is 947.7 cm^{-1} , which is near the peak of the ground state Q branch of the ν_3 vibrational mode.

FIGURE CAPTIONS (cont'd.)

12. Functional dependence of $\nu(\dot{\gamma})$ with pressure for a constant flux $\dot{\gamma}$. The points are the experimental data; the solid curves are the calculated dependence using Eq. (45').

Fig. 3

UAG

Fig. 4

Fig. 7

NORMALIZED PLOT OF MULTI-PHOTON ABSORPTION FOR POLYATOMIC MOLECULES

Fig. 9

LAS