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### Publication Date

1979-06-01

Peer reviewed



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

Presented at the Fourth International Conference  
on Laser Spectroscopy, Rottach-Egern, West Germany,  
June 11-15, 1979

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and C. Bradley Moore

June 1979

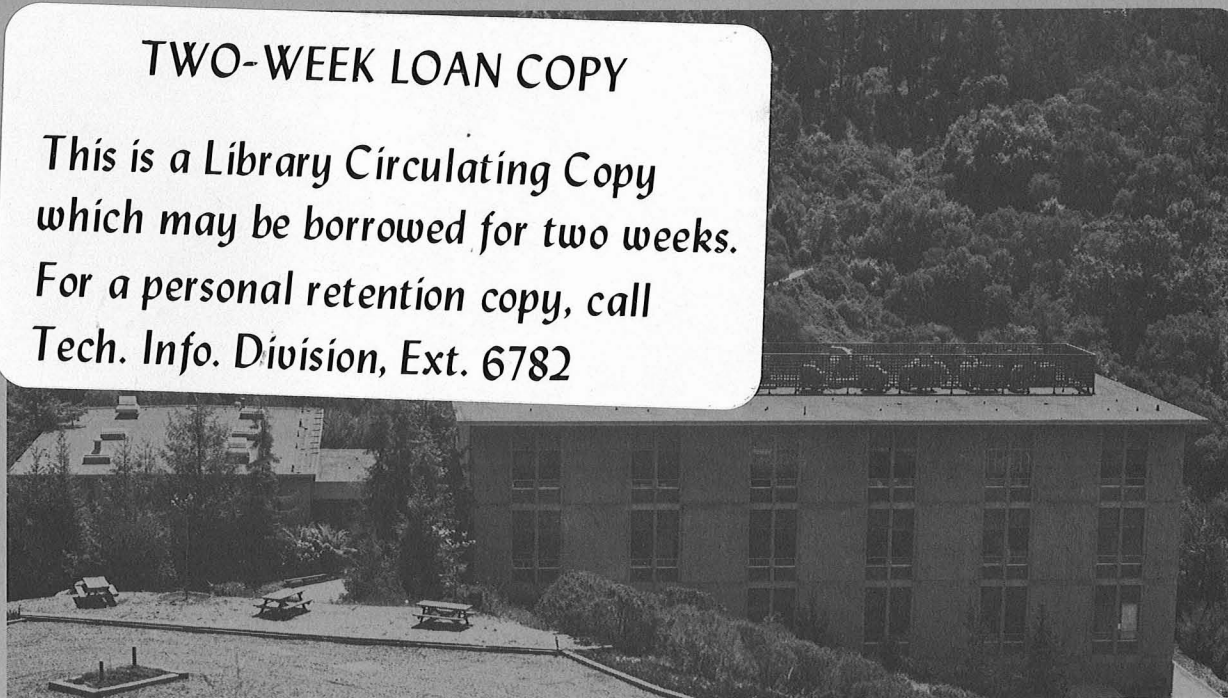
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### Introduction

Studies of multiphoton dissociation (MPD) over the past few years have led to a good semi-quantitative understanding of the process for SF<sub>6</sub> and similar molecules. Several reviews have appeared recently.<sup>1</sup> Applications have progressed to the point that a pilot plant is operating for the production of <sup>13</sup>C by MPD of CF<sub>3</sub>I.<sup>2</sup> The model developed for understanding MPD divides the vibrational energy levels of a molecule into three regions.<sup>3</sup> Region I includes the lowest, "discrete" levels of the vibrational modes that are nearly resonant with the laser frequency. Vibrational anharmonicity prevents exact resonances for the sequential absorption of several photons. However, the combined effects of rotational energy compensation, Coriolis shifts, and other perturbations, along with power broadening, permit the absorption of several photons. In region II, strong coupling among vibrational modes drains energy from the pumped mode and broadens vibration-rotation levels so that absorption occurs over a broad frequency range. Sequential absorption of photons becomes possible. In region III, where levels are above the dissociation threshold, this absorption continues, but with the competing process of dissociation occurring simultaneously. The boundary between regions I and II is poorly defined. From an operational point of view, region II begins when absorption becomes non-frequency selective for any molecule at any laser frequency of interest to the experimenter. In region II and especially in region III there is good evidence that energy is transferred rapidly among all vibrations of the excited molecule and that the rate of dissociation as a function of energy may be estimated using the RRKM theory.<sup>4</sup> The main features of the dynamics of molecules in regions II and III appear to apply rather generally to all types of molecules,<sup>5</sup> with the possible exception of very large ones.<sup>6</sup>

The excitation mechanism in region I has been studied extensively only for SF<sub>6</sub>. The dynamics in this region and in the transition from I to II depend strongly on detailed features of molecular structure and spectra. The great diversity of the latter implies a great variety in the corresponding MPD phenomena. Many questions remain to be answered. How small a molecule will exhibit MPD? How does MPD change when photons outside the 9 - 11 μm range are used? Can narrow resonances in MPD yield vs laser frequency occur, and for which molecules and fre-

quencies? What is the nature of the transition between regions I and II? How does it depend on energy level density, molecular structure, and vibrational mode pumped by the laser? In this paper two molecules  $C_2H_5Cl$  and  $D_2CO$  are studied. The spectroscopic and structural features of these two molecules are intermediate between those of  $SF_6$  and of diatomic molecules. For  $EtCl$ , hydrogen stretching vibrations are excited. Qualitatively new phenomena are observed. One purpose of the work on  $EtCl$  was to search for sharp resonances by using higher frequencies for excitation. The sharp resonances found may be useful for applications in selective photochemistry and laser isotope separation.  $D_2CO$  is studied to test the molecular size limit of collisionless MPD. The data also provide new and essential information for understanding the predissociation of formaldehyde.

### Ethyl Chloride MPD

Let us first consider the thermochemistry and linear spectroscopy of  $EtCl$ . The lowest reaction channel is molecular elimination to hydrogen chloride and ethylene. Only seven photons with  $\nu \geq 2900 \text{ cm}^{-1}$  are needed to overcome the  $58 \pm 2 \text{ kcal/mole}$  activation barrier.<sup>7</sup> The molecule is nearly a prolate symmetric top ( $\bar{\kappa} = -0.959$ ) with 18 non-degenerate vibrational modes.<sup>8</sup> There are 5 C—H stretch modes and they provide the dominant coupling between the molecule and the radiation field in this experiment. The fundamental absorption spectrum shows sharp rotational structures with measured widths limited only by instrument resolution of  $0.06 \text{ cm}^{-1}$ . At  $\nu_{CH} = 2$  there are 15 overtone and combination levels. The  $2.5 \text{ cm}^{-1}$  wide Q-branch of the first overtone indicates a fair amount of mixing of these levels with the low frequency vibrations. At  $\nu_{CH} = 3$  the total vibrational level density reaches 1300 per  $\text{cm}^{-1}$ .<sup>9</sup> The second overtone spectrum shows level widths that are wider than the P, R branch widths. Level mixing by anharmonic coupling and Coriolis coupling is strong.<sup>10</sup> Since the anharmonic defect of each individual C—H stretch mode is  $\sim 50 \text{ cm}^{-1}$ , the probability of populating high quantum states by exciting a single mode becomes miniscule.<sup>11</sup> However, the presence of a multitude of nearly degenerate vibrational modes makes it possible to find a path of excitation that involves combination levels. This path is resonant for the  $\nu = 0$  to 1, 1 to 2, and higher transitions. Figure 1 is a pictorial illustration of such a path to  $\nu = 2$  and the quasi-continuum. Only molecules with the proper/rotation- $\alpha$  quantum number will be excited at each laser frequency. Substantially more molecules will come into resonance if one transition in the path falls on a Q-branch. With the help of these resonances, the probability of absorbing  $n$  photons becomes large at modest intensities. Due to the large quantum of excitation at the stretch frequency, the quasi-continuous levels may be reached at  $n = 3$  or 4. Sequential absorption of more photons will drive the molecule to the dissociative states. Since the quasi-continuous levels are expected to have broad spectral characteristics, MPD yield would reflect the resonances of discrete level excitation and show enhancements that coincide with peaks in the fundamental and overtone spectra.

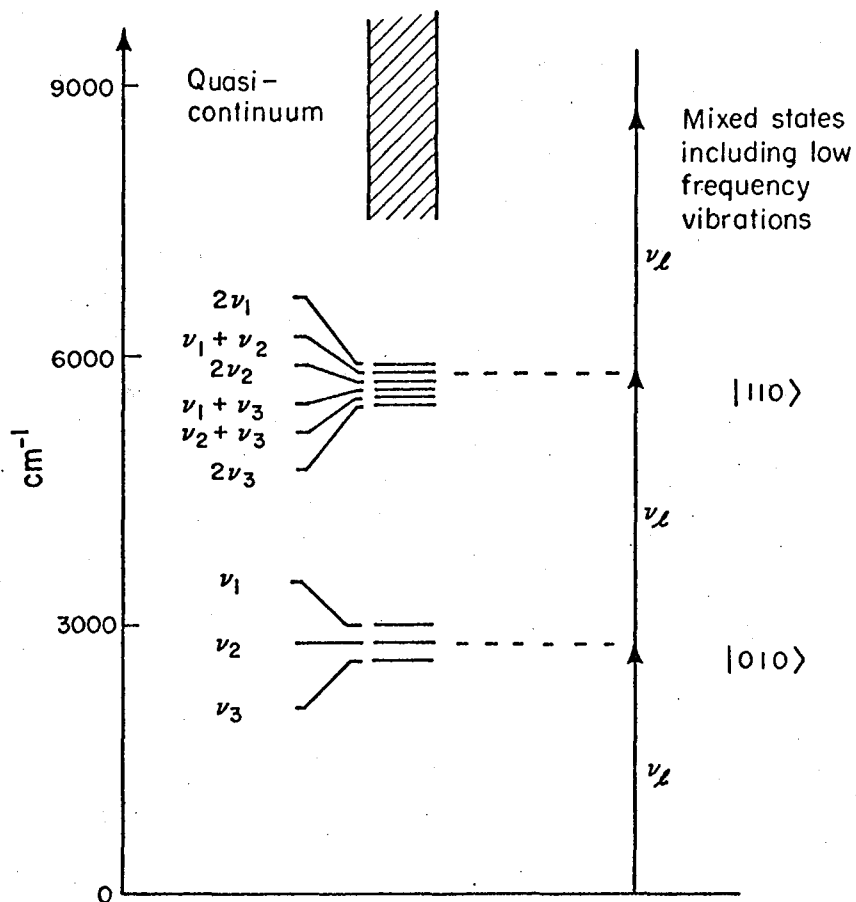


Fig. 1 Vibrational level diagram for molecule with 3 nearly degenerate modes. Arrows indicate resonant transition pathway to  $v = 3$  via:  $|000\rangle \rightarrow |010\rangle \rightarrow |110\rangle \rightarrow$  quasi-continuum. Low frequency vibrations are not included.

The experimental arrangement has been described elsewhere.<sup>12, 13</sup> Briefly, the tunable 3.3  $\mu\text{m}$  beam from a Nd:YAG laser pumped LiNbO<sub>3</sub> parametric oscillator was focused to the center of a Brewster angle cell where photolysis took place. From 3000 to 7200 pulses were used for each photolysis. Photolysis products were then analyzed with a flame ionization gas chromatograph (GC). The photolysis yield  $W_d(\nu)$  is given by the total area beneath the GC ethylene peak. An absolute calibration of the GC, combined with the effective focal volume estimate, gives an approximate absolute yield scale.

Results of the experiment have been reported in Refs. 12 and 13. We find that dissociation occurs throughout the entire spectral range studied. The shape and structure of the yield spectrum match those of the fundamental absorption spectrum (Fig. 2). If we divide the dissociation yield  $W_d(\nu)$  by the fundamental absorbance  $A_{01}(\nu)$  ( $A_{01}(\nu) = \sigma(\nu)N\ell$ ), the resulting curve correlates well with those of the first and second over-

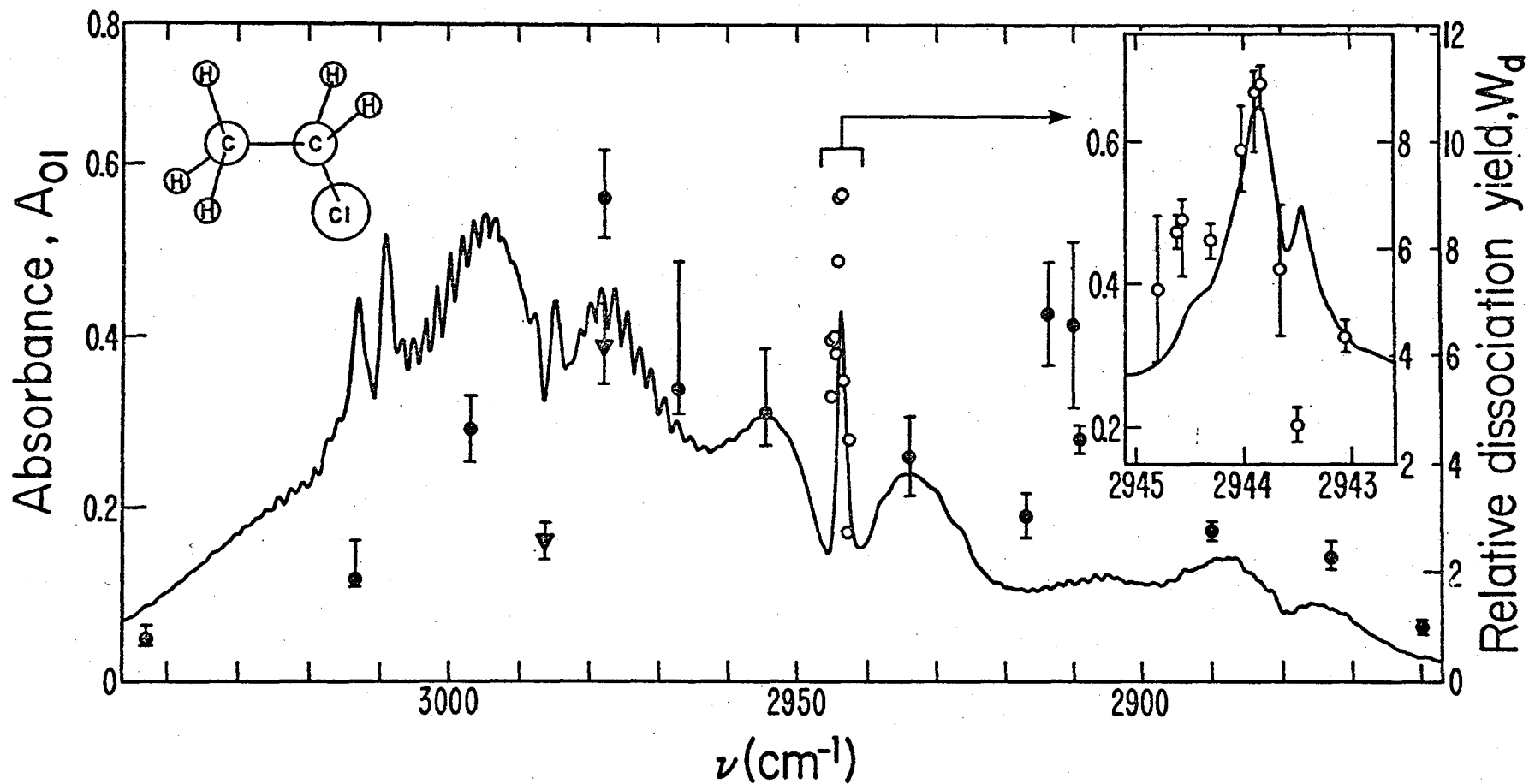


Fig. 2 Relative dissociation yield,  $W_d$ , and linear absorption spectrum,  $A_{01}$  (Nicolet 7199 FTIR with 1  $\text{cm}^{-1}$  resolution) vs frequency. All points ( $\bullet$ ) were measured at the peaks of absorption lines. Two points ( $\blacktriangledown$ ) were taken in valleys. A sharp resonance ( $\circ$ ) is shown enlarged with an absorption spectrum at 0.24  $\text{cm}^{-1}$  resolution. Two points near 2977  $\text{cm}^{-1}$  show sharp structure in a P-branch.

tone spectra (Fig. 3) Yields measured at the Q-branch at  $2944\text{ cm}^{-1}$  show that the frequency resolution of this MPD process is as good as  $0.4\text{ cm}^{-1}$  and may be limited only by the combined laser bandwidth ( $0.15 \pm 0.03\text{ cm}^{-1}$ ) and the power-broadened spectral width. Although the overtone spectra do not provide information on the strength of excited-state absorption, they do give the frequencies and approximate bandwidths of the more anharmonic transitions. The frequency match of the yield spectra ( $W_d$  and  $W_d/A_{01}$ ) with these linear absorption spectra establish the resonance excitation provided by 0 to 1, 1 to 2, and 2 to 3 transitions as discussed earlier. The excitations from 1 to 2 and then 2 to 3 represent a gradual transition from the discrete levels ( $v = 1$ ) to the quasi-continuum ( $v = 3$ ).

After establishing the dynamics of excitation through region I, it is possible to calculate the MPD yield following the formalism used by Grant et al.<sup>4</sup> Absorption in regions II and III is treated by stepwise, incoherent, single photon transitions in a driven harmonic oscillator. The process can be described by a series of rate equations. In region III, the competing process of dissociation is included. The set of rate equations can be solved for a given molecule when the absorption cross section  $\sigma(v)$  and laser intensity  $I(t)$  are specified. For this calculation, absorbed energy is assumed to be randomized before dissociation occurs so that rate constants obtained from the RRKM theory<sup>7</sup> can be used. The excited state absorption cross section is not known. However, several recent studies on  $\text{SF}_6$  and similar molecules have shown that the cross section of highly excited molecules is very slowly decreasing or even remains constant until dissociation is reached.<sup>14,15,16,17</sup> This is reasonable because when intramolecular energy transfer is fast compared to the excitation rate, the absorbing mode would remain in a state with a vibrational quantum number that puts it in region II. At the same time, energy is funneled from the laser field through this mode to other modes of the molecule. By adopting a cross section that is constant and equal to the average cross section for transition  $v = 1$  to 2, dissociation yields are calculated and compared with measured yields at several frequencies (Table 1). The agreement is quite satisfactory. The discrepancy at  $2913\text{ cm}^{-1}$  arises most probably because the absorbance at  $2913\text{ cm}^{-1}$  for the 1 to 2 transition is a few times higher than the average due to the presence of a Q-branch. The phenomenological model also successfully explains the fluence dependence (Fig. 4) and the pressure dependence of the dissociation.<sup>13</sup>

One of the new features of EtCl MPD is the sharp resonances in the yield spectrum. Based on this study it is possible to obtain some general ideas as to when structures should occur in MPD. The molecule must have a structured fundamental spectrum. It must have a path of at or near resonance excitation through the discrete levels to the quasi-continuum so that power broadening does not destroy the structure. Hence, small and medium size molecules with a single, isolated vibrational mode will usually not fall into this category. Molecules with three or more nearly degenerate modes have a high probability of ex-



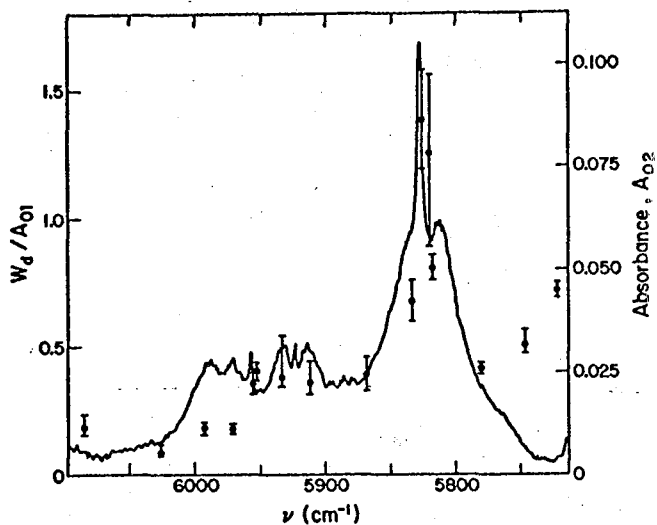


Fig. 3 (a) Relative dissociation yield,  $W_d(\nu/2)$ , divided by the absorbance,  $A_{01}(\nu/2)$  at  $0.24 \text{ cm}^{-1}$  resolution, from (●) in Fig. 2. The first overtone absorbance spectrum,  $A_{02}(\nu)$ , is also plotted at  $1 \text{ cm}^{-1}$  resolution (FTIR).

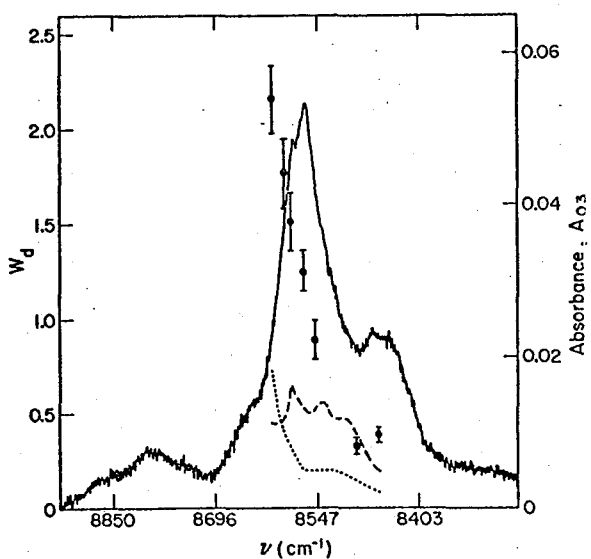


Fig. 3 (b) Relative dissociation yield  $W_d(\nu/3)$  and second overtone spectrum  $A_{03}(\nu)$  ( $2.5 \text{ cm}^{-1}$  resolution, Cary 17).  $A_{01}(\nu/3)$  ..... and  $A_{02}(2\nu/3)$  --- are also shown.

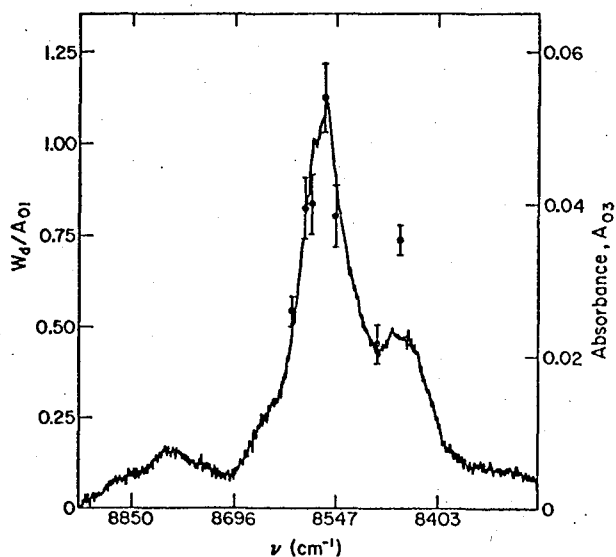


Fig. 3 (c)  $W_d/A_{01}(\nu/3)$  and the second overtone spectrum. The monotonic decrease of  $W_d$  in (b) becomes a broad resonance matching the second overtone spectrum when normalized.

Table 1 Calculated and measured  $C_2H_4$  yield at selected frequencies.

	P Branch		Q Branch	Q Overtone	
$\nu(\text{cm}^{-1})$	2976.6	2977	2943.8	2913	967.7
$\sigma_{01}^a (10^{-19} \text{ cm}^2)$	30	2	2	7	3
$\sigma_{12}^a$	3	3	3	3	-
$\sigma_{\ell, \ell+1}^a (\ell \geq 2)$	3	3	3	3	-
Yield (%)					
calculated	1.5	1.3	1.7	0.48	-
Yield (%)					
measured	$1.8 \pm 0.2$	$0.9 \pm 0.3$	$1.8 \pm 0.2$	$1.3 \pm 0.2$	$0.09 \pm 0.01$

hibiting dissociation with sharp resonances. A careful examination of fundamental and overtone spectra should often reveal possible resonant excitation paths. Level widths can show the onset of the quasi-continuum. More accurate assessments can be obtained if absolute intensities of transitions among excited states are available.

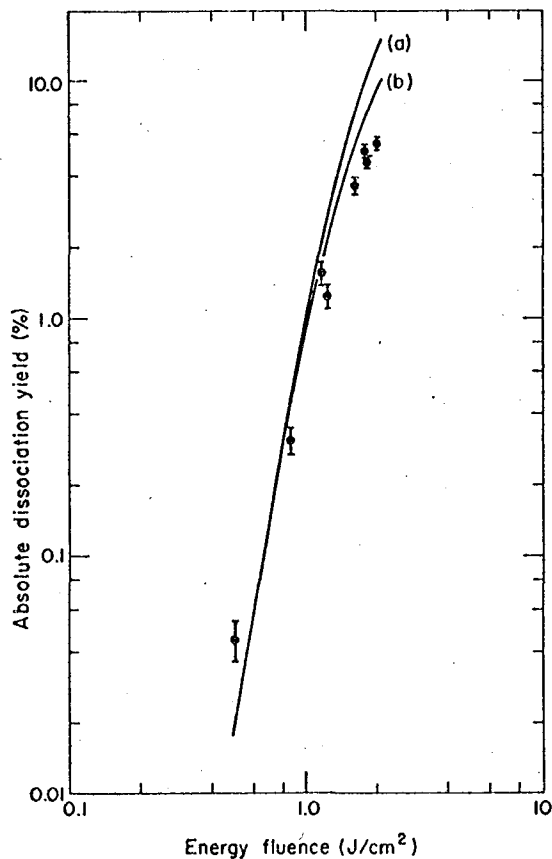


Fig. 4 Comparison of calculated ethylene yield with experimental yield vs laser fluence. (a) calculated,  $2976.8 \text{ cm}^{-1}$ ,  $\Delta\nu_{\ell} = 0.15 \text{ cm}^{-1}$ ; (b) calculated,  $2977 \text{ cm}^{-1}$ ,  $\Delta\nu_{\ell} = 2.5 \text{ cm}^{-1}$ ; ( $\diamond$ ) experimental data,  $\Delta\nu_{\ell} = 2.5 \text{ cm}^{-1}$ .  $\Delta\nu_{\ell}$  is laser bandwidth.

## Formaldehyde MPD

Several attempts to induce collisionless MPD in diatomic molecules have met with failure. What is then the limitation on molecular size and structure for collisionless MPD? The simple four-atom molecule, formaldehyde, is a good test for this limit. Only the deuterated isotope  $D_2CO$  has absorption that straddles the  $CO_2$  laser wavelengths. The vibrational density of states computed by direct count is only about 50 per  $cm^{-1}$  at 30,000  $cm^{-1}$  of internal energy.<sup>18</sup> Experiments have been performed to study total ir fluorescence, fluorescence from the C—D stretches, and the yield of CO from dissociation following TEA  $CO_2$  laser excitation at 975.9  $cm^{-1}$ . Intensity of emission from the C—D and C=O stretches is found to increase as the square of  $D_2CO$  pressure (Fig. 5). Although there is strong Coriolis coupling between the C—D stretch and C—D wagging modes,<sup>19</sup> no emission is observed at the stretch frequency around 2000  $cm^{-1}$  at pressures where gas kinetic collision times are longer than the laser pulse duration. These observations indicate that excitation to high vibrational levels does not occur under collisionless conditions in  $D_2CO$ . The lack of close compensation mechanisms to overcome anharmonicity has prevented absorption of several photons per molecule. Dissociation yield measurements support these observations. CO production occurs only at high pressure.<sup>20</sup> The yield increases as a high order of

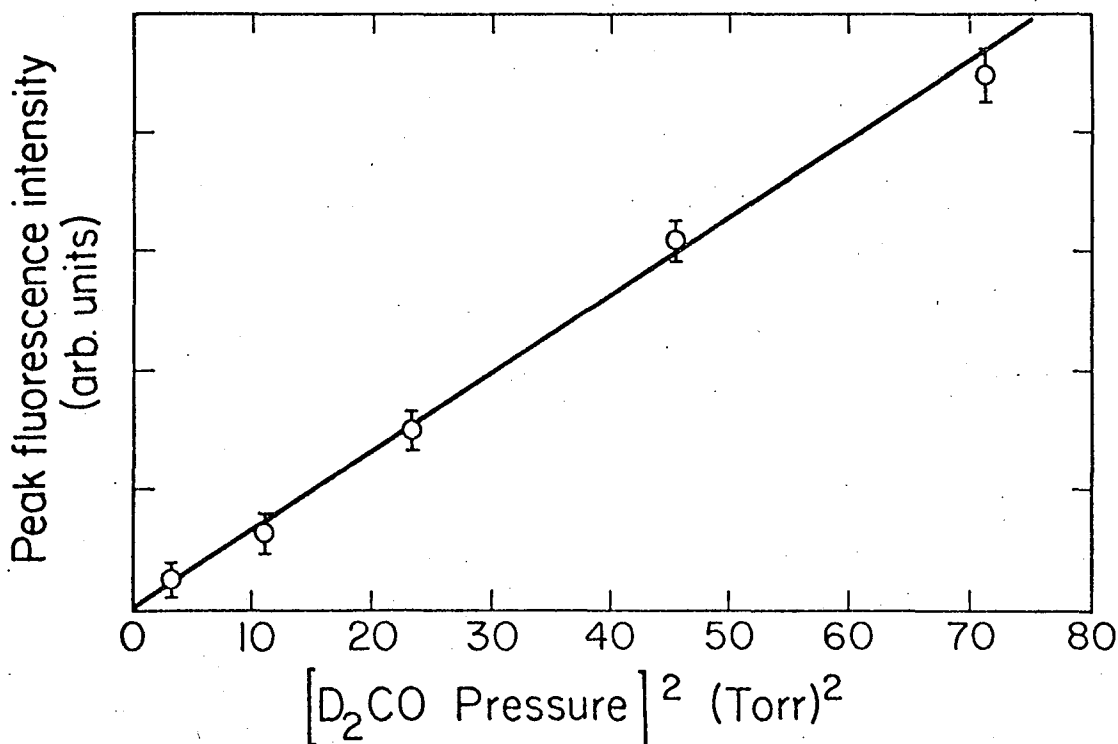


Fig. 5 5  $\mu m$  fluorescence from multiphoton excited  $D_2CO$  as a function of the square of  $D_2CO$  pressure.

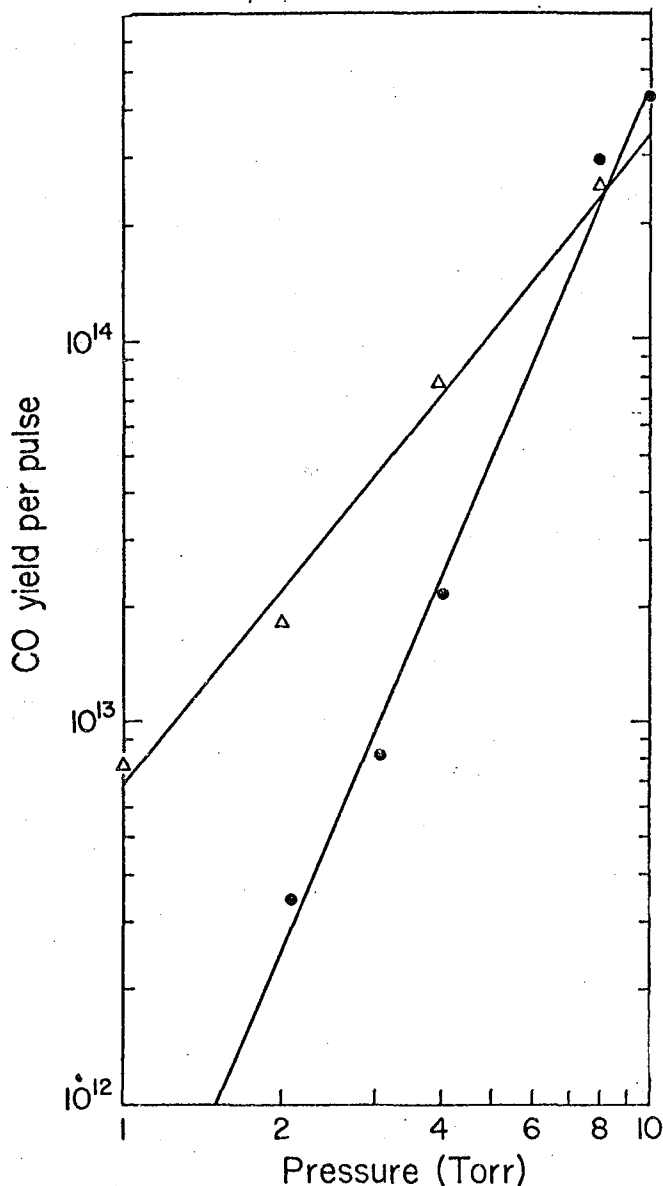


Fig. 6 Total CO yield vs  $D_2CO$  pressure. ● pure  $D_2CO$ ; △  $D_2CO$  + 15 Torr NO. NO replaces  $D_2CO$  as the collisional partner for rotational relaxation and also acts as a radical scavenger.

total reactant pressure (Fig. 6). This indicates that collisional V—V energy transfer and up-pumping play a crucial role in facilitating excitation. The study of  $D_2CO$  MPD is particularly interesting because its uv dissociation is well studied. Formation of radical products (D + DCO) has a threshold at  $323 \pm 3$  nm.<sup>21</sup> Theory and experiment have established a barrier for molecular product formation.<sup>22</sup> During infrared excitation, the molecule remains on the ground potential surface. It has been observed that 10% of the products appear through the radical channel (Fig. 7) when pumped by a  $CO_2$  laser at  $75 J/cm^2$ . Since the barrier height is close to the radical threshold, study of ratio of radical yield to molecular yield as a function of energy fluence may allow the estimation of absolute molecular dissociation rates and the barrier height for molecular dissociation.

#### Summary

The experiments on EtCl and  $D_2CO$  have provided answers to

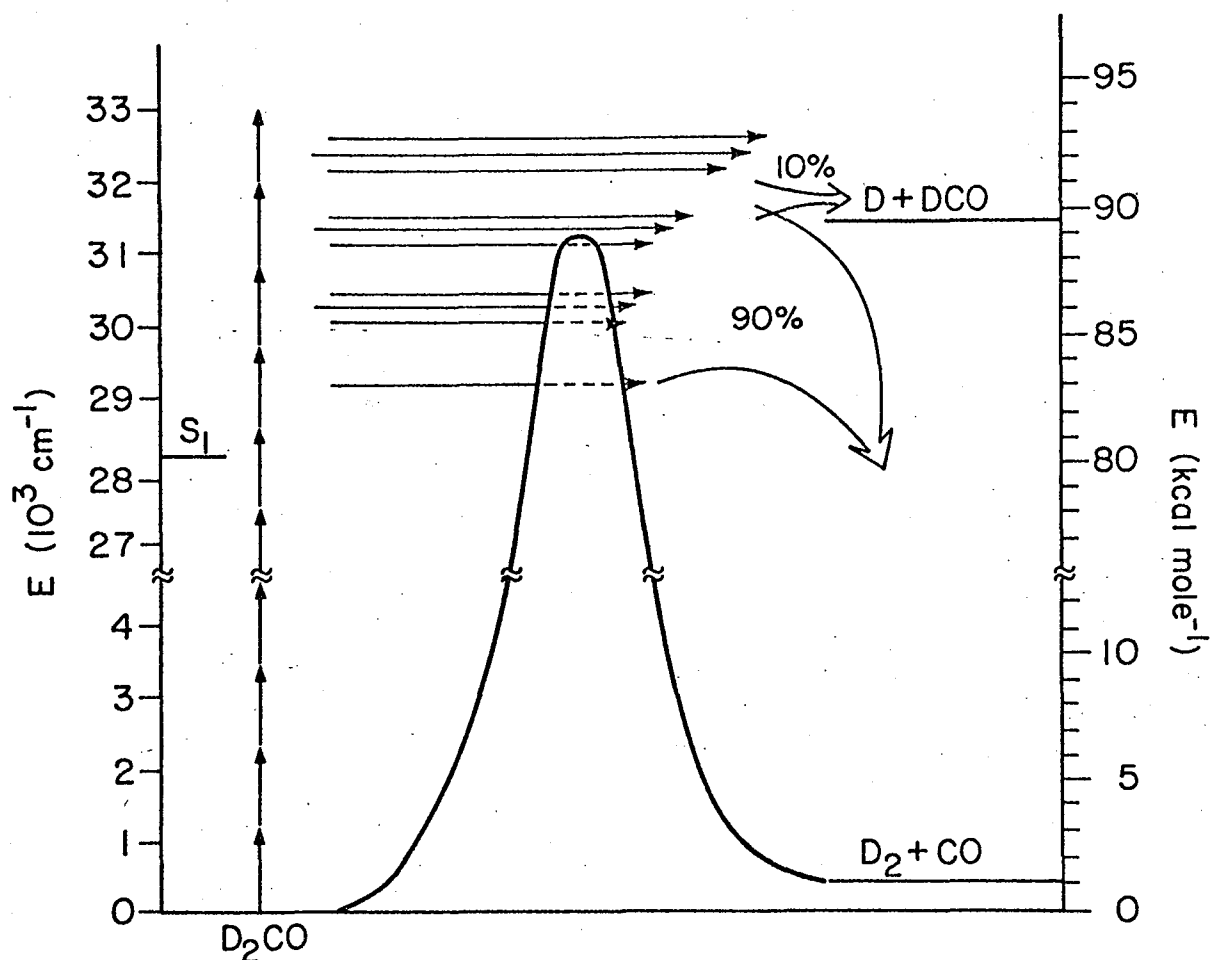


Fig. 7 Product distribution from  $\text{D}_2\text{CO}$  MPD at  $75 \text{ J/cm}^2$ . Molecular products result from both tunneling through and passing over the barrier.

some of the questions that were raised earlier in this paper. MPD dynamics are probably quite similar for all molecules in regions II and III but the dynamics in region I depend greatly on molecular structure and spectra. MPD behavior will vary greatly with structure. For  $\text{D}_2\text{CO}$ , intensities of  $1 \text{ GW/cm}^2$  were not sufficient to get the molecule through region I. Collisions are required. For  $\text{C}_2\text{H}_4$ , collision-free excitation is possible but dissociation still occurs only at such high intensities that spectral structure is almost completely smoothed by power broadening.<sup>23</sup> In  $\text{EtCl}$ , the presence of a sharp fundamental spectrum and anharmonic compensation by resonant combination band transitions have enabled the observation of sharp features in the dissociation spectrum. For molecules such as  $\text{SF}_6$ , dissociation occurs at low fluences but structure is lost due to a more complex spectrum.<sup>24</sup> For very large molecules like  $\text{UO}_2(\text{hfacac})_2 \cdot \text{THF}$ , resonances only a few  $\text{cm}^{-1}$  wide may occur in quite a different way.<sup>6</sup>

## Acknowledgments

We thank the Division of Advanced Systems Materials Production, Office of Advanced Isotope Separation, U.S. Department of Energy for research support under contract No. W-7405-Eng-48.

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