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A. H. Kung and Hai-Lung Dai

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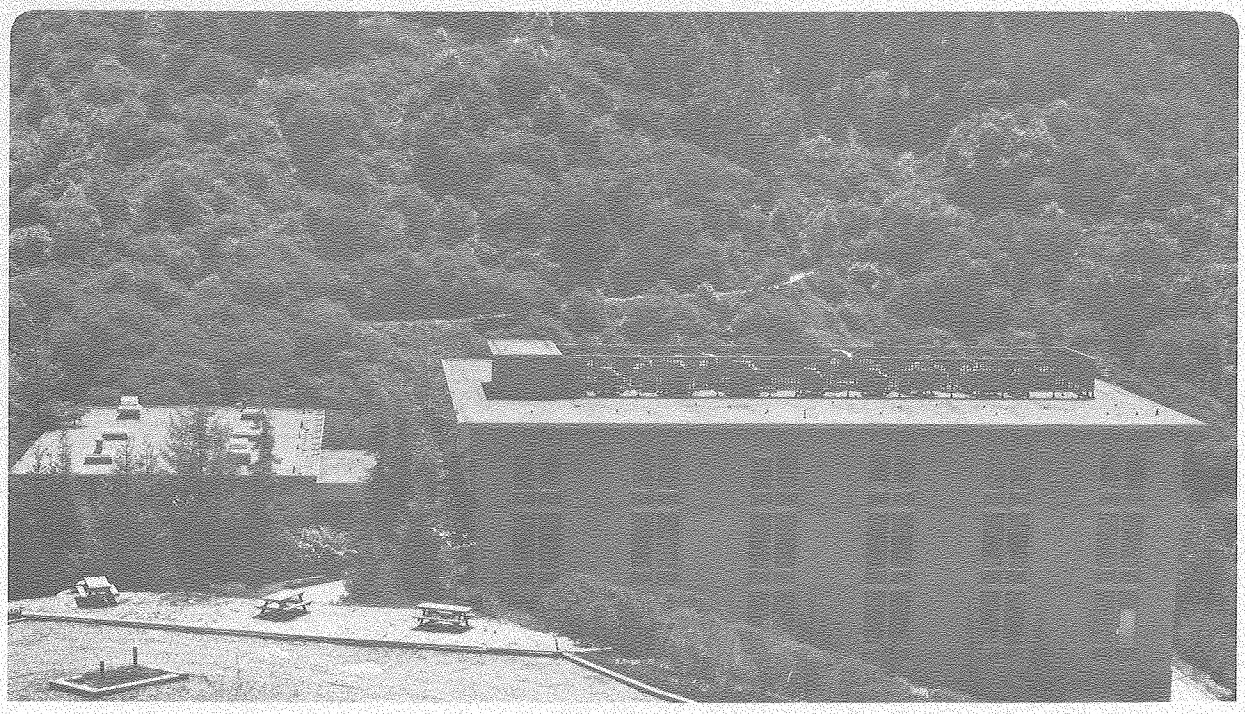

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RESONANT MULTIPHOTON DISSOCIATION OF ETHYL CHLORIDE AT 3.3 μm

by

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The interest in multiphoton dissociation (MPD) of molecules stems from the discovery of high isotopic selectivity for the process in 1974.[1] Recently enrichment ratios in excess of 10^4 have been achieved for deuterium separation using trifluoromethane[2,3] and > 30 with high yield for carbon 13 using CF_3I.[4] A pilot plant has been set up for large scale productions of carbon 13.[5] While these advances in practical applications are made, work is going on to understand the physics of the process. Most of the work is concentrated on molecules excitable by the CO_2 laser[6] for the obvious reason that the light source is easily available. However, a number of groups have also been studying excitation of the hydrogen stretches. The hydrogen stretch is of great interest because each quantum absorbed by the H-stretches is about three times the energy of a CO_2 laser quantum, and thus a higher fraction of the dissociation energy. On the other hand, hydrogen stretches have relatively higher anharmonicity and may be weakly coupled to the rest of the molecule. The effect of these on MPD needs to be explored.

Study of the H-stretches has been hindered by the lack of high power sources in the 3 μm region. Fixed frequency HF and DF lasers operating around 2.6 μm to 3.0 μm and 3.5 μm to 4.0 μm were used to study dissociation of methanol, formic acid and d-formaldehyde.[7,8,9,10] In all cases collisions are required to overcome anharmonicity for high excitation and dissociation. Nevertheless, at pressures around a Torr enrichment of the hydrogen isotope is achieved. As expected, the enrichment ratio decreases rapidly as reactant pressure increases. The HF lasers are only line tunable and do not give detailed spectroscopic information on the MPD process. They are not very suitable for mechanistic studies of excitation of H-stretching molecules. The optical parametric oscillator (OPO) has been used for such studies. The $LiNbO_3$ OPO, pumped by a Nd:YAG laser at 1.06 μm, tunes continuously from 1.4 μm to 4.0 μm. It provides a 10 nsec pulse of around 5 mJ and is focusable to 2 J/cm^2 and higher. Extensive studies on cyclopropane and ethyl chloride have used the OPO as the source. Hall et al. used the OPO to study cyclopropane ir multiple photon-induced chemistry.[11] There they show the unimolecular reaction of cyclopropane induced by absorption of 3.3 μm photons is different than by absorption of 10 μm photons in high pressures of argon (50- several hundred Torr). They interpret this as an indication of mode selective chemistry. No discussion is made of collision-free dissociation. The study of ethyl chloride takes a different approach. Collisions are allowed only after significant excitation and dissociation have occurred. The goal is to understand the excitation mechanism following absorption through the C-H stretching modes. Several results have been published in Refs. 12 and 13, and in a forthcoming paper.[14] Here we shall provide a more detailed description of the OPO used and additional evidence of the difference in excitation by a 3 μm and a 10 μm source.

The optical pump source for the OPO is a Raytheon model SS404 Nd:YAG oscillator amplifier system. The special feature of this system is a pair of Faraday rotators that are present to prevent self-oscillation among the Nd:YAG amplifiers and to eliminate beams specularly reflected from outside the system. A fused silica lens with - 2m focal length is placed between the oscillator and the first amplifier to produce a collimated beam at the output. The output beam has a FWHM of 4 mm, is 15 nsec in duration and is horizontally polarized. Typically 150 mJ to 200 mJ per pulse is used

for pumping the OPO. No additional optics is used between the Nd:YAG system output and the OPO.

Design of the OPO follows closely that given by Byer and Herbst.[15] It consists of an L-shaped cavity as shown in Fig. (1). On the input is a 45° incidence mirror

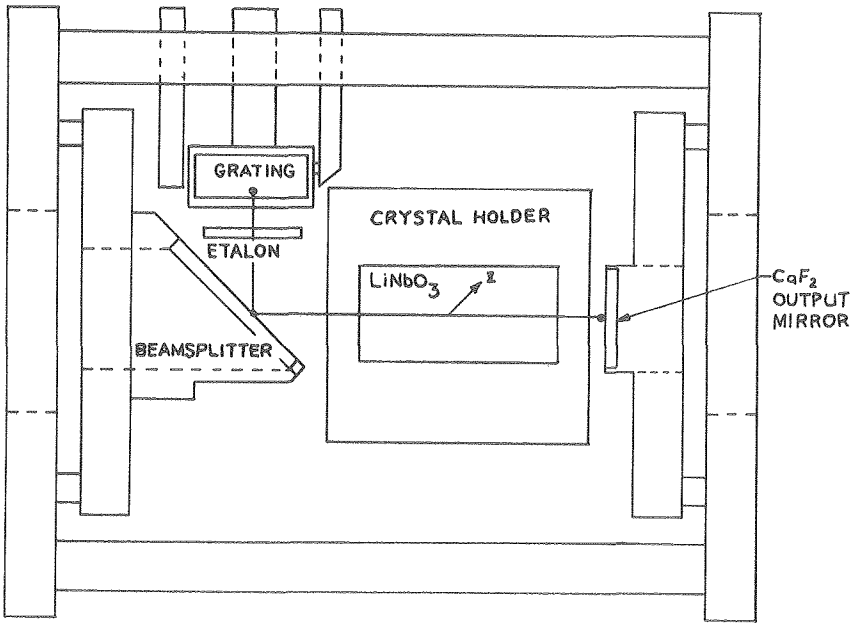

Fig. 1. Schematic of the 1.06 μm pumped, angle tuned $LiNbO_3$ singly resonant parametric oscillator.

dielectric coated for high reflection centered at 1.7 μm and high transmission (> 85%) at 1.06 μm for the proper polarization. A CaF_2 flat substrate coated for high reflection at 1.06 μm and 30% reflection from 1.4 μm to 2.0 μm is used as the output coupler. A Bausch and Lomb grating of 300 1/mm and blazed at 1.8 μm completes the optics of the OPO. The $LiNbO_3$ crystal is cut for phase-matching at 47° and is 1.5 cm in diameter and 5 cm long. It is polished and antireflection coated with SiO_2 at both end surfaces. The 1.06 μm beam makes a double pass through the crystal for the parametric generation. Tuning is achieved by rotating the grating angle and the phase-matching angle simultaneously.

The OPO is generally operated at 2 times above threshold. Output pulse energy, determined by a factory calibrated Scientech power meter, is typically 30 - 40 mJ. After filtering with an antireflection coated Ge flat, up to 7 mJ at 3.3 μm is available for the experiment. Peak to peak fluctuation is ± 15% (2σ) and long-term energy stability over 30 min. is better than 10%. The present output coupler, which is wedged at 30 sec and antireflection coated on the output side, behaves like a low finesse etalon at 3.3 μm. This results in an output spectrum that has six distinct peaks. The peaks are spaced at 0.6 cm^{-1} and each is 0.5 cm^{-1} wide. The full-width-half-maximum of the envelope through these peaks is 2 cm^{-1}. This is narrowed to 0.15 ± 0.03 cm^{-1} with the insertion of a 1 mm thick, finesse 7, etalon between the grating and the input mirror. A limited amount (1.5 cm^{-1}) of tuning is done by tilting just the etalon. The frequency stability and optical damage of the OPO are of concern. There is a ± 1 cm^{-1} drift over a 30 min. period for the output frequency when just the

grating is used. This drift is believed to be caused by the combined effects of mechanical vibrationas and laser heating of the $LiNbO_3$ crystal. With the grating and etalon, the frequency is stable to within 0.1 cm^{-1} over an extended period of time. Damage to coatings and crystal surfaces occurs. While the exact cause of damage has not been determined, it is possibly due to occasional excessive laser intensity and/or defective spots on the coating. This problem of crystal damage is mitigated by translating the damaged element to a clear aperture. Over the course of this experiment, two crystals were changed and repolished due to damage. At the operating level for photolysis in these experiments (nominally 30 MW/cm^2 at 1.06 μm) we estimate one damage spot is incurred for every 10 operating hours. If use of the OPO at 70% or less of the powers described can be tolerated, then damage-free operation should be possible.

The reaction studied is

$$C_2H_5Cl + nh\nu \rightarrow C_2H_4 + HCl$$

Absorption of seven photons $\nu \geq 2900$ cm^{-1} is required to overcome the activation energy of 58 ± 2 kcal/mole. Photolysis yield of ethylene is studied as a function of excitation frequency, energy fluence and reactant pressure. From Fig. 2, which com-

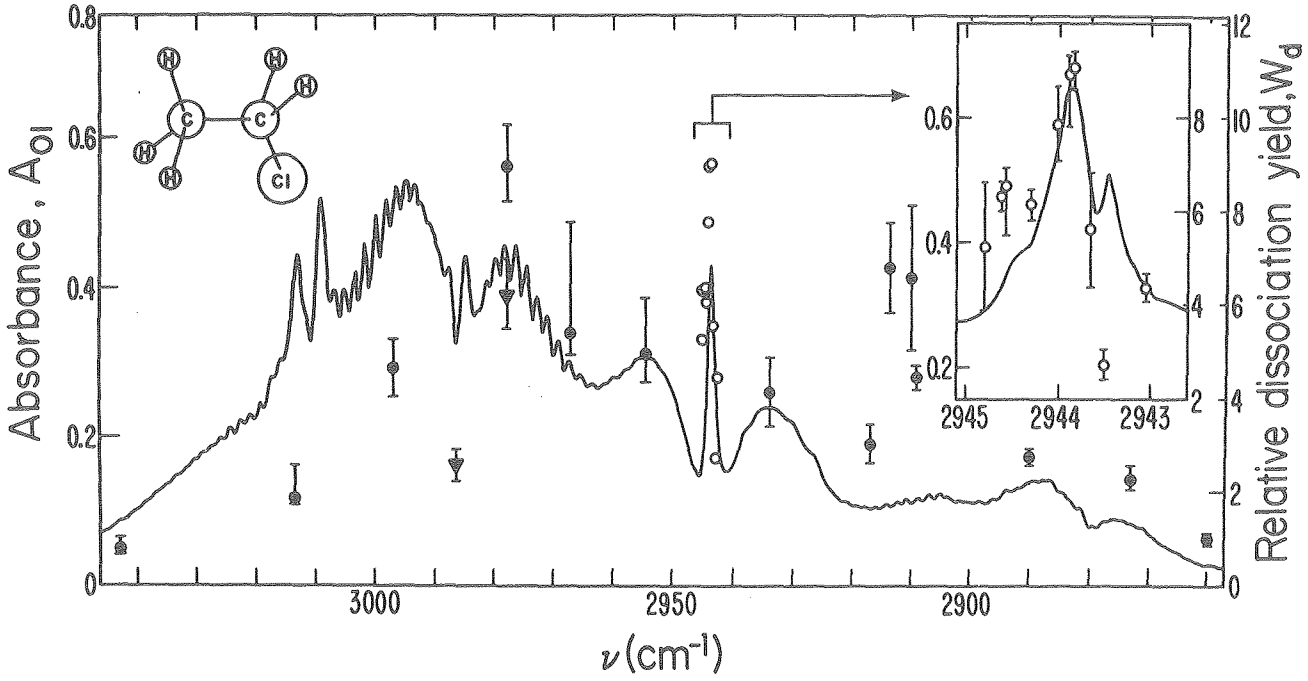

Fig. 2. Relative dissociation yield, W_d and linear absorption spectrum, A_{01}, vs frequency. All points (●) were measured at peaks of absorption lines. Two points (▼) were taken in valleys. From Ref. (12).

pares the photolysis yield with the fundamental absorbance, one obtains the following information on MPD by excitation of hydrogen stretch vibrations:

(1) MPD occurs throughout the entire spectral range for the five C-H stretch fundamentals. The yield spectrum follows approximately the same shape as the ordinary absorption spectrum. The relative yields are somewhat enhanced at longer wavelengths.

(2) High resolution in MPD yield can be achieved as exemplified by the sharp Q-branch at 2944 cm^{-1}. This resolution is limited only by the laser bandwidth and the power-broadened spectral width.

(3) The spectral structure of the fundamental absorption is preserved as shown by the yields of the Q-branch at 2944 cm^{-1} and the P-branch at 2977 cm^{-1}.

(4) Together with absorbance data of the first overtone, the yield enhancement at 2913 cm^{-1} is shown to be due to resonance with a $v = 1 \rightarrow 2$ Q-branch absorption.

The detailed spectroscopic absorbance and yield data obtained point to a resonant excitation mechanism.[12] In this mechanism, a resonant path of excitation is formed by involving several nearly degenerate C-H stretching modes. The occurrence of sharp peaks in MPD yields that coincide with structures given by ordinary absorption spectra results from this resonant excitation and the small number of photons required to reach quasi-continuum. Using the rate equation approach for this mechanism it is possible to calculate the absolute MPD yield.[14] This yield compares favorably with the experimental yield and fits the fluence dependence quite well (Fig. 3).

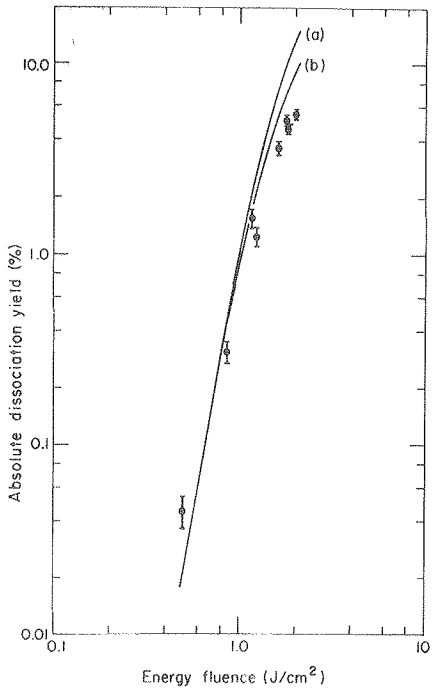

Fig. 3. Ethylene yield vs laser fluence in ethyl chloride MPD, (a) and (b) are calculated, (●) experimental data. From Ref. (13).

It also shows clearly that the decrease in yield with reactant pressure (Fig. 4) is the direct result of collisional deactivation of highly excited molecules (7 or more photons absorbed per molecule). The rate constants for dissociation are calculated using the RRKM theory.[16] Close agreement between calculation and experiment supports the assumption that energy randomization is extremely fast (in the psec or sub-psec timescale) and energy distribution is statistical near the dissociation threshold.

It is of interest to compare collision-free MPD for 3.3 μm excitation with 10 μm excitation. The 3 times higher energy per quantum at 3.3 μm makes it easy to reach

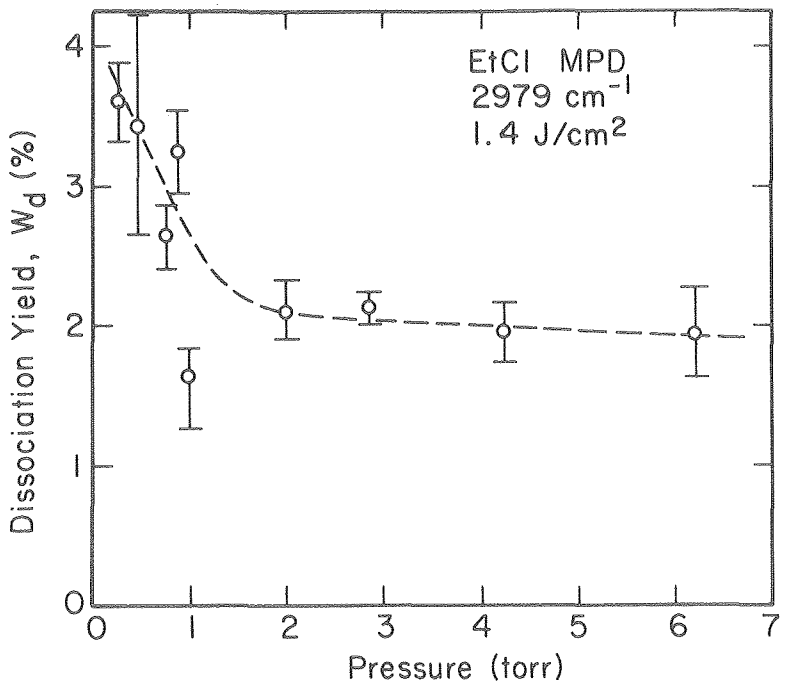

Fig. 4. Pressure dependence of ethylene production in ethyl chloride MPD. From Ref. (14).

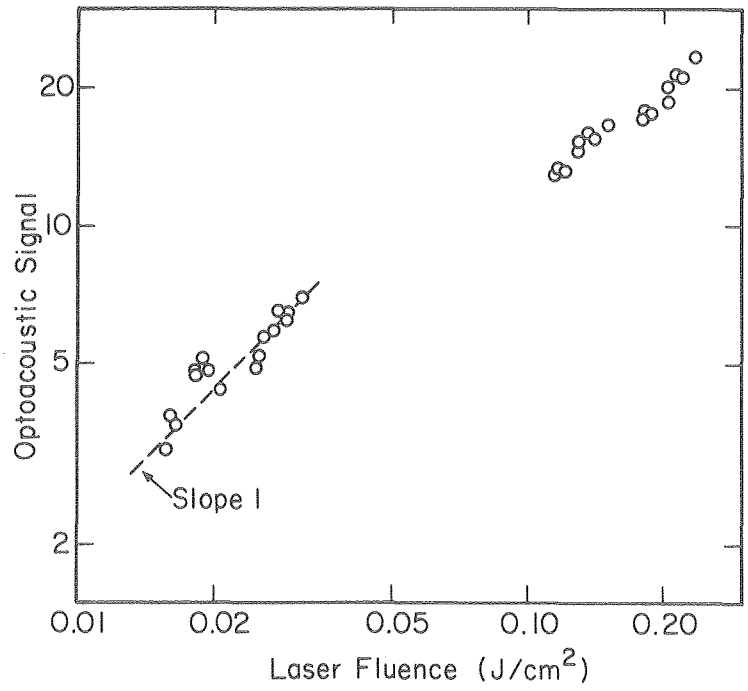

Fig. 5. Optoacoustic signal vs CO_2 laser fluence. From Ref. (14).

the quasi-continuum. Since only two or three photons are required to excite through the discrete levels, molecules with several hydrogen stretch modes and high vibrational level density at v = 2 or 3 will provide a resonant or near resonant absorption path. Only modest intensities will be required and sharp spectral structures can be preserved. These narrow resonances can be useful to obtain simple selective excitation schemes. At 10 μm the need to compensate for anharmonicity causes shifts and broadening in the MPD spectrum. Bottlenecking in the excitation path has been shown to exist that limits the efficiency of excitation. Additional evidence to this effect is shown by optoacoustic absorptions taken for ethyl chloride (Fig. 5). Saturation is clear at fluences around .5 J/cm^2. Similar measurement at 3.3 μm shows no evidence of saturation or bottlenecking. On the other hand, inexpensive 10 μm photons are easily available and the low MPD efficiency is more than compensated by the use of higher fluences. The advantages of both frequencies may be combined using two frequency excitations.

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