Frequency Doubled CO₂ Laser Induced Decomposition of Carbonyl Compounds: Cyclobutanone†

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This paper reports the first use of radiation derived from a TEA carbon dioxide laser by nonlinear upshifting techniques (second harmonic generation) in initiating multi-photon absorption and dissociation. The frequency doubled CO_2 laser has frequency coverage from 2180–1750 cm^{-1}. This frequency region is of importance as it allows pumping of the fundamental stretching modes of organic carbonyl groups (anhydrides, acyl chlorides and strained cyclic ketones), inorganic carbonyl groups, and carbon-tritium bonds. The laser has been used to excite cyclobutanone in the region of the carbonyl stretch. Efficient multiphoton absorption and two channel dissociation are observed. The product array is consistent with that observed upon excitation at 10 µm.

INTRODUCTION

The TEA CO_2 laser has been used in the majority of studies of infrared multiphoton absorption and dissociation. Other high intensity laser sources have only been employed or developed when the molecule under study does not absorb in the 9–11 µm region or if there is

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insufficient optical or wavelength selectivity in the absorption bands found in that region. The most obvious example of the latter is to be found in the development of high intensity laser sources at 16 μm for use in isotope enrichment of uranium.[1] In general, two classes of sources other than CO_2 lasers have been used in infrared multiphoton dissociation studies: optically pumped lasers with CO_2 drivers; and other high intensity lasers. In the first group we find studies using NH_3,[2] CF_4[3] and Raman shifted p-H_2 lasers[4] which have characteristic wavelengths longer than 10 μm. In the second group we find studies using other high intensity sources e.g., HF or DF lasers[5] and optical parametric oscillators[6] which in general have characteristic frequencies greater than 1000 cm^{-1}.

Given efficient nonlinear shifting techniques there would be obvious advantages to be gained from basing shifted infrared sources upon the efficient, scalable CO_2 laser. Nonlinear frequency conversion techniques for tunable infrared lasers have recently been reviewed.[7] Infrared nonlinear materials are available for both second harmonic and difference frequency generation. The use of tellurium crystals in doubling carbon dioxide lasers was reported at an early stage.[8] This material has the highest known nonlinear index; however, at high powers a parasitic nonlinear loss mechanism involving the absorption of one fundamental and one doubled photon to generate a free carrier (band gap = 0.34 eV) limits the available second harmonic energy.[9] Other nonlinear materials are reported to have far higher conversion efficiencies (>10%) e.g., $CdGeAs_2$,[10] $AgGaSe_2$[11] and $AgGaS_2$[11] but are less readily available.

In this paper we report upon the operation of a frequency doubled laser system using single crystal tellurium as the nonlinear medium. The laser system has been used to initiate multiphoton absorption and dissociation in cyclobutanone, a molecule which has been extensively studied following excitation with CO_2 laser radiation in the 10 μm region.[12] Multiphoton dissociation of this molecule involves competition between two low lying channels which yield exclusively molecular products. The product distribution has been well characterized following thermal,[13] photochemical[14] and 10 μm IR excitation.[12] The 10 μm IR results are still controversial and in order to compare the product distribution following excitation in the carbonyl stretch we have carried out further experiments at 10 μm. The differences in the observed product distributions are discussed.

EXPERIMENTAL

The experimental arrangement was extremely simple. The beam from a Lumonics Model 101 TEA CO_2 laser modified to allow closed cycle operation with either $^{12}CO_2$ or $^{13}CO_2$, propagated 2 m to a carbon aperture (1.2 cm diameter). The radiation then passed through the hexagonal face of a Te crystal 2 mm thick of approximately 2 cm width between faces cut at an angle of approximately 12°. The crystal was grown in the physics department of McGill University and cut and polished in the optical workshops of NRC. Both input and output surfaces were broadband AR coated for 5 and 10 μm (Interoptics Inc). The dielectric coatings transmitted over 90% of the radiation at both wavelengths and had damage thresholds greater than 1 J cm^{-2}. Further details of the design and operation of the crystals may be obtained from the authors. The beam output from the crystal passed through a piece of lithium fluoride which served to block the 10 μm radiation. At the incident power levels used the crystal operated in the saturated regime so that the pulse-to-pulse energy stability of the 5 μm output was at least as good as that of the 10 μm input ($\pm$3%). The 5 μm beam was then focussed at the centre of the reaction cell by a 20 cm focal length germanium lens AR coated for 5 μm radiation. The glass reaction cell had sodium chloride windows, was 3.8 cm long with an internal volume of 9.8 cm^3. The energy or intensity of the transmitted 5 μm beam were measured after the reaction cell by either a Gentec Model ED-200 pyroelectric detector or a Rofin Model 7415 photon drag detector. The laser operated on a 10:10:80::N_2:CO_2:He mix resulting in multimode pulses with a self mode locked spike of 100 ns pulsewidth followed by an exponentially decaying tail of 2 μs halfwidth containing 50% of the energy. The spatial profile of the 5 μm beam was measured by translating a 340 μm diameter pinhole across its profile. The beam was found to be gaussian with 1/e radius of 500 μm at the cell entrance window and 400, 450 and 550 μm after 1, 2, and 3 cm respectively.

The reaction cell was connected to a vacuum line, a cold finger and a Baratron 0→1 Torr pressure gauge. Samples could be removed for FTIR or GC analysis. The extent of reaction was measured from the presence of gases non-condensable at 77 K (liquid nitrogen bath), 113 K (iso-pentane slush bath) and by gas chromatography using a Porapak column. The gas chromatograph was calibrated with authentic

samples of ethylene, propylene, and cyclopropane. Ethylene (Phillips), propylene (Phillips), cyclopropane (Phillips), perfluoromethyl cyclohexane (PCR) and cyclobutanone (Aldrich) were better than 99% pure and were used following degassing by freeze-pump-thawing.

RESULTS

(a) Frequency doubled laser

The frequency doubled output energy, frequency, and observed conversion efficiency are shown for 8 CO_2 laser bands in Figure 1. As noted in the introduction the conversion efficiency of Te is energy dependent and higher output energy but lower conversion efficiency may be achieved at higher input energy. The results presented in Figure 1 represent a compromise between desired output energy and
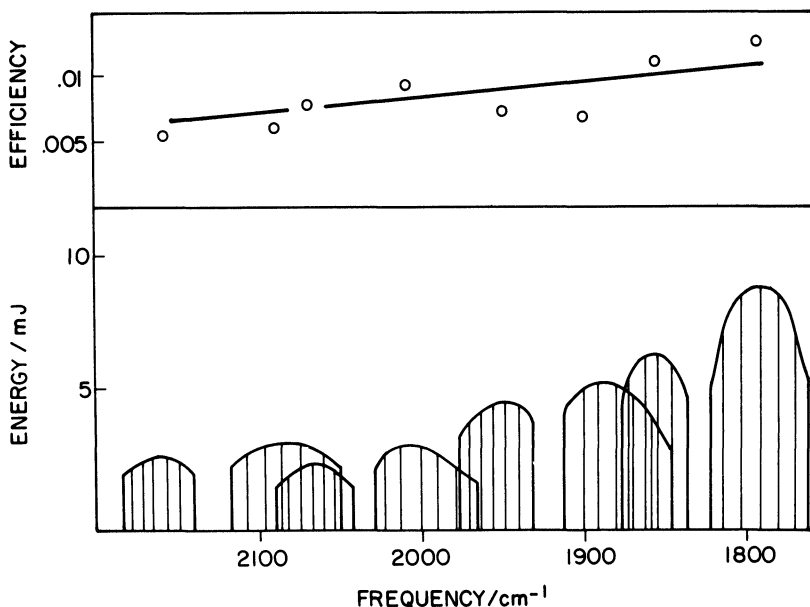

FIGURE 1 Output energy from the frequency doubling crystal. The lower panel shows the output energy as a function of the output frequency for various transitions of the $^{13}CO_2$ and $^{12}CO_2$ laser. The upper panel shows the conversion efficiency (defined as 5 μm energy/incident 10 μm energy).

the damage threshold of the dielectric coatings of the crystal. However the output energies obtained on the 10P $^{13}CO_2$ branch imply fluences of $\approx 2\,J\,cm^{-2}$ in the reaction cell, comparable to fluences used in the majority of studies at 10 μm.

The monotonic increase in conversion efficiency with increasing wavelength is noteworthy. It has recently been reported that frequency doubling of ammonia laser radiation at 12.8 μm may be achieved with efficiencies approaching 60%.[15,16] This observation is interpreted as evidence that the parasitic loss process, free carrier generation, involves one doubled and one undoubled photon.[9] The lines of the 10P $^{13}CO_2$ branch have a photon energy less than one third of the band gap in tellurium; however, there is no marked increase in conversion efficiency for the room temperature sample used here. The wavelength dependence of the conversion efficiencies reported here supports two photon absorption of two doubled photons as a significant loss mechanism in tellurium in the 9–11 μm region at these higher incident fluences.

(b) Photolysis of cyclobutanone at 5 μm

A preliminary investigation of the infrared multiphoton absorption spectrum of cyclobutanone near 5 μm revealed a peak cross-section at the frequency doubled $^{13}CO_2$ 10P10 line near 1810.8 cm^{-1}. This corresponds well with the maximum of the one photon absorption spectrum at 1818 cm^{-1}. However, a compromise between laser energy and molecular absorption resulted in the use of the frequency doubled $^{13}CO_2$ 10P16 line at 1800.5 cm^{-1} throughout this work.

The effect of incident fluence was investigated at 0.21 Torr. The dissociation yield was proportional to the fifth power of the incident fluence being 0.016 at 1 $J\,cm^{-2}$ (the dissociation yields are given as the reaction probability per pulse of the irradiated volume; the beam area is taken as $6.4 \times 10^{-3}\,cm^{-2}$ and volume as 0.024 cm^3). In these experiments the extent of reaction was assessed from the difference in the pressure of gases produced non-condensable at 113 K (mainly ethylene and carbon monoxide) and that of those non-condensable at 77 K (carbon monoxide $+ 4.5 \times 10^{-4}$ Torr vapor pressure of ethylene).

The effect of cyclobutanone pressure on the dissociation yield and product distribution was investigated at 1.3 $J\,cm^{-2}$ incident fluence.

The extent of reaction was monitored both by the technique described above and by GC analysis. The results were in excellent agreement and are shown in Figure 2. The GC analysis revealed ethylene and cyclopropane as sole products. The ratio of [ethylene]/[cyclopropane] is shown in Figure 3.

(c) Photolysis of cyclobutanone at 10 μm

The pressure dependence of IRMPD of cyclobutanone near 10 μm was investigated using the $^{12}CO_2$ 9P20 line at 2.3 J cm^{-2} incident fluence. GC analysis revealed ethylene, cyclopropane and propylene as reaction products. The extent of reaction was monitored by the two procedures described above. The ratio [propylene]/[propylene +
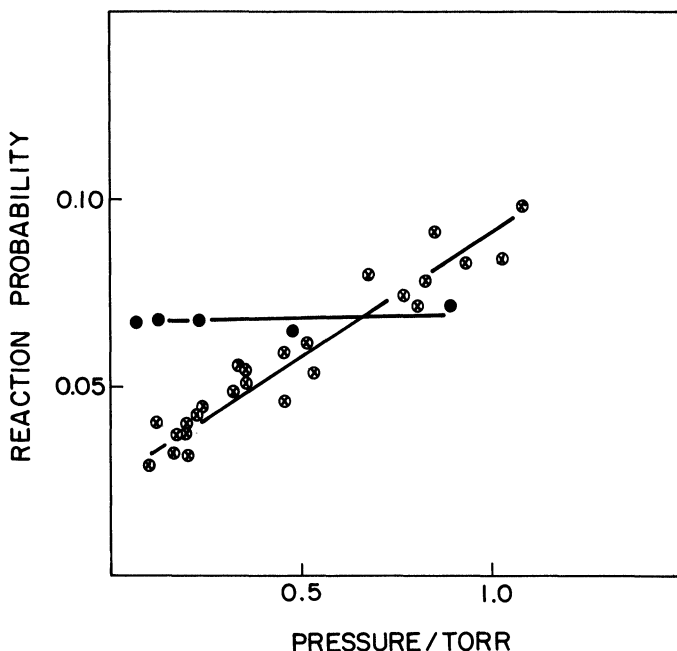
FIGURE 2 Infrared multiphoton dissociation of cyclobutanone as a function of pressure. Filled circles are data following irradiation with 1800 cm^{-1} radiation at 1.3 J cm^{-2}. Open circles are data obtained at 1046.85 cm^{-1} and 2.3 J cm^{-2} incident fluence. The reaction probability is defined as the fractional yield of ethylene from irradiated molecules.
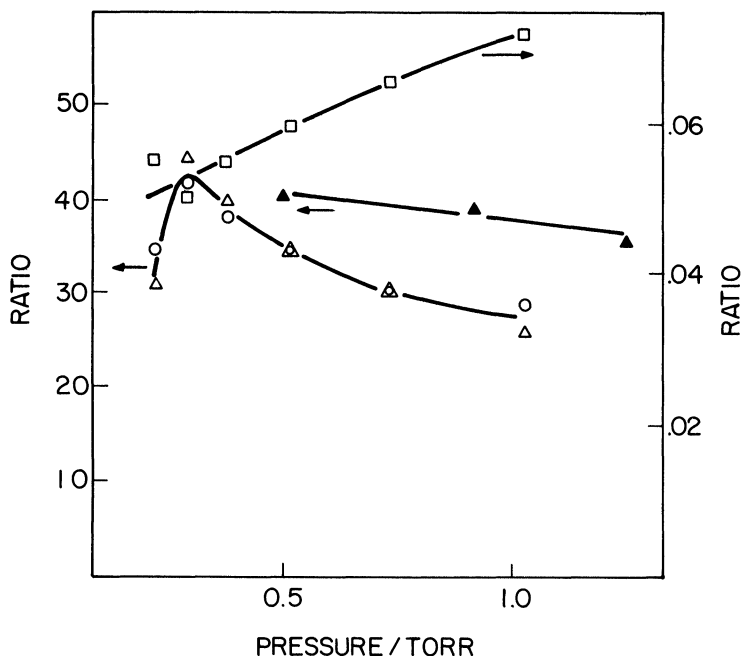
FIGURE 3 Variation of product yield ratios with cyclobutanone pressure. Filled symbols are data from $1800 \, cm^{-1}$ at $1.3 \, J \, cm^{-2}$, open symbols are data from $1046.85 \, cm^{-1}$ at $2.3 \, J \, cm^{-2}$. Triangles refer to the concentration ratio [ethylene]/[carbon monoxide] derived from pressure measurements (see text); circles refer to the ratio [ethylene]/[propylene + cyclopropane] derived from GC measurements; squares refer to GC determination of the ratio [propylene]/[propylene + cyclopropane] and require the right-hand ordinate.

cyclopropane] was measured by GC analysis. The product yield ratio of C_2 products to total C_3 products is the subject of some controversy and some care was taken in its determination. The GC technique described above was used and in the same experiment the pressure of products non-condensable at $77 \, K$ (P_1) and those non-condensable at $113 \, K$ (P_2) was recorded. Inspection of vapor pressure data shows that the ratio
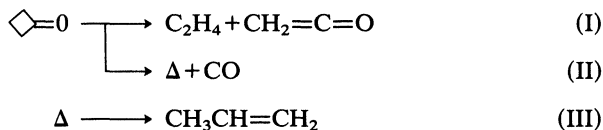
$$R_p = \frac{P_2 - P_1 + 0.00045}{P_1 - 0.00045}$$

where P_1 and P_2 are measured in Torr, is a very good approximation for the yield ratio [ethylene]/[carbon monoxide]. These three yield ratios are shown in Figure 3. Figure 2 shows the pressure dependence of the yield of the major reaction product (ethylene).

Discussion

These results show that the modest frequency doubled CO_2 laser described above can provide sufficient intensity to initiate multiphoton dissociation of cyclobutanone. The product yields and the pressure dependence of the $[C_2]/[C_3]$ yield ratio are qualitatively similar at the two excitation wavelengths; we will not attempt a quantitative comparison since these parameters depend subtly on many experimental variables.

Infrared multiphoton dissociation of cyclobutanone may be characterized by the following series of reactions:

$$\diamondsuit\!=\!0 \quad \begin{array}{l} \longrightarrow C_2H_4 + CH_2\!=\!C\!=\!0 \qquad (I) \\ \longrightarrow \Delta + CO \qquad\qquad\qquad (II) \end{array}$$

$$\Delta \longrightarrow CH_3CH\!=\!CH_2 \qquad\qquad (III)$$

Blades has measured the Arrhenius parameters for reactions (I) and (II) as $k_1 = 3.6 \times 10^{14} \exp(52000/RT) \, s^{-1}$ and $k_2 = 2.3 \times 10^{14} \exp(-58000/RT) \, s^{-1}$.[13] However, recent RRKM calculations question the reliability of the experimental data for the minor channel.[17] Blades from thermal data[13] and Koda et al. from IRMPD data[18] have concluded that propylene arises from unimolecular isomerization of cyclopropane molecules formed with sufficient internal energy. The excellent agreement between the yield ratios [ethylene]/[CO] and $[C_2]/[C_3]$ support this hypothesis although we accept that the formation of methylene from cyclopropane followed by insertion into ethylene is kinetically equivalent. Our failure to observe propylene in the experiments carried out at 5 μm may point to the involvement of multiphoton absorption at 10 μm in the production of propylene. Cyclopropane has a strong absorption band at 1030 cm^{-1} and unimolecular reaction along pathway (II) leaves 51.1 kcal/mol to be distributed among the degrees of freedom of the products.

The isomerization to propylene has an activation energy of 65.5 kcal/mol.[19] hence efficient multiphoton absorption and isomerization of the vibrationally excited cyclopropane formed through reaction (II) is not unlikely at 10 μm. However, it is improbable at 5 μm. This is because reaction (II) removes the absorbing CO chromaphore; at this frequency it is more likely that the ketene product undergoes secondary photolysis. Some support for these arguements may be gained by the observation of IRMPD of cyclopropane at 1053 cm^{-1} to yield both ethylene and propylene.[6]

Many authors have used the yield ratio $[C_2]/[C_3]$ to assess the energy distribution function of reacting molecules.[12,18,20–23] Some authors have argued that since (at 1073 cm^{-1}) the $[C_2]/[C_3]$ ratio decreased with cyclobutanone pressure while the average number of photons absorbed per molecule did not, that the initial distribution of excited molecules produced by the laser field was non-Boltzman.[20] Implicit in this assertion is the assumption that at higher pressures dissociation occurs from a distribution of molecules which have suffered collisions to establish a Boltzman distribution over the ensemble of molecules. There is some merit to these arguments as photon activation and collisional activation are inherently different processes; in particular photon activation proceeds through discrete steps with the possibility for competition between dissociation and absorption at each level. The same is true for collisional activation; however, the step size may be greatly different. These arguments are crucially dependent upon the constancy of the multiphoton absorption cross-section with pressure following 1073 cm^{-1} excitation. This condition may not be satisfied at other excitation frequencies and this may account for the discrepancy in results between studies carried out at 1073 cm^{-1} [18,20,21] and those carried out at 1043 cm^{-1}.[12,23]

In brief, studies at 1073 cm^{-1} find the $[C_2]/[C_3]$ ratio to fall with increasing pressure, indicating that the "temperature" of dissociating molecules increases with pressure.[18,20,21] Those at 1043 cm^{-1} find certain fluences where this ratio rises with increasing pressure indicating the reverse.[23] However, under all conditions at 1043 cm^{-1} the ratio [propylene]/[propylene + cyclopropane] falls indicating decreasing "temperature" at all fluences.[23] It was this discrepancy between the two "temperatures" indicated at 1046.9 cm^{-1} that prompted to investigate this frequency further. Our results are opposed to those from previous studies at this wavelength. The $[C_2]/[C_3]$ ratio falls and

the [propylene]/[propylene + cyclopropane] ratio rises with increasing pressure indicating an internal self-consistency as to the dependence of the trend in internal excitation of decomposing molecules with pressure and an agreement with the trends observed at 1073 cm^{-1}. However although we attempted to use the fluence where earlier work had established a increasing $[C_2]/[C_3]$ ratio $(2.2$ J cm$^{-2})$[23] our dissociation yields are consistently higher and suggest that we should compare with the earlier high fluence data $[3.5$ J cm$^{-2}]$.[23] If this is done the major discrepancy remaining concerns the propylene yield which the earlier workers report as falling from 10–2% of the total C_3 products over the pressure range 0.1 to 1.0 Torr. We can find no explanation for this discrepancy.

In conclusion the infrared multiphoton dissociation of cyclobutanone gives results which were qualitatively consistent at 1800, 1073 and 1047 cm^{-1}. Product analysis reveals that the importance of the secondary channel (II) and the isomerization of cyclopropane to propylene (III) increase with pressure. These observations may reflect the internal energy distribution of the ensemble of dissociating molecules and further work should only be carried out with accurate assessment of the energy deposition in these systems. The frequency doubled CO_2 laser is expected to find general utility in IRMPD dissociation studies and work is presently in progress on the IRMPD of metal carbonyls.

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