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THE SMALL MOLECULE LIMIT OF INFRARED MULTIPHOTON  
DISSOCIATION: COLLISIONAL EFFECTS IN  $D_2CO$

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The infrared multiphoton excitation of  $D_2CO$  was studied by monitoring infrared fluorescence from stretching modes of  $D_2CO$  following excitation in the bending modes. The dependence of the infrared multiphoton dissociation yield on laser wavelength, on laser power, and on reactant and foreign gas pressures was also studied. Severe bottlenecks to excitation through the first few steps are found. Vibration-to-vibration transfer of a bending quantum from one excited  $D_2CO$  molecule to another is a crucial step. Collision-induced changes of rotational quantum number must also play an important role.

KEY WORDS: Infrared multiphoton dissociation;  
formaldehyde;  $D_2CO$ ; collisions; infrared fluorescence.

INTRODUCTION

Infrared multiphoton dissociation (IRMPD) of polyatomic molecules has been described in terms of excitation through three regions of energy levels in a molecule:<sup>1-3</sup>

I. A region of discrete molecular states in which coherent processes and power broadening overcome mismatches between the laser frequency and an allowed molecular transition frequency caused by anharmonicity. II. A region termed the quasi-continuum (QC) in which the density of states is high enough to ensure absorption at any energy level. In

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this region, absorption can be described by a rate equations model. III. A dissociative continuum, in which continued excitation and dissociation are competing rate processes (Fig. 1).

The majority of studies of infrared multiphoton excitation (IRMPE) and IRMPD have dealt with collisionless processes in larger molecules.<sup>1-3</sup> The low density of states in small molecules raises the lower

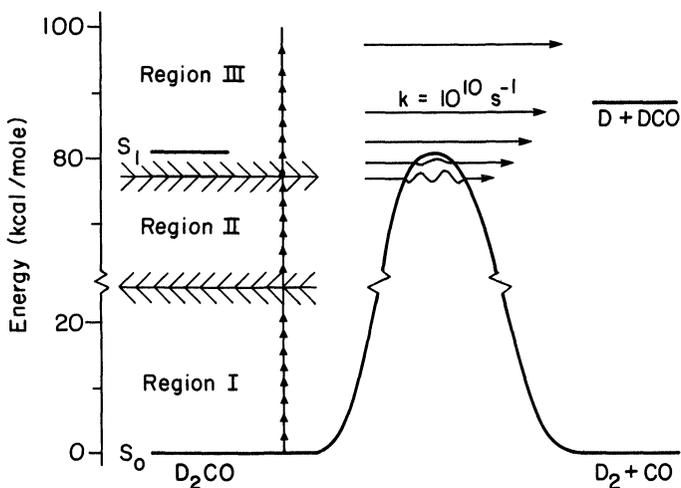
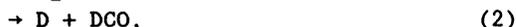


FIGURE 1 Potential energy diagram for  $D_2CO$ . The threshold for  $D+DCO$  is at 88.5 kcal/mole (Ref. 7) and the barrier top at 80.7 kcal/mole (Ref. 8). The boundary between regions II and III is set where the dissociation rate is  $\sim 10^7 s^{-1}$  and thus comparable to the collisional stabilization rate at 1 Torr. Arrows indicating dissociation are drawn at energies corresponding to rate increases of one order of magnitude each step (Ref. 9). The boundary between regions I and II is uncertain and depends critically on many experimentally controllable variables.

boundary of Region II to a relatively high energy. For triatomic molecules (e.g. OCS and D<sub>2</sub>O)<sup>1</sup> excitation stops at one quantum per molecule for fluences below 10 J/cm<sup>2</sup>.<sup>1</sup> However, dissociation of OCS at fluences of 50 J/cm<sup>2</sup> has been reported in a molecular beam.<sup>4</sup> In smaller molecules the laser frequency is resonant with a vibrational transition for only a few particular rotational states. Thus only a small fraction of the sample can undergo collision-free IRMPD. It has been well documented that if collisions cause rotational transitions to occur during the laser pulse, many more molecules may be excited through the "rotational bottleneck" and subsequently be dissociated.<sup>1</sup> In this paper the behavior of small molecules is explored using D<sub>2</sub>CO as an example.

Formaldehyde serves as a prototype for small molecule photochemistry.<sup>5</sup> In the UV, both molecular and radical dissociation channels,



have been identified and studied in detail.<sup>5-9</sup> The subsequent photochemistry in the radical system is well understood.<sup>10</sup> During IRMPD of formaldehyde, the molecule remains on the ground electronic state potential energy surface, Fig. 1. In the dissociative energy region, laser excitation competes with dissociation to molecular or radical products. The branching ratio between these two dissociation channels is a function of laser intensity since the dissociation thresholds are different and the dissociation rate constants vary with energy.<sup>11</sup>

IRMPD of formaldehyde has been reported in several works.<sup>12-18</sup> Deuterated isotopes of formaldehyde have absorption bands that overlap with CO<sub>2</sub> laser lines. In D<sub>2</sub>CO, the  $\nu_4$  (out-of-plane bend, 938 cm<sup>-1</sup>) and the  $\nu_6$  (in-

plane wag,  $989\text{ cm}^{-1}$ ) modes are strongly mixed by Coriolis interactions<sup>19</sup> and can be excited in the  $9.6\text{-}10.6\ \mu\text{m}$  region.  $\text{H}_2\text{CO}$  undergoes IRMPD when excited in its C-H stretching modes in the  $3.6\text{-}3.7\text{-}\mu\text{m}$  region.<sup>16</sup> IRMPD of formaldehyde has been observed to be strongly dependent on laser intensity and collisions have been found to enhance the dissociation yield.<sup>12-18</sup> State-selected studies of rotational and rovibrational collisional energy transfers have been carried out by IR-UV double resonance.<sup>20-23</sup>

In these experiments, infrared fluorescence was used to monitor the energy flow in IRMPE of  $\text{D}_2\text{CO}$ . In addition, the dependence of the IRMPD yield on excitation wavelength, laser power, and reactant and foreign gas pressures was studied. These measurements provide insights into the role of collisions in the IRMPE of  $\text{D}_2\text{CO}$  and probe the mechanism of and limitations on IRMPE and IRMPD in small molecules in general.

## EXPERIMENTAL

The excitation source in these experiments was a grating-tuned  $\text{CO}_2$  laser (Tachisto). The laser pulse consisted of a 70-ns spike followed by a  $1.3\text{-}\mu\text{s}$  tail with the total energy split almost equally between the two components. The laser beam was focused with either a NaCl lens having a 15-cm focal length or a Ge lens having a focal length of 25 cm, producing beam waists ( $1/e$  power points) of 0.08 and 0.10 cm, respectively. The laser was operated at a repetition rate of 1 Hz. The average laser power was maintained constant to within  $\pm 15\%$  over the course of an experiment as monitored by a Scientech power meter.

Infrared fluorescence was detected by either a Hg:Ge or

Cu:Ge photoconductive detector (SBRC), each 3 x 10 mm in size and cooled by liquid He. The Cu:Ge detector was equipped with a current-feedback amplifier (SBRC A320) and had a time constant of 80 ns. The Hg:Ge detector/amplifier (Keithley 104) system had a time constant of 300 ns. Fluorescence was focused onto the detector with a 5-cm diameter f/1 CaF<sub>2</sub> lens placed midway between the laser beam axis and the detector element. Scattered laser light was reduced by MgF<sub>2</sub> flats totaling 3-mm in thickness and a 6-mm thickness of CaF<sub>2</sub> flats, externally mounted over the 2-mm thick BaF<sub>2</sub> window on the detector dewar. An interference filter with 1% power points of 2026 and 2215 cm<sup>-1</sup> defined the viewing region to include most of the C-D stretching fundamental spectrum. A 4-cm long gas filter cell containing 700 Torr CO was also used to filter out CO (v-1-0) emission. Fluorescence signals were digitized (Biomation 8100) and averaged (Tracor-Northern 575A).

Dissociation yield experiments were performed in cylindrical pyrex reaction cells, 44-cm in length and having a 2.3-cm i.d. NaCl windows were affixed at Brewster's angle. The cell used for infrared fluorescence measurements was 30-cm long, 2.3-cm i.d., and had a 2.0-cm diameter CaF<sub>2</sub> window above the focus of the laser beam through which fluorescence was viewed.

Photolysis yields were determined by one of three techniques: quantitative gas chromatography (Varian 3600), pressure-rise (Celesco pressure transducer) in the photolysis cell, or mass spectrometry (AEI MS-10). Each technique was calibrated by appropriate standards (D<sub>2</sub>, HD, H<sub>2</sub>, and CO). The uncertainty in the absolute D<sub>2</sub> and CO<sub>2</sub> yields measured by gas chromatography (G.C.) analysis was <3%. Pressure-rise measurements agreed with G.C. analysis of the same photolysis sample to ± 3%. Photolyses were

typically 2700-3600 shots in duration.

Formaldehyde monomers were prepared from the appropriate polymers, [ $D_2CO$  and HDCO (Merck, Sharpe, and Dohme, each 98 atom % D) and  $H_2CO$  (Matheson, Coleman, and Bell)] as described elsewhere.<sup>18</sup> Ar and CO (Matheson Research Grade) and  $D_2$  (Matheson C. P., >99.5%) were all used without further purification. Infrared spectra, such as Fig. 2, were recorded using a Nicolet Model 7199 FTIR spectrometer.

## RESULTS

### Infrared Fluorescence

Infrared fluorescence from the C-D stretching modes of  $D_2CO$  was observed when the bending modes of  $D_2CO$  were excited by the  $CO_2$  laser radiation. The dependence of the fluorescence intensity on excitation wavelength in the 940- to  $950\text{-cm}^{-1}$  region was similar to the dissociation yield dependence shown in Fig. 2. A typical fluorescence trace of the  $5\text{-}\mu\text{m}$  fluorescence is shown in Fig. 3 for excitation at  $949.5\text{ cm}^{-1}$  with a fluence of  $133\text{ J/cm}^2$ . Analysis of the fluorescence trace yields two rapidly decaying components and a long tail; the latter is the result of thermal heating of the gas by V-T relaxation. The amplitude of the tail extrapolated back to zero time is approximately 1/6 that of the peak fluorescence amplitude. A CO gas filter placed in front of the detector had no effect on the decay curve indicating that the fluorescence did not originate from vibrationally excited product CO molecules. Emission from the first overtone of the pumped bending mode in  $D_2CO$  to the ground

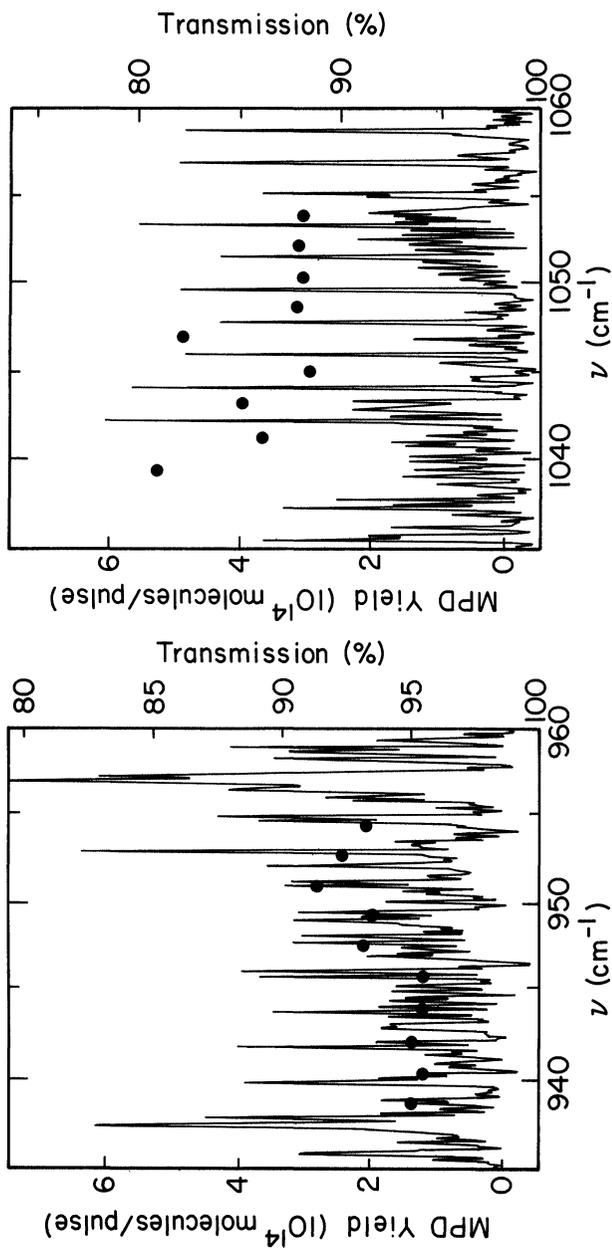


FIGURE 2 Wavelength dependence of the IRMPD yield of 8 Torr  $\text{D}_2\text{CO}$  irradiated with a laser fluence of  $160 \text{ J/cm}^2$ . Also shown is the infrared spectrum of 15 Torr  $\text{D}_2\text{CO}$  at  $0.1 \text{ cm}^{-1}$  resolution. Note the different transmittance scales.

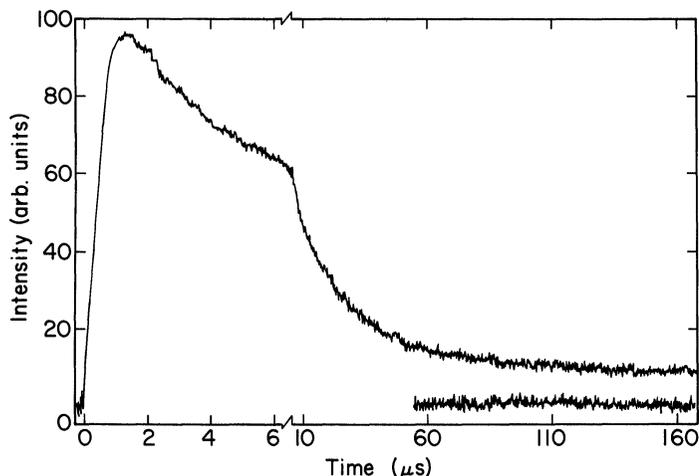


FIGURE 3 Infrared fluorescence at  $5 \mu\text{m}$  from 8.0 Torr  $\text{D}_2\text{CO}$  excited by a focused  $\text{CO}_2$  laser at  $949.5 \text{ cm}^{-1}$ . The fluence was  $133 \text{ J/cm}^2$ . The baseline was obtained from a similar trace taken on a slower time base. The long component of the signal is from thermal relaxation.

vibrational state was outside the bandpass of the filter.

The  $5\text{-}\mu\text{m}$  infrared fluorescence from  $\text{CO}_2$ -laser excited  $\text{D}_2\text{CO}$  was studied as a function of  $\text{D}_2\text{CO}$  pressure. In a system containing only  $\text{D}_2\text{CO}$ , the peak infrared fluorescence intensity increased quadratically with  $\text{D}_2\text{CO}$  pressure (Fig. 4). With 50 Torr Ar added to the system, rotational relaxation was complete (see below) and the fluorescence intensity maintained its quadratic dependence on  $\text{D}_2\text{CO}$  pressure.

The infrared fluorescence from 2.1 Torr  $\text{D}_2\text{CO}$  was studied as a function of Ar pressure (Fig. 5). The fluorescence intensity initially increased with less than a linear dependence on Ar pressure and then leveled off at Ar pressures above 30 Torr, demonstrating complete rotational

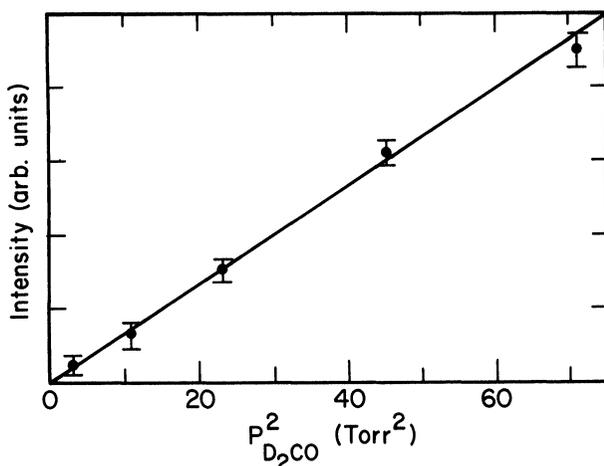


FIGURE 4 Peak infrared-fluorescence intensity at 5  $\mu\text{m}$  from IRMP excited D<sub>2</sub>CO as a function of the square of the D<sub>2</sub>CO pressure. The laser fluence was 133 J/cm<sup>2</sup> and the frequency was 949.5 cm<sup>-1</sup>.

relaxation. The time after the laser pulse at which the peak fluorescence intensity occurred did not change as a function of Ar pressure nor did the fluorescence decay rates.

#### Wavelength dependence of the dissociation yield

The MPD yield of D<sub>2</sub>CO was studied as a function of excitation wavelength. Photolyses were performed on 8 Torr of D<sub>2</sub>CO with a laser energy of 1.0 J/pulse and a fluence of 160 J/cm<sup>2</sup> for each laser line. Power broadening was on the order of  $\omega_R = \mu E/\hbar = 2 \text{ cm}^{-1}$ , where  $\omega_R$  is the Rabi oscillation frequency. The dissociation yield was measured by the increase in pressure in the photolysis cell after each photolysis was completed. The

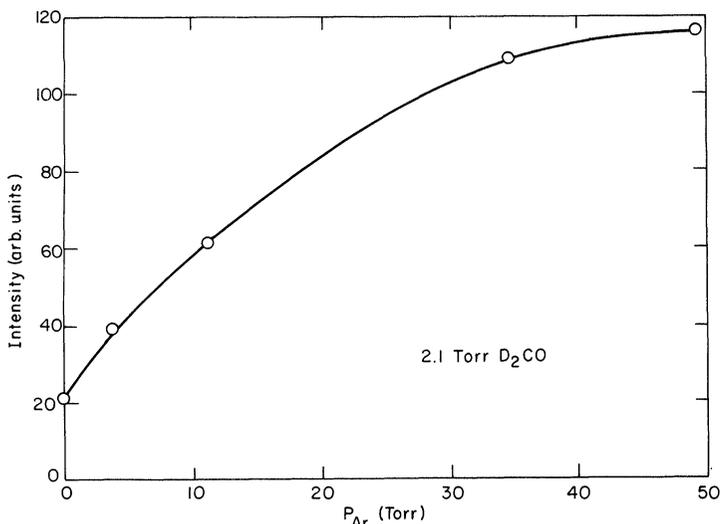


FIGURE 5 Peak infrared-fluorescence intensity at  $5 \mu\text{m}$  from 2.1 Torr  $\text{D}_2\text{CO}$  as a function of added Ar pressure. The laser fluence was  $133 \text{ J/cm}^2$  and the frequency was  $949.5 \text{ cm}^{-1}$ .

number of molecules dissociated per pulse,  $\bar{Y}$ , is shown in Fig. 2 as a function of excitation frequency along with the fundamental IR absorption spectrum of  $\text{D}_2\text{CO}$  in the ranges  $935\text{-}960$  and  $1035\text{-}1060 \text{ cm}^{-1}$ . The yield shows no striking correlation with peaks in the IR absorption spectrum at either one or two times the laser frequency. An enhancement of the dissociation yield is observed for excitation near  $1040 \text{ cm}^{-1}$  relative to excitation near  $940 \text{ cm}^{-1}$ .

The IRMPD yields of  $\text{D}_2\text{CO}$ ,  $\text{HDCO}$ , and  $\text{H}_2\text{CO}$  at several laser frequencies and intensities are listed in Table I. The dissociation yields of  $\text{D}_2\text{CO}$  and  $\text{HDCO}$  depend, respectively, on approximately the third and fifth power of laser intensity, in agreement with the results of Koren

et al.<sup>13</sup> H<sub>2</sub>CO shows minimal dissociation even at high intensities (>1 GW/cm<sup>2</sup>) at the CO<sub>2</sub>-laser line providing the best overlap with an H<sub>2</sub>CO vibration-rotation line or at wavelengths slightly red-shifted from that line.

#### Pressure dependence of the dissociation yield

The dependence of IRMPD yield on D<sub>2</sub>CO pressure was studied in the range from 1 to 10 Torr with excitation at 975.9 and 1039.4 cm<sup>-1</sup>. Analyses of the photolysis products at these excitation frequencies were performed by quantitative G.C. and measured pressure rise, respectively. The dissociation yield per pulse in pure D<sub>2</sub>CO is proportional to the (3.25 ± 0.35) power of pressure at 975.9 cm<sup>-1</sup> and a fluence of 175 J/cm<sup>2</sup> (Fig. 6) and to the (3.0 ± 0.3) power at 1039.4 cm<sup>-1</sup> and 290 J/cm<sup>2</sup>.

The addition of 15 Torr NO to the photolysis cell increased the D<sub>2</sub>CO dissociation yield at D<sub>2</sub>CO pressures lower than 8 Torr but reduced the dependence on D<sub>2</sub>CO pressure to the 1.7 power, Fig. 6, with excitation at 975.9 cm<sup>-1</sup> and 175 J/cm<sup>2</sup>. This reduced dependence on D<sub>2</sub>CO pressure is presumably due to rotational relaxation of D<sub>2</sub>CO by collisions with NO. The large dependence on D<sub>2</sub>CO pressure that remains indicates that D<sub>2</sub>CO-D<sub>2</sub>CO collisions play an important role in the excitation process in IRMPD of formaldehyde.

#### Photochemistry

The effect of photochemistry on the measured dissociation yields needs to be considered. It has been shown that the branching ratio for the radical decomposition channel in the IRMPD of D<sub>2</sub>CO is 0.10 ± 0.02

TABLE I Wavelength dependence of formaldehyde IRMPD yield.

CO <sub>2</sub> Laser Line	Frequency (cm <sup>-1</sup> )	$\bar{Y}$ (molec/pulse)
00°1-02°0	<u>D<sub>2</sub>CO<sup>a</sup></u>	
R(20)	1078.6	3.5 x 10 <sup>14</sup>
P(12)	1053.9	3.1
P(14)	1052.2	3.2
P(16)	1050.4	3.1
P(18)	1048.7	3.2
P(20)	1046.9	4.9
P(22)	1045.0	3.0
P(24)	1043.2	4.0
P(26)	1041.3	3.7
P(28)	1039.4	5.3
00°1-10°0		
R(20)	975.9	2.2 x 10 <sup>14</sup>
P(08)	954.5	2.1
P(10)	952.9	2.4
P(12)	951.2	2.8
P(14)	949.5	2.0
P(16)	947.7	2.1
P(18)	946.0	2.1
P(20)	944.2	1.2
P(22)	942.4	1.4
P(24)	940.5	1.2
P(26)	938.7	1.4
00°1-02°0	<u>D<sub>2</sub>CO<sup>b</sup></u>	
P(18) <sup>c</sup>	1048.7	3.8 x 10 <sup>14</sup>
P(18) <sup>d</sup>	1048.7	7.1 x 10 <sup>13</sup>

TABLE I (continued).

CO <sub>2</sub> Laser Line	Frequency (cm <sup>-1</sup> )	$\bar{Y}$ (molec/pulse)
00°1-02°0	<u>HDCO<sup>b</sup></u>	
P(18) <sup>c</sup>	1048.7	3.4 x 10 <sup>14</sup>
P(18)	1048.7	3.8 x 10 <sup>13</sup>
P(20)	1046.9	3.0 x 10 <sup>13</sup>
00°1-00°1		
P(18)	946.0	6.7 x 10 <sup>12</sup>
00°1-02°0	<u>H<sub>2</sub>CO<sup>b</sup></u>	
R(22)	1079.9	< 10 <sup>12</sup>
R(16)	1076.0	< 10 <sup>12</sup>
R(14)	1074.6	< 10 <sup>12</sup>
R(12)	1073.3	< 10 <sup>12</sup>
R(12) <sup>c</sup>	1073.3	< 10 <sup>12</sup>
00°1-10°0		
R(22) <sup>c</sup>	977.2	< 10 <sup>12</sup>

<sup>a</sup>D<sub>2</sub>CO pressure = 8 Torr, 25-cm focal length lens, incident energy = 1.0 J/pulse.

<sup>b</sup>Formaldehyde pressure = 8 Torr, 15-cm focal length lens, incident energy = 1.2 J/pulse.

<sup>c</sup>Incident energy = 1.9 J/pulse.

<sup>d</sup>Incident energy = 1.1 J/pulse.

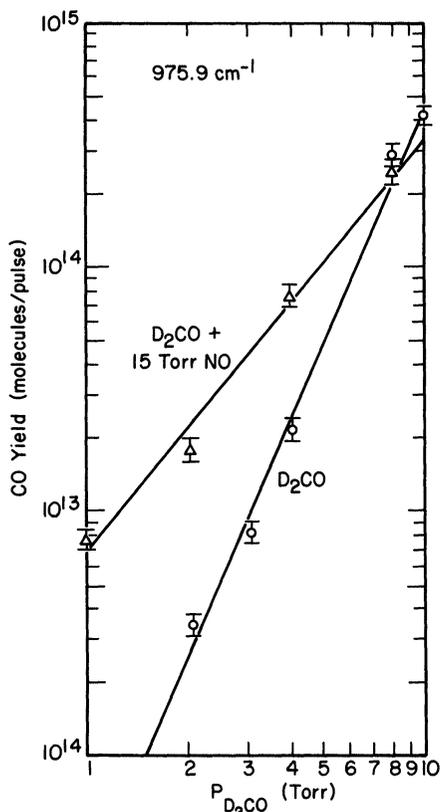


FIGURE 6 Pressure dependence of the CO yield from the IRMPD of  $D_2CO$  irradiated at  $975.9 \text{ cm}^{-1}$ . The laser energy was  $1.7 \text{ J/pulse}$  and the fluence was  $175 \text{ J/cm}^2$ . Least-squares fits give slopes of 3.25 for pure  $D_2CO$  and 1.7 for  $D_2CO + 15 \text{ Torr NO}$ . Products were analyzed by G.C.

with the laser conditions used in this work.<sup>18</sup> The chemistry that occurs following photodissociation of  $D_2CO$  to  $D + DCO$  in pure  $D_2CO$  and in  $D_2CO/NO$  mixtures is well understood.<sup>10</sup> The quantum yield for CO production is equal to the photodissociation quantum yield in pure  $D_2CO$ , and, with an NO pressure of 15 Torr and up to 10 Torr  $D_2CO$ , is within 2% of the photodissociation quantum yield in the mixtures as well.<sup>10,18</sup> Thus, the measured CO yield is a reliable measure of the dissociation yield in pure  $D_2CO$  and in  $D_2CO/NO$  mixtures.

The photochemistry and excitation mechanism in the IRMPD of  $D_2CO$  was investigated by photolyzing a mixture of 4

Torr each of H<sub>2</sub>CO and D<sub>2</sub>CO and analyzing the products mass spectrometrically. The relative D<sub>2</sub>:HD:H<sub>2</sub> yields were 1.0:0.1:<0.01, respectively, with 40 eV electrons used in the mass spectrometer in an effort to minimize cracking. The HD yield was a factor of two larger than that obtained in the photolysis of pure D<sub>2</sub>CO and cannot be accounted for by dissociation of the natural abundance of HDCO in H<sub>2</sub>CO. The increased HD yield resulted from radical dissociation of D<sub>2</sub>CO followed by the reaction  $D + H_2CO \rightarrow HD + HCO$ .

## DISCUSSION

D<sub>2</sub>CO displays the characteristics of a small molecule with respect to IRMPD. The density of vibrational states in D<sub>2</sub>CO,  $\rho_{\text{vib}}$ , is low compared to that in molecules such as SF<sub>6</sub> which undergo facile collisionless IRMPD under modest laser excitation. In D<sub>2</sub>CO,  $\rho_{\text{vib}} = 0.08, 0.7, 3.6$  and  $13/\text{cm}^{-1}$  at 5,000, 10,000, 15,000, and 20,000  $\text{cm}^{-1}$ , respectively. The effective density of states exceeds  $\rho_{\text{vib}}$  because Coriolis couplings spread oscillator strength among a number of rotational states. Stimulated-emission-pumping experiments probing vibrationally excited states of the ground electronic state of H<sub>2</sub>CO show that the onset of a QC is dependent on the rotational level of the molecule since Coriolis coupling matrix elements increase with increasing J and K.<sup>24</sup> For strong mixing  $\rho$  approaches  $(2J+1) \rho_{\text{vib}}/4$ .<sup>8,24</sup> In D<sub>2</sub>CO, the absorption of at least 5 CO<sub>2</sub>-laser photons in the discrete state region is probably required before the criterion for the applicability of a QC description,<sup>25,26</sup>

$$\Delta\omega_{\text{mol}} \gg \omega_{\text{R}} \gg \rho(E)^{-1}$$

can be met. Here,  $\Delta\omega_{\text{mol}}$  is the effective width over which the oscillator strength is distributed, and  $\rho(E)$  is the density of states at energy  $E$  to which allowed transitions can occur. The low density of states severely limits the opportunities for sequential transitions in region I and raises the energy of the transition into region II.

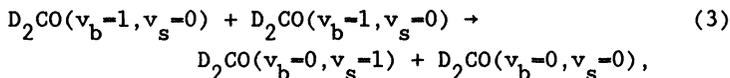
In the IRMPE of small molecules, bottlenecks to excitation in Region I resulting from mismatches between the laser frequency and allowed transition frequencies can be too large to be overcome by power broadening alone. The large rotational constants of  $\text{D}_2\text{CO}$  spread the lines of a vibrational band over 100 to 150  $\text{cm}^{-1}$ . Only a few  $J$ ,  $K_a$ ,  $K_c$  states of any given vibrational level can interact with the laser frequency. It is thus most unlikely that a molecule which resonantly absorbs a first photon will be resonant within  $\omega_R$  for absorption of a continued sequence of photons in the absence of collisions. Collisions which change rotational quantum numbers can help molecules to pass through bottlenecks by channelling molecules in each vibrational state into those rotational levels which are resonant with the laser frequency.<sup>1</sup> Collisions may also cause redistribution of energy among the vibrations of a single molecule or transfer vibrational energy from one molecule to another, vibration-to-vibration (V-V) energy transfer.

An important consequence of the rotational transition spacings being larger than typical anharmonicities, is that the usual red-shift of the IRMPD yield spectrum with respect to the one-photon absorption spectrum is not observed, Fig. 2. There are some stronger absorption features in the 1040  $\text{cm}^{-1}$   $\nu_6$  region than in the 940  $\text{cm}^{-1}$   $\nu_4$  region, but the total absorption strengths of the  $\nu_4$

and  $\nu_6$  modes are comparable. The yield enhancement at  $1040\text{ cm}^{-1}$  can be attributed to the location of the C-D stretching modes of D<sub>2</sub>CO whose fundamental absorption bands extend from  $2000$  to  $2275\text{ cm}^{-1}$ . Excitation by two  $940\text{-cm}^{-1}$  photons leaves a D<sub>2</sub>CO molecule below the C-D stretching levels while two  $1040\text{-cm}^{-1}$  photons bring the molecule into the heart of the C-D stretching vibration-rotation manifold. Fermi resonances between the stretching levels and bending overtones spread the transition probability for dipole-allowed transitions to more levels in this energy region, providing more available excitation pathways in the molecule. Collisional energy transfer from the bending modes to the stretches is also assisted by having the participating levels nearly resonant. Since collisions are required to reach the QC, collisional effects and power broadening wash out sharp frequency resonances in the dissociation yield spectrum. The yield spectrum cannot be expected to be closely related to the fundamental IR absorption spectrum.

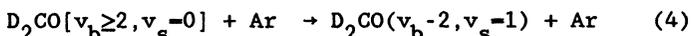
Measurements of infrared fluorescence from the C-D stretching modes help to elucidate the role of collisions in Region I in the IRMPE of D<sub>2</sub>CO. The quadratic dependence of the IR emission intensity on D<sub>2</sub>CO pressure implies that D<sub>2</sub>CO-D<sub>2</sub>CO collisions are required to populate the stretching modes. This demonstrates that there is a bottleneck to excitation and energy redistribution in the molecule at low energies. This bottleneck is not overcome by rotational relaxation as demonstrated by the emission retaining its quadratic dependence on D<sub>2</sub>CO pressure in the presence of 50 Torr of Ar. The most probable process involved in overcoming the excitation bottleneck is vibrational up-pumping via V-V energy transfer between two

$D_2CO$  molecules, each initially having one quantum of excitation in a bending mode,



where  $v_b$  denotes the number of quanta in the  $\nu_4$  and  $\nu_6$  modes. A molecule with excitation in the stretching manifold is produced, where  $v_s$  refers to the number of quanta in the  $\nu_1$  and  $\nu_5$  stretching modes of  $D_2CO$ . This process is endothermic by less than  $200 \text{ cm}^{-1}$  with pumping at  $950 \text{ cm}^{-1}$ . This energy transfer is nearly resonant for excitation at  $1050 \text{ cm}^{-1}$  and this, along with the larger density of states at multiples of  $1050 \text{ cm}^{-1}$ , is probably responsible for the reduced dissociation yield at  $950 \text{ cm}^{-1}$  relative to  $1050 \text{ cm}^{-1}$ .

If the initial absorption by  $D_2CO$  were a coherent multiphoton excitation in the bending mode to  $v_b > 1$ , Ar collisions would transfer molecules into stretching levels



and reduce the quadratic dependence on  $D_2CO$  pressure. The data are quadratic for  $D_2CO$  with 50 Torr Ar. Although the collision efficiencies for  $D_2CO$  and Ar coupling the bending and stretching manifolds in  $D_2CO$  are unknown, process (4) is expected to be rapid for 50 Torr Ar.<sup>27</sup>

Further confirmation of the importance of process (3) is the fact that IRMPD yields are approximately quadratic in  $D_2CO$  pressure when NO is present to bring about rotational relaxation. Thus the intermolecular transfer of a bending quantum, process (3), appears to be a crucial step in the IRMPE and IRMPD of  $D_2CO$ .

The decrease from cubic to quadratic of the dependence of the IRMPD yield on D<sub>2</sub>CO pressure in the presence of 15 Torr NO and the enhanced IR fluorescence with the addition of Ar shows that collisions are required to shift molecules among rovibrational levels so as to populate those with transitions in resonance with the laser. The large permanent dipole moment of formaldehyde gives rotational energy transfer rates about one order of magnitude greater than the gas kinetic collision rate.<sup>23</sup> Orr and coworkers<sup>20-23</sup> have observed that D<sub>2</sub>CO-D<sub>2</sub>CO collisions induce V-V transfer between the  $\nu_4$  and  $\nu_6$  bending modes of D<sub>2</sub>CO, which are strongly coupled by Coriolis interactions, with a rate comparable to that for pure rotational transitions,  $10^8 \text{ s}^{-1} \text{ Torr}^{-1}$ . Evans et al.<sup>16</sup> found that IRMPD of H<sub>2</sub>CO at 20 Torr using 3- $\mu\text{m}$  radiation was two orders of magnitude more efficient when their DF laser was operated multiline compared to single line at the same total energy. This demonstrates a very considerable bottlenecking for such a high pressure.

V-V energy transfer and rotational relaxation both contribute to IRMPE in D<sub>2</sub>CO. The dependence of 5- $\mu\text{m}$  IR fluorescence on the square of the D<sub>2</sub>CO pressure and the cubic dependence of the dissociation yield on D<sub>2</sub>CO pressure in pure D<sub>2</sub>CO can be described with the dissociation yield being given by  $\tilde{Y} \propto [\text{D}_2\text{CO}]^2 [\text{M}]^a$  where  $a$  depends on the rotational relaxation required. When pure D<sub>2</sub>CO is photolyzed,  $\text{M} = \text{D}_2\text{CO}$  and  $a = 1$ . The quadratic pressure dependence of the dissociation yield observed by Evans et al.<sup>16</sup> in H<sub>2</sub>CO with 3.6- $\mu\text{m}$  excitation could result from the need for fewer photons to reach the QC reducing the requirement for collisional processes to overcome bottlenecks in the discrete state region. In all probability the analogue of process (3) is not important.

Although V-V energy transfer processes play a pivotal role in excitation of  $D_2CO$  through Region I, they do not provide the mechanism for pumping through region II and into region III. Little dissociation of  $H_2CO$  was observed in an equimolar  $H_2CO/D_2CO$  mixture. Almost perfect isotopic discrimination between these two molecules is observed here and in the works of Koren *et al.*<sup>12-15</sup> and of Evans *et al.*<sup>16</sup> Dissociation is caused neither by thermal heating nor by a high vibrational temperature produced by V-V equilibration between  $H_2CO$  and  $D_2CO$ . Direct laser pumping of the molecule through Region II and into Region III is required.

## CONCLUSIONS

$D_2CO$  demonstrates the characteristics of a small molecule with respect to IRMPE and IRMPD. Bottlenecks to excitation occur after the absorption of one laser photon.  $D_2CO$ - $D_2CO$  collisions, most likely through collisional V-V transfer between two  $D_2CO$  molecules, each excited in a bending mode, populate the stretching manifold and overcome this bottleneck to further excitation. Buffer gas collisions are also required to change rotational and possibly vibrational quantum numbers so that the transitions of the absorbing molecule may be shifted into resonance with the laser at each step through Region I. Collisional energy transfer plays a crucial role in the IRMPD of small molecules. The types of vibrational and rotational energy transfer processes which are important will be as varied as the energy level structures of the molecules themselves.

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