# Infrared Multiphoton Dissociation of Octafluorocyclobutane with a Two-Frequency Q-Switched CO<sub>2</sub> Laser

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The infrared multiphoton dissociation of octafluorocyclobutane has been investigated by the use of two  $CO_2$  laser pulses of different frequency, synchronized by the same Q-switching mirror. The dissociation yield has been determined as a function of laser pulse energy, frequency of the dissociating pulse, substrate pressure, and interpulse delay. Accompanying transport phenomena (expansion and diffusion) were taken into account by the use of appropriate models. The kinetic behavior of highly vibrationally excited c-C<sub>4</sub>F<sub>8</sub> molecules indicates that collisional relaxation occurs at nearly gas kinetic rates.

### Introduction

The infrared multiphoton dissociation (IRMPD) of a number of polyatomic molecules has been investigated during the past few years. Nevertheless, little is known about the rate of relaxation of molecules in highly excited vibrational levels or the rate of dissipation of the energy deposited by infrared multiphoton absorption (IRMPA). This problem has been attacked by using two infrared lasers, either in double resonance (pump-probe) experiments<sup>1-15</sup> or two-frequency dissociation measurements.<sup>16-25</sup> The average number of absorbed photons in a two-frequency excitation experiment has recently been measured by the photoacoustic technique.<sup>26</sup> From these two-frequency experiments, a variety of results are obtained which depend on parameters such as the energy of the exciting pulse and the pulse duration.<sup>27</sup>

We have studied the infrared multiphoton dissociation (IRMPD) of octafluorocyclobutane  $(C_4F_8)$  using an experimental procedure in which the time interval between two laser pulses at different wavelengths could be varied. In terms of the well-established three-region model of multiphoton absorption, a laser at a frequency  $v_1$  resonant with the molecular absorption band of the molecule causes vibrational excitation up to the discrete levels or the quasicontinuum, depending on the fluence within the interaction region. The second laser, whose frequency  $v_2$  is redor blue-shifted with respect to  $v_1$ , pumps the excited molecules to the dissociation limit. In order to perform this experiment with an accurate determination of the pulse energy and duration, two tunable Q-switched  $CO_2$  lasers, synchronized by the same Qswitching mirror (QSM), have been used.

In this paper, we present a set of multiphoton dissociation measurements performed on  $C_4F_8$ , together with a theoretical model that accounts for complications introduced by transport phenomena.

#### **Experimental Section**

Figure 1 shows a schematic diagram of the experimental configuration. The laser cavities consist of two classic CO<sub>2</sub> lasers, coaxially pumped by a dc electric discharge, with a single hexagonal QSM having an axis of rotation in the plane of the cavities. The hexagonal mirror permits an 800-Hz pulse repetition rate. The electric discharge length is 270 cm for each 650-cm-long cavity, and the core diameter is 13 mm. In order to obtain a well-defined TEM<sub>00</sub> transverse mode, two 8-mm-diameter iris diaphragms were inserted into each cavity. Two 20-m radiusof-curvature output couplers with 65% reflectance were used. The two lasers can be tuned independently on the CO<sub>2</sub> transitions with two separate 150 line/mm gratings used in the Littrow configuration. If the surfaces of both gratings are perpendicular to the plane of the laser cavities, the two pulses are perfectly synchronized in time at the same position of the QSM. If one grating is moved in a vertical plane, on a circular trajectory centered on the QSM axis, the corresponding cavity is aligned for a different position of the QSM, leading to a time interval between the two pulses. With a repetition rate of 800 Hz, and a distance of 25 mm over which the grating can be moved accurately and automatically by a micrometric device, the time interval range is from -1 to +8 $\mu$ s, with a precision of  $\pm 10$  ns.

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Figure 1. Schematic diagram of the experimental apparatus. Abbreviations used are as follows: OC, output coupler; PY DT, pyroelectric detector; G, grating; PD, photodiode; 7904, oscilloscope; VISU 613, Tektronix CRT display.

The temporal profile of the laser pulses was determined with both a Ge:Au (77 K) detector and a pyroelectric detector with a boxcar integrator providing the time base. Pulses were found to be Gaussian in shape with a full width (at 1/e points) of 250  $\pm$  25 ns, the value used in calculations described in the Appendix. No self-mode locking was observed with the detectors and amplifiers used.

The advantages of such a device are evident: (i) high repetition rate (800 Hz), (ii) negligible jitter, (iii) accurate determination of temporal and spatial profiles of the pulses. The disadvantage is the very low output energy per pulse, about 1 mJ for a  $\sim 300$ ns (fwhm) Gaussian pulse, so that short focal length lenses (5 cm) are needed to obtain the high fluence required to induce MPA and IRMPD. With this experimental arrangement, the maximum fluence at the focal point is about 5 J/cm<sup>2</sup>.

With a coaxial beam geometry, the accurate alignment of the two focal points was verified by maximizing the two beam intensities, monitored by two beam splitters and a fast detector, after passage of the beams through a 400- $\mu$ m-diameter pinhole in the center of the cell. The focal point diameter was carefully measured to be 160  $\mu$ m by moving a 25- $\mu$ m pinhole across the focal spot diameter. The average diameter, measured over the 8-mm-long focal volume, is about 300  $\mu$ m. The cell, made from brass, 1.6-cm i.d., had an initial length of 6.6 cm which, in some experiments, was further reduced to 8 mm. The absence of wall-induced reaction at the cell entrance was verified by comparing the results obtained with the long and short path length cells, at the threshold of dissociation for C<sub>4</sub>F<sub>8</sub>.

In an earlier study of the IRMPD of  $C_4F_8$  with a TEA laser<sup>28a</sup> it was shown that the only product of the  $C_4F_8$  dissociation through IRMPD is tetrafluoroethylene ( $C_2F_4$ ), in agreement with kinetic studies of the thermal reaction.<sup>29</sup> In the present work, the dissociation measurements were performed with gas chromatographic analysis of the irradiated gas or by determing the increase of pressure due to the fact that one molecule of  $C_4F_8$  produces two of  $C_2F_4$ . The "one-color" (single-frequency) dissociation yields vs. energy and frequency of the exciting pulse were measured mainly with the gas chromatograph, while the "two-color" studies were performed with the pressure method. (See Figure 2 for an infrared spectrum of  $C_4F_8$  in the 10-µm range.)

In order to follow the exact evolution of the IRMPD vs. time delay between two pulses at different frequencies, the rate of



Figure 2. Infrared absorption spectrum of  $c-C_4F_8$  in the region of interest. Frequencies of CO<sub>2</sub> laser lines of the 10.6- $\mu$ m band used in this work are also indicated.

pressure increase was measured with a capacitance differential manometer (Barocell), coupled to a boxcar integrator. The time derivative signal from the boxcar is stored in a PDP 11/34 computer synchronously triggered by the micrometer device which raises the grating and introduces the interpulse delay. Note that in this experimental configuration the boxcar is being used to take the derivative of the pressure change vs. time and not as an averaging device. In order to reduce the apparent noise of the manometer, the time constant of the system was artifically increased to 1 s. The rate of pressure increase is read into the PDP 11/34 for a 500-ms interval every 3 s, each measurement corresponding to a 24-ns step of the interpulse delay. Such a device is quite sensitive and allows pressure increase measurements of about 3  $\mu$ torr/s with a signal-to-noise ratio of five.

The absolute dissociation probability was obtained by calibration of the system in a single-beam experiment. For a given time of irradiation and for a known pressure, the rate of pressure increase

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**Figure 3.** Dissociation yield of c-C<sub>4</sub>F<sub>8</sub> as a function of incident laser pulse energy, which was varied by changing the pressure of SF<sub>6</sub> in a filter cell. The initial pressure was 0.1 torr, and the laser frequency was 947.7 cm<sup>-1</sup> (P16). To obtain peak fluence at the focal point of the laser, the abscissa must be multiplied by *approximately*  $3 \times 10^3$ .

(boxcar signal) was compared to the absolute number of dissociated molecules per unit time determined from the gas chromatographic analysis of the irradiated  $C_4F_8$ . This calibration can only be done with the 8-mm path length cell and approximately collimated beam geometry, so that the absolute interaction volume can be estimated. The volume of the cell was also measured carefully. All the data presented, except those in Figures 3 and 4, were obtained with this collimated beam geometry.

## **Experimental Results**

In the present study, dissociation rates were determined as functions of substrate pressure (P), pulse energy (E), frequency of the second pulse  $(v_2)$ , and interpulse delay  $(\Delta t)$ . In the one-color study, the frequency of the pulse was fixed at 948  $\rm cm^{-1}$  (P16), which corresponds to the red side of the C<sub>4</sub>F<sub>8</sub> absorption band, as illustrated in Figure 2. Figure 3 illustrates the energy dependence of the dissociation yield, showing a strong threshold behavior characteristic of an IRMPD process. Note that, in this experiment, the path length of the cell is long (66 mm), so that the dissociation volume does not reach the cell windows regardless of the incoming pulse energy. For this reason, we have found, for the higher energies of Figure 3, a 3/2 power energy dependence.<sup>30-32</sup> However, at the threshold for dissociation, the interaction zone is limited to the focal point region ( $D \sim 160 \ \mu m$ ) where a fluence of about 0.5 J cm<sup>-2</sup> was determined. Figure 4 shows the effect of the substrate pressure (from 5 mtorr to 2.5 torr) on the dissociation yield. The slope of slightly less than one corresponds to an approximately constant dissociation probability. The turnover at the highest pressure may arise from a decrease in energy in the interaction zone due to absorption of the incoming beam. To reduce this problem, we decreased the path length of the cell to 8 mm, as previously described in the Experimental Section. The laser fluence is approximately uniform over this distance, unlike the case for the longer cell. The data presented in Figures 5-7, 9, and 10 were obtained with this collimated beam geometry, which allows us to determine an absolute dissociation probability.

In the two-color studies the frequency of the fixed pulse was 969 cm<sup>-1</sup> (R10), on the blue side of the  $C_4F_8$  absorption band. The moving pulse frequency was varied from 978 (R24) to 934



Figure 4. Dissociation yield of c-C<sub>4</sub>F<sub>8</sub> as a function of substrate pressure, with a laser pulse energy of  $\sim 0.5$  mJ in the P16 line. The total cell volume was 163 cm<sup>3</sup>.

 $cm^{-1}$  (P30) with a "hole" between 953 (P10) and 969  $cm^{-1}$  (R10), unfortunately corresponding to the center of the low-intensity spectrum.

Figures 5 and 6 show the enhancement of dissociation probability produced by the combination of both pulses vs. the interpulse delay, for two different moving pulse frequencies, 935 (P30) and 971 cm<sup>-1</sup> (R12), and for four different pressures, 0.05, 0.1, 1.0, and 5.0 torr. The horizontal "base line" in these diagrams corresponds to the sum of the dissociation probabilities independently produced by each pulse. The vertical line corresponds to the time coincidence of the two pulses.

A. Irradiation with R10 and R12 Pulses. As Figure 2 indicates, the absorption cross sections for the R10 and R12 lines are nearly identical. Thus, irradiation with these two pulses is the same, regardless of whether R12 preceeds R10 or vice versa. From Figure 5 the following observations can be made when the two laser pulses have nearly identical frequencies: (i) The dissociation probability is increased when the two pulses overlap in time, the maximum occurring when they are simultaneous. This indicates that the dissociation yield depends on intensity and not fluence. since the total fluence is independent of the pulse delay and, in fact, determines the base line. This suggests that molecular transport and/or relaxation are important on this time scale. (ii) The half-width of the dissociation probability enhancement decreases as pressure increases, implying that the relaxation of excited molecules is collisionally assisted. (iii) The dissociation yield enhancement, after a few microseconds, is below the base line at high pressure (>1.0 torr). (iv) The absolute value of the dissociation probability maximum decreases as pressure increases.

B. Irradiation with R10 and P30 Pulses. As indicated in Figure 2, the P30 pulse is very weakly absorbed, and causes no dissociation by itself. Figure 6 shows three different features when the laser pulse frequencies are well separated: (i) There is a significant time delay between the dissociation maximum and the pulse coincidence, unlike the R10/R12 case of Figure 5. (ii) The dissociation yield enhancement, after a delay of a few microseconds, is above the base line (sum of the one-pulse yields) at high pressure (>1.0 torr). (iii) The absolute value of the dissociation probability maximum decreases as pressure increases.

Figures 5 and 6 show that the dissociation enhancement depends strongly on the second pulse frequency. This effect has been more extensively studied, as shown in Figure 7, which also contains the low-intensity, one-photon absorption spectrum of octafluorocyclobutane. Regardless of the interpulse delay  $\Delta t$  there is a significant red shift in the dissociation spectrum with respect to the low-intensity one-photon spectrum. Similar observations have been made by Quack and Seyfang.<sup>28b</sup> Nevertheless, this red shift is more important for the R10 prepared excited molecules ( $\Delta t$ 

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Figure 5. The relation between the dissociation probability and the delay time between the R10 pulse (fixed in time) and the R12 "probe" pulse. Pulse energies are 500 (R10) and 400  $\mu$ J (R12). The horizontal line indicates the sum of dissociation probabilities independently produced by each pulse. The vertical line corresponds to the time coincidence of the two pulses. Pressures of C<sub>4</sub>F<sub>8</sub> are (a) 0.05 torr, (b) 0.10 torr, (c) 1.00 torr, (d) 5.00 torr.



Figure 6. This is the same as Figure 5 except that the "probe" pulse is now P30. Pulse energies are 450 (R10) and 200  $\mu$ J (P30).



Figure 7. Dissociation probability as a function of interpulse delay and frequency of the delayed pulse, when R10 is used as the exciting pulse. Pulse energies are 350-380 (R10) and 220  $\mu$ J (delayed pulse). The horizontal dashed line indicates the dissociation probability for the R10 pulse alone. Time delays are as follows: O,  $-1 \mu s$  (tunable pulse precedes R10 pulse); •, +1  $\mu$ s; +, 5  $\mu$ s. The dotted line indicates the low-power IR absorption spectrum of  $C_4F_8$ . Pressures of  $C_4F_8$  are (a) 0.5 torr and (b) 5.0 torr.

> 1  $\mu$ s) than for the unexcited ones ( $\Delta t = -1 \mu$ s). (Recall that  $\Delta t < 0$  indicates that the variable frequency pulse precedes the pulse fixed at R10 and that the variable pulse by itself causes essentially no excitation.)

#### Discussion

As far as we know, these results provide the first example of IRMPD with a Q-switched laser, with a typical pulse energy as low as  $\sim 1$  mJ. Pulse energies in experiments using CO<sub>2</sub> TEA lasers are typically 0.1-1 J. However, IRMPD under collisionless conditions in which ions are trapped in an ion cyclotron resonance chamber has been effected with a CW CO<sub>2</sub> laser with intensities of  $\sim 1-100 \text{ W cm}^{-2,33,34}$  The dissociation of large organometallic compounds in a molecular beam with 10-µm CW radiation has also been reported.<sup>35,3</sup>

In the present two-color experiments, the observation of similar behavior (as illustrated by Figures 5 and 6) over a pressure range of two orders of magnitude is quite striking. The excited molecules can be removed from the influence of the second laser pulse by three different mechanisms: (1) transport of the molecules out of the interaction region; (2) vibrational quenching of excited molecules by cold molecules (V-T and V-V transfer); (3) redistribution of excess vibrational energy within the excited molecules.

The analysis of the transport process depends on the relative magnitudes of the mean free path of the molecules ( $\lambda$ ) and the radius of the interaction region (R). If  $\lambda$  is equal to or larger than R, the transport process must be analyzed in terms of an expansion model,<sup>37-39</sup> which has been applied to a laser photochemistry



Figure 8. Calculated dissociation probability as a function of interpulse delay time, including transport phenomena but no first-order relaxation. Solid lines, transport calculated with a diffusion model at the pressures indicated; dashed line, transport calculated with an expansion model.

experiment by Stephenson and King.<sup>40a</sup> If  $\lambda$  is much smaller than R, the transport process may be described by a classic diffusion calculation as applied to laser photochemistry<sup>40b,c</sup> and to thermal diffusivity in the analysis of thermal lensing experiments.<sup>41</sup> Intermediate cases, with  $1.0 > \lambda/R > 0.1$ , cannot be rigorously analyzed. The laser photochemistry experiments discussed by Stephenson and co-workers<sup>40</sup> differ from ours in that the probe laser pulse has a much shorter time duration than the pump laser pulse and can be treated as a  $\delta$  function in time. The analysis carried out in the Appendix leads to an expression for the dissociation yield of the form:

$$Y(\Delta t) \propto \int_{-\infty}^{\infty} \exp[-n(t - \Delta t)^2 / T_p^2] dt \times \int_{-\infty}^{t} \frac{\exp[-m(t'/T_p)^2] dt'}{(m+n)R^2 + Z} \{A \exp[(t'-t)/\tau] + B\}$$

where  $Z = c^2(t - t')^2$  for the expansion model and  $Z = 4D(t - t')^2$ t) for the diffusion model. In the above expression,  $\Delta t$  is the time separation between the two pulse centers, and  $T_{p}$  is the width at the 1/e points. The coefficients m and n differ from unity if the excitation and dissociation processes have a nonlinear dependence on intensity. In addition, c is the most probable velocity, and Dis the diffusion coefficient (defined further in the Appendix). The values used in these calculations were  $c = 1.62 \times 10^{-5}$  cm ns<sup>-1</sup> and  $D = 1.65 \times 10^{-8} \text{ cm}^2 \text{ ns}^{-1}$  at 1 torr. Both m and n were assumed to be unity. A is the maximum enhancement of the dissociation yield and B is the plateau in the yield obtained for well-separated pulses at high pressures. The constants A and Bare adjusted to fit the experimental results and to obtain the relaxation time for the excited molecules,  $\tau$ . For a given type of experiment (R10/R12 or R10/P30), the ratio A/B is estimated from an experiment with a small transport effect (high pressure), so that the maximum and the plateau values of the theoretical curves fit the experimental data, regardless of  $\tau$ . The remaining parameter,  $\tau$ , is determined by fitting the above expressions to the experimental values of the dissociation yield enhancement at each pressure.

Figure 8 shows pure transport phenomena at pressures from 20 mtorr to 5 torr calculated with the diffusion model and with an interaction zone radius of 150  $\mu$ m. In these curves, the relaxation rate expression,  $A \exp(-t/\tau) + B$ , has not been included in the dissociation yield calculations. Note that under these

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Figure 9. A comparison of experimentally determined dissociation probabilities (points) and those calculated with the assumption of first-order relaxation times indicated on the figure (solid lines). The excitation pulse was R10 and the "probe" pulse was R12. Pressures of  $C_4F_8$  were (a) 0.10 torr; (b) 5.00 torr.

conditions only the three upper curves, with the mean free path  $\lambda$  small compared to *R*, are valid. The dashed curve represents the calculation based on the expansion model, which is independent of pressure.

When this model is applied to the case where the "pump" and "probe" pulses are essentially at the same wavelength (i.e., the R10/R12 system), the designations of "first" and "second" pulse become irrelevant, and  $Y(-\Delta t) = Y(\Delta t)$ . This was taken into account in the yield calculations.

The method described above has been applied to the experimental data with the results shown in Figures 9 and 10. The solid lines indicate calculated dissociation yield enhancements for three different values of  $\tau$ , the first-order relaxation time. For the R10/P30 experiments, the parameters A and B determined from the 5-torr experiments were also used at all the other pressures. At high pressures (Figures 9b and 10b), the effect of diffusion is a small perturbation on the relaxation. However, the relaxation times that best fit the data (0.40  $\mu$ s for R10/R12 and 0.65  $\mu$ s for R10/P30) are comparable to the pulse convolution width ( $T_p$ ), and this introduces considerable uncertainty into the determination of  $\tau$ . The above relaxation times correspond to collisional rate constants of 0.5 and 0.3  $\mu$ s<sup>-1</sup> torr<sup>-1</sup> for the R10/R12 and R10/P30 systems, respectively.

In the R10/P30 experiments, the time delay of  $\sim 0.5 \ \mu s$  between the pulse coincidence and the dissociation maximum can arise from either of two effects. First, if the relaxation time is roughly 0.25 to 4 times the pulse duration, the population of levels that absorb at the P30 wavelength will be proportional to the intensity of the exciting pulse integrated up to the time of the second pulse. Second, molecules in vibrational levels that can absorb the P30 pulse and dissociate may be produced from R10-excited molecules by collisions. This second explanation appears to be ruled out by the fact that the time delay between the pulse coincidence and



Figure 10. The same as Figure 9, but with R10 as the exciting pulse and P30 as the "probe" pulse.

dissociation yield maximum was found to be nearly the same at pressures of 10 and 50 mtorr.

At low pressures (Figures 9a and 10a), the effect of expansion is a significant perturbation on the observed relaxation. As Figure 10a indicates, there is little difference between the calculated dissociation yields for values of  $\tau$  ranging from 1  $\mu$ s to  $\infty$  (the curve labeled "no relaxation"). In other words, gas expansion alone introduces a "relaxation" effect with a time constant of a few microseconds. For this reason, the values of  $\tau$  giving the best fit to the experimental data (1.5  $\mu$ s for R10/R12 and 5.0  $\mu$ s for R10/P30) cannot be considered very accurate. However, additional evidence for a very fast collisional relaxation process is provided by the data in Figure 6, a and b, from which it is evident that an increase in pressure from 50 to 100 mtorr decreases the half-width of the dissociation probability enhancement (and hence the relaxation time) by about 25%. At these pressures  $\lambda/R$  is ~1 to 2, and the transport process is expansion, which is approximately independent of pressure (see above). Since the average number of collisions occurring in a  $1-\mu s$  time interval is very small at these pressures, the excited system relaxes at a nearly gas kinetic rate, indicating a very large cross section for this process.

The relaxation rate constants derived from the low-pressure data cited above (Figure 6, a and b) are an order of magnitude larger than those observed in the high-pressure experiments. In addition to the uncertainty introduced by transport phenomena and the finite pulse width, the discrepancy could result from a combination of two relaxation processes, one of which has a rate constant corresponding to the low-pressure value and the other with a rate constant corresponding to the high-pressure value. For example, the relaxation rates measured at low pressures could pertain to rapid V-V energy transfer among highly excited vibrational levels, while the slow process observed at higher pressures could be a subsequent relaxation (V-T,R energy transfer) of the vibrationally excited molecules. At a pressure of 100 mtorr, the V-T,R process would have a time constant of  $\sim 20-25 \,\mu$ s, which

would be undetectable because the expansion process is faster by an order of magnitude. In the experiments at 5 torr, the fast V-V process would have a time constant of  $\sim 0.03-0.1 \ \mu s$ , which is too fast to observe on the time scale of the experiment. However, this fast decay would decrease the magnitude of the maximum in the dissociation probability curve, as is observed. In any case, it does not appear reasonable to ascribe the observed relaxation rate to collisionless intramolecular energy redistribution, which would be expected to occur on a picosecond time scale in a large molecule such as  $C_4F_8$ . Although the lifetime for  $C_4F_8$  (as estimated from RRKM theory) can be quite long for molecules just above threshold for a reaction, the present experiments are sensitive only to molecules produced below threshold by the first laser pulse and promoted over threshold by the second pulse. Hence, the lifetime does not affect the yield as a function of time delay between the laser pulses.

The positive or negative value of the plateau with respect to the base line can be explained in terms of a red shift of the infrared absorption spectrum when the temperature of the medium is increased. This plateau corresponds to a totally thermalized hot core, the disappearance of which depends on diffusional effects and bulk gas cooling. The low vibrational levels probed by the higher energy R12 pulse are depleted by increasing the temperature, leading to a decrease in dissociation yield. In contrast, the population of the higher vibrational levels, probed by the redshifted frequency pulse (P30) is increased, producing a positive value of the plateau with respect to the base line.

Although the dissociation yield is not linearly proportional to the absorption cross section probed by the dissociating pulse, Figure 7 shows qualitatively the red shift of the "hot"  $C_4F_8$  spectrum. Note that at high pressure (5 torr) the dissociation spectrum is fairly flat regardless of the interpulse delay, provided that the moving pulse arrives after the fixed one (R10). Within the frequency range of the probing pulse it is not possible to define a maximum in this spectrum. On the other hand, the dissociation spectra obtained at 0.5 torr are more dependent on the interpulse delay. The dissociation spectrum 1  $\mu$ s after the time coincidence of the two pulses shows a peak with a red shift of about 20  $cm^{-1}$ . At 0.5 torr and with such short time delays, both transport effects and V-T relaxation can be neglected. This leads us to ascribe the red shift of the spectrum to a distribution of vibrational levels corresponding to a metastable multiple temperature distribution.<sup>42-44</sup> For longer interpulse delays the perturbing effects of transport phenomena are not negligible and the interpretation of dissociation spectra becomes difficult. The decrease of the dissociation yield when the pressure is increased is explained by the relaxation of the R10 excited species on the time scale of the pulse width.

#### Conclusion

The present study has demonstrated the possibility of dissociating molecules through IRMPD with the focussed beam of a Q-switched  $CO_2$  laser. A pronounced threshold behavior has been observed for the dissociation yield vs. the fluence, characteristic of a multiphoton absorption process. The results obtained in two-frequency excitation experiments indicate a very efficient collisional process for the relaxation of an ensemble of highly excited vibrational levels of the quasicontinuum. The dissociation yield variations, measured vs. the probing pulse frequency, show a red-shifted spectrum both for nonequilibrated, vibrationally excited molecules and for thermalized molecules.

The two-frequency Q-switched  $CO_2$  laser system appears to be a very powerful instrument for the study of systems which do not need high fluences, so that the laser beams may be used unfocussed in order to avoid the perturbations of transport effects. Resonant energy transfer experiments could also be readily performed with this arrangement, especially if shorter pulses are used. Acknowledgment. This research was carried out at Brookhaven National Laboratory under Contracts DE-A02-76CH00016 (E.P., R.E.W.) and DE-AC02-78ER04940 (G.W.F.) with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

#### Appendix

In order to calculate the dissociation yield occurring from the interaction of a laser pulse with excited molecules initially prepared by another laser pulse, the local density of excited molecules in space must be known at an arbitrary time after the first pulse. The dissociation yield calculation is the result of the integration over space of this local density at a specific time, convoluted with the spatial and temporal profiles of the second laser beam.

Although several pump-probe experiments of the type described here have been reported, a detailed data analysis for laser pulses with a time duration comparable to the time interval between pulses has not been described. For this reason, we consider this problem in some detail below. In the work of Stephenson and King,<sup>40a</sup> the treatment was simplified by the assumption that both pump and probe pulses were  $\delta$  functions in time. This was valid for the probe laser, with a pulse width of  $\sim 10$  ns, but the pump pulse width of  $\sim 100$  ns was comparable to the observed relaxation times of a few microseconds. In later papers<sup>40b,c</sup> the temporal dependence of the pump laser pulse is explicitly considered, but the experimental arrangement permits the probe laser pulse to be represented by a  $\delta$  function in time. In the work of Hackett et al.,<sup>22</sup> both pump and probe pulses had widths of  $\sim 80$  ns with the pulse tails of a few microseconds that are typical of CO<sub>2</sub> TEA lasers. In spite of this, they report interpulse delays as short as 200 ns, and one would expect the relaxation times in their experiments to be affected by the finite pulse width. In later work, a plasma shutter was used to reduce the laser pulse width.45

Schematically, the two-pulse excitation and dissociation experiments can be represented by the equations

$$C_4F_8 + h\nu_1 \xrightarrow{I_1(t)} C_4F_8^*$$
$$C_4F_8^* + h\nu_2 \xrightarrow{I_2(t)} 2C_2F_4$$

where  $C_4F_8^*$  is vibrationally excited  $C_4F_8$ . Defining  $P = [C_2F_4]/2$ ,  $F = [C_4F_8]$ ,  $\rho = [C_4F_8^*]$ , we obtain the equations

$$dP/dt = \sigma_2' I_2(t)\rho(t)$$

$$P(t) = \sigma_2' \int_{-\infty}^t I_2(t') \rho(t') dt'$$
(A-1)

where  $\sigma_2'$  is the cross section for absorption of an  $h\nu_2$  photon by  $C_4F_8^*$  to give *P*. For both the pump and probe pulses, the cross section is purely phenomenological, and we are ignorant of the details of the photon-molecule interaction. The yield of product is then just  $Y = 2P(\infty)$  or, defining  $\sigma_2 = 2\sigma_2'$ 

$$Y = \int_{-\infty}^{\infty} \sigma_2 I_2(t') \rho(t') dt' \qquad (A-2)$$

Since the time-dependent form of the pulse  $I_2(t)$  is known, we require only the density of vibrationally excited  $C_4F_8^*$ ,  $\rho(t)$ , to obtain the yield. Unfortunately,  $\rho$  is a function of both space and time with its distribution being affected by the shape and intensity of the two pulses  $I_1(t)$  and  $I_2(t)$ , as well as by transport processes and relaxation phenomena.

The effect of transport depends on the ratio of the mean free path to the minimum radius of the interaction region. If this ratio is small (case A) a model based on a Fick's law diffusion calculation can be used. The approach here is entirely analogous to that used by Bialkowski, et al.<sup>40b,c</sup> and by Bailey et al.<sup>41</sup> On the other hand, if the mean free path is long compared to the interaction region (case B), the problem is that of a gas expanding into a vacuum, which has been the subject of a number of

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mathematical analyses.<sup>37-40a</sup> In both cases, cylindrical symmetry, with the laser propagation direction as the axis, is assumed. Because of the small attenuation of the laser beam along the cylinder axis, the density of excited molecules along this axis is assumed to be constant, and only the radial part of the diffusion problem is needed.

Case A. The parallel with the problem treated by Bailey et al. is apparent if one replaces their  $1/a^2$  (thermal diffusivity) by the diffusion coefficient D, and their  $\delta T(\mathbf{r},t)$  (temperature excursion) by  $\rho(\mathbf{r},t)$ , the density of excited molecules as a function of distance from the cell axis and time. The molecular diffusion coefficient is given in terms of the temperature T, the mass, the collision cross section  $\pi \sigma_{coll}^2$ , and the molecular density  $\rho_0$  by

$$D = (3/8\pi^{1/2})(kT/M)^{1/2}/\sigma_{\rm coll}^2\rho_0$$
(A-3)

The value for the collision cross section was taken from the data collection of Ireton et al. $^{46}$ 

The appropriate partial differential equation for  $\rho(\mathbf{r},t)$  is

$$\frac{\partial \rho(\mathbf{r}',t')}{\partial t'} = D\nabla^2 \rho(\mathbf{r}',t') - \tau^{-1} \rho(\mathbf{r}',t') + I_1'(\mathbf{r}',t') \rho_0 - I_2'(\mathbf{r}',t') \rho = (D\nabla^2 - \tau^{-1}) \rho(\mathbf{r}',t') + I_1'(\mathbf{r}',t') \rho_0 - I_2'(\mathbf{r}',t') \rho \quad (A-4)$$

The latter two terms represent the rate of production of excited molecules by the first laser pulse and their removal by the second pulse. This equation can be readily solved if it is assumed that the last term is small compared to the other terms. The second term accounts for the relaxation of excited molecules with a lifetime of  $\tau$ . The pump laser pulse is assumed to be Gaussian in both space and time:

$$I_1'(\mathbf{r}',t')\rho_0 = \rho_0 \sigma_1 I_1(0,0) \exp[-m(r'/R)^2] \exp[-m(t'/T_p)^2]$$
(A-5)

In this expression,  $T_p$  is the temporal width at the 1/e points, R the analogous beam radius, and the factor m is introduced to allow for a nonlinear dependence of the multiphoton absorption on laser intensity. The initial molecular density of ground-state molecules (assumed to be constant) is  $\rho_0$ , and  $\sigma_1$  is the *effective* multiphoton cross section.

The radial part of the Green's function for  $\rho(r,t)$  is

$$G(\mathbf{r},t|\mathbf{r}',t') = [4\pi D(t-t')]^{-1} \exp\left[-\frac{(\mathbf{r}-\mathbf{r}')^2}{4D(t-t')}\right] \exp[-(t-t')/\tau] \quad (A-6)$$

giving

$$\rho(\mathbf{r},t) = \int_{-\infty}^{t} dt' \int_{0}^{\infty} r' dr' \int_{0}^{2\pi} d\phi' G(\mathbf{r},t) \mathbf{r}',t') I_{1}'(\mathbf{r}',t') \rho_{0} = \int_{-\infty}^{t} \exp[-(t-t')/\tau] dt' \int_{0}^{\infty} r' dr' \int_{0}^{2\pi} d\phi' [4\pi D(t-t')]^{-1} \exp\left[-\frac{(\mathbf{r}-\mathbf{r}')^{2}}{4D(t-t')}\right] I_{1}'(\mathbf{r}',t') \rho_{0} \quad (A-7)$$

An implicit assumption in the above expression is that the effective radius of the sample cell is so large compared to that of the interaction region (R) that an upper limit of  $r = \infty$  can be used.

The angle  $\phi'$  is defined so that

$$(\mathbf{r} - \mathbf{r}')^2 = r^2 + r'^2 - 2rr' \cos \phi'$$

giving

$$I_{1}(0,0)\rho_{0}\sigma_{1} \exp[-m(r'/R)^{2}] \exp[-(\mathbf{r} - \mathbf{r}')^{2}/4D(t - t')] = I_{1}(0,0)\rho_{0}\sigma_{1} \exp[-r^{2}/4D(t - t')] \exp\{-[(m/R^{2}) + 1/4D(t - t')]r'^{2}\} \exp[rr'\cos\phi'/2D(t - t')]$$
(A-8)

Then

$$\rho(r,t) = I_1(0,0)\rho_0\sigma_1 \int_{-\infty}^{t} [dt'/4\pi D(t-t')] \exp[-m(t'/T_p)^2] \times \exp[-(t-t')/\tau] \exp[-r^2/4D(t-t')] \int_{0}^{\infty} r' dr' \exp[-[(m/R^2) + 1/4D(t-t')]r^2] \int_{0}^{2\pi} \exp[rr'\cos\phi'/2D(t-t')] d\phi'$$
(A-9)

The integral over  $\phi'$  can be evaluated by use of

$$J_0(ix) = (1/\pi) \int_0^{\pi} \exp(\pm x \cos \alpha) \, \mathrm{d}\alpha \qquad (A-10)$$

to become

$$2\pi J_0[irr'/2D(t-t')]$$
 (A-11)

where  $J_0$  is the zero-order Bessel function of the first kind.

The integration over r' can be carried out by use of Weber's first exponential integral<sup>47</sup>

$$\int_0^{\infty} J_0(\gamma x) \exp(-p^2 x^2) x \, dx = (1/2p^2) \exp(-\gamma^2/4p^2) \quad (A-12)$$

where  $\gamma = ri/2D(t - t'), p^2 = mR^{-2} + [4D(t - t')]^{-1}$ .

Combining this with the result from the integration over  $\phi'$ , we obtain the last two integrals of eq A-9

$$\frac{\pi}{\frac{m}{R^2} + \frac{1}{4D(t-t')}} \exp\left\{\frac{\frac{r^2/4D^2(t-t')^2}{4\left[\frac{m}{R_2} + \frac{1}{4D(t-t')}\right]}\right\}$$
(A-13)

This combines with the other factors of eq A-9 to give the final result for the density of excited molecules:

$$\rho(r,t) = I_1(0,0)\rho_0\sigma_1 \int_{-\infty}^{t} dt' \exp[-m(t'/T_p)^2] \exp[-(t-t')/\tau] \frac{R^2}{R_2 + 4mD(t-t')} \exp\left[-\frac{mr^2}{R^2 + 4Dm(t-t')}\right]$$
(A-14)

Next we introduce the second laser pulse, which has the same temporal and spatial properties as the first laser pulse, but is centered at a time  $\Delta t$  after the initial pulse.

$$I_{2}'(r,t) = I_{2}(0,0)\sigma_{2} \exp[-n(t - \Delta t)^{2}/T_{p}^{2}] \exp[-nr^{2}/R^{2}]$$
(A-15)

The yield of product molecules is then given by

$$Y(\Delta t) = I_2(0,0)\sigma_2 \int_{-\infty}^{\infty} dt \exp[-n(t - \Delta t)^2 / T_p^2] 2\pi L \int_{0}^{\infty} \rho(r,t) \exp(-nr^2 / R^2) dR$$
(A-16)

In this expression,  $I_2(0,0)$ ,  $\sigma_2$ , and *n* are analogous to  $I_1(0,0)$ ,  $\sigma_1$ , and *m* in eq A-5; also, *L* is the cell length. Introducing the previously obtained expression for  $\rho(r,t)$ , we have  $Y(\Delta t) =$ 

$$2\pi L I_{1}(0,0) I_{2}(0,0) \sigma_{1} \sigma_{2} \rho_{0} \int_{-\infty}^{\infty} dt \exp[-n(t-\Delta t)^{2}/T_{p}^{2}] \times \int_{-\infty}^{t} \frac{dt' \exp[-m(t'/T_{p})^{2}] \exp[-(t-t')/\tau]}{R^{2} + 4mD(t-t')} R_{2} \times \int_{0}^{\infty} r \, dr \exp\left\{-r^{2}\left[\frac{m}{R^{2} + 4Dm(t-t')} + \frac{n}{R^{2}}\right]\right\}$$
(A-17)  
$$Y(\Delta t) = 2\pi I_{1}(0,0) I_{2}(0,0) \sigma_{1} \sigma_{2} \rho_{0} R^{2} L \int_{-\infty}^{\infty} dt \exp[-n(t-\Delta t)^{2}/T_{p}^{2}] \int_{0}^{t} dt' \exp[-(t-\Delta t)^{2}/T_{p}^{2}/T_{p}^{2}] \int_{0}^{t} dt' \exp[-(t-\Delta t)^{2}/T_{p}^{2}/T_{p}^{2}] \int_{0}^{t} dt' \exp[-(t-\Delta t)^{2}/T_{p}^{2}$$

$$\frac{L^{\prime}}{t^{\prime}} / \tau ] \exp[-m(t^{\prime}/Tp)^{2}] \frac{R^{2}}{2[(m+n)R^{2} + 4Dmn(t-t^{\prime})]}$$
(A-18)

<sup>(46)</sup> Ireton, R. C.; Ko, A.-N.; Rabinovitch, B. S. J. Phys. Chem. 1974, 78, 1984.

<sup>(47)</sup> Abramowitz, M.; Stegun, I. A. "Handbook of Mathematical Functions"; Dover: New York, 1965; eq 11.4.29.

In practice, we determine the *increase* in yield above B, the base line yield measured when the two pulses are widely separated, and diffusion can be neglected (high-pressure limit). The constants before the integrals in eq A-18 are not known from experiment and are taken into account by replacing the relaxation term  $\exp[-(t)]$  $(-t')/\tau$  with  $B + A \exp[-(t-t')/\tau]$ .

In the absence of transport or relaxation (i.e., D = 0 and  $\tau =$  $\infty$ ), the integral over t' can be evaluated exactly in terms of the error function, with the result

$$Y(\Delta t) = 2\pi [I_1(0,0)I_2(0,0)\sigma_1\sigma_2\rho_0 R^2 L(A + B)T_p(\pi/m)^{1/2}/4(m+n)] \int_{-\infty}^{\infty} dt \exp[-n(t - \Delta t)^2/T_p^2][1 + \operatorname{erf} (m^{1/2}t/T_p)]$$
(A-19)

Case B. When the mean free path is long compared to the radius of the irradiated region, i.e., at low pressures, the diffusion

$$c = (2kT/M)^{1/2}$$

The final expression is

$$Y(\Delta t) = \text{constant} \times \int_{0}^{\infty} dt \exp[-n(t - \Delta t)^{2}/T_{p}^{2}] \int_{0}^{t} dt' [A \exp[-(t - t)^{2}/T_{p}^{2}] \frac{R^{2}}{2[(m + n)R^{2} + c^{2}mn(t - t)^{2}]} (A-20)$$

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## $\beta$ -Cyclodextrin Inclusion Complexes with $\alpha$ -Diimineruthenium(II) Photosensitizers

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Binding interactions of ruthenium(II)  $\alpha$ -dimine photosensitizers with  $\beta$ -cyclodextrin (CD) were studied in aqueous solution by using an excited-state lifetime method. Only complexes possessing phenyl-substituted ligands exhibited significant interaction with CD. Binding occurred via inclusion of the phenyl group in the CD cavity. Multiple binding was observed in deaerated solution for those complexes containing more than one phenyl substitutent. Lifetime vs. CD concentration titrations were successfully described by a simple model. Binding of CD to the Ru(II) complexes shields the complexes from the oxygen quenching. Shielding increases as the number of bound CD's increases. Solvent exposure parameters are shown to provide information on both solvent accessibility and sensitizer-CD interactions in the inclusion complex.

#### Introduction

A large number of organic molecular systems have been studied as a means to generate microheterogeneous aqueous solutions. In particular, there has been an enormous amount of work concerning the binding, phase transfer, and catalytic activity of cyclodextrins.<sup>1</sup> There has also been an increasing amount of interest in the photochemistry and photophysics of organic compounds and their interactions with cyclodextrins.<sup>2-8</sup> However, there have been no studies to date concerning the interactions of cyclodextrins with transition-metal complexes.

Ruthenium(II) complexes have long been used as model systems for electron transfer reactions, catalysis, and solar energy conversion.<sup>9-11</sup> Success in these applications requires an intimate understanding of the environment of the complex. We have previously studied the interactions of several  $RuL_3^{2+}$  (L is substituted 2,2'-bipyridine or 1,10-phenanthroline) sensitizers with micellar systems.<sup>12-18</sup> We report here the extension of our studies to include the interaction of  $\alpha$ -dimineruthenium(II) complexes with  $\beta$ -cyclodextrin (CD).

## **Experimental Section**

The ligands and our abbreviations are as follows: 1,10phenanthroline (phen), 5-methyl-1,10-phenanthroline (Mephen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me<sub>2</sub>phen), 5,6-dimethyl-1,10-phenanthroline (5,6-Me2phen), 3,4,7,8-tetramethyl-1,10phenanthroline (Me<sub>4</sub>phen), disulfonated 4,7-diphenyl-1,10phenanthroline ((PhSO<sub>3</sub><sup>-</sup>)<sub>2</sub>phen), 4,7-diphenyl-1,10-phenanthroline (Ph<sub>2</sub>phen), and 5-phenyl-1,10-phenanthroline (Phphen). The complexes were synthesized as described elsewhere.<sup>12</sup>

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