

without correction for beam inhomogeneity; that is, to the same level of approximation as in Figure 4.

Three observations are worth making. (1) In the quantitative interpretation of data, beam inhomogeneity needs to be taken into account, especially at low dosages. (2) The empirical eq 17 is not an exact relationship, because neither of the curves in Figure 5A is a horizontal straight line. According to the dashed curve, the parameter  $A$  in (17) varies by a factor of  $\sim 2$  while  $\exp(-v_{\text{act}}/v_{\text{abs}})$  varies by a factor of  $\sim 3000$ . (3) All relationships shown in Figure 5 increase up to  $v_{\text{act}} \sim 5$  and appear to become constant when  $v_{\text{act}} > 5$ .<sup>18</sup> This feature is shown most clearly by the solid curve in Figure 5B, which is based on the exact harmonic oscillator, eq 20. The maximum value of  $f/x_{\text{act}}$  is about 5, which means that the amount of laser-induced reaction is greater than the fraction of activated molecules predicted by the simple harmonic oscillator model.

## References and Notes

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- (18) Because  $f/x_{\text{act}}$  approaches unity in the limit as  $v_{\text{act}}$  becomes large, the crosses in Figure 5 represent the function  $\ln(1-f)/\ln(1-x_{\text{act}})$ , which does not approach any mathematically required limit as  $v_{\text{act}}$  becomes large.  $\ln(1-f)/\ln(1-x_{\text{act}})$  practically reduces to  $f/x_{\text{act}}$  except in the three experiments in which  $v_{\text{act}} > 6$ . The use of  $\ln(1-f) = -\ln(c_0/c)$  in place of  $f$  seems logical for expressing amount of reaction in an inquiry which probes the chemical kinetics.

# Megawatt Infrared Laser Chemistry of $\text{CCl}_2\text{F}_2$ Derived from the Excitation of Two Distinct Vibrational Modes<sup>1</sup>

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**Abstract:**  $\text{CCl}_2\text{F}_2$  was pulse irradiated at  $921\text{ cm}^{-1}$ , where a  $\text{CCl}_2$  stretching mode is excited, and at  $1088\text{ cm}^{-1}$ , where a  $\text{CF}_2$  stretching mode is excited. Laser-induced reactions at the two frequencies are practically identical, both qualitatively and quantitatively. Major reaction products are  $\text{ClF}_2\text{CCClF}_2$  and  $\text{CClF}_3$  and account for  $\sim 83\%$  of decomposition. Minor products formed initially are  $\text{ClF}_2\text{CCCl}_2\text{F}$  and  $\text{CCl}_3\text{F}$ ; there was no evidence for  $\text{C}_2\text{F}_4$ . A reaction mechanism involving primary C-Cl bond scission is indicated. Conversion of  $\text{CCl}_2\text{F}_2$  per flash ( $f$ ) was as high as 13%; radiant energy absorbed ( $E_{\text{abs}}$ ) was as high as 107 kJ/mol. The plot of  $\ln f$  vs.  $E_{\text{abs}}^{-1}$  is linear with a slope of  $-419\text{ kJ/mol}$ , which is in good agreement with  $-E_{\text{act}}$  for thermal decomposition of  $\text{CCl}_2\text{F}_2$ . When  $\text{CCl}_2\text{F}_2$  is excited at  $921\text{ cm}^{-1}$  in the presence of  $\text{CBr}_2\text{F}_2$  (which does not absorb at  $921\text{ cm}^{-1}$ ), the absence of organic bromochlorides from the reaction products suggests that reaction takes place in two stages:  $\text{CCl}_2\text{F}_2$  decomposes very quickly after excitation from a nonequilibrium molecular energy distribution, while  $\text{CBr}_2\text{F}_2$  reacts thermally after V-T/R relaxation of the absorbed energy.

One of the hopes of infrared laser chemists is that excitation of different vibrational modes will lead to specifically different reactions. A good substrate with which to test this concept is  $\text{CCl}_2\text{F}_2$ , for which the following evidence leads to the expectation of two competing reaction channels: The laser-induced decomposition of the trifluoro analogue,  $\text{CClF}_3$ , involves a free-radical mechanism, while that of  $\text{CCl}_3\text{F}$  involves a carbene mechanism.<sup>2</sup> The corresponding primary processes for  $\text{CCl}_2\text{F}_2$  are<sup>3</sup>



Reactions 1 and 2 are readily distinguished by the nature of the overall reaction products. In the case of (1) one would expect to find  $\text{ClF}_2\text{CCClF}_2$  and other free-radical products, such as  $\text{CClF}_3$ , while in the case of (2) one would expect to find  $\text{C}_2\text{F}_4$ .

$\text{CCl}_2\text{F}_2$  has two strong absorption bands in the  $\text{CO}_2$  laser's tunable range.<sup>4,5</sup> The band centered at  $923\text{ cm}^{-1}$ , of  $b_2$  symmetry, is formally an antisymmetric  $\text{CCl}_2$  stretching mode; the band centered at  $1098\text{ cm}^{-1}$ , of  $a_1$  symmetry, is formally a symmetric  $\text{CF}_2$  stretching mode. Ngai and Mann<sup>5</sup> describe the dominant normal-coordinate displacements as follows: For the  $923\text{-cm}^{-1}$  band, C-Cl stretching, 50%; FCCl bending, 26%. For the  $1098\text{-cm}^{-1}$  band, C-F stretching, 59%; C-Cl stretching, 13%.

The thermal decomposition of  $\text{CCl}_2\text{F}_2$  has been studied at 1 atm between 700 and 900 K.<sup>6</sup> The products are those characteristic of a free-radical mechanism initiated by reaction 1:  $\text{CClF}_3$ ,  $\text{CCl}_3\text{F}$ , and the products of their decomposition.  $\text{ClF}_2\text{CCClF}_2$  is unstable under these conditions. There is also an unidentified white powder formed.

The ultraviolet photolysis of  $\text{CCl}_2\text{F}_2$ <sup>7,8</sup> produces decomposition by both mechanisms 1 and 2. Rebert and Ausloos<sup>7</sup> find that at 213.9 nm, about 91% of the decomposition occurs

via (1). However, as the wavelength of irradiation decreases to 147.0 nm, more than 80% of the decomposition occurs via (2).

Decomposition of  $\text{CCl}_2\text{F}_2$  following excitation of the  $\text{CCl}_2$  stretching mode with a  $\text{CO}_2$  laser has been examined under both continuous wave<sup>9,10</sup> and pulsed<sup>11-13</sup> conditions. Continuous wave irradiation results in the formation of free-radical products. Prolonged pulse irradiation, under some conditions, results in the formation of some  $\text{C}_2\text{F}_4$ .<sup>11,12</sup>

In the present paper we report on the infrared laser chemistry of  $\text{CCl}_2\text{F}_2$  at both  $921\text{ cm}^{-1}$ , where the  $\text{CCl}_2$  stretching mode is excited, and at  $1088\text{ cm}^{-1}$ , where the  $\text{CF}_2$  stretching mode is excited. Attention will be paid to the nature of reaction products, reaction and excitation mechanism, and the amount of reaction as a function of the amount of absorbed energy. Mathematical symbols will conform to previous definitions.<sup>14</sup>

## Experimental Section<sup>15</sup>

**Materials.** Gases were purchased from Matheson Gas Products or PCR Inc. All were of the highest purity available. All reactant gases were checked for purity by infrared and gas-liquid chromatographic (GLC) analysis, and were purified by distillations if necessary. All gases were handled and outgassed by standard vacuum-line techniques.

**Reaction Cells.** Most of the experiments were done in 3-cm glass cells with KCl windows. The inner cross-sectional area was  $3.8\text{ cm}^2$ , as compared with a beam size of  $2.30\text{--}2.44\text{ cm}^2$ . Experiments using the disk calorimeter were done with special cells, with  $0.014\text{ cm}^3$  dead volume, described elsewhere.<sup>14</sup>

**Laser.** The laser system has been described in a previous paper.<sup>14</sup> Because the laser output at  $921\text{ cm}^{-1}$  is relatively weak, the beam was concentrated at both frequencies from  $5.8$  to  $\sim 2.3\text{ cm}^2$  by means of a converging lens, and then made approximately parallel by means of a diverging lens. The beam homogeneity, as measured by the fractional standard deviation  $\sigma_D$ , was about 13% at  $1088\text{ cm}^{-1}$  and 62% at  $921\text{ cm}^{-1}$ . The high standard deviation at  $921\text{ cm}^{-1}$  was unavoidable because the laser beam was rectangular (long and thin rather than round). The effective pulse duration was  $\sim 270\text{ ns}$ .

**Dosimetry.** The accuracy of the dose measurements was improved progressively during a 2-year period. All quantitative measurements reported in this paper were made by a split-beam monitoring system, as described in Figure 2 of the previous paper.<sup>14</sup> Meter M1 was always a pyroelectric detector. Meter M2 was either pyroelectric or a disk calorimeter. The sensitivity of the pyroelectric detectors was found to vary with incident energy ( $J$ ) and was not uniform over the absorbing surface. When the relative positions of beam and detector were kept constant, the sensitivity  $V/J$  (where  $V$  = pyroelectric peak voltage) was represented adequately by

$$V/J = S_0/(1 + 0.178V) \quad (3)$$

Values of  $S_0$  were found to be 1.63 and  $1.54\text{ V/J}$ , respectively, for two detectors. The short-term precision of the pyroelectric measurements is about 2%. However, over longer periods we noted puzzling changes of 2-10% at the higher doses. We therefore repeated the measurements for neat  $\text{CCl}_2\text{F}_2$  with a disk calorimeter, whose sensitivity is accurate, being determined by direct electrical calibration in each experiment.<sup>14</sup> The two sets of measurement were quantitatively consistent.

**GLC Analysis.** A Varian Model 1700 instrument, equipped with a 1-mm Porapak Q column and a thermal conductivity detector, was used. Gas samples were introduced directly from the reaction cell through a Varian six-port valve.<sup>15</sup> The detector signal was recorded and processed digitally by a Spectraphysics Autolab System I computing integrator. It was possible to resolve and determine, in the presence of largely unreacted  $\text{CCl}_2\text{F}_2$ , the following compounds with the following accuracies: the major products  $\text{CClF}_3$  and *sym*- $\text{C}_2\text{Cl}_2\text{F}_4$ , 20%; the minor products  $\text{CCl}_3\text{F}$ ,  $\text{Cl}_2\text{FCCF}_2\text{Cl}$ , and a *cis-trans* mixture of  $\text{ClFC=CClF}$  (the two isomers are not resolved), within a factor of 2.

**Infrared Analysis.** A Perkin-Elmer Model 567 instrument was used. Spectra were taken directly on the reaction cells before and after laser irradiation and were recorded in different colors on a single chart, with

careful attention being paid to equalizing the baselines and sensitivities. The infrared measurements were to monitor the disappearance of  $\text{CCl}_2\text{F}_2$ , to confirm the GLC measurements for the amounts of the major products, and to confirm the absence of certain possible reaction products. For quantitative analysis, optical densities (OD) were measured at  $1213\text{ cm}^{-1}$  (the position of a  $\text{CClF}_3$  peak),  $1156\text{ cm}^{-1}$  (a peak of  $\text{CCl}_2\text{F}_2$ ), and  $1048$  and  $845\text{ cm}^{-1}$  (peaks of  $\text{C}_2\text{Cl}_2\text{F}_4$ ). The actual equations were:

$$\begin{aligned} 1213\text{ cm}^{-1} & \quad L^{-1}(\text{OD}) = 0.0661y + 0.0010z \\ 1156\text{ cm}^{-1} & \quad L^{-1}(\text{OD}) = 0.01510x + 0.0002y + 0.0002z \\ 1048 + 845\text{ cm}^{-1} & \quad L^{-1}\sum(\text{OD}) = 0.0004x + 0.0004y + 0.0305z \end{aligned}$$

where  $L$  is the optical path length (in cm),  $x = \Delta P_{\text{CCl}_2\text{F}_2}$ ,  $y = P_{\text{CClF}_3}$ , and  $z = P_{\text{C}_2\text{Cl}_2\text{F}_4}$ ; pressures are in Torr. The known minor products do not absorb significantly at precisely these wavelengths.

The infrared determination of the absence of certain possible reaction products was most important in the case of  $\text{C}_2\text{F}_4$ , whose GLC retention time is identical with that of  $\text{CClF}_3$ . Authentic samples of  $\text{C}_2\text{F}_4$  have a strong absorption band with peaks at  $1326$  and  $1339\text{ cm}^{-1}$ . Infrared spectra taken after irradiation of neat  $\text{CCl}_2\text{F}_2$  were completely free of any hint of absorption in this spectral range, where none of the other substances absorbs. We thus set an upper limit of 5% of the total product to the amount of  $\text{C}_2\text{F}_4$  formed in any experiment involving neat  $\text{CCl}_2\text{F}_2$ . As a control experiment, when IR photolysis takes place in the presence of hydrogen compounds, we have no trouble at all in detecting  $\text{C}_2\text{F}_4$ .

## Results

**Conversion per Flash.** Results obtained for 12 Torr of  $\text{CCl}_2\text{F}_2$  at  $1088$  and  $921\text{ cm}^{-1}$  are shown in Figure 1. As before,<sup>14</sup>  $f(\%)$  denotes percent of conversion of reactant, per flash, calculated on the basis of the irradiated volume rather than the total volume of  $\text{CCl}_2\text{F}_2$ .  $E_{\text{abs}}$  was measured with a disk calorimeter. The experimental points obtained at the two frequencies of irradiation fall on a single line, well within their experimental errors. Because the two frequencies were chosen so as to excite different vibrational modes, we conclude that the amount of reaction is independent of the mode of excitation, depending simply on the amount of absorbed energy per mole.

In previous work<sup>2,14</sup> it was found that plots such as those of Figure 1 are approximate straight lines with negative slopes that are very close to the activation energy  $E_{\text{act}}$  for thermal reaction of the given substance. In the present case, the data are adequately reproduced by a straight line whose negative slope is  $419 \pm 40\text{ kJ}$ . The activation energy for thermal reaction of  $\text{CCl}_2\text{F}_2$  has been reported<sup>9</sup> as  $420\text{ kJ/mol}$ , in good agreement, although the virtual identity of the two values is statistically fortuitous. The bond dissociation energy of the C-Cl bond, whose scission we believe to be the primary process, is  $350\text{ kJ/mol}$ . As before,<sup>2,14</sup> we conclude that reaction does *not* take place by a mechanism of laser-induced temperature jump followed by pyrolysis.

**Test for Nonthermal Mechanism.** To provide further proof, duplicate mixtures of 11.5 Torr of  $\text{CCl}_2\text{F}_2$  and 5.6 Torr of  $\text{SiF}_4$  were laser irradiated at two frequencies. At  $921\text{ cm}^{-1}$ , where  $\text{CCl}_2\text{F}_2$  absorbs and  $\text{SiF}_4$  is transparent,  $0.18\text{ J/cm}^2$  was absorbed per flash and 0.24% of  $\text{CCl}_2\text{F}_2$  decomposed per flash. At  $1031\text{ cm}^{-1}$ , where  $\text{SiF}_4$  absorbs and  $\text{CCl}_2\text{F}_2$  is transparent,  $0.40\text{ J/cm}^2$  was absorbed per flash but there was no detectable decomposition of  $\text{CCl}_2\text{F}_2$  ( $<0.01\%$  per flash).  $\text{SiF}_4$  was inert in both experiments. If  $\text{CCl}_2\text{F}_2$  were decomposing after the absorbed energy had become random thermal energy, the temperature jump would have been about doubled at  $1031\text{ cm}^{-1}$  and the decomposition of  $\text{CCl}_2\text{F}_2$  would have been markedly greater than at  $921\text{ cm}^{-1}$ .

**Reaction Products.** The two major reaction products from neat  $\text{CCl}_2\text{F}_2$ ,  $\text{C}_2\text{Cl}_2\text{F}_4$  and  $\text{CClF}_3$ , account for  $81 \pm 13\%$  of

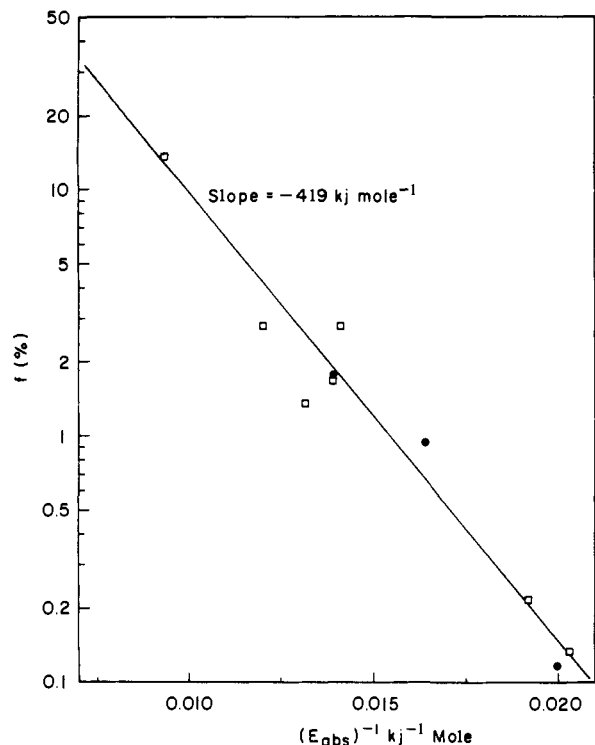


Figure 1. Infrared laser chemistry of  $\text{CCl}_2\text{F}_2$  at  $921\text{ cm}^{-1}$  (solid circles) and at  $1088\text{ cm}^{-1}$  (squares).

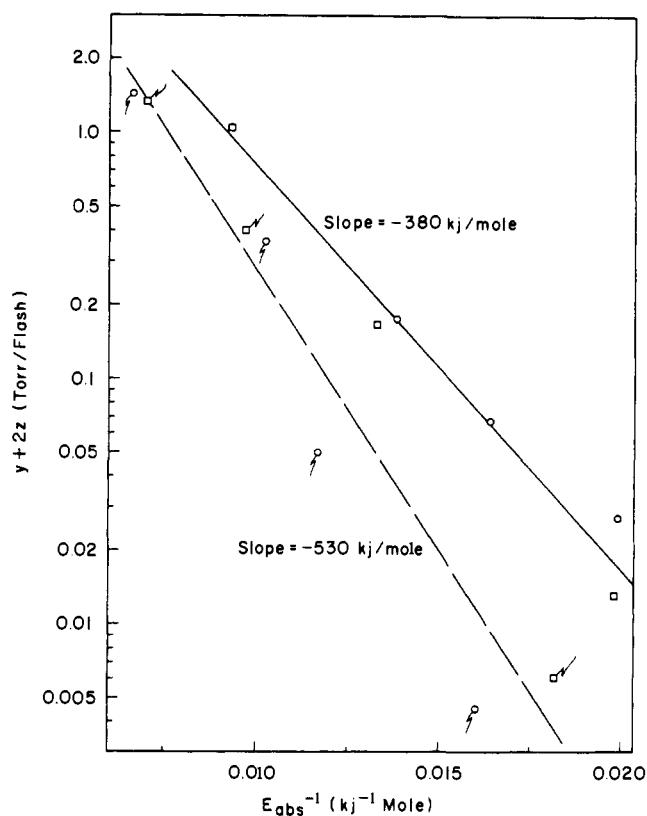


Figure 2. Total carbon of major reaction products,  $\text{C}_2\text{Cl}_2\text{F}_4$  ( $2z$ ) and  $\text{CClF}_3$  ( $y$ ) in infrared laser chemistry of  $\text{CCl}_2\text{F}_2$ : circles,  $921\text{ cm}^{-1}$ ; squares,  $1088\text{ cm}^{-1}$ . Data shown with "lightning bolts" were obtained by GLC analysis and pyroelectric energy measurement and are represented approximately by the dashed line. Other data were obtained by IR analysis and disk calorimetry.

$\text{CCl}_2\text{F}_2$  conversion, based on carbon balance. The identified minor products,  $\text{CCl}_3\text{F}$  and  $\text{C}_2\text{Cl}_3\text{F}_3$ , account at most for an additional 8%. This comprises all products we see within the

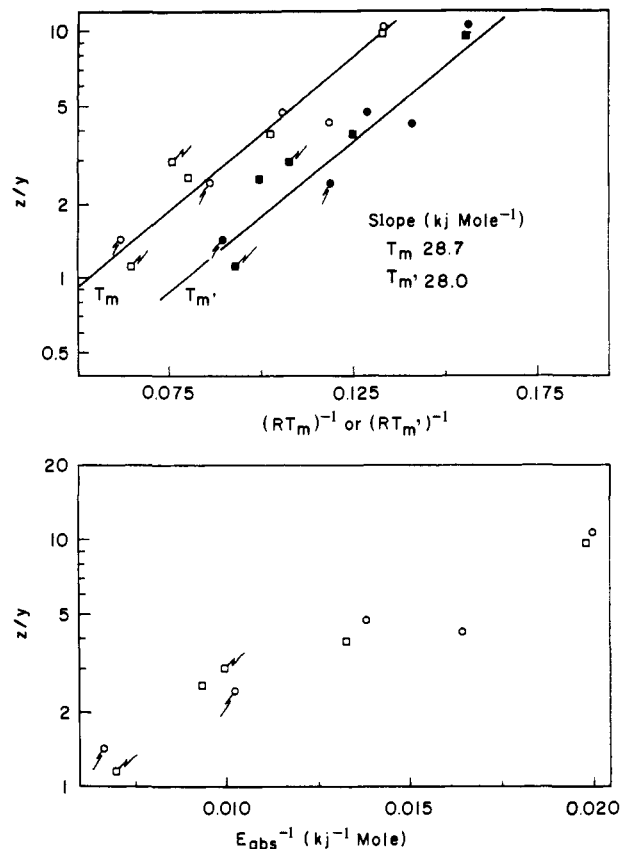
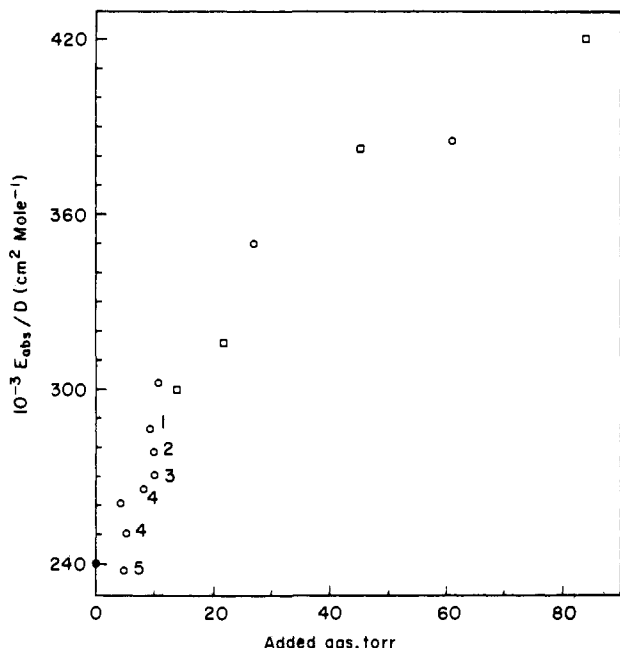


Figure 3. Ratio of major reaction products,  $z = \text{C}_2\text{Cl}_2\text{F}_4$ ,  $y = \text{CClF}_3$ . Symbols for data points are the same as in Figure 2. In the upper figure, data points as a function of  $T_M'$  are shown as filled circles and filled squares.

first 10% conversion. After prolonged photolysis,<sup>15</sup>  $\text{ClFC}=\text{CClF}$  isomers are identified, as well as an unidentified product whose relatively long GLC retention time suggests a molecular weight greater than 150. It is clear from the above that a small ( $\sim 10$ ) percent of reaction goes to products that have not been identified. However,  $\text{C}_2\text{F}_4$ , which one might expect to find according to a carbene mechanism (eq 2), accounts at most for half of this residue.

Within the accuracy of our data, there are no differences in either the nature or the relative amounts of the reaction products upon changing the frequency of excitation. Figures 2 and 3 show this for the two major products;  $z$  and  $y$  denote partial pressures of  $\text{C}_2\text{Cl}_2\text{F}_4$  and  $\text{CClF}_3$ , respectively. The earlier sets of data (indicated by "lightning bolts") were obtained with pyroelectric detection, GLC analysis, and 3-cm glass cells in which the irradiated fraction  $\phi$  was  $\sim 0.63$ . The later set of data was obtained with the disk calorimeter, infrared analysis, and a 2.6-cm Olszyna cell<sup>14</sup> in which  $\phi$  was  $\sim 0.76$ . As can be seen in Figure 2, there is a systematic difference between the two data sets. However, within each set, the results obtained at  $921\text{ cm}^{-1}$  mesh well with those obtained at  $1088\text{ cm}^{-1}$ . We do not know at this time whether a systematic difference is due to the difference in detection and analysis, or whether it is a real effect caused by the difference in  $\phi$  and cell length. After the rapid primary decomposition step, probably according to (1), the subsequent product-forming reaction steps, at the pressures and temperatures likely to prevail, may be expected to have half-lives of at least microseconds, and probably tens of microseconds. On this time scale, the mixing of laser-heated gas with surrounding unirradiated gas must be significant, and therefore the product-forming reactions probably take place at a lower effective temperature in the 3-cm cell.



**Figure 4.** Photophysics of  $\text{CCl}_2\text{F}_2$  in the presence of added gases: unlabeled circles,  $\text{SiF}_4$ ; unlabeled squares,  $\text{N}_2$ . Other data points are as follows: 1,  $\text{CH}_4$ ; 2,  $\text{CF}_2\text{Br}_2$ ; 3,  $\text{CF}_2\text{Cl}_2$ ; 4,  $\text{O}_2$ ; 5,  $\text{NO}$ .

Figure 3 shows plots of the product ratio  $z/y$  vs.  $E_{\text{abs}}^{-1}$  as well as  $(RT_m)^{-1}$  and  $(RT_m')^{-1}$ .  $T_m$  is the temperature reached when  $E_{\text{abs}}$  adiabatically becomes random thermal energy;  $T_m'$  is the analogous temperature when the T-jump is accompanied by perfect mixing of irradiated with unirradiated gas in the cell. It is clear that  $z/y$  increases with decreasing amount of absorbed energy, indicating that the two product-forming reactions differ in activation energy. We believe (see Discussion) that both products are formed in bimolecular reactions of  $\text{CClF}_2$  radicals. Thus the slopes of the semilogarithmic plots vs.  $(RT_m)^{-1}$  or  $(RT_m')^{-1}$  indicate a probable value for the difference in activation energy of  $\sim 28$  kJ/mol. The plot vs.  $E_{\text{abs}}^{-1}$  is included because it shows more clearly how well the product ratios obtained on excitation of the two different vibrational modes agree. The product ratios should be relatively unaffected by systematic errors.

**Photophysics.** Within the experimental error,  $E_{\text{abs}}$  for neat  $\text{CCl}_2\text{F}_2$  at 12 Torr was proportional to the average dose  $\bar{D}$  in the cell, both at  $921\text{ cm}^{-1}$  and at  $1088\text{ cm}^{-1}$ .  $E_{\text{abs}}$  varied from 40 to 150 kJ/mol. Average values obtained for  $10^{-3}E_{\text{abs}}/\bar{D}$  (in  $\text{cm}^2\text{ mol}^{-1}$ ) at  $921\text{ cm}^{-1}$  were  $241 \pm 12$  by disk calorimetry and  $244 \pm 21$  by pyroelectric measurement. At  $1088\text{ cm}^{-1}$ , the corresponding average was  $260 \pm 26$  by pyroelectric measurement. From the spectrophotometric optical densities we calculate that  $10^{-3}E_{\text{abs}}/\bar{D}$  for chaotic (incoherent) radiation of low intensity is  $1250\text{ cm}^2\text{ mol}^{-1}$  at  $921\text{ cm}^{-1}$  and  $500\text{ cm}^2\text{ mol}^{-1}$  at  $1088\text{ cm}^{-1}$ . Thus we observe the interesting phenomenon that even relative spectrophotometric absorption coefficients may not be applied at  $\text{MW}/\text{cm}^2$  coherent intensities without the risk of serious error.

Owing to mistuning of the laser, measurements with the disk calorimeter were made at  $1087\text{ cm}^{-1}$  rather than at  $1088\text{ cm}^{-1}$ .  $10^{-3}E_{\text{abs}}/\bar{D}$  was found to be  $216 \pm 16\text{ cm}^2\text{ mol}^{-1}$ , 17% smaller than at  $1088\text{ cm}^{-1}$ . By comparison, the spectrophotometric absorbance decreases by 10%.

**Effects of Added Gases.** A detailed summary of our numerous experiments is given elsewhere.<sup>1b</sup> We shall briefly consider some representative results, which are listed in Tables I, and II, and in Figure 4.

With the possible exception of the paramagnetic gases  $\text{NO}$  and  $\text{O}_2$ , the addition of a second gas brings on a significant

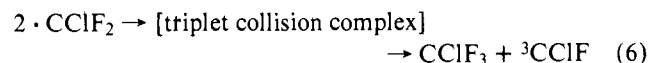
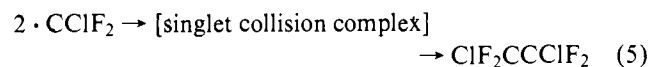
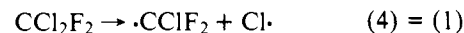
increase in the amount of energy that is absorbed (Figure 4). However, experiments involving the addition of inert gases ( $\text{N}_2$  and  $\text{SiF}_4$  in Table II) show that the effectiveness at which a given amount of excitation energy can induce chemical reaction characteristically decreases. In the presence of radical trapping agents such as  $\text{O}_2$  and  $\text{NO}$  at sufficiently low pressures, the total conversion per flash actually increases, presumably due to suppression of the reverse of reaction 1, and  $\text{CF}_2\text{O}$  appears as major product (Tables I and II). The reaction of  $\text{O}_2$  with trihalomethyl radicals, including  $\cdot\text{CClF}_2$ , is a familiar reaction and results in the formation of carbonyl dihalides.<sup>17,18</sup> Because the same product ( $\text{CF}_2\text{O}$ ) rather than an organic nitroxide is formed in the presence of  $\text{NO}$ , we inferred from the work of Modica<sup>19</sup> that the presence of  $\text{CF}_2$  as primary reaction intermediate (eq 2) can be ruled out. However, owing to recently published work by Burks and Lin,<sup>20</sup> such a conclusion is now disputable and the experiment with  $\text{NO}$  is not diagnostic of reaction mechanism.

The addition of  $\text{H}_2$  or any hydrocarbon results in the formation of  $\text{C}_2\text{F}_4$  and/or  $\text{CH}_2=\text{CF}_2$  as major product. That  $\text{CH}_2=\text{CF}_2$  can be formed by a free-radical mechanism has been shown by several authors.<sup>21,22</sup>  $\text{C}_2\text{F}_4$  could result from hydrogen abstraction,  $\text{CClF}_2\cdot + \text{RH} \rightarrow \text{HCClF}_2 + \text{R}\cdot$ , followed by thermolysis of  $\text{HCClF}_2$ <sup>23</sup> in the laser-heated gas.

The experiments with added  $\text{HCClF}_2$  and  $\text{CBr}_2\text{F}_2$  have special significance and will be taken up in the Discussion. When neat  $\text{CBr}_2\text{F}_2$  was irradiated at  $1088\text{ cm}^{-1}$  where it absorbs strongly,<sup>24</sup> the only product detected by either IR or GLC analysis was  $\text{BrF}_2\text{CCBrF}_2$ . When a 12 Torr/9 Torr mixture of  $\text{CCl}_2\text{F}_2$  and  $\text{CBr}_2\text{F}_2$  was irradiated at  $921\text{ cm}^{-1}$ , where  $\text{CCl}_2\text{F}_2$  absorbs strongly and  $\text{CBr}_2\text{F}_2$  does not, the only bromine compound detected in the product was  $\text{BrF}_2\text{CCBrF}_2$ . The amounts of  $\text{CBrClF}_2$  and  $\text{BrF}_2\text{CCCIF}_2$ , if formed at all, were below the limits of detection (about 2% of the decrease in  $\text{CCl}_2\text{F}_2$ ) by either GLC or IR.  $\text{BrF}_2\text{CCCIF}_2$  would have given a well-resolved GLC peak and practically unobscured IR absorption in the region of its very strong absorption peak at  $804\text{ cm}^{-1}$ .<sup>25</sup> The GLC peak due to  $\text{CBrClF}_2$  might have been obscured, but the very strong triple-peaked IR absorption band<sup>24</sup> at  $866, 872, 876\text{ cm}^{-1}$  should have been easily visible as a shoulder on the double-peaked  $\text{CF}_2\text{Cl}_2$  band at  $880, 887\text{ cm}^{-1}$ .

## Discussion

**Reaction Mechanism.** The two most important reaction products obtained in the IR photolysis of  $\text{CCl}_2\text{F}_2$  are  $\text{C}_2\text{Cl}_2\text{F}_4$  and  $\text{CClF}_3$ . Equations 4-6 indicate our "best estimate" of the mechanism of their formation. The reasons for choosing these reactions rather than plausible alternatives will now be explained.



To show that the primary step is (4) rather than (2), we argue as follows. (a) The reaction products of IR photolysis in the absence of added reactive gases are typical products for a free-radical mechanism. (b)  $\text{C}_2\text{F}_4$ , the most likely product of a  $\text{CF}_2$  mechanism, is not found. We believe that  $\text{C}_2\text{F}_4$  would survive under the experimental conditions because in the IR photolysis of  $\text{CCl}_3\text{F}$ , the detected products are the three  $\text{C}_2\text{Cl}_2\text{F}_2$  isomers and  $\text{Cl}_2$ ,<sup>2</sup> showing that  $\text{Cl}_2$  does not add to fully halogenated  $\text{C}=\text{C}$  double bonds in analogous molecules under similar conditions. (c) The major reaction product,  $\text{C}_2\text{Cl}_2\text{F}_4$ , which we believe to be formed by combination of

**Table I.** Megawatt Infrared Laser Chemistry of 12 Torr of CCl<sub>2</sub>F<sub>2</sub> with Added Gases at Comparable Pressures

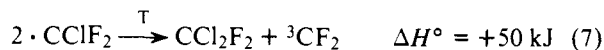
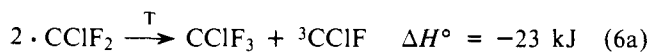
Added gas	Frequency, <sup>a</sup> cm <sup>-1</sup>	Products
None	921, 1088	C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub> > CClF <sub>3</sub> > CCl <sub>3</sub> F > C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>
O <sub>2</sub>	921	CF <sub>2</sub> O >> C <sub>2</sub> Cl <sub>3</sub> F <sub>4</sub> > CClF <sub>3</sub>
NO	921	CF <sub>2</sub> O > C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub> > CCl <sub>3</sub> F; NOCl
H <sub>2</sub>	921, 1088	C <sub>2</sub> F <sub>4</sub> >> C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub> ; HCl
CH <sub>4</sub>	921, 1088	CH <sub>2</sub> =CF <sub>2</sub> >> C <sub>2</sub> F <sub>4</sub> ; HCl
C <sub>2</sub> H <sub>4</sub>	1088	C <sub>2</sub> F <sub>4</sub> > CH <sub>2</sub> =CF <sub>2</sub> > C <sub>2</sub> H <sub>2</sub> ; HCl
HCClF <sub>2</sub>	1088	C <sub>2</sub> F <sub>4</sub> >> C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub> ; HCl
CBr <sub>2</sub> F <sub>2</sub>	921	C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub> > C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>

<sup>a</sup> Frequency of irradiation.

•CClF<sub>2</sub> radicals according to (5), could conceivably be formed by insertion of CF<sub>2</sub> into the C–Cl bond: CF<sub>2</sub> + Cl–CClF<sub>2</sub> → Cl–CF<sub>2</sub>–CClF<sub>2</sub>. To show that this reaction is unimportant, a gaseous mixture of CCl<sub>2</sub>F<sub>2</sub> and HCClF<sub>2</sub> was irradiated at 1088 cm<sup>-1</sup>, where both gases absorb similarly and strongly. The primary laser-induced reaction of the latter is HCClF<sub>2</sub> → CF<sub>2</sub> + HCl.<sup>14</sup> This reaction also takes place in the presence of CCl<sub>2</sub>F<sub>2</sub> because we found that HCClF<sub>2</sub> is partly decomposed. However, the major reaction product is C<sub>2</sub>F<sub>4</sub> rather than C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub> (Table I).

Concerning the mechanism of formation of CClF<sub>3</sub>, which is the second-most important reaction product, we thought at first that CClF<sub>3</sub> might be formed by fluorine abstraction according to •CClF<sub>2</sub> + CCl<sub>2</sub>F<sub>2</sub> → CClF<sub>3</sub> + •CClF. However, the following facts indicate that the analogous bromine and chlorine abstractions, which should be faster,<sup>16</sup> are kinetically unimportant under identical or similar conditions. (a) CBrClF<sub>2</sub> is not formed in detectable amounts when CCl<sub>2</sub>F<sub>2</sub> is photolyzed at 921 cm<sup>-1</sup> in the presence of CBr<sub>2</sub>F<sub>2</sub> at comparable pressure. (b) The remarkable efficiency of C-12/C-13 isotope separation, when CCl<sub>2</sub>F<sub>2</sub> is laser-irradiated at appropriate wavelengths,<sup>11</sup> could not have been achieved had there been rapid Cl-atom exchange between •CClF<sub>2</sub> and CCl<sub>2</sub>F<sub>2</sub>.

We chose the mechanism shown in (6) after considering whether the formation of triplet-state products, resulting from the statistically probable triplet collisions of two free radicals, is energetically feasible. According to data in the JANAF Tables,<sup>3</sup> standard enthalpies of formation Δ*H*<sub>f</sub><sup>o</sup> (in kJ/mol) are –182 for <sup>1</sup>CF<sub>2</sub>, 12 for <sup>3</sup>CF<sub>2</sub>,<sup>26</sup> 239 for <sup>1</sup>CCl<sub>2</sub>, and 285 for <sup>3</sup>CCl<sub>2</sub>.<sup>26</sup> It is clear that the triplet state of CX<sub>2</sub> is greatly stabilized, relative to the singlet state, by substitution of Cl for F. On adopting a mean value of those for <sup>3</sup>CF<sub>2</sub> and <sup>3</sup>CCl<sub>2</sub>, we obtain Δ*H*<sub>f</sub><sup>o</sup> = 148 kJ/mol for <sup>3</sup>CClF, and thus arrive at the following thermochemistry:



It appears that for triplet radical–radical reaction, C–F abstraction is exothermic while C–Cl abstraction is endothermic. If the stated mechanism (4)–(6) is correct, the difference in activation energy, *E*<sub>6</sub> – *E*<sub>5</sub>, is estimated from the upper plots in Figure 3 as ~28 kJ.

We are currently planning experiments to test the presence of <sup>3</sup>CClF and examine its eventual conversion to stable products more decisively. According to the mechanism stated in eq 4–6, the disappearance of CCl<sub>2</sub>F<sub>2</sub> (–*x*) should be related to the formation of C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub> (*z*) and CClF<sub>3</sub> (*y*) by –*x* = 2*y* + 2*z*. The experimental ratio of –2(*y* + *z*)/*x* is 0.96 ± 0.12, essentially unity.

**Excitation Mechanism.** It is clear, from the good correspondence of results obtained at 921 and at 1088 cm<sup>-1</sup>, that

**Table II.** Semiquantitative Photochemistry and Photophysics at 921 cm<sup>-1</sup> for CF<sub>2</sub>Cl<sub>2</sub> (12 Torr)

Added gas, Torr	10 <sup>-3</sup> <i>E</i> <sub>abs</sub> / <i>D</i> , <sup>a</sup> cm <sup>2</sup> mol <sup>-1</sup>	<i>E</i> <sub>abs</sub> = 90 kJ/mol <sup>b</sup> <i>f</i> / <i>f</i> <sub>0</sub>	<i>z</i> / <i>z</i> <sub>0</sub>
None	242	1.00	1.00
N <sub>2</sub> (22.1)	317	0.1	0.03
O <sub>2</sub> (5.2)	248	2.2	0.16
(7.9)	266	0.8	0.04
NO (8.4)	232	2.2	0.73
SiF <sub>4</sub> (4.8)	261	0.2 <sub>5</sub>	0.2 <sub>5</sub>
CH <sub>4</sub> (9.4)	279		
CBr <sub>2</sub> F <sub>2</sub> (9.2)	286	0.6 <sup>c</sup>	0.83 <sup>c</sup>

<sup>a</sup> Average values for 60 < *E*<sub>abs</sub> < 120 kJ/mol; typical standard deviation is ±20. <sup>b</sup> Obtained by interpolation. *E*<sub>abs</sub> measured with pyroelectric detectors; *f*/*f*<sub>0</sub> and *z*/*z*<sub>0</sub> measured by GLC; *z* = C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub>/flash. <sup>c</sup> (*quasi-E*<sub>abs</sub>)/*E*<sub>abs</sub> = 0.94<sub>5</sub> (from *f*/*f*<sub>0</sub>), 0.98<sub>5</sub> (from *z*/*z*<sub>0</sub>); average 0.97.

the laser-activated molecules at the moment of reaction retain practically no memory of the original mode of excitation. The sequence of microscopic events leading up to primary reaction is of course of interest. We shall describe an experiment whose outcome is particularly revealing.

When 12 Torr of CCl<sub>2</sub>F<sub>2</sub> is irradiated at 921 cm<sup>-1</sup> in the presence of 9 Torr of CBr<sub>2</sub>F<sub>2</sub>, energy is absorbed only by CCl<sub>2</sub>F<sub>2</sub>, yet both substances react to yield free-radical products. CCl<sub>2</sub>F<sub>2</sub> gives C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub> as major product, CBr<sub>2</sub>F<sub>2</sub> gives C<sub>2</sub>Br<sub>2</sub>F<sub>4</sub> as the only detected product, suggesting the intermediate formation of both •CClF<sub>2</sub> and •CBrF<sub>2</sub>. Yet significantly, there is no trace of the bromochloride ClF<sub>2</sub>CCBrF<sub>2</sub>, whose formation would have been surely expected had the two free-radical species been present simultaneously. Thus the reactions of CCl<sub>2</sub>F<sub>2</sub> and CBr<sub>2</sub>F<sub>2</sub> appear to be time resolved. We believe that CCl<sub>2</sub>F<sub>2</sub> (which absorbs at 921 cm<sup>-1</sup>) decomposes first, while CBr<sub>2</sub>F<sub>2</sub> decomposes later, after an appropriate lag period to allow for intermolecular energy transfer, and mostly after the temperature jump. Because of the known high rate constants for the combination of halomethyl radicals,<sup>16</sup> it is plausible to propose that the CClF<sub>2</sub> radicals will have largely decayed to stable products during the lag period, before the formation of CBrF<sub>2</sub> radicals is well underway. After the temperature jump, one would expect the thermal reaction of CBr<sub>2</sub>F<sub>2</sub> to be faster by several orders of magnitude than that of CCl<sub>2</sub>F<sub>2</sub>, because of the lower bond dissociation energy, 265 kJ/mol for C–Br vs. 350 kJ/mol for C–Cl. As far as we know, this is the first instance of *chemical* proof that the reaction of laser-activated CCl<sub>2</sub>F<sub>2</sub> molecules is photochemical rather than thermal.

Further insight is provided by the amount of reaction of CCl<sub>2</sub>F<sub>2</sub>. As shown by typical results in Table II, when *E*<sub>abs</sub> = 90 kJ/mol, conversion per flash (*f*) and amount of C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub> produced per flash (*z*) in the presence of CBr<sub>2</sub>F<sub>2</sub> are only slightly smaller than the corresponding values, *f*<sub>0</sub> and *z*<sub>0</sub>, obtained when *E*<sub>abs</sub> = 90 kJ/mol in the absence of CBr<sub>2</sub>F<sub>2</sub>. Because the magnitude of the T-jump of the laser-heated gas will be considerably smaller in the presence of CBr<sub>2</sub>F<sub>2</sub>, the near absence of any effect due to CBr<sub>2</sub>F<sub>2</sub> on *f* and *z* further confirms the previous conclusion that the primary step for CCl<sub>2</sub>F<sub>2</sub> reaction takes place *before* the T-jump is well under way. Expressed in terms of *E*<sub>abs</sub>, at 90 kJ/mol in the presence of CBr<sub>2</sub>F<sub>2</sub>, laser-activated CCl<sub>2</sub>F<sub>2</sub> decomposes essentially with the same yield and chemistry per flash as it would in the absence of CBr<sub>2</sub>F<sub>2</sub> at 87 ± 2 kJ/mol (Table II, footnote *c*).

This result becomes revealing of microscopic events when analyzed in terms of number of gas-kinetic collisions. In a gas phase consisting of 12 Torr of CCl<sub>2</sub>F<sub>2</sub> and 9 Torr of CBr<sub>2</sub>F<sub>2</sub>, the average number of collisions experienced by a CCl<sub>2</sub>F<sub>2</sub> molecule during the 270 ns effective duration of the laser pulse

is  $\sim 80$  with  $\text{CCl}_2\text{F}_2$  molecules and  $\sim 60$  with  $\text{CBr}_2\text{F}_2$  molecules. The collision number,  $Z_{10}$ , for V-T/R relaxation from the lowest excited vibrational state to the ground state of  $\text{CCl}_2\text{F}_2$  is 212 collisions,<sup>27</sup> so that the laser pulse duration is about one half-life. By comparison, the maximum percent of V-T/R energy transfer for  $\text{CCl}_2\text{F}_2$  in the actual experiment is  $3 \pm 2\%$ .<sup>28</sup> As is well known (and expressed mathematically by the Lambert-Salter rule<sup>29</sup>), collisional V-T/R energy transfer is efficient only from states of low vibrational excitation energy. Our results therefore indicate that, prior to reaction, at most a small fraction of the vibrational excitation energy resides in low-energy modes.

Even more remarkable is the evident unimportance of V-V energy transfer between  $\text{CCl}_2\text{F}_2$  and  $\text{CBr}_2\text{F}_2$ . These two molecules are as nearly alike (in structure, symmetry, and chemical type) as two distinct molecules can be, short of being isotopic variants of the same molecular species. The normal-mode frequencies for analogous vibrations range from fairly similar to near resonant.<sup>24</sup> In particular, the two C-F stretching modes of  $\text{CCl}_2\text{F}_2$  at 1101 and 1159  $\text{cm}^{-1}$  are within 20  $\text{cm}^{-1}$  of the analogous normal-mode frequencies of  $\text{CBr}_2\text{F}_2$ . The C-Cl stretching mode at 667  $\text{cm}^{-1}$  is within 50  $\text{cm}^{-1}$  of the analogous C-Br stretching mode. The torsional mode at 318  $\text{cm}^{-1}$  is within 20  $\text{cm}^{-1}$  of a bending mode of  $\text{CBr}_2\text{F}_2$ . If the excitation energy of  $\text{CCl}_2\text{F}_2$  were residing in, or exchanging rapidly into, any of these modes, one might reasonably expect<sup>30</sup> that more than a maximum of  $3 \pm 2\%$  of the energy is transferred to vibrational modes of  $\text{CBr}_2\text{F}_2$ . The fact that it does not happen indicates that the vibrational energy of  $\text{CCl}_2\text{F}_2$ , prior to reaction, remains narrowly localized.

Following earlier analysis,<sup>2,3</sup> we conclude from the agreement of the slope of Figure 1 with the experimental activation energy for thermolysis, that the laser-induced reaction takes place from a molecular energy distribution which closely resembles a Boltzmann distribution of energy in a single vibrational mode. Let us suppose that resemblance mirrors reality. Then what is the frequency of the single mode? In the present experiment the excitation frequency is 921  $\text{cm}^{-1}$ . We have seen that the energy is not likely to reside in the two higher-frequency modes of  $\text{CCl}_2\text{F}_2$ , because of the unimportance of energy transfer to  $\text{CBr}_2\text{F}_2$ . Nor is it likely to reside in several of the lower frequencies, for the same reason, and also because of the unimportance of V-T/R energy transfer. This does not leave much choice, and the simplest choice is that the energy remains localized in the original mode of excitation, perhaps because the molecules are "locked" coherently onto the laser frequency.<sup>2,31</sup>

Finally, it must be pointed out that if this explanation can be accepted, the molecules, while locked onto the laser frequency, undergo vibrational motions which are different from the kind of motion normally called translation along the reaction coordinate. However, at some time shortly after the laser pulse, the frequency lock becomes sufficiently weak that the molecules become able to escape from the forced mode of motion and, at constant energy, explore other regions of phase

space. Those molecules which possess enough energy to react will, in due course, find a reaction channel and go on to products. Judging by the Monte Carlo calculations of Bunker and Hase<sup>32</sup> for a somewhat more complex process, the isomerization of  $\text{CH}_3\text{NC}$ , the time required for finding a reaction channel is of the order of  $10^{-9}$  to  $10^{-11}$  s, starting at a random point in phase space, at energies comparable to those required for reaction here. By comparison, the mean time between successive (gas-kinetic) collisions of a  $\text{CCl}_2\text{F}_2$  molecule, under the present conditions, is  $\sim 2 \times 10^{-9}$  s. Thus, at the end of the period of forced motion, most molecules with enough energy to react will react before the next collision occurs, regardless of their mode of excitation. The model can therefore explain the observation, in the case of  $\text{CCl}_2\text{F}_2$ , that the amount of reaction depends only on  $E_{\text{abs}}$  and is independent of the mode of excitation.

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