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IR Multiphoton Dissociation Dynamics of Octafluorocyclopentene: Time-Resolved Observation of Concerted Products :CF_2 and Hexafluorobutadiene

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Real time observation of :CF_2 and hexafluorobutadiene (HFBD) generated simultaneously in the concerted IR multiphoton dissociation of octafluorocyclopentene (OFCP) is reported. The formation rate of both the transients, i.e., hot HFBD and :CF_2, which have an overlapping absorption at 250 nm, fits to a single exponential, with a rate constant $(2.0 \pm 0.1) \times 10^6\ s^{-1}$. The fast exponential decay of the transient signal up to 100 μs is assigned to electrocyclic isomerization of HFBD to hexafluorocyclobutene with a rate constant $k = (5.7 \pm 0.2) \times 10^4\ s^{-1}$, whereas the slower decay on the millisecond time scale suggests :CF_2 dimerization to form C_2F_4, with a bimolecular rate constant $(4.5 \pm 0.1) \times 10^7\ M^{-1}\ s^{-1}$. RRKM calculation for the unimolecular dissociation of OFCP and isomerization of HFBD gives an average energy of OFCP as 383 ± 10 kJ/mol and of nascent HFBD as 202 ± 5 kJ/mol, corresponding to the experimental rates. The nascent vibrationally hot HFBD exhibits a red shift of 50 nm in the transient absorption spectrum.

1. Introduction

Infrared multiple photon excitation (IRMPE) is now a general technique available for inducing unimolecular reaction under collision-free conditions. In recent papers,[1-4] a few novel routes of dissociation and isomerization from the ground electronic state have been observed in the IRMPE of polyatomic molecules. It has some advantages over thermal reaction. The time-dependent evolution of the reaction can be studied, and the energy distribution in the nascent product fragments can be evaluated.[3,5,6] There are some reports concerned with energy disposal among the fragments.[7-9] However, a limited number of studies are reported on time-resolved measurements of unimolecular reaction rates.[9-11] These studies are also important in understanding the average energy involved in the unimolecular dissociation process and the distribution of excess energy among the fragments.

The dynamics of photodissociation via electronic excitation of small molecules are studied extensively[12-16] where dissociation occurs on a time scale comparable to molecular vibrational periods (<1 ps). However, the long time required for sequential absorption of many CO_2 laser photons during the 100 ns pulse ensures that the vibrational energy acquired in the reactant is statistically distributed. In that case, the product flux is expected to be isotropic. In the IRMPD of small molecules, product formation often occurs during the laser pulse.[17] The observed time dependence is a convolution of the reaction rate and the true profile of the laser. The dissociation at moderate fluences of medium- to large-sized molecules with large activation energies, however, can be slow enough to observe product formation after the laser pulse.

We report here a time-resolved absorption spectroscopic investigation on the IR multiphoton dissociation of OFCP generating :CF_2 and hexafluorobutadiene (HFBD) as unstable primary products. Kinetics reveal their undergoing further reactions: the former dimerizes to tetrafluoroethylene, and the latter isomerizes to its thermodynamically stable isomer hexafluorocyclobutene (HFCB). RRKM calculations are made to gain insight into the energetics of the dissociation of OFCP and of the isomerization of the nascent vibrationally hot HFBD.

2. Experimental Section

A grating-tuned multimode TEA pulsed CO_2 laser (Lambda Physik EMG-201E-CO_2) was used for the irradiation of OFCP. A typical laser pulse consisted of a 100 ns spike followed by a tail of 1 μs. A schematic diagram of the experimental setup is shown in Figure 1. A specially designed stainless steel cell of 290 cm^3 volume fitted with one pair KCl windows orthogonal to the other pair quartz windows was used in the IR/UV crossed-beam configuration. Radiation from the pulsed tunable CO_2 laser was partially condensed by a 100 cm focal length BaF_2 lens to obtain a parallel beam with the required energy fluence.

The spectroscopic UV probe beam from a Xe lamp (150 W) with associated optics, monochromator ($f = 3.5$), fast photomultiplier (1P28), and signal processing system (Gould Biomation 4500) was part of a computer (LS1-11/23)-controlled kinetic spectrophotometer (Applied Photophysics, U.K.). The fast rising photon drag detector signal was used to trigger the Biomation transient digitizer. The resolution of the Biomation is 10 ns. In some of the experiments, the monitoring Xe lamp was used in pulsed mode for better illumination in the UV region, and the CO_2 laser was triggered at a preset time when the lamp intensity reaches a maximum and remains steady over a period of −200 μs. In the present experimental setup the parallel CO_2 laser beam used for irradiation and the UV-monitoring beam cross orthogonally (Figure 1). The geometry for the overlap of excitation laser beam with the monitoring beam for deriving actual optical absorption in a crossed-beam arrangement has been analyzed in detail.[18,19] Since the monitoring beam diameter is somewhat larger than the IR beam dimension in the present experiments, an overlap correction was made to evaluate the actual optical density of the transient species.

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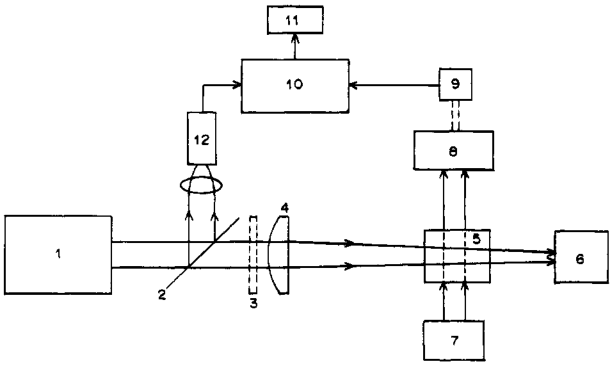

Figure 1. Schematic diagram of the experimental setup for the transient absorption studies: 1, TEA CO_2 laser; 2, beam splitter; 3, attenuator; 4, BaF_2 lens; 5, stainless steel cell; 6, energy meter; 7, xenon lamp; 8, monochromator; 9, PMT; 10, Biomation digitizer/averager; 11, *Y–T* plotter; 12, photon drag detector.

The perfluoro compounds used in this experiment, octafluorocyclopentene (C_5F_8) and hexafluorobutadiene (C_4F_6), were purchased from PCR Research Chemicals Inc. (Gainesville, FL). The purity of all the materials was checked by gas–liquid chromatography. Prior to use, all condensable materials were degassed by at least five freeze–pump–thaw cycles.

Gas phase ultraviolet spectra was taken on a Hitachi Model 330 recording spectrophotometer (Japan) with wavelength range of 185–2600 nm.

3. Results and Discussion

Infrared multiphoton absorption and dissociation (IRMPA and IRMPD) are universal phenomena[20–23] that occur upon excitation of strong IR absorption bands of molecules with intense, pulsed laser radiation. The most crucial aspect of the IRMPA as preparation technique for unimolecular reactions is knowledge of the excitation level and its control by the laser fluence. The average excitation level and its distribution function contain information on the IR-MP mechanism. The distribution function of highly excited molecules, probed by spectroscopic methods such as IR fluorescence and Raman scattering,[24] has a steeper high-energy tail and is narrower than the Boltzmann function. The high-energy distribution tail determines the characteristics of unimolecular dissociation of the ensemble of MP-excited molecules. Invariably, IRMPE gives rise to a broad, but narrower than the normal Boltzmann, vibrational state distribution of the reactant before dissociation. Thus, the range of parent energies involved in unimolecular dissociation depends on the competition between optical pumping and dissociation of the energized molecule with specific rate $k(E)$, where E is the reactant energy.

3.1. Laser-Induced Chemistry. Our earlier investigation,[2] employing IR laser frequency corresponding to the ring deformation mode of octafluorocyclopentene, has shown that the only channel opening up in the decomposition of OFCP is to generate $:CF_2$ and C_4F_6 as primary products. Both the primary products are unstable and undergo further reactions. The $:CF_2$ dimerizes to give C_2F_4. The nescent hexafluorobutadiene (HFBD), $C_4F_6^{\dagger}$, is formed with an energy above its isomerization threshold (about 148 kJ mol^{-1}) and thereby isomerizes to hexafluorocyclobutene (HFCB), the thermodynamically stable isomer. A five-center ring-opening mechanism is responsible for the primary yields. Such a process is likely to follow Woodward–Hoffmann rules for pericyclic reaction.[25] In concerted processes the simultaneous bond breaking and formation results in an exit channel barrier.[26] In the case of c-C_5F_8, the exit energy barrier may be considered as due to rearrangement of bonds as the reaction proceeds from the transition state to the products. A fraction of the exit channel energy is likely to be converted into the internal energy of the products.[26] Further, it has been observed in the IR multiphoton-induced reaction that most of the excess energy above the unimolecular dissociation threshold remains as internal energy of the products.[27] Therefore, a significant fraction of the total energy released will be partitioned in favor of internal degrees of freedom of the products, which may undergo further reactions.

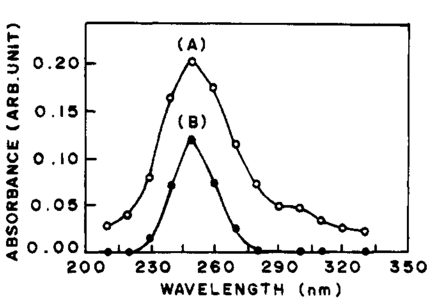

Figure 2. Transient UV absorption spectra generated in the IR multiphoton dissociation of 2 Torr of OFCP at a laser fluence of 1 J/cm^2: (A) at 5 μs after the CO_2 laser pulse (○) and (B) at 150 μs after the CO_2 laser pulse (●).

3.2. Observation of Transients in the OFCP Dissociation. On irradiation of OFCP at 982 cm^{-1}, a transient UV absorption band appears at 250 nm immediately after the CO_2 laser pulse. The transient absorption signal grows very fast and reaches its maximum OD_{max} in 5 μs. Thereafter, it decays exponentially to one-third level in 150 μs and finally vanishes in 10 ms time. The time-resolved absorption spectrum of the transient generated in the IR multiphoton excitation of 2 Torr of OFCP has been recorded from 210 to 330 nm at 5 μs after the CO_2 laser pulse with an energy fluence of 1 J/cm^2. Figure 2A exhibits the transient spectrum. Standard computer software was used to calculate the optical density (OD) values as a function of wavelength, from the time-resolved signals obtained at different monitoring wavelengths. The transient spectrum at 5 μs shows a broad absorption band around 210–330 nm with a peak at 250 nm. The time-resolved absorption spectrum was also recorded at 150 μs, which shows a narrow band around 225–280 nm (Figure 2B). When the 150 μs spectrum was subtracted from the 5 μs one, the corrected spectrum at 5 μs also shows a broad absorption band from 210 to 330 nm, with an absorption maximum at 250 nm.

3.2.1. Characterization of Hot HFBD. To characterize the species responsible for the transient absorption, a separate set of experiments was carried out by monitoring the spectra of vibrationally hot hexafluorobutadiene (HFBD) generated by irradiating neat HFBD with the CO_2 laser pulse. The experimental setup was identical to that described above, and the cell was filled with 2 Torr of HFBD. The CO_2 laser was tuned at a frequency corresponding to the absorption of HFBD, i.e., at 10R(12), and the laser energy fluence was kept at 1 J/cm^2. The transient absorption signal exhibits a fast rise, reaches a maximum within a couple of microseconds, and then decays exponentially. The time-resolved spectrum from 200 to 350 nm was recorded at 5 μs after the CO_2 laser pulse. The wavelength corresponding to the maximum absorbance was observed at 250 nm. The spectral shape is similar to the corrected transient absorption spectrum at 5 μs generated in the IRMPD of OFCP.

The ground state electronic absorption spectrum of HFBD has a strong absorption peak at 200 nm.[28] The observed 50 nm red shift from the ground state absorption maximum is apparently due to the vibrational excitation in the HFBD.

It is known that extinction coefficients depend on temperature. As a result, the shape of the absorption band with its wavelength for maximum absorbance also changes as a function of temperature in the gas phase.[29] The vibrational excitation level of HFBD can be varied by changing the CO_2 laser energy fluence for the irradiation of HFBD. By so doing, it is observed that the λ_{max} shifts toward the red, and the spectral shape broadens as a function of increasing laser fluence from 0.1 to 1 J/cm^2 for the irradiation of HFBD. However, the postirradiated IR spectrophotometric analysis reveals that the HFBD is partially isomerized to form hexafluorocyclobutene (HFCB) at laser energy fluences around 1 J/cm^2.

The above results clearly show that the new UV absorption at 250 nm obtained upon irradiation of OFCP at 982 cm^{-1} was due to HFBD. In the infrared multiphoton dissociation of polyatomic molecules, it is generally observed that the dissociation energy level is much higher than that of the threshold energy required for its dissociation. The criteria which determine such a dissociation level are on the one hand the up-pumping rate of excitation and on the other hand the internal energy-dependent rate of dissociation. At any particular laser intensity, the optical excitation rate constant decreases, as higher excitation levels are reached, because of a decrease in the absorption cross section, whereas the unimolecular dissociation rate constant rapidly increases with increase in the internal energy of the molecule. The probability of further excitation beyond a certain excitation level would be too small. In other words, a limiting multiphoton excitation level would be reached where the molecule decomposes before it can absorb the next laser photon.[30]

Nevertheless, the primary product energy distribution at the time of formation depends on the multiphoton excitation level of the reactant OFCP molecule. In an earlier study,[2] we have observed that the primary product HFBD is formed with sufficient energy so that it undergoes isomerization by overcoming an activation barrier of about 148 kJ/mol. However, subsequent collision of HFBD with argon has been shown to deenergize the HFBD molecule and prevent its isomerization to HFCB. The above consideration suggests that the primary product energy distribution in HFBD is above its threshold for undergoing isomerization to form HFCB. However, the same amount of energy acquired in HFBD may be sufficient to show a 50 nm red shift in the transient spectra.

3.2.2. Characterization of :CF_2. Figure 2B shows the transient absorption spectrum, at 150 μs after the CO_2 laser irradiation of OFCP, which has an optical absorption in the UV region with a maximum absorbance at 249 nm. The spectral features, with a long lifetime, agree with the well-known absorption spectrum[3,31-34] of :CF_2 $\tilde{A}\ ^1B_1 \leftarrow \tilde{X}\ ^1A_1$ band system at λ = 225–280 nm.

The molar extinction coefficient, ϵ, of :CF_2 is determined in the following manner. Time-resolved experiments are carried out at different laser fluences and OFCP pressures. The dissociation yield, α, is determined for each experiment:

$$\alpha = \ln\{[\mathrm{OFCP}]_0/[\mathrm{OFCP}]_n\}/n \qquad (1)$$

where $[\mathrm{OFCP}]_0$ and $[\mathrm{OFCP}]_n$ are the OFCP concentrations before and after irradiation with n pulses. In the nearly parallel beam geometry used in these experiments, the laser-induced decomposition is uniform, and the partial pressure of :CF_2 in the irradiation zone is related to α by the expression

$$[P_{:\mathrm{CF_2}}]_{\mathrm{beam}} = \alpha V_{\mathrm{cell}} P_{\mathrm{i}}/V_{\mathrm{beam}} \qquad (2)$$

where V_{beam} is the volume of the cylindrical irradiation beam geometry and P_{i} is the initial pressure of OFCP. The optical density at λ = 249 nm and 150 μs, i.e., at the completion of the fast decaying component, was determined and plotted as a function of $[P_{:\mathrm{CF_2}}]_{\mathrm{beam}}$. From the slope of such a plot, the molar extinction coefficient for the :CF_2 generated in the IRMPD of OFCP was evaluated to be ϵ = 2200 ± 100 L mol^{-1} cm^{-1}. The molar extinction coefficient of :CF_2 has been variously reported from ϵ = 2100 (ref 34) to 4600 cm^{-1} M^{-1} (ref 32) by different groups depending on the system. It is known that ϵ of :CF_2 is very much dependent on its internal energy,[31-34] and our value corresponds to an effective vibrational temperature T_v = 1130 ± 20 K for the :CF_2 formed in the IRMPD of OFCP.

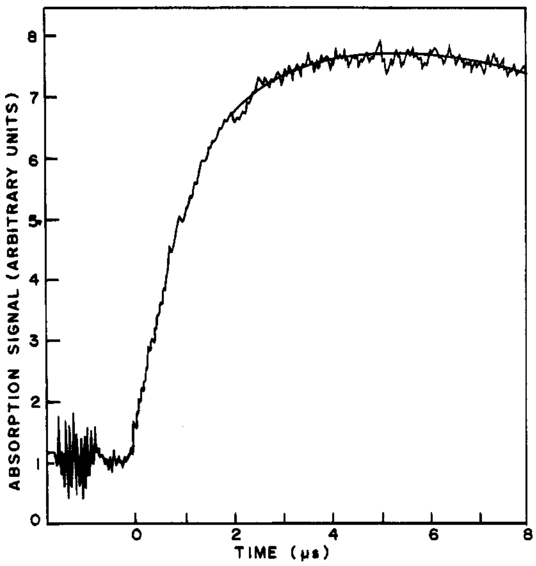

Figure 3. Growth of the optical absorption signal at 250 nm due to hot HFBD and :CF_2 generated in the IRMPD of 2 Torr of OFCP at a laser energy fluence of 1 J/cm^2.

The observed bandwidth of the transient spectrum together with the above ϵ gives the oscillator strength f = 0.03 ± 0.006, in close agreement with the reported values for :CF_2 at the 249 nm band.[33,34]

3.3. Kinetics of OFCP Decomposition. The rate of growth of optical absorption due to hot HFBD and :CF_2 can give information on the kinetics of its formation from the decomposition of the multiphoton excited OFCP,

$$[\mathrm{OD}]_t = [\mathrm{OD}]_{\mathrm{max}}[1 - \exp(-kt)] \qquad (3)$$

where k represents energy-dependent mean rate constant for the multiphoton decomposition of OFCP† under the experimental conditions. The experimental observation of the growth of the transient absorption signal due to the products is shown in Figure 3. The optical densities at various time, $[\mathrm{OD}]_t$, are calculated from the transient signal. The rate constant, $k = (2.0 \pm 0.1) \times 10^6$ s^{-1}, which has been evaluated from the slope of the plot $\ln([\mathrm{OD}]_{\mathrm{max}} - [\mathrm{OD}]_t)$ vs time, corresponds to the unimolecular dissociation of OFCP. The growth rate of the transient when monitored at various other wavelengths around 210–330 nm produced the same rate constant within experimental error. This suggests that the :CF_2 and hot HFBD transients are produced simultaneously in the IR multiphoton dissociation of OFCP, presumably via a concerted channel.

3.4. Time-Resolved Isomerization of HFBD. The initial decay of the optical absorption signal due to the transients produced in the IRMPD of 2 Torr of OFCP is shown in Figure 4. The plot of ln(signal) vs time give a straight line with a slope indicating a decay constant $k = (5.67 \pm 0.2) \times 10^4$ s^{-1}. By varying the OFCP pressure between 0.5 and 3 Torr, the

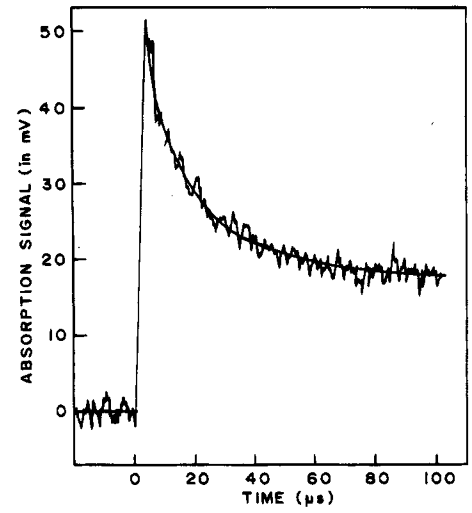

Figure 4. Exponential decay of the optical absorption signal monitored at 250 nm in the IRMPD of 2 Torr of OFCP at a laser energy fluence of 1 J/cm^2.

decay constant remained within ±10% of the above value. In the direct irradiation studies of HFBD (cf. section 3.2) similar decay was also observed. By correlating the static cell experimental results[2] obtained in the irradiation of neat OFCP, which has produced HFCB as the final product, this decay has been assigned to the electrocyclic isomerization of vibrationally hot HFBD to form HFCB. Similar studies have been reported earlier by Glat and Yogev[35] with their time-resolved infrared fluorescence technique.

At a OFCP pressure of 2 Torr, the nascent HFBD undergoes about 300 collisions with OFCP before its isomerization. It may be of interest to see whether collisions can quench the isomerization reaction, i.e., HFBD → HFCB, thereby generating stable HFBD as the final product. While the weak collider argon has been found to stabilize HFBD, strong colliders such as SF_6/OFCP still give HFCB as the final product.[2] However, at higher pressure the overall decomposition yield of OFCP has been found to be decreasing. It seems that although the dissociation rate of the parent molecule OFCP decreases at higher OFCP pressure, the HFBD isomerization rate does not decrease significantly. That is, the collisional deactivation is not in competition with the isomerization of vibrationally hot HFBD. It is likely that the irradiated volume has an elevated vibrational temperature where the collisional partners are also hot, causing collisional deactivation insignificant.

3.5. Dimerization of $:CF_2$ Radicals. The decay of the transient absorption signal in millisecond time scale is shown in Figure 5. The decay of the optical absorption signal fits to second-order kinetics, plots of (optical density)$^{-1}$ vs time being linear, with a rate constant $k_2 = (4.55 \pm 0.1) \times 10^7$ L mol^{-1} s^{-1}. This slow second-order rate constant is representative of the chemistry of the relatively unreactive $:CF_2$ which may dimerize rather than undergoing addition reactions with the small amount C_2F_4 generated in situ.[36] From the known temperature dependence of dimerization kinetics[33] of $:CF_2$

$$k_2 = 2.5 \times 10^6 T^{1/2} \exp(-200/T) \ \text{L mol}^{-1}\,\text{s}^{-1} \qquad (4)$$

we evaluate a temperature associated with the $:CF_2$ to be 630 ± 15 K during their lifetime. Considering the high system pressure and millisecond time scale of the measurement, this temperature is assigned to the overall temperature of the irradiated thermalized ensemble. The slow decay of $:CF_2$ radicals generated in our IRMPD experiments is commensurate with the suggestion[37] that the initial approach of two $:CF_2$ radicals, in their ground electronic singlet state, is repulsive.

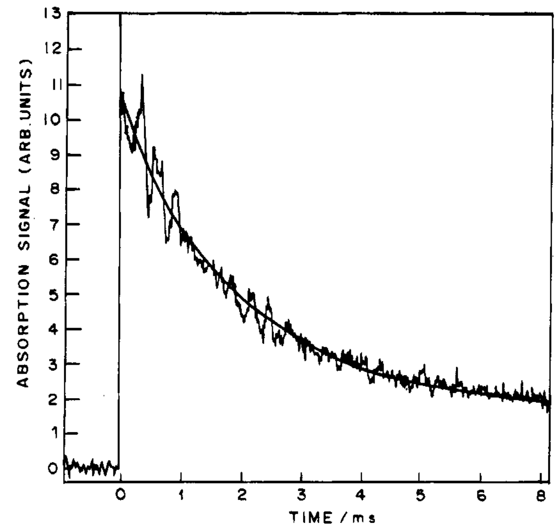

Figure 5. Decay of the optical absorption signal at 249 nm on the millisecond time scale in the IRMPD of 2 Torr of OFCP at a laser energy fluence of 1 J/cm^2.

3.6. Evaluation of Rate Constants Using RRKM Theory.[38] A RRKM calculation for the unimolecular rate of dissociation of OFCP and of isomerization of HFBD leads to an estimate of the internal energy of the OFCP and HFBD molecules.

The RRKM rate constant $k(E^*)$ is calculated by using

$$k(E^*) = -\frac{G(E^\dagger = E - E_0)}{hN(E^*)} \qquad (5)$$

where E_0 is the threshold energy for dissociation/isomerization, E^* is the excitation energy, $N(E^*)$ is the density of states for the molecule at E^*, and $G(E^\dagger)$ is the sum of states of critical configuration up to an excess energy $E^\dagger$. Sums and densities of states are calculated using Whitten–Rabinovitch formulas.[39]

A frequency factor of log A (s^{-1}) = 14.5 and an activation barrier of E_{act} = 214.5 kJ/mol have been reported for the unimolecular dissociation of 3-cyclopentenone,[40] which generates CO and 1,3-butadiene as products. As the dissociation mechanism of octafluorocyclopentene and 3-cyclopentenone has similar π-bond participation during five-centered $:C<$ elimination in their transition states, a similar frequency factor and barrier of activation may be assumed for the dissociation of OFCP.

A rigid activated complex has been assumed for the concerted CF_2 elimination from OFCP. The skeletal deformation mode at 1003 cm^{-1} has become the reaction coordinate, and other related vibrational frequencies are adjusted until agreement is reached between the A factor and the corresponding values calculated from the predicted entropy of activation.

A frequency factor of log A (s^{-1}) = 12.1 and an activation barrier of E_{act} = 148 kJ/mol have been reported for the isomerization of 1,3-hexafluorobutadiene to hexafluorocyclobutene.[41] Here also a rigid activated complex has been assumed, and a skeletal deformation mode at 295 cm^{-1} has been considered as the reaction coordinate. The frequencies taken for the activated complex and other parameters used in the RRKM calculations are given in Table 1.

The resulting k values (i.e., rate constants) as a function of the excess energy above the dissociation reaction threshold of OFCP and isomerization threshold of HFBD for their consecutive dissociation and isomerization reactions are shown in Figure 6. In correspondence with the dissociation rate of 2×10^6 s^{-1},

TABLE 1: Parameters Used in RRKM Calculations[a]

OFCP molecule (ref 50)	activated complex
1772, 1402, 1386, 1373, 1330, 1300, 1219, 1180, 1146, 1003, 985*, 889*, 697, 696, 665*, 631*, 614*, 599*, 506*, 445(2)*, 431(2), 418*, 347, 310(2), 274, 250, 234, 187, 180, 100	as for molecule except those with asterisk replaced by 700, 600, 460, 450(3), 400, 340(2), 368, and 1003 dropped to become reaction coordinate, $\log(A/s^{-1}) = 14.5$ critical energy = 214.5 kJ mol^{-1} reaction path degeneracy = 1
HFBD molecule (ref 51)	**activated complex**
1796, 1768, 1381, 1329, 1184, 1130, 968, 939, 705*, 633*, 624*, 576*, 552*, 530, 468, 418, 378, 330, 321, 295, 260*, 210*, 190*, 170	as for molecule except those with asterisk replaced by 900(3) 850, 800, 310, 280, 250, and 295 dropped to become reaction coordinate $\log(A/s^{-1}) = 12.1$ critical energy = 148 kJ/mol^{-1} reaction path degeneracy = 1

[a] Vibrational wavenumbers are in cm^{-1}.

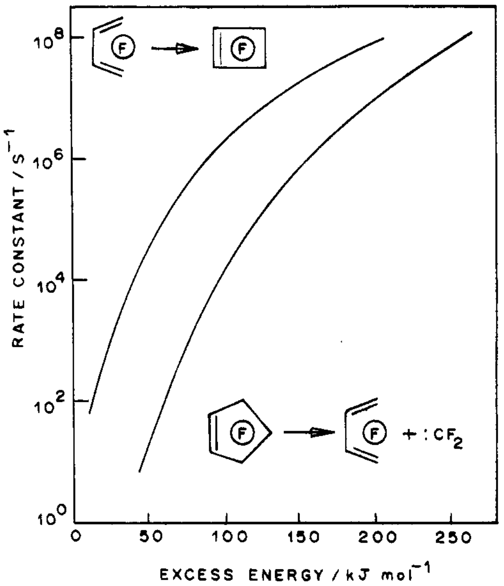

Figure 6. Plot of RRKM rate constants k/s^{-1} vs excess energy for the unimolecular dissociation of octafluorocyclopentene and isomerization of hexafluorobutadiene.

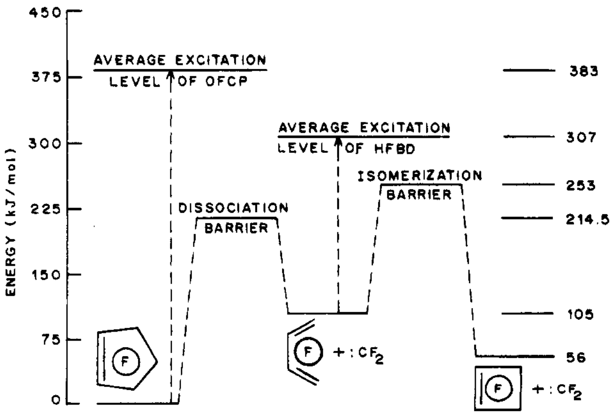

Figure 7. Energy level diagram for the consecutive dissociation of OFCP and isomerization of HFBD. The energy barrier for the dissociation and isomerization and all heats of formation are taken from refs 40 and 41 and from Benson (Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976).

one obtains a mean excitation energy of OFCP to be about 383 ± 10 kJ/mol, whereas an isomerization rate of 5.67×10^4 s^{-1} in HFBD corresponds to an average energy of 202 ± 5 kJ mol^{-1}. The relevant energetics are depicted in Figure 7.

3.7. Product Energy Distribution. In IRMPD reaction, the partitioning of the released energy in the internal and translational degrees of freedom of the products depends on the structure of the transition state and the location of its barrier to dissociation.[27,42,43] The product rovibronic energy distribution following CO_2 laser-induced dissociation has been found to be in agreement with the theoretical results considering transition state geometry.[44,45] The kinetic energy distribution is usually peaking at $E_{KE} = 0$ for simple bond rupture reactions.[27] However, a higher kinetic energy release in the products has been observed in several CO_2 laser-induced unimolecular reactions. This is observed due to significant exit channel barriers involved in the reactions. The role of exit channel barrier appears to be more prominent in concerted reactions where bond breaking and formation occur simultaneously.[2] However, in the apparently simple bond breaking reaction, i.e., IRMPD of ethyl vinyl ether,

$$CH_2CHOCH_2CH_3 \rightarrow CH_2CHO + CH_2CH_3 \qquad \Delta H_0{}^\circ = 230\ \text{kJ/mol}$$

Lee et al.[42] found a small exit barrier. This is due to the stabilization of fragments compared to the transition state, as the CO double bond formation takes place in the CH_2CHO. A similar situation is expected also in case of OFCP dissociation due to the stabilization energy for $^\bullet CF_2{-}CF{=}CF{-}CF_2{}^\bullet \rightarrow CF_2{=}CF{-}CF{=}CF_2$. As a result, significant kinetic energy release in the products is expected in the case of OFCP dissociation.

The vibrational state distributions in the products are sensitive to the location where the original bond breaks along the reaction coordinate, i.e., the position of the transition state within the reactive potential surface.[46,47] If the bonds which are to be broken are greatly extended in the transition state, significant vibrational excitation in the products may be expected. In unimolecular reaction it has been observed that most of the excess energy above the unimolecular dissociation threshold remains as internal energy of the products.[27] In the dissociation of OFCP, the $:CF_2$ and HFBD product fragments, which have available large number of low-frequency vibrational modes, will carry away most of the internal energy. The vibrational energy can be shared among the 24 vibrational modes of HFBD and three modes of $:CF_2$. If statistical partitioning of the energy is assumed,[48] the HFBD will have about 90% of the internal energy released in products. A modest 202 kJ/mol of internal energy has been acquired by HFBD, as evaluated from its RRKM rate of isomerization. Assuming statistical distribution, about 21 kJ/mol of internal energy is expected to be associated with the $:CF_2$. This is in agreement with the experimental result that the nascent HFBD is formed so highly vibrationally excited that it undergoes a prompt isomerization reaction even though it has to overcome an activation energy barrier of about 148 kJ mol^{-1}.

In the process of infrared multiphoton excitation the parent molecule absorbs many photons in rapid succession, until the energy-dependent dissociation rate becomes comparable to the optimal pumping rate. A lifetime limited excitation level which has a fairly large amount of excess energy, over and above the molecular threshold energy for dissociation, is reached by this means. For a molecule dissociating from such a highly energized level E^*, an amount $(E^* - \Delta H)$ of excess energy will be available for partitioning between the products degrees of freedom, where ΔH is the reaction enthalpy. Further, if the reaction mechanism involves concerted processes in which bonds are broken and formed simultaneously, the partitioning of energy will depend on the substantial potential energy barrier in the exit channel. The percentage of exit channel energy appearing in the product translational energy has been reported to be 30%[49] to 70%.[42] Assuming that about 50% of the exit barrier energy is partitioned in the product kinetic energy, the endothermicity of the OFCP dissociation producing $:CF_2$ and HFBD has been computed to be about $\Delta H = 105 \pm 10$ kJ mol^{-1}. This has also been included in the energy diagram of OFCP dissociation, which is shown in Figure 7.

4. Conclusions

Real time UV absorption spectroscopy has been used to study the infrared multiphoton-induced concerted dissociation of octafluorocyclopentene (OFCP) to produce hexafluorobutadiene (HFBD) and $:CF_2$ as primary products. The time-resolved growth of HFBD and $:CF_2$, which have an overlapping transient absorption spectra around 250 nm, has been assigned to the multiphoton dissociation rate of OFCP, with a rate constant $k = (2.0 \pm 0.1) \times 10^6$ s^{-1}. The initial exponential decay has been assigned to the isomerization of HFBD to form the stable cyclic isomer HFCB, with a rate constant $k = (5.7 \pm 0.2) \times 10^4$ s^{-1}, whereas the slower millisecond decay has been assigned to $:CF_2$ dimerization producing stable C_2F_4, with a rate constant $k_2 = (4.5 \pm 0.1) \times 10^7$ M^{-1} s^{-1}. Unimolecular rate constants for the decomposition of OFCP and the isomerization of HFBD are computed on the basis of RRKM modeling. An average energy associated with the dissociating OFCP and the nascent product HFBD has been evaluated to be about 383 ± 10 and 202 ± 5 kJ mol^{-1}, respectively.

Both the primary products hexafluorobutadiene (HFBD) and $:CF_2$ are characterized by transient absorption spectroscopy. The transient absorption spectra at 150 μs after the CO_2 laser pulse exhibit a band at 225−280 nm characteristic of $:CF_2$, whereas the corrected spectrum at 5 μs, which reveals a broad absorption band around 210−330 nm with a peak at 250 nm, has been assigned to the vibrationally hot HFBD. The nascent hot HFBD which has 202 kJ mol^{-1} internal energy shows a red shift of 50 nm in the transient absorption spectrum. The CF_2 vibrational temperature is found to be 1130 ± 20 K after 150 μs of the CO_2 laser pulse, whereas an overall temperature of the thermalized ensemble on the millisecond time scale is computed to be 630 ± 15 K. The dissociation of OFCP appears to be endothermic by 105 ± 10 kJ mol^{-1}.

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