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# Real Time Optical Observation of Nascent Hexafluorobutadiene in the IR Multiphoton Dissociation of Decafluorocyclohexene

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Real time observation of retro-Diels–Alder dissociation of decafluorocyclohexene into tetrafluoroethylene and hexafluorobutadiene induced by transversely excited atmospheric pulsed $CO_2$ laser is reported. The formation rate and the red-shifted absorption spectra of nascent hexafluorobutadiene suggest substantial internal energy incorporation, which appears to be sufficient for its undergoing electrocyclic transformation to hexafluorocyclobutene at a rate corresponding to the decay kinetics. When the above IR multiphoton dissociation of decafluorocyclohexene occurs in presence of oxygen, UV light emission due to $COF_2^*$ is observed.

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, limited number of studies are reported on time resolved measurements of unimolecular reaction rates.[9–11] These studies are also important to understand 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 in 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.

The gas phase thermal and photochemical reaction of decafluorocyclohexene (DFCH) has been studied earlier.[18,19] The observed products are perfluoro-1-methylcyclopentene, perfluoro-1,2-dimethylcyclopentene, perfluoromesitylene, perfluoromethylenecyclopentane and some polymeric perfluorinated liquid. In contrast, clean retro-Diels–Alder (RDA) reaction has been observed by us[1] in the IR multiphoton dissociation of DFCH induced by transversely excited atmospheric (TEA) $CO_2$ laser. The RDA reaction is a typical example of the generalized pericyclic reaction of Woodward and Hoffmann[20] which passes through a minimum activation energy barrier when it proceeds in a concerted fashion in the ground electronic state. The activation energy required for the unimolecular decomposition has been supplied exclusively as vibrational excitation by means of IR laser irradiation.

The RDA product energy distribution in the translational degrees of freedom has been reported recently by Lee et al.[21] However, the energy distribution in the internal degrees of freedom is not yet probed. The preliminary results on the time resolved observation of a primary RDA product hexafluorobutadiene (HFBD) have been reported in a short communication.[1a] This paper reports on the dynamics of RDA dissociation of DFCH by monitoring HFBD with the help of time resolved absorption spectroscopy. It is of interest to study whether the nascent primary products are formed in highly vibrationally energized state so that they undergo further reaction to form the final stable product.

## Experimental

A grating-tuned multimode transversely excited atmospheric (TEA) pulsed $CO_2$-laser (Lambda Physik EMG-201E-$CO_2$) was used for the irradiation of DFCH. A typical laser pulse consisted of 100 ns spike followed by a tail of 1 μs. A schematic diagram of the experimental set up is shown in Fig. 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 get 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 (LSI-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

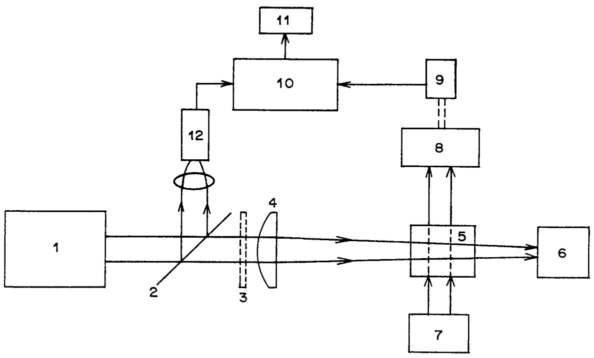

Fig. 1. Schematic diagram of the experimental set-up for the transient absorption studies: 1—TEA $CO_2$ laser, 2—Beam splitter, 3—Attenuator, 4—$BaF_2$ lens, 5—Stainless steel cell, 6—Energy meter, 7—Xenon lamp, 8—Monochromator, 9—PMT, 10—Biomation digitizer/Averager, 11—Y-T Plotter, 12—Photon drag detector.

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 ca. 200 μs. In the case of emission studies the Xe-lamp was off.

In the present experimental setup the parallel $CO_2$ laser beam used for irradiation and the UV-monitoring beam cross orthogonally (Fig. 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 analysed in detail.[22,23] Since the monitoring beam diameter is somewhat larger than the IR beam dimension in the present experiments, overlap correction was made to evaluate the actual optical density of the transient species.

The perfluoro compounds used in this experiment, decafluorocyclohexene ($C_6F_{10}$) and hexafluorobutadiene ($C_4F_6$) were purchased from PCR Research Chemicals Inc. (Gainesville, Florida, U.S.A.). 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 to 2600 nm

## Results and Discussion

Infrared multiphoton absorption and dissociation (IRMPA and IRMPD) are universal phenomena that occur upon excitation of strong IR absorption bands with intense, pulsed laser radiation. The widely accepted model of IRMPE[24–26] assumes that the vibrational structure of polyatomic molecules can be described by an initial set of discrete anharmonic states followed by a dense manifold of states referred to as the quasi-continuum. The discrete region is characterized by coherent excitation, while in the quasi-continuum vibrational relaxation gives rise to incoherent transitions. Further excitation through the quasi-continuum leads finally to unimolecular dissociation. The enormous progress made in this field in the last decade both in theory and in experiments has been recently reviewed by Lupo and Quack.[27] 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 contains information on the IR-MP mechanism. The distribution function of highly excited molecules, probed by spectroscopic methods such as IR fluorescence and Raman scattering,[28] 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 internal and translational energy distributions of the product fragments largely reflect the dynamics of the IR multiphoton excitation, and 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.

**1. Observation of Transient Intermediate in the RDA Reaction:** Upon irradiation of DFCH at 976 $cm^{-1}$ a transient UV-absorption band at 250 nm was observed immediately after the $CO_2$ laser pulse. The absorption signal due to the transient species grows very fast, reaches a maximum value $OD_{max}$ in about 4 μs, followed by an exponential decay at a longer time scale.

The time resolved absorption spectrum of the transient generated in the IR-multiphoton excitation of 2 Torr (1 Torr=133.322 Pa) DFCH has been recorded from 200—350 nm at 4 μs after the $CO_2$ laser pulse with the energy fluence of 1 J $cm^{-2}$. Figure 2(b) exhibits the transient spectrum. A standard computer software was used to calculate the absorbance values as a function of wavelength, from the time resolved signals obtained at different monitoring wavelengths. In the transient spectrum, maximum optical density $OD_{max}$

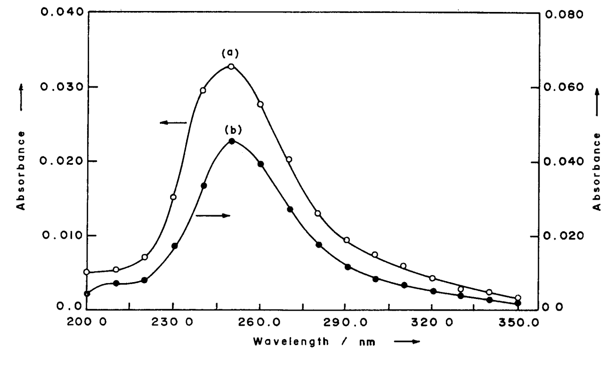

Fig. 2. Transient UV-absorption spectra generated in the IR multiphoton excitation of (a) 2 Torr HFBD at 4 μs after the $CO_2$ laser pulse ○ and (b) 2 Torr DFCH at 4 μs after the $CO_2$ laser pulse ●.

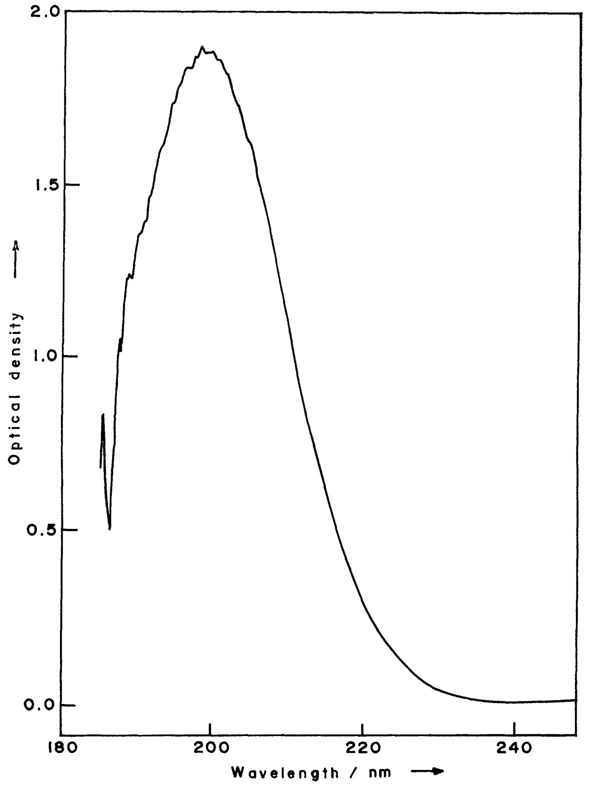

Fig. 3. UV-absorption spectra of hexafluorobutadiene in the gas phase.

was observed at 250 nm.

To characterize the species responsible for the transient absorption, a separate set of experiment 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 set-up was identical as 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 maximum by a microsecond and then decays exponentially. The time resolved spectrum from 200—350 nm recorded at 4 μs after the $CO_2$ laser pulse is shown in Fig. 2(a). The wavelength corresponding to the maximum absorbance was observed at 250 nm. The spectral shape is similar to the transient absorption spectrum generated in the IRMPD of DFCH.

The ground state electronic absorption spectrum of HFBD has a strong absorption peak at 200 nm[29] as shown in Fig. 3. 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.[30] 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 $\lambda_{max}$ shifts towards 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 post irradiated 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 DFCH at 976 cm$^{-1}$ was due to the hot band of 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 short. In other words a limiting multiphoton excitation level would be reached where the molecule decomposes before it can absorb the next laser photon.[31]

Nevertheless, the primary product energy distribution at the time of formation depends on the multiphoton excitation level of the reactant DFCH molecule. In the earlier study,[1] 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 36 kcal mol$^{-1}$. However, subsequent collisions 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. And the same amount of energy acquired in HFBD may be sufficient to show 50 nm red shift in the transient spectra.

**2. Kinetics of DFCH Decomposition:** The rate of growth of optical absorption due to hot HFBD can give information on the kinetics of its formation from the decomposition of the multiphoton excited DFCH,

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

where $k$ represents energy dependent mean rate constant for the multiphoton decomposition of DFCH$^{\dagger}$ under the experimental conditions. The experimental observation of the growth of the transient absorption signal due to hot HFBD is shown in Fig. 4. The rate constant, $k=(1.12\pm0.1)\times10^6$ s$^{-1}$, has been evaluated from the slope of the plot $\ln([\mathrm{HFBD}]_{\max}-[\mathrm{HFBD}]_t)$ vs. time (Fig. 5), corresponding to the unimolecular dissociation of

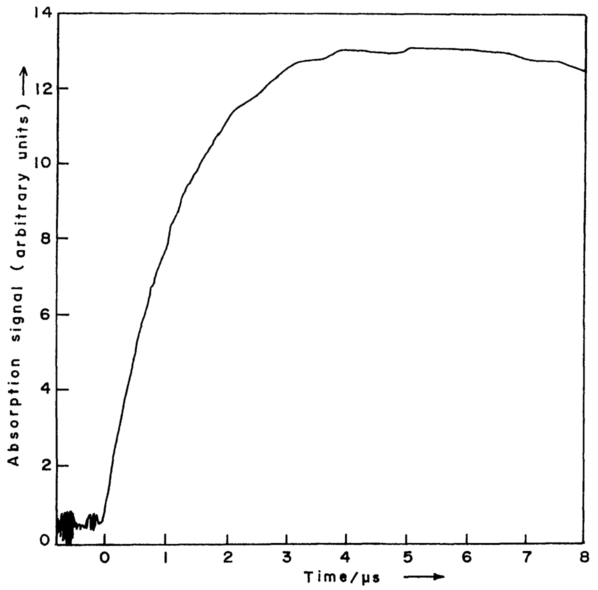

Fig. 4. The growth of the optical absorption signal at 250 nm due to hot HFBD generated in the IRMPD of 2 Torr of DFCH at a laser fluence of 1 J cm$^{-2}$.

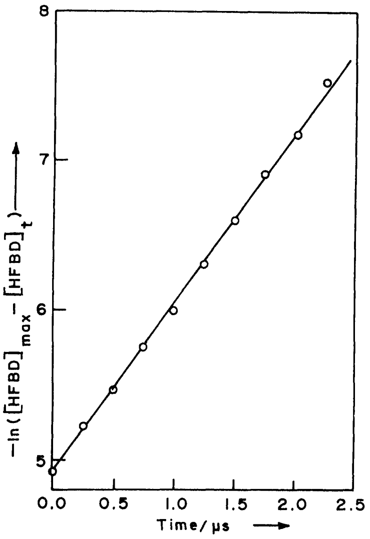

Fig. 5. Plot of ln ($[HFBD]_{max}-[HFBD]_t$) vs. time, generating the DFCH unimolecular dissociation rate constant $k=1.12\times10^6$ s$^{-1}$.

DFCH.

**3. Multiphoton Decomposition Level of DFCH:** The activation energy for the RDA decomposition of DFCH is not known. The hydrogen analogue, $C_6H_{10}$ has an overall activation energy[32] of about 66 kcal mol$^{-1}$ for the RDA decomposition. In view of the fact that C–C bonds are only involved in the RDA reaction, the activation energy for DFCH decomposition is expected to be close to that of cyclohexene. Further, the multiphoton excitation of the molecule by the IR laser must impart an appreciably larger amount of energy to the molecule, than is required to traverse the energy barrier for dissociation, to induce rapid unimolecular decomposition before vibrational-translational and/or rotational relaxation occurs.

The initial internal energy ($E$) associated with the excited DFCH can be evaluated in a simplest approximation by using the expression[33] for the energy dependent unimolecular rate constant, i.e.

$$\begin{aligned} k(E) &= A\,[(E-D)/E]^{s-1} \\ &= 1.12\times10^{6}\ \mathrm{s}^{-1}, \end{aligned} \qquad (2)$$

where $s$ is the number of vibrational degrees of freedom and $A$ is the frequency factor. The unimolecular dissociation rate $k(E)$ increases drastically with increasing ($E-D$) but the rate of such an increase drops as the number of vibrational degrees of freedom $s$ is increased. With proper estimation of the frequency factor and using 50—60% of the degrees of freedom, the rate constant has been shown to be in good agreement with RRKM rates.[33] A frequency factor of log $A$ (s$^{-1}$)=15.2, can be estimated by comparison with the unimolecular dissociation of cyclohexene[32] which generates ethylene and butadiene as products. If a dissociation energy ($D$) of 66.2 kcal mol$^{-1}$ and 21 degrees of freedom are used for this calculation, one obtains the internal energy of the dissociating DFCH molecule to be 101.6±2 kcal mol$^{-1}$.

**4. Time Resolved Isomerization of HFBD:** The decay of the optical absorption signal due to the hot HFBD produced in the IRMPD of DFCH is shown in Fig. 6. The plots of ln (signal) vs. time as shown in Fig. 7, generated a straight line with a slope indicating a decay constant, $k=(4.5\pm0.2)\times10^4$ s$^{-1}$. In the direct irradiation studies of HFBD (Section 1) similar decay was also observed. By correlating the static cell experimental results (Ref. 1) obtained in the irradiation of neat DFCH, which has produced HFCB as the final product,

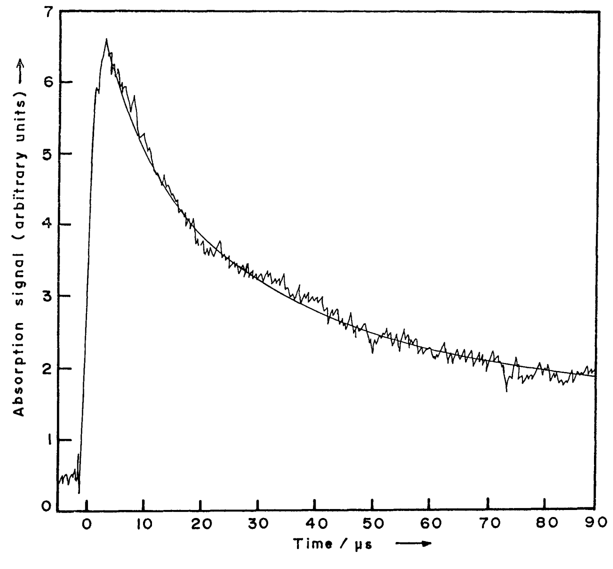

Fig. 6. The decay of the optical absorption signal at 250 nm.

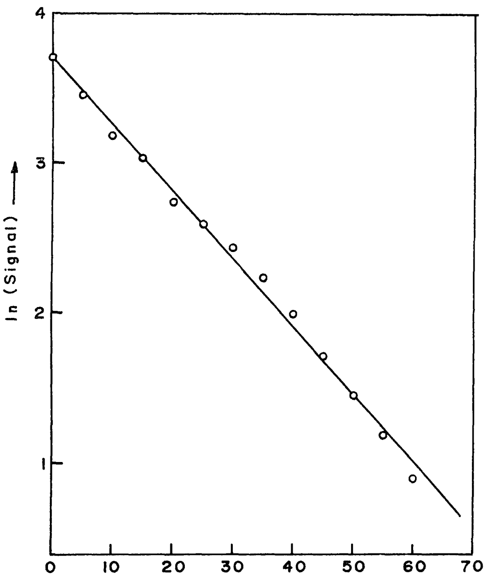

Fig. 7. Plot of the decay signal to an exponential function, generating a rate constant of $k$=4.5×$10^4$ s$^{-1}$.

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[34] with their time resolved infrared fluorescence technique.

**5. Internal Energy of Nascent HFBD:** The excess multiphoton excitation energy, over and above that required for the decomposition of DFCH, would be available as internal energy of the product molecules, i.e. tetrafluoroethylene (TFE) and hexafluorobutadiene (HFBD), and can be utilized in part, for driving the isomerization reaction,

$$\mathrm{HFBD} \longrightarrow \mathrm{HFCB}. \qquad (3)$$

From the thermal work of Schlag and Peatman,[35] the rate constant for the isomerization reaction is known to be,

$$k = 10^{12.03} \exp(-35800/RT)\ \mathrm{s}^{-1}.$$

An estimation of the internal energy associated with the nascent HFBD could be made from the observed time resolved isomerization rate constant, $k$=4.5×$10^4$ s$^{-1}$ by using Eq. 2 mentioned above. By using $D$= 35.8 kcal mol$^{-1}$ and log $A$ (s$^{-1}$)=12.03 obtained from the thermal data, and by assuming that half of the oscillators are effective here also in HFBD isomerization i.e. $s$=12, the internal energy associated with the nascent HFBD, $E$, has been evaluated to be 45.5±1 kcal mol$^{-1}$.

**6. Chemiluminescence with Oxygen:** When the above IR multiphoton dissociation of DFCH was carried out in presence of oxygen (a mixture of 2 Torr DFCH and 6 Torr $O_2$), $COF_2$ was detected as a major product as determined by IR spectrophotometric analysis. In the time resolved experiment of the above system, a transient emission band around 270 nm has been observed. The transient emission grows very fast to a maximum by 5 μs and decays exponentially with a rate constant $k$=1.1×$10^5$ s$^{-1}$. The emission spectrum has been observed at $\lambda$=230—350 nm, with a peak at 270 nm. By comparison with the spectral shape and emission lifetime reported in the literature,[36] the species responsible for emission has been assigned to $COF_2$.

It is known[36] that vibrationally excited $C_2F_4$ reacts with oxygen molecule to generate electronically excited $COF_2$, via a dioxetane intermediate, followed by emission of UV photon. In the present RDA reaction of DFCH, the primary tetrafluoroethylene (TFE) product is apparently formed with sufficient excitation energy to surpass the barrier of activation for the reaction $C_2F_4+O_2 \rightarrow COF_2$.

**7. Product Energy Distribution:** In IRMPD reaction, the released energy is partitioned in the internal and translational degrees of freedom of the products.[37] The distribution of energy in different vibrational, rotational and translational degrees of freedom depends on the structure of the transition state and the location of its barrier to dissociation.[38,39] The product rovibrational energy distribution following $CO_2$ laser induced dissociation has been found to be in agreement with the theoretical results considering transition state geometry.[40,41] The kinetic energy distribution is usually peaking at $E_{KE}$=0 for simple bond rupture reactions.[37] 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 occurs simultaneously.[2] However, in the apparently simple bond breaking reaction i.e., IRMPD of ethyl vinyl ether,

$$\mathrm{CH_2CHOCH_2CH_3} \longrightarrow \mathrm{CH_2CHO} + \mathrm{CH_2CH_3}$$

Lee et al.[38] 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 DFCH dissociation due to the stabilization energy for $\cdot CF_2\text{-}CF{=}CF\text{-}CF_2\cdot \rightarrow CF_2{=}CF\text{-}CF{=}CF_2$. As a result, significant kinetic energy release in the products is expected in case of DFCH dissociation. By investigating a few RDA reactions in the molecular beam, Lee et al. have reported[21] that typically about 23 kcal mol$^{-1}$ of the available energy is partitioned as translational energy of the products. A similar 23 kcal mol$^{-1}$ of translational energy may be assumed to be partitioned in the RDA products of DFCH.

It would be interesting to compare the product energy distribution of decafluorocyclohexene to that of cyclohexene. In their concerted RDA dissociation of ground state cyclohexene, as found by Lee et al.,[21] the product translational energy distribution has been determined by the dynamics of the exit barrier potential energy release. As a consequence, the translational energy distribution has been found to be unaffected by the variation of the dissociation energy level of the molecule. A similar translational energy distribution may also be expected in the RDA dissociation fragments of DFCH, where the exit barrier appears due to a similar bond rearrangements. However, the cyclohexene product energy distribution in the internal degrees of freedom is not reported.

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.[42,43] 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 IRMPD reaction it has been observed that most of the excess energy above the unimolecular dissociation threshold remains as internal energy of the product.[37] In the dissociation of DFCH, the TFE 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 12 modes of TFE. If statistical partitioning of the energy is assumed,[44] the HFBD will have about two-thirds of the internal energy released in products. 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 36 kcal mol$^{-1}$.

A modest 45.5 kcal mol$^{-1}$ of energy acquired in HFBD is evaluated (cf. Section 5) from its transformation rate. Assuming a statistical distribution of internal energy between the RDA reaction products of DFCH, i.e. HFBD and TFE, about 22.7 kcal mol$^{-1}$ of internal energy is expected to be associated with the TFE. The translational energy of 23 kcal mol$^{-1}$ is also expected to be shared between the products. Assuming momentum conservation, about 14.2 kcal mol$^{-1}$ goes to TFE. Thereby, a total energy acquired by TFE is about 37 kcal mol$^{-1}$. Considering that both the reactant translational and vibrational energy can contribute in overcoming the activation barrier of a bimolecular reaction, an upper limit of the activation energy required for $C_2F_4+O_2 \rightarrow COF_2$ reaction has been assessed to be $E_{act} \leq 37$ kcal mol$^{-1}$.

## Conclusions

Real time studies on the infrared multiphoton induced retro-Diels–Alder (RDA) dissociation of decafluorocyclohexene (DFCH) are reported. One of the primary products hexafluorobutadiene (HFBD) generated in the RDA reaction of DFCH has been characterized by real time UV kinetic absorption spectroscopy. Time resolved spectra of the nascent HFBD reveals a 50 nm red shift, which suggests that a substantial amount of energy is associated with the HFBD during its formation.

The time resolved growth of HFBD has been assigned to the multiphoton dissociation rate of DFCH, with $k=10^6$ s$^{-1}$, and the decay has been assigned to the isomerization of HFBD to form the stable cyclic isomer, with a rate constant $k=4.5\times10^4$ s$^{-1}$. The average energy associated with the dissociating DFCH and the nascent RDA product HFBD has been evaluated to be about 102 and 45 kcal mol$^{-1}$ respectively.

The energy acquired by the other primary product tetrafluoroethylene (TFE) has been assessed as 37 kcal mol$^{-1}$, which appears to be sufficient for initiating the chemiluminescent reaction $C_2F_4+O_2 \rightarrow COF_2^*$, followed by emission of a UV photon around 270 nm.

Discussions of this work with J. P. Mittal and K. V. S. Rama Rao are gratefully acknowledged.

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