

SENSITIZED DECOMPOSITION OF DECAFLUOROCYCLOHEXENE BY IR-MULTIPHOTON-EXCITED SF₆ IN A CO₂ LASER FIELD

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Summary

On irradiation of mixtures of SF₆ and decafluorocyclohexene (DFCH) at CO₂ laser frequencies absorbed only by SF₆, retro Diels-Alder decomposition of DFCH was obtained. A massive intermolecular vibrational energy transfer from IR-multiphoton-excited SF₆ to the cold DFCH molecule seems to occur with a probability of 0.03 per collision. The decomposition yield per pulse was studied as a function of the partial pressures of SF₆, DFCH and the argon buffer as well as the laser fluence and frequency. The maximum decomposition was observed at the 10 P(30) CO₂ laser line which is red shifted by about 13 cm⁻¹ with respect to the ν_3 fundamental of SF₆ at 948 cm⁻¹.

1. Introduction

Vibrational energy transfer from IR-laser-excited donor molecules to acceptor molecules up to the dissociation level is a topic of current interest [1]. Isotope selectivity in a sensitized decomposition has recently been observed [2]. In another case electronic energy transfer has been suggested to explain the prompt sensitized decomposition following IR multiphoton excitation of the acceptor [3]. The sensitized decomposition of the acceptor molecules by such indirect means depends on various parameters such as the efficiency of the pump laser, the rates of vibrational relaxation and the energy transfer from the primary excited species.

CO₂-laser-induced retro Diels-Alder (RDA) decomposition of decafluorocyclohexene (DFCH) to tetrafluoroethylene (TFE) and hexafluorobutadiene (HFBD) followed by isomerization of the nascent HFBD to thermodynamically stable hexafluorocyclobutene (HFCB) has recently been observed in a study performed in this laboratory [4]. In this paper we describe our investigations of the induction of the RDA decomposition of DFCH by energy transfer from SF₆ resonantly pumped by a CO₂ laser at a frequency not absorbed by DFCH. The sensitized decomposition of DFCH has been studied as a function of the partial pressures of DFCH, SF₆ and an inert buffer gas argon, the laser fluence and the frequency. Consideration

of the results suggests that a massive intermolecular vibrational energy transfer is responsible for the observed sensitized decomposition of DFCH.

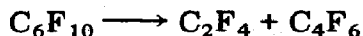
2. Experimental details

The source of IR radiation was a pulsed CO₂ transversely excited atmospheric pressure laser (Lumonics model 103-2) operating at 0.5 Hz. A typical laser pulse contains 50% of its energy in a spike with a full width at half-maximum of 100 ns and the rest in a 2 μs tail. A factory-calibrated pyroelectric detector (Lumonics model 20 D) was used to measure the pulse energy. A photon drag detector (Rofin model 7415) was employed to measure the pulse shape and specific laser lines were detected by means of a spectrum analyser (Optical Engineering Co.).

A stainless steel cell 2.5 cm long and 3.1 cm in diameter was used for irradiation. It was provided with two polished KCl end windows which were held in position by Viton O-rings. Each component of the mixture was admitted into the cell at a measured pressure and condensed through a Teflon stopcock into a side-arm at 77 K. The progress of the reaction was monitored by IR spectrophotometry (Perkin-Elmer model 577) and the final product analysis was carried out by gas chromatography [4]. A BaF₂ lens of focal length 100 cm was used to vary the fluence and to maintain a near-parallel laser beam geometry throughout the cell. The DFCH and SF₆ were obtained from PCR Research Chemicals Inc. (Gainesville, FL) and Matheson (U.S.A.) respectively.

3. Results

In our experiments mixtures of DFCH and SF₆ were irradiated using various CO₂ laser lines originating from the P branch of the 10.6 μm band, which has a frequency close to the ν₃ band of SF₆ at 948 cm⁻¹. In most of the experiments the 10 P(20) line at 944 cm⁻¹ was employed for irradiation. Blank experiments using pure components were carried out to establish that direct dissociation of either DFCH or SF₆ did not occur to any appreciable extent at the fluence levels of 1 - 3 J cm⁻² employed in this work. When the mixtures were irradiated, an appreciable decomposition of DFCH and almost no decomposition of SF₆ was observed. The decomposition products in all cases were TFE and HF₂C=CF₂, as determined by gas chromatography analysis. Under the experimental conditions employed TFE and HF₂C=CF₂ were obtained in almost equivalent yields; a small amount of HFBD (up to 5% of HF₂C=CF₂) was also detected. The overall relationship between the yields of the above products and the DFCH consumed was found to be stoichiometrically equivalent to the reaction



With repeated laser pulse irradiation, an exponential decrease in the concentration of DFCH was observed. The fractional decomposition α per pulse is given by

$$[\text{DFCH}] = [\text{DFCH}]_0 \exp(-\alpha n)$$

where n is the number of laser pulses supplied to the sample and $[\text{DFCH}]_0$ and $[\text{DFCH}]$ are the initial and final concentrations of DFCH after n pulses.

3.1. Role of SF_6 pressure

Mixtures of 3 Torr DFCH with 1 - 30 Torr SF_6 were irradiated with the 10 P(20) line of a $10.6 \mu\text{m}$ CO_2 laser at an energy fluence of 2.69 J cm^{-2} . α increased with the SF_6 partial pressure as shown in Fig. 1, curve a. Saturation was observed at high SF_6 pressures where 50% of the DFCH in the irradiation volume decomposed per pulse.

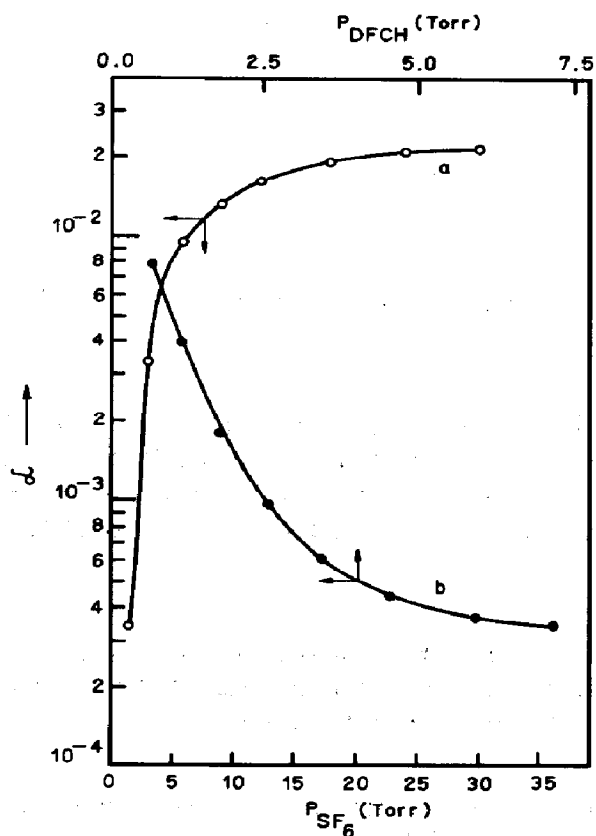


Fig. 1. Curve a, semilogarithmic plot of α vs. the SF_6 pressure (the DFCH pressure was kept constant at 3 Torr; the 10 P(20) laser line was used at a fluence of 2.69 J cm^{-2}); curve b, semilogarithmic plot of α vs. DFCH pressure (the SF_6 pressure was kept constant at 3 Torr; the 10 P(20) laser line was used at a fluence of 2 J cm^{-2}).

3.2. Role of DFCH pressure

Mixtures of 3 Torr SF_6 with various DFCH pressures from 0.5 to 10 Torr were irradiated with the 10 P(20) laser line at an energy fluence of 2 J cm^{-2} . α decreased with increasing DFCH pressure as shown in Fig. 1, curve b. No detectable dissociation of DFCH was observed at a pressure ratio $P_{\text{SF}_6}:P_{\text{DFCH}}$ of 1:6 under the same irradiation conditions.

3.3. Role of total pressure

α increased with increasing total pressure at a $P_{\text{SF}_6}:P_{\text{DFCH}}$ ratio of 2:1 as indicated in Fig. 2. The laser line used was 10 P(20), *i.e.* 944 cm^{-1} , and the fluence was 2.69 J cm^{-2} .

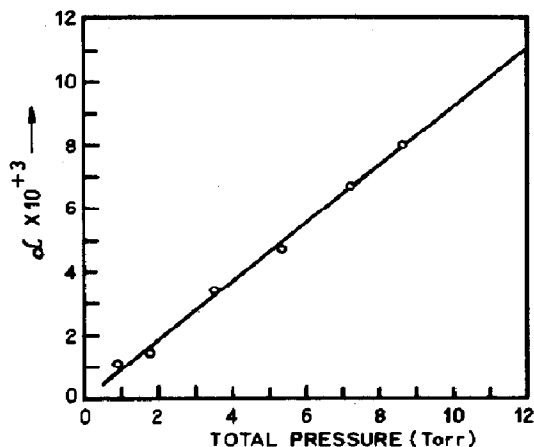


Fig. 2. α vs. total pressure of SF_6 and DFCH at a $P_{\text{SF}_6}:P_{\text{DFCH}}$ ratio of 2:1 (energy fluence, 2.69 J cm^{-2} ; laser line, 10 P(20)).

3.4. Role of argon pressure

Various amounts of argon were added to a mixture of 1.2 Torr DFCH and 3.6 Torr SF_6 . The gas mixtures were irradiated with the 10 P(20) CO_2 laser line at a fluence of 2.69 J cm^{-2} . α decreased with increasing argon pressure as can be seen in Fig. 3, in which α^{-1} is plotted as a function of the argon pressure.

3.5. Role of laser fluence

A mixture of 3.6 Torr SF_6 and 1.2 Torr DFCH was irradiated with the 10 P(20) CO_2 laser line at various energy fluences in the range $1.32 - 3.4 \text{ J cm}^{-2}$. α was found to increase with increasing fluence (Fig. 4).

3.6. Role of optical frequency

Mixtures of 3.6 Torr SF_6 and 1.2 Torr DFCH were irradiated at an energy fluence of 1.32 J cm^{-2} using various CO_2 laser lines ranging from P(14) to P(38) of the $10.6 \mu\text{m}$ band. α was found to be a maximum at 10 P(30), *i.e.* at 935 cm^{-1} , and decreased on each side of this line as shown in Fig. 5.

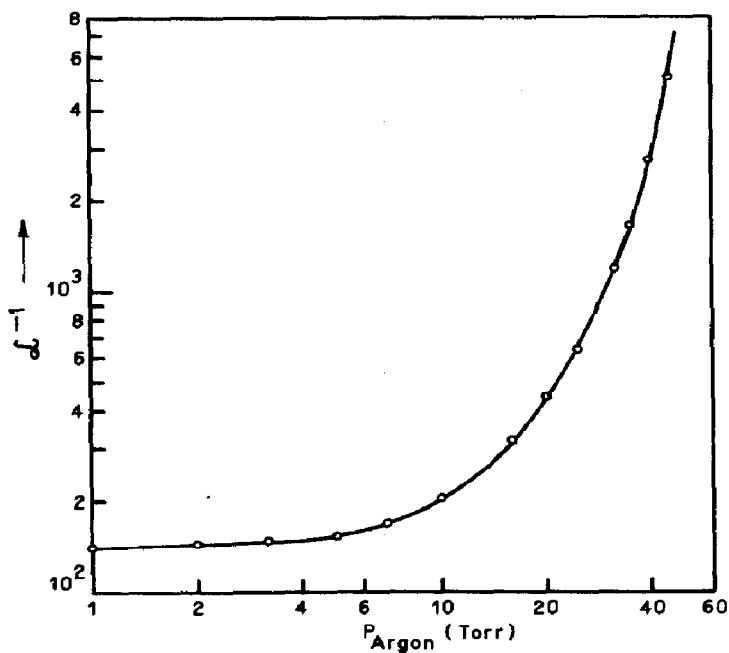


Fig. 3. Log-log plot of α^{-1} vs. the partial pressure of argon added to a mixture of 1.2 Torr DFCH and 3.6 Torr SF_6 ; 10 P(20) laser line was used at an energy fluence of 2.69 J cm^{-2} .

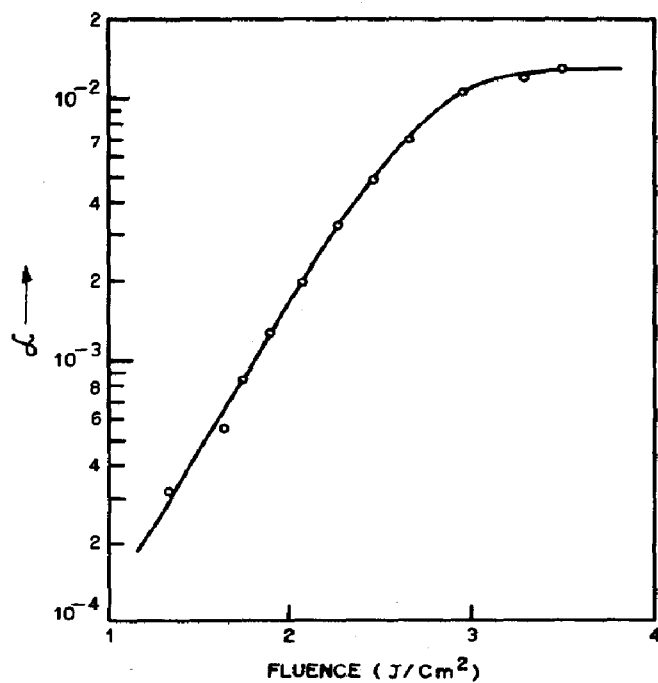


Fig. 4. α vs. the laser energy fluence (CO_2 laser line, 10 P(20); gas mixture, 1.2 Torr DFCH and 3.6 Torr SF_6).

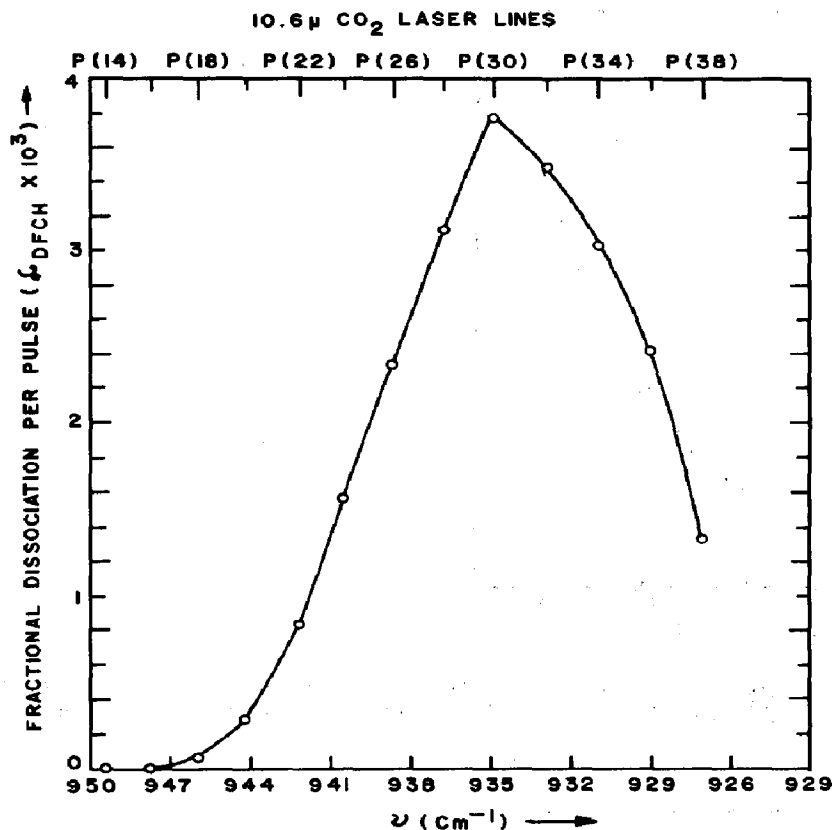
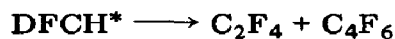
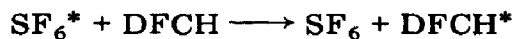
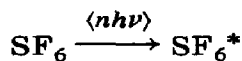


Fig. 5. α vs. the optical frequency ν corresponding to various CO₂ laser lines of the 10 μ m band (energy fluence, 1.32 J cm⁻²; gas mixture, 1.2 Torr DFCH and 3.6 Torr SF₆).

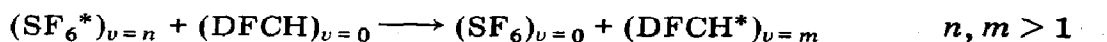
4. Discussion

The energy required for the decomposition of DFCH is obtained by collisional energy transfer from vibrationally excited SF₆ to DFCH:



The minimum energy required for the unimolecular decomposition of DFCH is not yet clearly established but is expected to be substantially greater than 66 kcal mol⁻¹, which is the activation energy for the dissociation of the protonated analogue cyclohexene. The final products obtained in both the present work on sensitized decomposition and our previous investigation

[4] of the direct IR-laser-induced decomposition of DFCH at laser frequencies absorbed by DFCH were TFE and perfluorocyclobutene. Neither TFE nor the HFBCB-HFBD mixture were obtained in the pyrolysis of DFCH [5]. This suggests that the present laser-driven reaction proceeds through a different channel to that of the pyrolysis where the products formed were even of a qualitatively different nature. Therefore it appears that in the laser-driven reactions the vibrational energy content of the molecule is utilized for the chemical reaction well before it undergoes vibrational-translational (V-T) relaxation. Further, the initial decomposition channel is most likely to give perfluorobutadiene, which has a sufficiently large internal energy content (about 54 kcal mol⁻¹ [4]) at the time of its formation to undergo isomerization to the cyclic isomer which is the final product. This large amount of energy (more than 66 kcal mol⁻¹) in the acceptor DFCH molecules must be acquired either by a massive energy transfer involving collision between highly excited SF₆ and DFCH or energy pooling via low quantal energy exchange involving SF₆*-DFCH and DFCH*-DFCH* collisional processes. Energy pooling by low quantal exchange is tenuous and can take place only over a prolonged time during which V-T relaxation is certain to occur, resulting in thermal heating. Since the products obtained are very different from those of pyrolysis, we consider that DFCH*-DFCH* energy pooling collisional processes are less important and that the observed chemical decomposition is the result of massive energy transfer, *i.e.* a vibrational energy exchange equivalent to a large number of quanta in a single intermolecular collision:



It is important to note that the SF₆*-DFCH collisions required for energy exchange involve SF₆* molecules which have a wide distribution of vibrational excitation. In fact the multiphoton excitation of SF₆ during the laser pulse competes with energy loss by collisions with DFCH. In view of the large cross section for $\nu_{0 \rightarrow 1}$ photon absorption by SF₆ we expect almost all SF₆ molecules in the irradiation volume V_{irr} to be excited to the first or the first few levels within the first few nanoseconds of the 100 ns pulse. Collisions of DFCH essentially involve SF₆ molecules which are excited to the first or higher levels of vibrational excitation. The excitation loss by collisional energy transfer is rapidly compensated by laser photon absorption. When such excitation in SF₆ during the laser pulse time τ is considered, the total number of SF₆*-DFCH collisions occurring in the irradiated volume V_{irr} during the pulse time is given by $3 \times 10^{16} Z P_{\text{SF}_6} P_{\text{DFCH}} V_{\text{irr}} \tau$. A small fraction of these collisions is likely to result in a massive energy transfer leading to the molecular dissociation of DFCH. The number of DFCH molecules dissociating per pulse is given by $3 \times 10^{16} \alpha V_{\text{cell}} P_{\text{DFCH}}$ where α , as defined earlier, is the experimentally determined fractional dissociation of DFCH per pulse. The probability η that a massive energy transfer leading to chemical decomposition occurs on collision is therefore given by

$$\eta = \frac{\text{DFCH molecules decomposed}}{\text{SF}_6^* \text{-DFCH collisions}}$$

$$= \frac{\alpha V_{\text{cell}}}{Z P_{\text{SF}_6} \tau V_{\text{irr}}}$$

Under the present experimental conditions $V_{\text{irr}} = 0.9 \text{ cm}^3$, $V_{\text{cell}} = 19 \text{ cm}^3$, $\tau = 100 \text{ ns}$ and the collision frequency Z for SF_6 -DFCH collisions is $0.916 \times 10^7 \text{ Torr}^{-1} \text{ s}^{-1}$. Hence

$$\eta = 23\alpha/P_{\text{SF}_6}$$

Typical values of η calculated from the results of Figs. 1, 2 and 4 are summarized in Table 1, which shows that the probability η of massive energy transfer per collision is about 1.5% - 5% over a wide range of SF_6 partial pressures.

It is interesting to note that the single collision probability for a massive energy transfer is independent of total pressure in the experiments where the $[\text{SF}_6]/[\text{DFCH}]$ ratio is constant (data from Fig. 2; $\eta = 0.03$). When the relative concentration of the laser absorber SF_6 increases, as in the case of Fig. 1, curve a, η remains almost constant but decreases slightly to 0.017 at a high $[\text{SF}_6]/[\text{DFCH}]$ ratio of 10 where about 50% of the available DFCH molecules in the irradiation volume undergo dissociation. We consider that the apparent decrease in η is due only to the decreased availability of DFCH

TABLE 1

SF_6 -sensitized dissociative energy transfer probability for DFCH

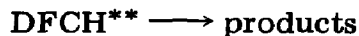
Figure from which data are taken	SF_6 pressure (Torr)	DFCH pressure (Torr)	Laser energy fluence (J cm^{-2})	η
1, curve a	3.0	3.0	2.69	2.54×10^{-2}
	6.0	3.0	2.69	3.72×10^{-2}
	12.4	3.0	2.69	3.01×10^{-2}
	30.0	3.0	2.69	1.652×10^{-2}
1, curve b	3.0	0.6	2.00	6.01×10^{-2}
	3.0	1.1	2.00	2.53×10^{-2}
	3.0	2.5	2.00	7.53×10^{-3}
	3.0	7.2	2.00	2.69×10^{-3}
2	0.6	0.3	2.69	4.38×10^{-2}
	2.4	1.2	2.69	3.22×10^{-2}
	3.6	1.8	2.69	3.02×10^{-2}
	5.8	2.9	2.69	3.15×10^{-2}
4	3.6	1.2	1.32	2.05×10^{-3}
	3.6	1.2	2.27	2.07×10^{-2}
	3.6	1.2	2.47	3.14×10^{-2}
	3.6	1.2	3.5	8.32×10^{-2}

molecules at these high conversions. In other words, if more DFCH were available, commensurate with the increased availability of SF₆* molecules at high SF₆ pressures, η would still have been about 0.03.

When the [SF₆]/[DFCH] ratio is decreased by increasing the DFCH concentration (Fig. 1, curve b), η decreases markedly, e.g. $\eta = 0.0027$ at [SF₆]/[DFCH] = 0.42 at a fluence of 2 J cm⁻². At 3 Torr SF₆ and 7 Torr DFCH, each SF₆ molecule collides about six times with DFCH during the 100 ns laser pulse. The mean excitation build-up time available for an SF₆ molecule between collisions is only about 16 ns compared with a build-up time of as much as 30 - 100 ns available for the case of 3.0 Torr SF₆ and 0.6 Torr DFCH for which η is as high as 0.056.

Another factor which determines η is the laser fluence, e.g. η increases from about 0.002 at $\phi = 1.3$ J cm⁻² to a saturation value of 0.08 at $\phi = 3.5$ J cm⁻² in experiments where the [SF₆]/[DFCH] concentrations are kept constant (data in Fig. 4). In this series of experiments the partial pressures of SF₆ and DFCH are such that the DFCH molecules collide with SF₆ molecules which have 30 - 100 ns excitation build-up times.

The above considerations establish that the criteria for massive energy transfer seem to be an adequate excitation build-up time for the donor excitation and an adequate laser fluence. It is not known how much energy is in fact transferred in such a massive energy transfer collision process. The only known examples where unambiguous estimates have been made are in the chemical activation and thermal decomposition experiments [6] where an average energy transfer of some 10 - 15 kcal mol⁻¹ takes place on collision. It is probable that similar magnitudes of energy transfer are involved in the present case of SF₆*-DFCH collisions and that the acceptor DFCH molecules are either (i) propelled into a quasi-continuum and undergo non-resonant laser absorption or (ii) undergo further collisional activation and thereby acquire sufficient energy for decomposition:



By massive energy transfer we imply process (1) whereby the product acquires further energy via (2) or (3) and finally decomposes.

4.1. Frequency dependence of the sensitized decomposition

As seen from Fig. 5, the fractional dissociation α per pulse rapidly increases as the excitation frequency decreases. The maximum decomposition occurs when the 10 P(30) line (935 cm⁻¹) is used which is red shifted as much as 13 cm⁻¹ with respect to the ν_3 mode of the SF₆ absorption maximum at 948 cm⁻¹. It is known that both the multiphoton excitation and

multiphoton decomposition spectra of most polyatomic molecules are red shifted with respect to the fundamental frequency [7] commensurate with the criteria for quasi-continuum absorption of polyatomic molecules. However, in experiments with pure DFCH it was found that the most efficient laser frequency for inducing RDA decomposition of the molecule is 976 cm^{-1} which is red shifted only 2 cm^{-1} with respect to its IR absorption maximum at 978 cm^{-1} [4]. In contrast, in the case of sensitized decomposition the ν_3 mode of donor SF_6 is red shifted 30 cm^{-1} with respect to DFCH absorption at 978 cm^{-1} , and the maximum decomposition frequency at 935 cm^{-1} is still further red shifted. It is rather surprising that the endothermicity factor for intermolecular vibrational energy transfer from $\text{SF}_6(\nu_3) \rightarrow \text{DFCH}(\nu!)$ should have increased. Since such large red shifts are not generally experienced, it appears that the coupling mode for vibration-vibration transfer may not necessarily be the same as that at 978 cm^{-1} but may involve some other fundamental or combination mode of DFCH which has no IR absorption in this region.

5. Conclusions

The RDA decomposition of DFCH can be induced by intermolecular vibrational energy transfer from CO_2 -laser-excited SF_6 to cold DFCH. The difference between the products obtained in thermolysis [5] and those obtained in the present laser-induced process is a strong indication that thermal effects may not be involved in the latter process. The sensitized decomposition spectrum is red shifted and sharp compared with the rather broad multiphoton excitation spectrum of SF_6 [7]. Saturation in the decomposition yield was observed at high SF_6 pressures and high laser fluences.

Acknowledgments

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