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TEA CO_2 Laser-Induced Photodissociation of UF_6 Via Interspecies *V–V* Energy Transfer from Multiple Photon Excited Halomethanes

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Abstract. The dissociation of UF_6 sensitized by multiple photon excitation of a series of halomethanes: CF_4, CF_3Cl, and CF_2Cl_2 has been investigated. The roles of various experimental parameters like exciting frequency, fluence and pressures of sensitizer/UF_6 on the dissociation yield were studied to examine (1) the characteristics of the sensitizer/UF_6 system and (2) the coupling of vibrational energy between two molecular systems. The efficiency of the energy transfer process was estimated on the basis of long range dipole–dipole interaction to gain an understanding of the dissociation process.

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Molecules such as SF_6 and halomethanes that are strong absorbers of CO_2 laser radiation have found various applications in laser physics and chemistry. After the successful isotope-selective infrared multiphoton dissociation (IRMPD) of SF_6 and halomethanes, recent attention has focused on laser-induced chemical reactions [1] and on reactions of other molecules sensitized by such laser-excited species [2]. Although such molecules can be pumped to dissociation with intense CO_2 laser radiation, at relatively low laser fluence it is possible to achieve a moderate level excitation. Under near resonant conditions, this excitation energy can be transferred to other molecules for which direct laser excitation is not readily accomplished.

It is well known that there is no measurable absorption of CO_2 laser radiation by UF_6 at room temperature, even through its hot bands [3]. However, IR photochemistry of UF_6 can conveniently be studied using CO_2 laser radiation where energy transfer can be effected to its ν_3 mode ($625\ \mathrm{cm}^{-1}$) from a sensitizer having good absorption in 9–11 μm region and some vibrational mode near $625\ \mathrm{cm}^{-1}$. SF_6-sensitized IRMPD of UF_6 by CO_2 laser was first reported by us [4] and subsequently SF_6 was used as a sensitizer for studies involving dissociation and energy transfer on UF_6 and many other polyatomics [5, 6].

In the present work, we have chosen a series of halomethanes CF_4, CF_3Cl and CF_2Cl_2 for performing dissociation of UF_6 via *V–V* energy transfer processes.

Table 1. Molecular parameters for the sensitizers

Molecule	Pump mode [cm^{-1}]	Exciting line [cm^{-1}]	Transferring mode near ν_3 of UF_6	Bond energy [kcal/mole]
CF_4	$\nu_2+\nu_4$ 1067	9*R*(12) 1073	ν_4 630	$D(R-F)=100$ [36]
CF_3Cl	ν_1 1105	9*R*(30) 1084	ν_2 781	$D(R-Cl)=81$ [23]
CF_2Cl_2	ν_1 1101	9*R*(30) 1084	ν_2 667	$D(R-Cl)=76$ [23]
SF_6	ν_3 948	10*P*(20) 944	ν_4 615	$D(S-F)=92$ [37]
UF_6			ν_3 625	$D(U-F)=68$ [38]

The criteria for choosing such sensitizers, in particular this series of halomethanes are: (1) they have a varying absorption ranging from weak (combination band) to strong (fundamental) in the CO_2 laser region; (2) they have favourable vibrational levels for energy transfer processes; (3) their dissociation energy is higher than UF_6 and (4) they are chemically inert towards UF_6. The various molecular parameters for these sensitizers are shown in Table 1. The roles of various experimental parameters like exciting frequency, fluence and pressure of sensitizer/acceptor on the dissociation processes were studied. The efficiency of the energy transfer process was estimated on the basis of long range dipole–dipole interaction. This gave fruitful information about the dissociation mechanism relating the role of the absorption characteristics of the sensitizer and relative energy levels of the sensitizer and acceptor molecules.

1. Experimental

A Lumonics 103-2 grating tuned TEA CO_2 laser operating at 0.5 Hz was used as the excitation source for the absorbers. The irradiations involving UF_6 were carried out in 10 cm long and 100 cm^3 volume nickel cell equipped with monel valve and polished KCl end-windows on viton O-rings. The all-metal gas handling vacuum system and the cell were leak tested and evacuated to 10^{-4} Pa while baking. The cell was well passivated by prolonged exposure to a UF_6/halomethane mixture for several days. The irradiations involving neat halomethanes were carried out in another nickel cell never exposed to UF_6, but were also carried out in a pyrex cell and the same cell used for mixture irradiation to check for cell material problems and dark reaction.

The temporal profile of the laser pulse as monitored by a photon drag detector (Rofin) consisted of a 100 ns initial spike followed by a 1 μs tail. The pulse energy was measured by a calibrated pyroelectric detector (Lumonics 20D). For low fluence experiments, the laser pulse was suitably attenuated by polyethylene films. For higher fluence the laser was focused by a BaF_2 lens ($f = 40$ cm) and different fluence conditions were obtained by changing the distance of the cell from the focal point. Care was taken not to focus the beam inside the cell to avoid any dielectric breakdown.

The relative changes in the sample concentrations were monitored by IR spectrometry (Perkin Elmer 577) at appropriate wavelengths for measuring the cell averaged dissociation yield per pulse. This is defined as $-\ln(1-x)/n$, where x denotes the dissociated fraction after n pulses of irradiation. In the case of the CF_2Cl_2/UF_6 system, the product analysis was also carried out by an indigeneously built gas chromatograph (Porapak Q, 52° C, H_2 carrier gas, thermal conductivity detector) after removing the undecomposed UF_6.

2. Results

2.1 *The* CF_4/UF_6 *System*

CF_4 is a tetrahedral molecule with fundamental band frequencies $\nu_1 = 904$, $\nu_2 = 437$, $\nu_3 = 1265$, and $\nu_4 = 630\ cm^{-1}$ [7]. Of the four only ν_3 and ν_4 are infrared active. In this system, irradiations were carried out with the 9R(12) line of the CO_2 laser, the line which is commonly used for pumping the 16 μm CF_4 laser, resonating with the $(\nu_2 + \nu_4)$ combination band. However, the absorption cross section of this band is rather small $\sim 10^{-20}\ cm^2$ [8] (i.e. <0.1 photon absorbed per molecule at an energy fluence up to about 1 J cm^{-2}).

Three series of irradiations, namely neat CF_4, neat UF_6 and the CF_4/UF_6 mixture were carried out. Neat CF_4 and neat UF_6 were irradiated in a pressure range of 0.66–6.65 kPa. The mixtures were irradiated (1) keeping the CF_4 pressure constant at 0.66 kPa and varying the UF_6 pressure from 0.66 to 6.65 kPa and (2) similarly varying the CF_4 pressure while keeping the UF_6 pressure constant at 0.66 kPa. In each experiment, the fluence was progressively increased up to the point where the dielectric breakdown could be visibly seen.

Infrared spectrometry of irradiated neat CF_4 and neat UF_6 did not show any detectable dissociation in the pressure and fluence range studied. Similarly, in case of the mixtures no photodissociation in either species could be observed under any combination of pressures and fluence conditions i.e. dissociation yield per pulse $<1 \times 10^{-5}$.

Therefore it is apparent that the energy absorbed by the system is very small and for the same reason Koren et al. [9] failed to observe any fluorescence in the range 600–1500 cm^{-1} from laser-excited CF_4. Interest in developing the 16 μm laser has led to detailed high resolution spectroscopy studies of the pump $(\nu_0 \rightarrow \nu_2 + \nu_4)$ and lasing band $(\nu_2 \rightarrow \nu_2 + \nu_4)$ of CF_4 [10, 11]. The combination band $(\nu_2 + \nu_4)$ has a rich sub-structure such that with a free-running CO_2 laser resonances are almost guaranteed. In fact in most cases more than one transition is pumped and consequently several different lines of CF_4 are observed to lase. The strength of the well-known 615 cm^{-1} emission stems from a cluster of lines belonging to different tetrahedral species when pumped by a normal multimode TEA CO_2 laser. However, we attempted to compensate the poor absorption of CF_4 by employing higher substrate pressure (up to 13.3 kPa) and fluence (10 J cm^{-2}). Even then no photodissociation of UF_6 could be induced in the system. This could be understood in terms of its poor absorption and also inadequate energy flow in the required ν_4 mode of CF_4 due to the fact that the $(\nu_2 + \nu_4)$ mode is coupled strongly to the ν_2 mode via 615 cm^{-1} laser emission. Therefore, although the energy defect in V–V energy transfer between ν_4 of CF_4 and ν_3 of UF_6 is about 5 cm^{-1} (almost resonant), net energy accumulation in the ν_3 mode of UF_6 is too small to effect the photodissociation.

2.2 *The* CF_3Cl/UF_6 *System*

The CF_3Cl molecule has nine vibrational modes [12] of which the ν_1 mode was excited by the 9R(30) CO_2 laser line (1084 cm^{-1}). Similar sets of experiments as described previously were carried out. Up to a fluence level of 1 J cm^{-2} there were no detectable dissociation in either neat CF_3Cl or neat UF_6 systems. However, at a fluence of

0.3 J cm^{-2} or above a net dissociation of UF_6 was observed after several hundred pulses while the CF_3Cl concentration remained unchanged in the mixture. In a typical CF_3Cl/UF_6 mixture (5:1), the decomposition yield was found to be 1×10^{-4} per pulse at 0.5 J cm^{-2} fluence and 4 kPa total pressure.

The dissociation of UF_6 in the mixture was accompanied by the development of a new peak in the IR spectrum at 1270 cm^{-1} which is similar to the observation in SF_6/UF_6 system [4]. The other two peaks at 1210 and 1100 cm^{-1} as found in latter system could not be observed in the present case because of spectral congestion in this region from CF_3Cl absorption [12]. The intensity of the observed peak was found to have direct bearing on the amount of UF_6 decomposed. Chemical analysis of the white yellow deposit on the window indicated the presence of uranium.

Taking into account the present observations and comparing with the results of SF_6/UF_6 system [4], we believe a similar mechanism must be operating for CF_3Cl-sensitized dissociation of UF_6. Following multiphoton absorption – Eq. (1) – and intermode relaxation ($\nu_1 \to \nu_2$) in CF_3Cl – Eq. (2) – V–V energy transfer takes place to the ν_3 mode of UF_6 – Eq. (3):

$$CF_3Cl \longrightarrow CF_3Cl(\nu_1) \tag{1}$$

$$CF_3Cl(\nu_1) \longrightarrow CF_3Cl(\nu_2) \tag{2}$$

$$CF_3Cl(\nu_2) + UF_6 \rightarrow UF_6(\nu_3) + CF_3Cl + 156\ cm^{-1}. \tag{3}$$

Although the rate of intermode vibrational relaxation of CF_3Cl is not reported, it can be presumed to have values similar to those of systems like CH_3F [13, 14], CH_3Cl [15] which have been determined by IR fluorescence techniques. For CH_3F the rate of intermode transfer from the pumped mode ν_3 (1049 cm^{-1}) to ν_6 (1182 cm^{-1}) and ν_2, ν_5 (1464, 1466 cm^{-1}) are 0.78 and 0.64 ms^{-1} Pa^{-1} respectively. For CH_3Cl, the rate for ν_6 (1015 cm^{-1}) to ν_3 (712 cm^{-1}) transfer is 0.57 ms^{-1} Pa^{-1}. Assuming similar rates for intermode relaxation for CF_3Cl and also for the interspecies V–V energy transfer between CF_3Cl and UF_6, the excitation of UF_6 can occur well within the laser pulse duration.

Following this there could be two alternative or concurrent processes. The first possibility is that such energy transfer can eventually pump sufficient vibrational energy into UF_6 to cause its dissociation [5]. However, at the working fluence level the multi-photon excitation in CF_3Cl is limited to about 5–6 photons. On the other hand, if UF_6 is excited to its quasi-continuum it can absorb further CO_2 laser photons thereby undergoing dissociation via broadened and red-shifted binary ($\nu_2 + \nu_3$) (1157 cm^{-1}) [16] and/or tertiary combination bands ($\nu_3 + \nu_5 + \nu_6$) and ($\nu_2 + \nu_3 - \nu_5$) [17].

2.3 *The* CF_2Cl_2/UF_6 *System*

With the same experimental set up the sensitized dissociation of UF_6 by CF_2Cl_2 was studied. The CO_2 laser being tuned across the ν_1 band of CF_2Cl_2. Various parametric studies involving laser frequency, fluence, pressure, etc., were carried out for this molecule, which is expected to give better yields due to its spectroscopic features.

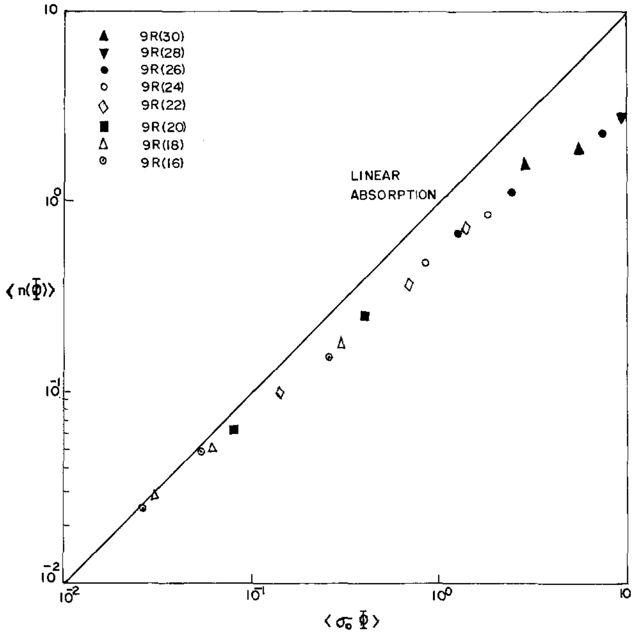

Fig. 1. Average number of photons absorbed per molecule $\langle n(\Phi) \rangle$ for CF_2Cl_2 as a function of $\langle \sigma_0 \Phi \rangle$. The data were obtained at several frequencies using various CO_2 laser lines within the ν_1 band of CF_2Cl_2 in the pressure range 40–133 Pa

a) Multiphoton Absorption (MPA) *Measurements.* Conventional measurements of absorbed laser energy by CF_2Cl_2, corrected for window losses, were taken by simultaneously monitoring the incident and transmitted energy using calibrated pyroelectric detectors. Various excitation frequencies and fluences were used to estimate $\langle n(\Phi) \rangle$, the average number of photons absorbed per molecule. Based on the MPA data collection by Judd [18] for various molecules, we have similarly plotted our result in the format of $\langle n(\Phi) \rangle$ versus $\langle \sigma_0 \Phi \rangle$ (Fig. 1). It was found that after scaling out the small signal absorption cross section σ_0 and the excited population fraction $\langle f \rangle$, the number of photons absorbed per molecule $\langle n(\Phi) \rangle$ at a fluence Φ scales as Φ^{γ}. For $\langle \sigma_0 \Phi \rangle / \langle f \rangle$ less than 1, γ is unity while it is about 2/3 for $\langle \sigma_0 \Phi \rangle / \langle f \rangle > 1$.

At low CF_2Cl_2 pressure (up to about 133 Pa), $\langle n \rangle$ can be considered practically constant to within the experimental error which is typically about 1–2 in the fluence range of 0.2–0.5 J cm^{-2}. This could be due to the fact that collisions are not very important during the laser pulse duration. The fraction of molecules (also termed q-factor [19]) excited by the pulse can be determined by saturating the energy absorption when an inert gas like argon is added to CF_2Cl_2 at sufficiently low pressure so that the mixture is free of CF_2Cl_2–CF_2Cl_2 collisions. The ratio of $\langle n \rangle$ at $P_{Ar} = 0$ and $\langle n \rangle_{sat}$ at $P_{Ar} = P_{sat}$ indicated that about 5% of molecules interact with the field at a fluence of 0.5 J cm^{-2}. This is similar to the value reported by Alonso et al. using 929.07 cm^{-1} CO_2 laser irradiation [20]. However when the CF_2Cl_2 pressure was increased, $\langle n \rangle$ increased due to rotational hole-filling and intermolecular V–V energy exchange assisted by collisions. At a fluence level of 0.5 J cm^{-2}, $\langle n \rangle$ takes a constant value in the range of 1.33–4 kPa of CF_2Cl_2 suggesting that all the molecules in the ground state ($\simeq 38\%$) become resonant with the field during the laser pulse. However, there could be some contribution to the absorption through hot bands lying close to the pumped ν_1 mode. At this fluence level CF_2Cl_2 absorbs about 10–12 photons ($\simeq 10000\ cm^{-1}$) and in such an energetic state can undergo rapid intramolecular and intermolecular *V–V* energy transfer (Sect. 2.3b) to populate the ν_2 level (667 cm^{-1}) considerably. Addition of UF_6 facilitates the energy distribution further by transferring the energy from $CF_2Cl_2(\nu_2)$ to UF_6 (ν_3) by near-resonant *V–V* exchange.

b) Multiphoton Dissociation (MPD) *Measurements.* Various groups have studied the MPD of CF_2Cl_2 by exciting either near 923 cm^{-1} (antisymmetric CCl_2 stretch) or near 1098 cm^{-1} (symmetric CF_2 stretch) [21–22]. Using single frequency excitation at these two bands, the laser-induced dissociations were observed to be practically the same. In the present studies we used the latter mode of excitation. Under 9*R*(30) excitation neat CF_2Cl_2 underwent MPD with a fluence threshold of 0.6 J cm^{-2}. IR spectroscopy and GC analysis revealed the formation of various products, namely $C_2F_4Cl_2$ (IR peaks at 1048 and 845 cm^{-1}), C_2F_4 (1339 cm^{-1}) and CF_3Cl (1213 and 770 cm^{-1}). The dissociation patterns were similar in the fluence and pressure (0.66–6.6 kPa) range studied. IRMPD of CF_2Cl_2 occurs via two channels with nearly the same endothermicity:

$$CF_2Cl_2 \begin{cases} \to CF_2Cl + Cl & \Delta H = 78\ \text{kcal mole}^{-1} \quad (4) \\ \to CF_2 + Cl_2 & \Delta H = 74\ \text{kcal mole}^{-1}. \quad (5) \end{cases}$$

The branching ratio measurements have been reported in bulk and molecular beam photolysis under various fluence conditions. Krajnovitch et al. [23] has shown that the Cl_2:Cl ratio at 6 J cm^{-2} is 0.12 and that this ratio changed by less than 25% over the fluence range of 0.3–6 J cm^{-2}. The bulk photolysis experiments [22, 24] reported maximum CF_2 fractional yield of about 7% in good agreement with the molecular beam studies. However the product analysis of bulk photolysis in various studies is not unambiguous. While in certain experiments [21b] CF_3Cl and $C_2F_4Cl_2$ were observed with no C_2F_4 production, in other cases the products were $C_2F_4Cl_2$ and C_2F_4 [21c]. In the present studies, we have observed that $C_2F_4Cl_2$, CF_3Cl, and C_2F_4 were the major products, but sometimes a small amount of uncharacterized product was also detected. This could be due to polymerization of C_2F_4 to some extent or COF_2 originating from reaction of CF_2 with traces of O_2. Judging from these various reports, it is quite likely that the bulk photolysis products are dependent on the experimental conditions like excitation frequency, fluence, pressure, etc. As some of the products may have absorption at the excitation frequency they can lead to secondary products as well and can complicate the diagnosis of the primary products.

However, when exciting with 9*R*(30) line, the dissociation of only UF_6 in a CF_2Cl_2/UF_6 mixture (5:1) could be observed at a much lower fluence of 0.3 J cm^{-2}. The possibility of CF_2Cl_2 dissociation prior to UF_6 can be ruled out at this fluence level. On the contrary, it was observed that UF_6 is an efficient quencher for dissociation of CF_2Cl_2 as we could not measure any dissociation of CF_2Cl_2 even at higher fluence (>1 J cm^{-2}) when the mixture contained more UF_6 than CF_2Cl_2. In a mixture, therefore, the CF_2Cl_2 MPD threshold must be higher than that in the neat CF_2Cl_2 system. The dissociation yield of UF_6 in a typical mixture ($CF_2Cl_2:UF_6 = 5:1$) of 4 kPa total pressure was found to be 5×10^{-3} per pulse at a fluence level of 0.5 J cm^{-2}. However when such typical mixture was irradiated at progressively higher fluence level, CF_2Cl_2 also started decomposing at about 0.8 J cm^{-2} along with increasing UF_6 dissociation.

The dissociation of UF_6 alone in a mixture was accompanied by the development of new peaks in the IR spectrum at 1270 and 1210 cm^{-1} which are similar to the other sensitizer/UF_6 system. These could be due to some volatile fluorides resulting from the F atom reaction with cell materials. But in the case of dissociation of both CF_2Cl_2 and UF_6, IR spectroscopy and GC analysis revealed that CF_3Cl was the major product with very little formation of C_2F_4 and $C_2F_4Cl_2$. Apart from its formation from MPD of CF_2Cl_2, additional CF_3Cl could be formed from the reaction of F and CF_2Cl radicals originating from the dissociation of UF_6 and CF_2Cl_2 respectively. However, reaction of F atoms with CF_2Cl_2 to give CF_2Cl is insignificant which otherwise could have increased the yield of $C_2F_4Cl_2$. From the above results it is clear that a similar mechanism as described in Sect. 2.2 is operative in this system too. However one expects an efficient *V–V* energy transfer in this case compared to CF_3Cl because of the smaller energy defect of 42 cm^{-1} and indeed this was reflected in much better dissociation yield for UF_6 under similar conditions as compared to the CF_3Cl system.

Pyrolysis of CF_2Cl_2 or UF_6 in the system by laser-induced temperature jumps can be ruled out in view of efficient *V–V* energy transfer processes. Hot tube pyrolysis and high power (400 W) CO_2 laser irradiation of CF_2Cl_2 proceeds with a high conversion to CF_3Cl in an overall nearly thermally neutral reaction [25] which is quite different to the MPD products. Even for a fully *V–T* relaxed system, the calculated temperature jump [26] using an average multiphoton excitation cross section for CF_2Cl_2, average fluence in the irradiation volume and thermodynamic properties of CF_2Cl_2 and UF_6, was found to be about 350 K. This would be too low a temperature for pyrolytic dissociation of UF_6 and CF_2Cl_2 which are stable up to about 1200 K [27] and 1150 K [25] respectively.

Role of the Excitation Frequency. Mixtures of 3.33 kPa CF_2Cl_2 and 0.66 kPa UF_6 were irradiated with an energy per pulse of 0.5 J cm^{-2} for various excitation frequencies from 9*R*(30) (1084.6 cm^{-1}) to *R*(16) (1076 cm^{-1}). As the frequency was tuned across the ν_1 band of CF_2Cl_2, the dissociation yield of UF_6 decreased with longer wavelength excitation (Fig. 2). For excitation frequencies which are still further away from the band centre no detectable MPD could be seen for either species even under high fluence condition. This decrease in yield actually follows

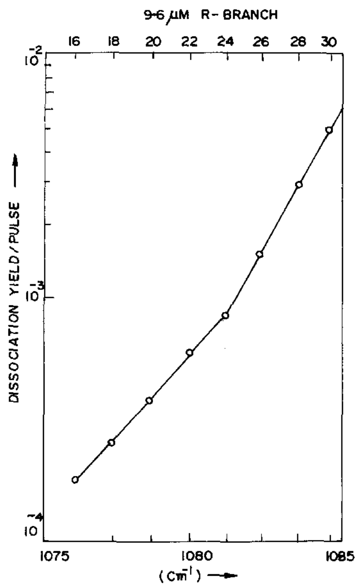

Fig. 2. UF_6 dissociation yield per pulse as a function of irradiation frequencies for 5 : 1 CF_2Cl_2/UF_6 mixture. The total pressure is 4 kPa and the laser fluence 0.5 J cm^{-2}

CF_2Cl_2 absorption features where the cross section decreased by an order of magnitude in the frequency range employed in the experiments. It appears that the frequency dependence can probably be correlated with the absorbed energy in such a way that equal absorbed energy implies equal dissociation probability.

Role of Pressure. In a series of experiments the dissociation of UF_6 was studied using 9*R*(30) excitation (0.5 J cm^{-2}) where CF_2Cl_2 was added in the range of 0.26–3.33 kPa to a constant UF_6 pressure of 0.66 kPa. The dissociation of UF_6 was observed only above 0.66 kPa of CF_2Cl_2 added. Figure 3 shows the dissociation yield versus CF_2Cl_2 pressure on a log-log scale and is roughly proportional to $P^{6\pm1}_{CF_2Cl_2}$ in the range of 1.33–3.33 kPa. This general behaviour is due mainly to the fact that energy absorption in the system increases with increase in CF_2Cl_2 pressure and the energy transferred via $V-V$ processes lead to generation of UF_6 molecules which are excited to a higher average level (Sect. 2.3a). The observation by Angelie et al. [5a] of a sharp acceleration in the UF_6 dissociation rate with number of laser pulses has also been explained by similar reasoning.

The role of V–V energy transfer in MPA of CF_2Cl_2 was studied by Mazur [28]. The intramolecular distribution of energy among various modes after multiphoton absorption of CF_2Cl_2 was observed by following the spontaneous Raman scattering signals appearing on a 20–30 ns time scale. It was also found that the ν_8-pumped mode (923 cm^{-1}) retains an excess energy compared to other connecting modes up to at least 10000 cm^{-1} excitation energy. Above this limit, it was found that 667, 923 and 1098 cm^{-1} modes received about equal energy after the redistribution.

The fact that part of the energy absorbed get transferred to UF_6 was verified in a separate study [29] by looking at the infrared fluorescence (IRF) of CF_2Cl_2 at 9.6 μm and of UF_6 at 16 μm in a laser-excited CF_2Cl_2/UF_6 mixture. It was observed that simultaneously with the increase of $\langle n \rangle$ with UF_6 pressure, there is a decrease in 9.6 μm fluorescence and a growth of 16 μm fluorescence intensity. The observed decrease of 9.6 μm intensity could be understood as the energy was siphoned off to UF_6 from $CF_2Cl_2^{\ddagger}$ via $V-V$ energy transfer while the increase in 16 μm fluorescence is caused by IRF from such excited UF_6 molecules. The fast rise of 16 μm IRF (<1 μs limited by the rise time of the detection system) suggested that intermolecular V–V energy transfer from CF_2Cl_2 to UF_6 is complete within the laser pulse duration.

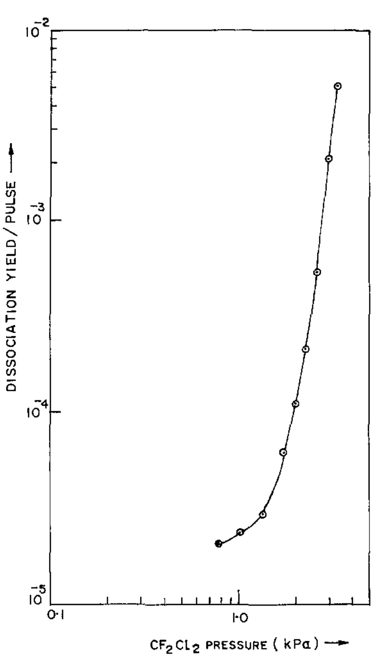

Fig. 3. UF_6 dissociation yield per pulse versus CF_2Cl_2 pressure in a mixture where the UF_6 pressure was kept constant at 0.66 kPa. The pulse energy was 0.5 J cm^{-2} for the exciting 9*R*(30) CO_2 laser line

3. Discussion

The observations presented in this study can be used to examine (1) the characteristics of the sensitizer/UF_6 system and (2) the coupling of vibrational energy between two molecular systems in general. Comparison of the dissociation yield in each case can provide information about the extent to which the vibrational degrees of freedom in the two species have coupled.

In dealing with the mechanism of vibrational energy flow in polyatomic molecules whose specific vibrational mode is excited by a laser, it is the general consensus that the intramode V–V dominates the intermode V–V energy transfer. Therefore, a local vibrational quasi-equilibrium distribution is attained within the laser-pumped mode prior to the establishment of the steady state distribution among all the modes. In the final stage of relaxation the V–T/R energy transfer occurs from modes having low fundamental frequencies. The studies on the vibrational relaxation of a number of small polyatomic molecules support this mechanism and are reviewed in detail by Flynn [30].

The role of *V–V* energy transfer being undoubted in the present studies, we can estimate the vibrational relaxation probabilities in each case on the basis of long range dipole–dipole interaction. The probability for transition from state 1 to state 2 induced by a time-dependent perturbation $V(t)$ in the first order Born approximation is given by [31]:

$$P_{12}=\hbar^{-2}\left|\int_{-\infty}^{+\infty} V_{12}(t)\exp(i\Delta\omega t)dt\right|^2, \tag{6}$$

where $V_{12}(t)=\langle 1|V(t)|2\rangle$.

It is known that the probability will be greatest when $V_{12}(t)$ has Fourier components at frequency $\Delta\omega$. For a *V–T* process where $\Delta\omega$ is large and the process occurs through the lowest vibrational level, this may be achieved on the repulsive part of the interaction potential where V_{12} changes rapidly with time. However, in *V–V* processes it is possible for $\Delta\omega$ to be quite small or even zero for a resonant energy transfer. In such cases, the attractive part of the interaction potential may introduce significant Fourier components at frequency $\Delta\omega$ into $V(t)$. That such long-range dipole–dipole interactions could induce near resonant *V–V* transfer was first pointed out by Mahan [32] and was subsequently improved by Sharma and Brau and Stephenson et al. [33].

Evaluating the Born approximation, the vibrational relaxation probability is obtained as:

$$P(b,v)=\hbar^{-2}C^2\left|\frac{2\Delta\omega}{bv^2}K\left(\frac{b\Delta\omega}{v}\right)\right|^2, \tag{7}$$

where K is a modified Bessel function, and C is a constant containing the dipole matrix elements and an appropriate rotational average. This probability (7) must be integrated over the impact parameter b and the velocity v with appropriate weighting factors to obtain the average vibrational relaxation probability $\langle P\rangle$ for comparison with the experiment. The non-resonant $(\Delta\omega \neq 0)$ *V–V* relaxation probability due to long-range forces using the Sharma-Brau cut-off is given by:

$$\langle P\rangle=\frac{4\pi^4C^2\Delta\omega\mu}{\sqrt{3}h^2d^3v^*kT}\exp(-\mu v^{*2}/2kT), \tag{8}$$

where $C=1/3\ [\text{d.m.}^A]_{12}\times[\text{d.m.}^B]_{12}$, where $[\text{d.m.}^A]_{12}$ is the $1\rightarrow 2$ vibrational dipole matrix element for molecule A and v^* is given by $(2d\Delta\omega kT\mu^{-1})^{1/3}$. The above Eq. (8) gives a behaviour similar to that given by SSH theory i.e. $\ln\langle P\rangle \sim \Delta\omega^{2/3}$ and $\sim T^{-1/3}$. These matrix elements can be determined from measurements of the integrated infrared absorption (S_m) which is related to them by [34]:

$$\text{d.m.}=0.3646\,(S_m/\nu)^{1/2}, \tag{9}$$

where d.m. is in Debye, S_m is in km mole^{-1} and ν is the band centre frequency in cm^{-1}.

From the available spectroscopic and kinetic data, the vibrational energy transfer probabilities were evaluated for UF_6/sensitizer systems using the above treatment. For one-quantum transfer, the probabilities are given in Table 2, which indicate that energy transfer can occur to UF_6 very efficiently from CF_2Cl_2 and SF_6. The last entry in the table, i.e. SF_6, was kept to compare the earlier results with the present set of sensitizers. The estimated one-quantum transfer probability in the SF_6/UF_6 system agrees with the value of 2.8×10^{-11} cm^3 s^{-1} at 300 K reported by Kim et al. [6].

Table 2. Vibrational energy transfer probabilities for various sensitizers with UF_6 ($\nu_3=625$ cm^{-1}, d.m. = 0.38 D [39]) using long-range dipole–dipole interaction

Sensitizer	Modes [cm^{-1}]	d.m. [D]	$C(S/UF_6)$ [erg cm^3] × 10^{40}	$\langle P\rangle$
CF_4	$\nu_2+\nu_4$ (1067)	0.0099	–	–
	ν_4 (630)	0.0534 [40]	67.64	0.0276
CF_3Cl	ν_1 (1105)	0.226	–	–
	ν_2 (781)	0.069 [40]	87.40	0.0062
CF_2Cl_2	ν_1 (1101)	0.183	–	–
	ν_2 (667)	0.198 [40]	250.80	0.369
SF_6	ν_3 (948)	0.388	–	–
	ν_4 (615)	0.134 [41]	169.70	0.239

Once the vibrational energy transfer cross sections are known, the whole process can be described by a rate equation in a similar formalism to the energy grained master equation (EGME) [35]. The difference here is that the optical pumping terms are replaced by collisional pumping. When the laser-excited sensitizer molecule collides with UF_6 molecule and exchanges energy E_{ij} between the initial state i and final state j of UF_6, three options are possible: an up-collision with $j>i$ (equivalent to optical absorption of one vibrational quantum) with a rate r^u, a down-collision with $j<i$ (equivalent to stimulated emission of one vibrational quantum) with a rate r^d and a non-productive event when $j=i$.

Therefore, the rate equation for UF_6 is

$$dN_i/dt=r^u_{i-1}N_{i-1}+r^d_{i+1}N_{i+1}-(r^u_i+r^d_i+r^{dis}_i)N_i, \tag{10}$$

where N_i is the population at the level i and r^{dis}_i is the dissociation rate at this level.

Such excitation can either proceed to the dissociation threshold or it can result in the excitation of UF_6 in its quasi-continuum (QC) as discussed earlier. In the first case, the above rate equation can describe the whole process, while in the latter case further absorption of laser photons by QC-excited UF_6 molecules must include optical pumping terms at an appropriate time in the rate equation which requires a very careful analysis. The collisional rates r^u and r^d depend on the vibrational population of the sensitizer which is governed by the working laser fluence and molecular absorption cross section at the exciting frequency. Therefore, when the estimated energy transfer probabilities of the three sensitizers are normalised with respect to the absorption strength of ν_3 of SF_6, it is found that CF_3Cl is about fifty times less efficient than CF_2Cl_2, and that CF_4 is almost ineffective in inducing dissociation of UF_6 due to its poor absorption and strong radiative coupling of the pumped mode to ν_2 instead of the required ν_4 mode.

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References

1. (a) N. Bloembergen, E. Yablonovitch: In *Laser Spectroscopy III*. Springer Ser. Opt. Sci., Vol. 7 (Springer, Berlin, Heidelberg 1977) p. 86
   (b) R.V. Ambartzumyan, Yu.A. Gorokhov, V.S. Letokhov, G.N. Makarov: Sov. Phys. JETP **42**, 993 (1976)
   (c) W. Fuss, J. Hartmann: J. Chem. Phys. **70**, 5486 (1979)
2. (a) J.I. Steinfeld: In *Laser induced Chemical Processes*, ed. by J.I. Steinfeld (Plenum, New York 1981) p. 243
   (b) W.E. Farneth, G. Flynn, R. Slater, N.J. Turro: J. Am. Chem. Soc. **98**, 7877 (1976)
   (c) A. Fahr, R.D. Bates, Jr.: Chem. Phys. **105**, 449 (1986)
3. D.M. Cox, A. Grauck: J. Molec. Spectrosc. **81**, 207 (1980)
4. R.S. Karve, S.K. Sarkar, K.V.S. Rama Rao, J.P. Mittal: Chem. Phys. Lett. **78**, 273 (1981)
5. (a) C. Angelie, M. Cauchetier, J. Paris: Chem. Phys. **66**, 129 (1982)
   (b) M. Cauchetier, M. Luce, C. Angelie: Chem. Phys. Lett. **88**, 146 (1982)
   (c) C.T. Chin, H.Q. Hou, Y.H. Bao, T.H. Li: Chem. Phys. Lett. **101**, 69 (1983)
   (d) A. Mele, F. Salvetti, E. Molinari, M.L. Terranova: J. Photochem. **32**, 265 (1986)
6. K.C. Kim, S. Freund, R.K. Sander, D.F. Smith, W.B. Person: J. Chem. Phys. **78**, 32 (1983)
7. G. Herzberg: In *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York 1956) p. 167
8. J.J. Tiee, C. Wittig: J. Appl. Phys. **49**, 61 (1978)
9. G. Koren, I. Levin, M. Dahan, U. Oppenheim: J. QE-**16**, 1380 (1980)
10. A.Z. Grasyuk, V.S. Letokhov, V.V. Lobko: Sov. J. Quantum Electron. **10**, 1317 (1980)
11. C.W. Patterson, R.S. McDowell, N.G. Areson, R.F. Begley, H.W. Galbraith, B.J. Krohn: J. Molec. Spectrosc. **80**, 71 (1980)
12. E.K. Plyler, W.S. Benedict: J. Res NBS **47**, 202 (1951)
13. R.S. Sheorey, G.W. Flynn: J. Chem. Phys. **72**, 1175 (1980)
14. H. Nakane, S. Tsuchiya: Laser Chem. **7**, 141 (1987)
15. J.T. Knudtson, G.W. Flynn: J. Chem. Phys. **58**, 2684 (1973)
16. J.J. Tiee, C. Wittig: Opt. Commun. **27**, 377 (1978)
17. J.A. Horsley, P. Rabinowitz, A. Stein, D.M. Cox, R. Brickman, A. Kaldor: J. QE-**16**, 412 (1980)
18. O.P. Judd: J. Chem. Phys. **71**, 4515 (1979)
19. Yu.R. Koomilskii, V.S. Marchuk, E.A. Ryabov: Sov. J. Quantum Electron. **12**, 1139 (1982)
20. E.M. Alonso, A.L. Peuriot, V.B. Slezak: Appl. Phys. B **40**, 39 (1986)
21. (a) J.L. Lyman, S.D. Rockwood: J. Appl. Phys. **47**, 595 (1976)
    (b) G.A. Hill, E. Grunwald, P. Keenh: J. Am. Chem. Soc. **99**, 6521 (1977)
    (c) G. Folchar, W. Braun: J. Photochem. **8**, 341 (1978)
22. (a) D.S. King, J.C. Stephenson: Chem. Phys. Lett. **51**, 48 (1977)
    (b) R.J.S. Morrison, E.R. Grant: J. Chem. Phys. **71**, 3537 (1979)
23. D. Krajnovitch, F. Huisken, Z. Zhang, Y.R. Shen, Y.T. Lee: J. Chem. Phys. **77**, 5977 (1982)
24. R.J.S. Morrison, R.F. Loring, R.L. Farley, E.R. Grant: J. Chem. Phys. **75**, 148 (1981)
25. M.P. Freeman, D.N. Travis, M.F. Goodman: J. Chem. Phys. **60**, 231 (1974)
26. N.G. Basov, A.N. Oraevsky, A.V. Pankarov: In *Chemical and Biochemical Application of Lasers*, ed. by C.B. Moore, vol. 1 (Academic, New York 1974) p. 203
27. L. Brewer, L.A. Bromley, P.W. Gilles, N.L. Lofgren: In *Chemistry of Uranium, Collected Papers*, ed. by J.J. Katz, E. Rabinovitch (US Atomic Energy Commission, Oak Ridge 1958) p. 219
28. E. Mazur: In *Atomic and Molecular Processes with Short Intense Laser Pulses*, ed. by A.D. Bandrauk (Plenum, New York 1988) p. 329
29. R.S. Karve, S.K. Sarkar, K.V.S. Rama Rao, J.P. Mittal: In *Lasers and Applications*, ed. by H.D. Bist, J.S. Goela (McGraw-Hill, New Delhi 1984) p. 403
30. (a) G.W. Flynn: Acc. Chem. Res. **14**, 334 (1981)
    (b) G.W. Flynn, E. Weitz: Adv. Chem. Phys. **47**, 185 (1981)
31. J.T. Yardley: In *Introduction to Molecular Energy Transfer* (Academic, New York 1980) p. 130
32. B.H. Mahan: J. Chem. Phys. **46**, 98 (1967)
33. (a) R.D. Sharma, C.A. Brau: J. Chem. Phys. **50**, 924 (1969)
    (b) J.C. Stephenson, R.E. Wood, C.B. Moore: J. Chem. Phys. **48**, 4790 (1968)
34. K. Fox, W.B. Person: J. Chem. Phys. **64**, 5218 (1976)
35. J.R. Barker: J. Chem. Phys. **72**, 3686 (1980)
36. T. Shimanouchi: NSRDS-NBS **39** (1972)
37. S.W. Benson: Chem. Rev. **78**, 23 (1978)
38. D. Hildenbrand: J. Chem. Phys. **66**, 4478 (1977)
39. K.C. Kim, W.B. Person: J. Chem. Phys. **74**, 171 (1981)
40. K. Narahari Rao: In *Molecular Spectroscopy: Modern Research*, Vol. 3 (Academic, New York 1985) Chap. 3
41. W.B. Person, K.C. Kim: J. Chem. Phys. **69**, 1764 (1978)