

TEA CO₂ laser-induced reaction of CH₃NO₂ with CF₂HCl: A mechanistic study

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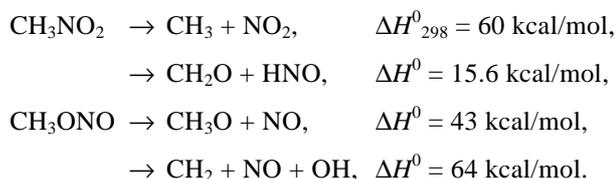
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Abstract. Dissociation of nitromethane has been observed when a mixture of CF₂HCl and CH₃NO₂ is irradiated using pulsed TEA CO₂ laser at 9R (24) line (1081 cm⁻¹), which is strongly absorbed by CF₂HCl but not by CH₃NO₂. Under low laser fluence conditions, only nitromethane dissociates, whereas at high fluence CF₂HCl also undergoes dissociation, showing that dissociation occurs via the vibrational energy transfer processes from the TEA CO₂ laser-excited CF₂HCl to CH₃NO₂. Time-resolved infrared fluorescence from vibrationally excited CF₂HCl and CH₃NO₂ molecules as well as UV absorption of CF₂ radicals are carried out to elucidate the dynamics of excitation/dissociation and the chemical reactions of the dissociation products.

Keywords. Nitromethane; excitation dissociation; energy transfer; infrared fluorescence; CF₂ radicals.

1. Introduction

Dissociation of nitro compounds continues to be a topic of current research due to their important role in explosive materials and atmospheric chemistry^{1–5}. Nitromethane (CH₃NO₂), the first member of this series is the most studied molecule in this class^{6–10}. It has been shown to undergo dissociation into following primary channels on excitation.



In order to avoid the surface effects of the reactor and secondary reactions at high temperature, gas phase photodissociation has been used to understand the primary processes and dissociation products. In the UV photolysis (320–280 nm) of gaseous nitromethane, dissociation into CH₃ and NO₂ radicals is the most efficient [*f* = 0.6]

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primary process⁶. Isomerisation of CH_3NO_2 to CH_3ONO and subsequent decay of the latter to CH_3O and NO was observed in molecular beam study⁷ in the TEA CO_2 laser excitation of CH_3NO_2 . Isotopic selectivity in ^{15}N during dissociation of CH_3NO_2 was disclosed even when vibrational bands having no isotope shifts were pumped⁸. Reactions of nitromethane with other simple molecules have also been reported. Thomsen *et al*⁹ studied the reaction of nitromethane with H and D atoms and showed the formation of $\text{CH}_3(\text{NO})\text{OH}$ adduct. In the CO_2 laser-initiated reaction between nitromethane and H_2 under high fluence conditions¹⁰, bright visible luminescence from CN species was observed.

This molecule has a very weak absorption in the CO_2 laser emission range¹¹. Therefore, CF_2HCl was selected as energy transfer reagent to induce its dissociation because there are quite a few fundamental frequencies¹² which are close to that of CH_3NO_2 and a high probability of energy transfer is expected. Table 1 gives the different frequencies for both the molecules. In this work, we have studied the dissociation of CH_3NO_2 by energy transfer from CO_2 laser-excited CF_2HCl and secondary chemical reactions of the dissociation products when CF_2HCl also undergoes multiphoton dissociation. Time-resolved infrared fluorescence from these molecules as well as UV absorption of CF_2 radicals is investigated to elucidate the dynamics of excitation and dissociation.

2. Experimental

Dissociation of nitromethane was studied in a stainless steel cell under low as well as high fluence conditions. The laser beam was focussed in the middle of the cell (away from the cell walls) to avoid any wall effects. The fluence was varied by using lenses of appropriate focal length and changing the input energy by inserting polyethylene sheets in the beam. Laser energy was measured using a Gentec pyroelectric detector.

Table 1. Vibrational frequencies (cm^{-1}) of CF_2HCl ¹² and CH_3NO_2 ¹¹.

Frequency	CH_3NO_2	CF_2HCl
\mathbf{n}_1	2972	3021
\mathbf{n}_2	1397	1312
\mathbf{n}_3	1377	1107
\mathbf{n}_4	658	809
\mathbf{n}_5	918	596
\mathbf{n}_6	3065	412
\mathbf{n}_7	1443	1351
\mathbf{n}_8	1087	1127
\mathbf{n}_9	1586	365
\mathbf{n}_{10}	477	
\mathbf{n}_{11}	3065	
\mathbf{n}_{12}	1482	
\mathbf{n}_{13}	1100	
\mathbf{n}_{14}	605	
\mathbf{n}_{15}	*	

* A_2 twisting vibrations in CH_3NO_2 are not allowed in the IR as well as Raman¹¹

The temporal profile of the laser pulse had a 150 ns (FWHM spike) followed by a 2 μ s tail. The spike contained two-thirds of the total pulse energy. Low fluence dissociation was studied in a small cell (4.7 cm long, total volume = 32 cm³). The cell was fitted with two polished KCl windows. Mixtures of CH₃NO₂ and CF₂HCl were irradiated at a CO₂ laser fluence of 0.5 J cm⁻² for 1000 pulses at 9R (24) line (1081 cm⁻¹) of CO₂ laser which is strongly absorbed by CF₂HCl but not by CH₃NO₂. Depletion of CH₃NO₂ and CF₂HCl was monitored by gas chromatography and FTIR spectrometry. In gas chromatography, the products were analysed on a 6-foot column of silicone grease and detected using a flame ionisation detector. For detection of H₂ and NO, molecular sieves and porapak-Q columns were used with a thermal conductivity detector. Quantitative analysis could not be done because of the complexity of the reaction products and nonavailability of standards.

Time-resolved experiments were carried out in a specially designed stainless steel cell fitted with a pair of KCl windows orthogonal to another pair of quartz windows in an IR/UV crossed beam configuration. A cw spectroscopic UV probe beam from a pulsed mode operated Xe lamp (150 W) with associated optics, monochromator ($f = 3.5$), PMT (IP 28) and signal processing system (Gould Biomation 4500, 10 ns resolution)¹³ was used for detection of transients in CO₂ laser irradiation. The CO₂ laser is triggered at a time when the pulsed lamp intensity reaches a maximum and remains steady over a period of 200 μ s. The complete operation from firing of CO₂ laser to data collection is computer controlled. The signal is averaged for 64 shots and data are transferred to the computer for further processing.

The experimental set up used for infrared fluorescence has been described in detail earlier^{14,15}. Briefly, experiments were performed in a cell having two orthogonal pairs of windows. Fluorescence was detected by an InSb (at 77 K) photovoltaic detector (Judson J-10D) equipped with a matched preamplifier and sapphire window. The signals were averaged on a digital oscilloscope. The rise time of this system is $\approx 5 \mu$ s. The IRF spectrum of CF₂HCl on exciting its \mathbf{u}_3 mode by 1081 cm⁻¹ CO₂ laser line shows two bands at 4.6 and 3.3 μ m¹⁴. The 4.6 μ m band is due to the overtone of the pumped mode and the 3.3 μ m is due to the fundamental \mathbf{u}_1 . Using a filter, fluorescence was recorded only in the 3–4 μ m range. Since the frequency modes of CF₂HCl and CH₃NO₂ are close (≈ 50 cm⁻¹), the combined fluorescence was collected and the IRF signal for CH₃NO₂ was obtained by subtracting the fluorescence from neat CF₂HCl.

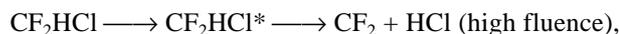
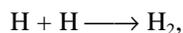
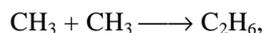
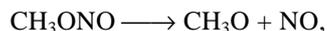
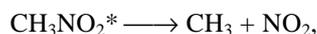
3. Results and discussion

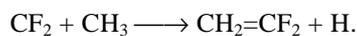
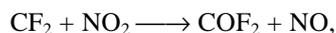
3.1 Effect of fluence and pressure

Dissociation of nitromethane was observed when a mixture of CF₂HCl (8 torr) and CH₃NO₂ (8 torr) is irradiated at 9R(24) laser line under low fluence conditions (0.5 J/cm²). Under this pressure and fluence condition, the average number of photons absorbed $\langle n \rangle$ is approximately unity¹⁴. Typical results indicated about 10% dissociation in CH₃NO₂ while CF₂HCl did not dissociate after 1000 pulses of irradiation. In this case, the primary products are CH₃ and NO₂ leading to stable products like C₂H₆, NO₂, CH₄, NO, H₂ etc. Neat CH₃NO₂ did not show any dissociation under these conditions as it absorbs very weakly at this frequency¹¹. The dissociation threshold fluence for CF₂HCl is reported to be 1.5 J/cm²¹⁶ and hence it is not expected to decompose under low fluence conditions. However, by increasing the fluence

(10 J/cm²), typically 50% of CH₃NO₂ decomposed along with dissociation of CF₂HCl to the extent of 15%. The products in this case were identified as CH₂=CF₂, C₂F₄, HCl, COF₂, NO, H₂, CH₄ and in trace amounts, C₂H₆. In both low and high fluence experiments, dissociation of CH₃NO₂ in the mixture proceeds by absorption of laser photons mainly by CF₂HCl and subsequent transfer of energy to nitromethane by collisional processes from vibrationally excited CF₂HCl. This mechanism was further supported by the following two observations. First, decreasing the partial pressure of CF₂HCl decreases the dissociation of CH₃NO₂ and, second, addition of an inert gas (32 torr) to a CF₂HCl + CH₃NO₂ mixture showed a threefold increase in the CF₂HCl dissociation, whereas the dissociation of nitromethane decreases tenfold. In the first case, as the partial pressure of the laser energy absorber decreases, the total energy absorbed by the system decreases and hence the dissociation yield. Whereas in the second case, CF₂HCl dissociation increased due to rotational hole filling and vibrationally excited nitromethane is de-excited due to collisions with inert gas molecules resulting in the loss of dissociation yield. The mechanism of rotational hole filling in IRMPD has been found to be operative for enhancing the multiphoton dissociation yield. This is affected by collisionally re-populating the rotational levels which are depleted by the resonant laser excitation. Hence, the process of multiphoton and energy transfer to the nitromethane compete under the high fluence conditions unlike only energy transfer processes under low fluence conditions.

At high laser fluence when CF₂HCl also dissociates, CF₂ and HCl are also present in addition to CH₃ and NO₂ in the mixture. As a result of multiphoton dissociation of CF₂HCl, CF₂ is produced in the vibrationally excited state with typical vibrational temperature of ≈ 1000 K¹⁷. Therefore, all these primary products can react in a complex manner to produce the different observed products. The other products like COF₂ and NO could be formed by the reaction of CF₂ with NO₂¹⁸. Isomerisation of excited CH₃NO₂ to CH₃ONO⁷ and the dissociation of the latter into CH₃O and NO could also contribute to total NO yield. Formation of CH₄ can be explained by the reaction of CH₃ radicals with CH₃NO₂, since the activation energy for this process is shown to be only 11 kcal/mol¹⁹. From the study of reactions of CF₂ radicals with various species²⁰, formation of CH₂=CF₂ appears to be due to the reaction of CF₂ with CH₃ radicals. Although the kinetic parameters of this reaction are not known, it is expected to have very low activation energy. Under the low fluence conditions, H atoms are produced through rapid dissociation of methoxy radicals² generated in the photolysing mixture. Therefore, the observed photochemistry of the mixture at low and high CO₂ laser fluence can be understood in terms of the following reactions:





3.2 Time-resolved UV absorption of CF₂

CF₂ was monitored by its optical absorption at 249 nm ($\bar{A} \leftarrow X$)^{13,21,22} as a function of time and partial pressure of the nitromethane. Under low fluence conditions, no absorption signal was observed for CF₂ in agreement with the FTIR product analysis. However, under high fluence irradiation, a transient absorption signal was observed for CF₂. In the absence of nitromethane, the CF₂ signal increases sharply for about 3 μs followed by a gradual increase up to several microseconds (figure 1a). However, when monitored over millisecond time scale (not shown in the figure), the decay of CF₂ signal was observed and the decay was found to be of second order. With the addition of CH₃NO₂, the CF₂ signal intensity decreased and the decay showed a bimodal behaviour (figure 1b), an initial fast decay in about 10 μs followed by a slow decay. The fast component was found to be quite sensitive to nitromethane pressure in the mixture. The initial fast decay followed by the non-zero base line in figure 1b indicates that CF₂ reacts with CH₃ and NO₂, i.e. the decomposition products of CH₃NO₂ and not

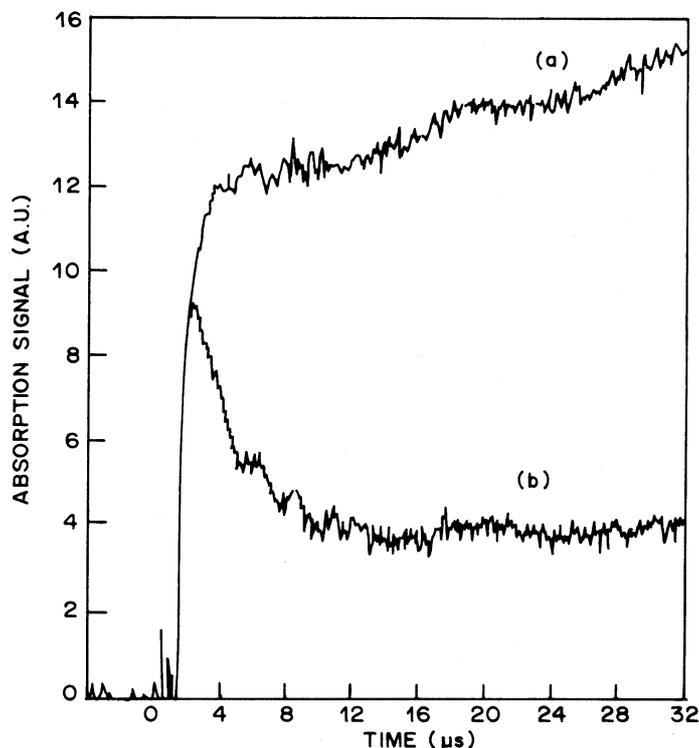


Figure 1. UV absorption signal of CF₂ (fluence $\sim 10 \text{ J/cm}^2$). (a) 10 Torr of CF₂HCl and (b) 10 Torr CF₂HCl + 10 Torr of CH₃NO₂.

CH₃NO₂ itself. In the latter case, CF₂ signal should have decayed to the baseline. Decay to the non-zero baseline can be explained in terms of transient species concentration which react with CF₂ as well as among themselves. However, the decay depends on the pressure of CH₃NO₂ because of the fact that with the increasing CH₃NO₂ pressure the dissociation yield per pulse of CH₃NO₂ increases which resulted in higher concentration of CH₃ and NO₂ and hence a faster decay is observed.

After the CF₂ radical is produced it can react with either (1) CF₂, (2) NO₂ or (3) CH₃. The rate constants for the first two processes are known^{10,18} and would correspond to much slower decay rates than the experimentally observed rates considering the dissociation yield per pulse and the concentration of the transient species. Thus, the observed decay of CF₂ radical in the first 10 μs is assigned to the reaction of CF₂ with CH₃. This reaction being a radical–radical reaction will have very low activation energy. In the present experimental setup where both the species are generated transiently and the concentrations are not well-defined, it was not possible to measure the rate constant for this reaction.

Usually, in IRMPD the dissociation yield of the molecule decreases with increasing pressure of the buffer gas after the initial enhancement which is due to rotational hole filling^{23,24}. However, a buffer molecule having normal vibrational modes resonant with the modes of the excited molecule is very efficient in quenching its yield, compared to noble gases or other non-resonant molecules. In this set of experiments, when 30 torr Ar was added to 10 torr of CF₂HCl, the UV absorption signal of CF₂ increased three times as compared to neat CF₂HCl experiments. With the addition of about 2 torr of CH₃NO₂, the CF₂ signal decreased more than 25%. The decrease in the CF₂ signal is indicative of effective quenching of vibrationally excited CF₂HCl molecules.

3.3 Infrared fluorescence studies

CF₂HCl (5 torr) was irradiated at 9R(28) line under low fluence condition and the infrared fluorescence from the **u**₁ mode recorded (figure 2a). The signal rises to a maximum in 7 μs and then decays to about 80% in 120 μs. Under these conditions no IRF is observed in pure CH₃NO₂. However, on irradiation of a mixture of CF₂HCl (5 torr) and CH₃NO₂ (4.7 torr) the peak IRF intensity increases and the decay is about 50% only (figure 2b). Subtraction of IRF signal of figure 2a from that of figure 2b gives the IRF signal from nitromethane and is shown in figure 3a.

CF₂HCl and CH₃NO₂ have some modes with close values of vibrational frequency. In particular the **u**₃ mode of CF₂HCl at 1107 cm⁻¹¹², which is pumped by the 9R(24) laser line can near resonantly transfer the energy to **u**₁₃ mode of CH₃NO₂ at 1100 cm⁻¹^{8,11}. To check for the presence of vibrationally excited CH₃NO₂, the time-resolved infrared fluorescence from the **u**₁ mode of CH₃NO₂ was monitored when CF₂HCl was excited. In earlier work¹⁴, we reported infrared fluorescence from the **v**₁ mode of CF₂HCl following CO₂ laser excitation in the **u**₃ mode. Figure 2a shows the IRF signal from the **u**₁ mode of CF₂HCl in the absence of nitromethane. As can be seen from figure 2a the signal decays to about 80% in 120 μs time. However, in the presence of CH₃NO₂ (figure 2b), the peak IRF intensity increases and after about 50 μs, the signal decays slowly. In this case, the total decay is only 50% in 120 μs. To confirm that the slow decaying part is not due to rise in the total pressure of the system, another experiment was done in which CH₃NO₂ was substituted by SF₆. SF₆ was chosen because it does not have any fundamental frequency in the range of 3–4 μm which can

give fluorescence and the total number of atoms are the same as in CH₃NO₂. This experiment showed that though the rise time of the signal remaining unaffected, the total intensity decreased considerably and the decay is more than 90% in about 10 μs due to deactivation of CF₂HCl fluorescence by SF₆ and SF₆* itself does not contribute to the IRF in the 3–4 μm region.

In IRF studies on CF₂HCl¹⁴, we have shown that ν_1 mode of CF₂HCl is populated via collisions of molecules initially in the laser excited u_3 ($u = 1$) level. When a particular mode is excited by CO₂ laser at moderate fluences, most of the molecules are in the $\nu = 1$ level. Higher levels of that mode equilibrate via the V-V ladder climbing processes. This type of processes is quite efficient since they are nearly resonant and have been shown to reach steady state in ~ 30 collision²⁵. At longer times, intermode equilibration starts and various other modes are excited depending on the energy defect between the modes, different couplings and the pathways. Decay in the fluorescence of

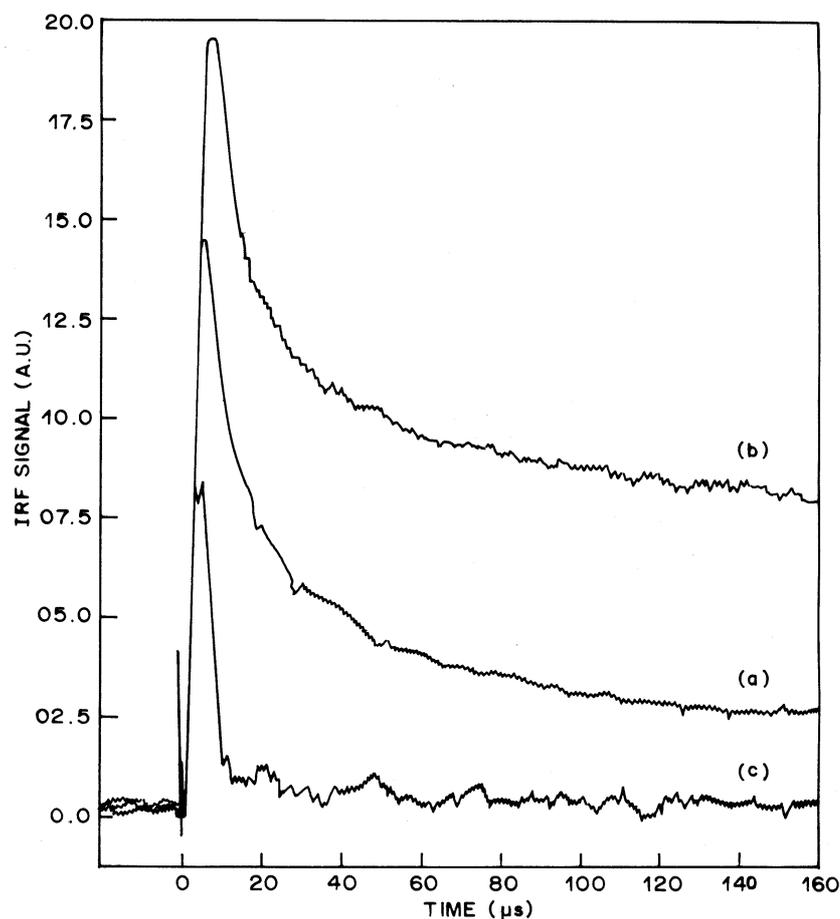


Figure 2. Infrared fluorescence signal in the region of 3 to 4 μm. (a) 5 Torr of CF₂HCl, (b) 5 Torr CF₂HCl + 4.7 Torr of CH₃NO₂, (c) 5 Torr CF₂HCl + 5 Torr of SF₆.

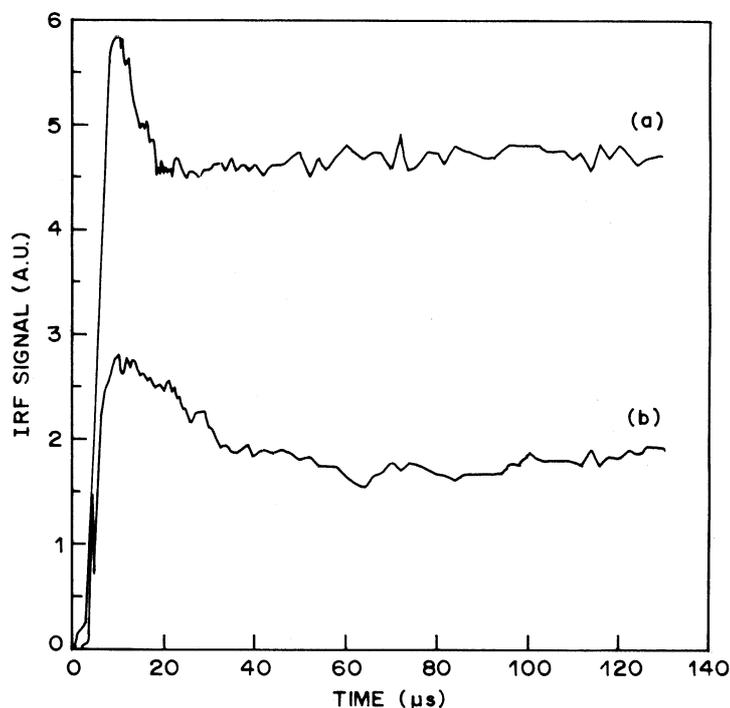


Figure 3. Infrared fluorescence signal in the region of 3–4 μm . (a) Subtracted signal of figures 2b and 2a, (b) 0.5 Torr SF_6 + 12 Torr CH_3NO_2 .

any mode is largely governed by the outflow of energy from $\nu = 1$ level of that mode since the reverse processes are also near resonant and equally efficient.

During the process of collisional excitation of these modes, if a different molecule is present which quenches the initial pumped level, a significant decrease in the IRF intensity is expected and the decay of the fluorescence may be much faster as observed experimentally when SF_6 is added to the CF_2HCl . The fluorescence from u_1 mode shows a decrease in intensity and a fast decay (see figure 2c). In case of CH_3NO_2 most of the above processes remain the same, except that in the process of collisions with CF_2HCl , CH_3NO_2 gets excited and emits fluorescence in the same region as of CF_2HCl . In this case the time evolution of IRF is resultant of these two processes.

Subtraction of pure CF_2HCl IRF signal from that of the mixture ($\text{CF}_2\text{HCl} + \text{CH}_3\text{NO}_2$) generates a resultant signal which comprises fluorescence from CH_3NO_2 alone and the changes brought by the increased number of collisions in the system (figure 3a). This resultant IRF signal shows a comparatively slow rise followed by a sharp decrease for about 10 μs and finally a slow decaying component up to 120 μs . The rise of the signal is largely due to the emission from u_1 mode of CH_3NO_2 . The sharp decrease for 10 μs is originates from the quenching of the u_1 fluorescence of CF_2HCl by the increased number of collisions in the system. The same behaviour is reflected in the IRF of the mixture (figure 2b), where after reaching the maxima, the decrease is sharper for 20 μs as compared to the pure CF_2HCl infrared fluorescence decay. A similar behaviour has been reported in the time-resolved infrared fluorescence of collisionally excited CF_4 by laser pumped SF_6 ²⁶.

In order to make sure that fluorescence of figure 3a indeed due to vibrationally excited CH₃NO₂, SF₆ was tried as another sensitizer for CH₃NO₂. In this experiment 0.5 torr of SF₆ was added to 12 torr of CH₃NO₂ and the mixture irradiated at 10 P(20) CO₂ laser line corresponding to the ν_3 mode of SF₆. The weak IRF signal obtained in 3 to 4 μm region is shown in figure 3b. The absorption coefficient of SF₆ for 10P(20) line is very high, thus its pressure was kept low to avoid thermal heating of the sample. The IRF signal from this system is shown in figure 3b. This signal does not contain the sharp decrease after reaching maxima as in figure 3a since there is no quenching of the fluorescence from the parent. This in turn supports the assignment of the sharp decay in figure 3a to quenching of ν_1 fluorescence of CF₂HCl by CH₃NO₂. Both the signals (figure 3a and 3b) have qualitatively the same nature, thus the slowly decaying fluorescence signal in the region of 3–4 μm is due to collisionally excited CH₃NO₂ molecules. However, because of the limited detector response (1–5.5 μm), it was not possible to monitor the pumped mode.

4. Conclusion

In summary, we have shown that dissociation of nitromethane occurs via the vibrational energy transfer processes from the CO₂ laser-excited CF₂HCl. Under low fluence conditions, dissociation of only nitromethane is observed. However, at high fluence CF₂HCl also dissociates. The products identified under high fluence are CH₂=CF₂, COF₂, CH₄, NO and C₂F₄. Infrared fluorescence studies show that there is an increase in the fluorescence intensity in the 3–4 μm region when nitromethane is added to the CF₂HCl. The rise of the signal has been assigned to the emission from the ν_1 mode of CH₃NO₂. Based on the decrease in time-resolved UV absorption of CF₂ radicals and its decay to nonzero baseline, CH₂=CF₂ has been suggested as originating from the reaction of CF₂ with CH₃.

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