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IR MPD OF CDF_3 IN TWO-FREQUENCY IR FIELDS

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Abstract The effectiveness of various sets of laser frequencies was analyzed for two-frequency MPD of CDF_3 molecule at the different pressures of buffer gas. It was shown that MPD yield increased compared to either single-frequency or two adjacent frequencies irradiation.

INTRODUCTION

Infrared multiple photon dissociation (IR MPD) of molecules by multiple-frequency IR laser fields is based on multistep, resonant excitation of successive vibrational states of molecules with different frequencies [1]. This approach is especially suited to IR MPD of light, small molecules wherein the on-set of quasi-continuum of vibrational levels begins at fairly high internal energy. Very high laser intensity and fluence that are normally required for single frequency IR MPD of this type of molecules are expected to be reduced in multiple-frequency IR MPD as the latter efficiently removes bottle-necking in pumping.

Evseev et al. [2] have recently demonstrated a highly selective and efficient MPD in $^{13}CF_2HCl/^{12}CF_2HCl$ using multiple frequency excitation. We have adopted similar experimental

scheme for getting simultaneous, two frequency emission from a single TEA CO_2 laser [2,3] and have examined two-frequency IR MPD of CDF_3 in its ν_5 band. The advantage of getting two frequencies from a single laser is that the two beams propagate at small angles and in same direction. The difficulty in matching and reproducing overlap volume, which occurs while using two separate lasers, is practically eliminated. Earlier multiphoton excitation and dissociation of CDF_3 have been studied by a number of workers [4-8] using single IR laser frequency and $\sim$ 100 nsec FWHM pulses. Recently, Herman [9] has investigated two-frequency IR MPD of CDF_3 employing two independent CO_2 lasers. In the present work, we have studied MPD process for CDF_3 molecule in two-frequency IR fields. It is shown that for suitable choice of two-frequency set within P- and R-branches of ν_5 band of CDF_3, MPD yield increased compared to either single-frequency or two adjacent frequencies irradiation.

EXPERIMENTAL

All two-frequency and single-frequency irradiations were carried out with a line tunable TEA-CO_2 laser built in Laser Division, BARC. In two-frequency experiments, basic laser cavity was formed with ZnSe (R=10 m) output coupler and a grating (60 lines/mm). Various sets of diaphragms (two circular apertures (1.2 cm diameter) typically separated by various distances) were placed inside the cavity nearer to grating to obtain various combinations of two frequencies. Laser lines were checked with spectrum analyzer (optical engg. Model No.16-A). Temporal profile, as monitored by photon drag detector (Rofin, Model No.7415), consisted of a 100 nsec spike

followed by a few μsec tail. Energy of each of the two beams was almost equal and was measured by a calibrated pyroelectric detector (Lumonics Model No.50 D). For photolysis, both the beams were focussed into the centre of a pyrex cell (volume ~ 160 cc) by a ZnSe lens (f = 20 cm). Focal fluence was estimated by measuring the circular focal spot size (area ~ 0.005 cm^2) from burn pattern on a perspex sheet.

For getting two beams on two adjacent frequency lines, e.g. 10 [R(10) + R(12)] or 10[R(18) + R(20)], the curved output coupler was replaced by a flat ZnSe mirror, keeping rest of the experimental set up the same. Single frequency experiments were carried out with this configuration but blocking one of the two beams lasing on two adjacent frequencies.

CDF_3 (purity ~ 98%, D atom % ~ 98%), concentration was determined by quantitative IR spectrophotometry (Perkin Elmer Model 180) with typical reproducibility better than ± 1% using ν_5 band of CDF_3 at 980 cm^{-1}. Argon and nitrogen (purity > 99%) were used as such.

RESULTS AND DISCUSSIONS

Photolysis of CDF_3 was carried out either in neat form or with Ar or N_2 as a function of exciting frequencies and buffer gas pressure. CDF_3 dissociation extent in each run is described in terms of "reaction volume per pulse, V_R", which is given by

$$V_R = \text{Specific dissociation rate, } d_D \times \text{Cell volume, } V_{cell} \quad (1)$$

The specific dissociation rate of CDF_3, d_D, is given by

$$\frac{N_n}{N_o} = (1 - d_D)^n \qquad (2)$$

where N_o and N_n being initial and final concentration of CDF_3 after irradiation with 'n' number of pulses.

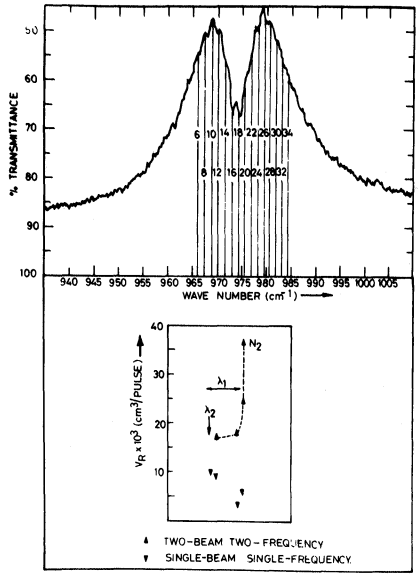

FIGURE 1. $\sqrt{_5}$ band profile of CDF_3 (7 torr; path length 10cm) along with R-branch lines of CO_2 laser (10.6 μm). (Inset) variation of V_R with exciting frequency(ies) for 2 torr CDF_3 buffered with 54 torr Ar.

Figure 1 gives the $\sqrt{_5}$ band profile for CDF_3 with its P- and R- branches at 10.2 μm and 10.3 μm respectively. It also shows relative position of various R-branch lines of CO_2 laser in its 10.6 μm band. Five sets of two-frequencies, [R(8)+ R(18)], [R(10) + R(18)], [R(10) + R(20)], [R(10) + R(12)] and [R(18) + R(20)] were used for irradiation.

Figure 2 gives V_R dependence on Ar pressure for two sets, viz., [R(10) + R(20)] and [R(10) + R(18)]. It also shows similar dependence for N_2 as buffer gas for [R(10) + R(20)] excitation.

It can be seen from Fig.2 that excitation with [R(10) + R(20)] gives relatively better yield compared to that with [R(10) + R(18)] in lower pressure regions of Ar. However, in the pressure range studied, both sets of frequencies tend to give similar yield at higher pressures, maintaining an up-

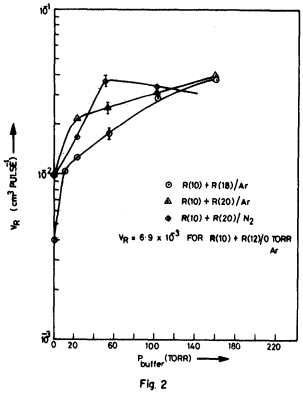

Fig. 2

FIGURE 2. Dependence of V_R with buffer gas pressure for various two-frequency excitation.

ward trend with P_{Ar}. Use of N_2 as buffer gas, in contrast, for [R(10) + R(20)]excitation leads to slower peaking of V_R and early fall with increasing buffer gas pressure.

Table 1 summarises results obtained for two- and single-frequency experiments. Results of the single beam, single frequency experiments (run no. (6) - (9)) followed the low intensity absorption spectrum. R(18) and R(20) lines, which were weakly absorbed, gave lower yields compared to that for the strongly absorbed R(10) and R(12) lines. In the two beam configuration using adjacent frequency pair (run no. (1) and (4)), yield improved compared to single beam experiments as

TABLE I Yields in MPD of CDF_3 (2 torr)

		Wave lengths λ_1	λ_2	Focal fluences Φ_1 J/cm^2	Φ_2	P_{buffer} (Torr)	V_R x 10^3 cm^3/pulse
Two frequencies	1.	R(12)		18	18	54 Ar	16.9
	2.	R(18)		18	18	54 Ar	17.8
	3(a)	R(20)	R(10)	18	18	54 Ar	24.2
	(b)	R(20)				54 N_2	36.3
Two beams	4.	R(20)	R(18)	18	18	54 Ar	8.8
	5.	R(8)		18	18	22 Ar	16.0
Single beam Single frequency	6.	R(10)	-	18	-	54 Ar	8.5
	7.	R(12)	-	18	-	54 Ar	8.4
	8.	R(18)	-	18	-	54 Ar	3.0
	9.	R(20)	-	18		54 Ar	5.8

expected. From these two sets of studies, it is possible to estimate the expected yield in two beam configuration of well-separated frequency pairs, viz., [R(10) + R(20)] and [R(10) + R(18)] in the absence of any advantages offered by such multiple frequency excitation. The results reported in ref.[9] for IR MPD of 20 mtorr CDF_3/20 torr Ar by 10R(12) line prepulse indicate that dissociation probability remained nearly constant for excitation range of 940 - 990 cm^{-1} for second frequency. However, variations in the laser beam intersection angle, pulse energy of either laser, focal spot size and mode quality in the course of wavelength scan introduced a random error of $\pm$ 25% to the two frequency data. In the present studies, since all two-frequency experiments were done ir same geometry using a single laser, most of the difficulties associated in ref.[9] were eliminated. Our results show that well-separated two-frequency excitation in ν_5 band certainly provides significant enhancement in the yield compared to single frequency or two adjacent frequencies excitation (compare run no. (1) and (4) with (2) and (3a) and see the inset of Fig.1). It can also be seen that yield improved better with [R(10) + R(20)] combination compared to [R(10) + R(18)] in photolysis of 2 torr CDF_3 buffered with 54 torr Ar. This effect was still more pronounced for the use of N_2 as buffer gas (cf. run no. 3(b) where more than two-fold enhancement was obtained compared to [R(10) + R(12)] excitation under similar conditions.

Multiple-frequency excitation is expected to overcome anharmonicity bottleneck in pumping through resonance transitions and enables a molecule reach its quasi-continuum at low energy fluence. Though anharmonicity is very low in the ν_5 manifold of CDF_3 ($X_{55} \approx -0.25$ cm^{-1}) [10,11], single frequency

IR MPD "action spectrum" does indicate a red-shift and is broader than low-intensity absorption spectrum [6,9]. The two-frequency IR MPD data reported by Herman [9] seem to indicate a red shift ranging from 0 to 20 cm^{-1} and a broadening of 60 -100 cm^{-1}. Our results show that despite small anharmonicity, two-frequency excitation in ν_5 band certainly provides a small, nevertheless, significant enhancement in yield for appropriate combinations of frequencies. The major bottleneck for yield enhancement continues to be still dominated by depletion of rotational level population under pumping.

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