

TWO-FREQUENCY CO₂ LASER MULTIPLE-PHOTON DISSOCIATION AND DYNAMICS OF EXCITED STATE ABSORPTION IN CDF₃[†]

Irving P. HERMAN

Physics Department, University of California, Lawrence Livermore National Laboratory, Livermore, California 94550, USA

Received 27 August 1982

The two-frequency multiple-photon dissociation probability in CDF₃ is studied as a function of wavelength, fluence and pulse separation using two pulsed CO₂ lasers. When the ν_2 mode of CDF₃ is excited by an R(12), 10.3 μ prepulse, the probability for subsequent dissociation is approximately constant from 940 to at least 990 cm⁻¹. A model of excited state absorption in CDF₃ is presented to help explain these results. Implications for deuterium separation are also discussed.

1. Introduction

Two-frequency infrared laser multiple-photon dissociation (2 ν MPD) experiments have been performed by several investigators to better understand the dynamics of infrared absorption in polyatomics from the ground state and from vibrationally excited levels. The overall conclusion of these studies in SF₆ [1] and OsO₄ [2] is that the wavelength-dependent profile of 2 ν MPD, with the laser frequency of the second pulse varied, is red shifted from the single frequency MPD (1 ν MPD) spectrum, which itself is red shifted from the ground state absorption spectrum. Consequently, the net fluence requirements are lower for 2 ν MPD than for 1 ν MPD when the weak prepulse is tuned near the 1 ν MPD peak and the delayed main pulse is at a slightly longer wavelength. The importance of 2 ν MPD in determining molecular vibrational energy structure and in applications, such as isotope separation, is well established.

Recent studies of multiple-photon absorption (MPA) and 1 ν MPD of CDF₃ have sparked considerable interest because CDF₃ is an example of a

“small” molecule from a multiple-photon interaction perspective [3], and because of applications toward deuterium separation [4–7]. The cross section for 1 ν MPD in essentially collision-free samples of CDF₃ ($\approx$ 50 mTorr partial pressure) can be increased by at least a factor of 10 with the addition of sufficient buffer gas ($\geq$ 20 Torr argon), as monitored by fluorescence of the vibrationally excited DF MPD nascent product [8] or by gas chromatographic observation of the C₂F₃ product [4]. Using 2 ns fwhm laser pulses, absorption in CDF₃ increased ten-fold when 1 atm of argon was added [6]. These experiments show that, in contrast to larger polyatomics, under collisionless conditions only a small fraction of thermally populated CDF₃ states undergo MPA, resulting in a striking bimodal vibrational distribution [9].

The very small first-order anharmonicity contributions in the CO₂ laser-pumped ν_2 mode in CDF₃ [10] contrasts the much larger anharmonicity of many other molecules investigated by MPD (for example, see refs. [1,2]). In studies of MPA, with fluences up to 20 J/cm² [11], and in preliminary studies of 1 ν MPD in CDF₃ [8,12], there is no apparent red shift from the low fluence absorption spectrum and very little spectral broadening. Studies of 2 ν MPD in CDF₃ can more sensitively sample the averaged excited state absorption profile and determine whether frequency shifts or

[†] Work performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

broadening appear in excited CDF_3 .

Deuterium separation by CO_2 laser MPD of $\text{CDF}_3/\text{CHF}_3$ is the most outstanding example of laser isotope separation, as demonstrated by single step enrichment factors exceeding 20000 : 1 [4–7,13] and very large (> 1000 : 1) D/H selectivity in absorption [6]. 2ν MPD could further improve these parameters by selecting a weak prepulse at the 1ν MPD maximum, and a main pulse at a lower frequency, if the 2ν MPD exhibited a red shift and/or significant broadening.

The experiments described in this study examined the 2ν MPD probability along only a few cuts in the multidimensional parameter space describing the range of experimental variables: the prepulse and main pulse fluence and wavelength, the prepulse/main pulse time delay, and photolysis mixture components. A limited number of parameter variations were chosen to best examine excited state absorption strengths, red shifts and frequency broadening; the selected studies also coincided with the parameter range of interest for deuterium separation.

Each of the many theories of MPA and MPD found in the literature (for example, see ref. [14] and ref. [3]) hinges on the strength and spectral profile of absorption in polyatomics that are vibrationally excited to the so-called quasi-continuum. No experimentally tested and otherwise satisfactory theory of excited state absorption has yet been formulated which would provide the framework for detailed analysis of MPA and MPD. (See ref. [15] for one in-depth attempt.) Consequently, a simple density of states model of excited state CDF_3 absorption was developed and is described here to help explain the 2ν MPD observations. Though many details of MPA were purposely omitted from this model because of the dearth of spectroscopic data, it still serves as a starting point for describing excited state absorption in CDF_3 and other molecules.

In sections 2 and 3 the experimental procedure and results are detailed. These observations are discussed in section 4, and are further analyzed in section 5, where the excited state absorption model is presented. Section 6 describes the impact of these 2ν MPD results on deuterium separation.

2. Experimental procedure

In most of the described runs a Lumonics 103 (L-103) CO_2 laser and a Lumonics 602 (L-602) modified-amplifier CO_2 laser provided the two independent laser frequencies. Both provided line-tuneable, multimode pulses of ≈ 100 ns fwhm, with a small ≈ 500 ns tail. In early experiments, the large transverse discharge area in the L-602 constituted the gain region for two laterally-displaced and parallel optical cavities, which provided independent frequency and fluence control at two different lines. Though the mode quality of the two L-602 lasers was superior to that of the L-103, overall operation with the L-103 and one L-602 laser was preferred to the dual L-602 mode, because pulse delays could be adequately controlled only with the two independent oscillators. Though with L-602 dual laser operation on the same line the output pulses were essentially simultaneous, the strong $10.4\ \mu$ band P lines were found to precede the R lines by ≈ 100 ns, while strong $9.4\ \mu$ band lines were delayed after these R line laser pulses by ≈ 100 ns. Relatively weaker lines, though still with 2 J/pulse output, were further delayed by 500–2000 ns. Attempts to delay P(20), $10.6\ \mu$ past R(12), $10.3\ \mu$ by inserting and angle-tuning several parallel crystal flats (BaF_2 , CaF_2 , NaCl) in the P(20), $10.6\ \mu$ cavity were successful only with unacceptable losses in pulse energy. Consequently, two-frequency infrared photolysis was predominantly studied with the L-103 and (single laser) L-602 discharges fired by independent SCR-based timing circuits, typically with pulse separations of $(\pm) 1.5$ – $50\ \mu\text{s}$. There was unacceptable pulse-to-pulse jitter in pulse delay for nominal pulse separations less than $\approx 1.5\ \mu\text{s}$.

The two lasers were directed into the pyrex photolysis cell (45 cm long, 33 mm i.d., KCl Brewster windows) in a manner ensuring maximum spatial overlap of the two beams with collinear propagation. This is shown in fig. 1 along with typical operating parameters. Both lasers were independently focused at the center of the cell by two 1 m focal length BaF_2 lenses. Variations in the pulse fluence along the cell length were minimized by slowly focusing each laser, and by utilizing the shortest cell possible consistent with no laser

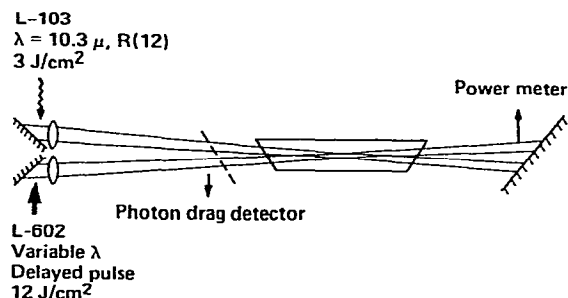


Fig. 1. The experimental arrangement for the two-frequency MPD studies, with typical experimental parameters denoted. The two lenses both have a 1 m focal length.

damage to the cell windows. Maximum beam overlap was assured by minimizing the intersection angle of the two co-propagating beams (≈ 40 mrad), and using long focal length focusing optics. Pulse fluences were determined by measuring the pulse energy with a thermopile detector, and the laser cross-sectional area by the burn marks produced on cardboard inserted at various points along the beam path (with the photolysis cell temporarily removed). The incident pulse energies were varied by inserting a combination of CaF_2 , BaF_2 and NaCl crystal flats before the focusing lenses. Using a flat profile, the beam diameter at the focus was typically ≈ 4.0 mm, and ≈ 4.5 mm at either end of the 10 cm long laser overlap region. Therefore, fluences in the intersection volume varied by $\pm 10\%$; the volume-averaged fluences are cited below. Maintaining the same focal beam spot size for each scanned wavelength was quite essential in the wavelength dependence studies. The beam diameter at the focus of either laser could be slightly changed by adjusting the circular aperture placed in each laser cavity. In the two-wavelength studies, the focal diameter of the fixed wavelength laser was maintained at a constant value that was slightly larger than that of the variable wavelength beam.

The degree of beam overlap was adjusted with the cell and laser fluence attenuators in position by examining the laser burn patterns in symmetrical positions before and after the cell. Both maximum and consistent run-to-run overlap were crucial for satisfactory data. Due to the slowly focus-

ing lasers and short cell lengths, the beam paths within the photolysis cell can be approximated by intersecting solid cylinders. (As shown above, this is a good approximation in the overlap region. Outside this region, the beams slowly expand to ≈ 6 mm.) For cylinders of equal radius R and intersection angle θ , the overlap volume is $(16\pi/3) R^3 / \sin \theta$. The ratio of this intersection volume to the volume swept out by either beam alone was 0.245 ± 0.03 . To ensure a constant volume ratio, the beam focus diameters were adjusted to a specific value, and the intersection angle was controlled to ± 4 mrad of the 40 mrad target value.

Before each run the relative pulse delay was set to the desired value, using a photon drag detector placed in front of the photolysis cell for the temporal measurements. The pulse separations were set to a value in the range 1.5–2.5 μs (which is greater than the pulse width), except for the runs summarized in fig. 3 where the pulse delay was purposely varied. In figs. 4–6, the pulse delays were carefully set and monitored; in the stated operating range the pulse separation uncertainty was $\pm 0.3 \mu\text{s}$.

Mixtures of 20 mTorr CDF_3 /20 Torr argon were used in the photolysis runs. The CDF_3 was 98% D, and was used as obtained from Stohler except for cryogenic removal of non-condensables. It was found to contain $< 0.1\%$ C_2F_4 as determined by gas chromatography. The Ar was 99.99% pure, and was used with no further purification.

The data presented in each figure (figs. 2–6) were taken in random order within one or two days. Typically, ≈ 25 pulses irradiated the photolysis cell for each datum point, corresponding to less than 10% reactant depletion. The 15 s time between pulses allowed satisfactory mixing of the cell contents. The MPD probability was then determined by measuring the ratio of C_2F_4 product to remaining CDF_3 by gas chromatography, as detailed in previous reports [4,6]. Corrections were made to account for the small deviations from constant per-pulse product formation due to depletion. In all cases the fractional photoproduct yield per pulse was normalized by the beam overlap volume using the expression given above. The normalization procedure described here averages

the details of the beam profile and the effects of relatively weak laser focusing within the 2ν MPD interaction volume. The absolute calibration is uncertain by an estimated $\approx \pm 20\%$; however, the relative calibration is superior to this within any series of runs in which any parameter, other than the laser wavelength, is varied.

3. Experimental results

The data in fig. 2 were obtained with both L-602 lasers tuned to R(12), $10.3\ \mu$, with zero time delay. In the right curve only one beam was incident on the reaction vessel, with the fluence denoted by the abscissa. For the left curve the other beam also irradiated the cell with fluence fixed at $3.7\ \text{J}/\text{cm}^2$. Yield values exceeding unity indicate significant dissociation in regions outside the overlap volume. Note that at low fluences the left curve is the single laser curve shifted to the left by $\approx 3\ \text{J}/\text{cm}^2$.

In the experiments summarized in fig. 3 the main pulse was delayed after the prepulse by a variable time. The prepulse was the R(12), $10.3\ \mu$ line with $3\ \text{J}/\text{cm}^2$ fluence, while the main pulse at P(20), $10.6\ \mu$ had a much higher fluence, $14\ \text{J}/\text{cm}^2$. With either pulse alone incident on the photolysis mixture, the normalized dissociation probability is 0.01. When the time ordering of the pulses was reversed, and the leading edge of the "prepulse"

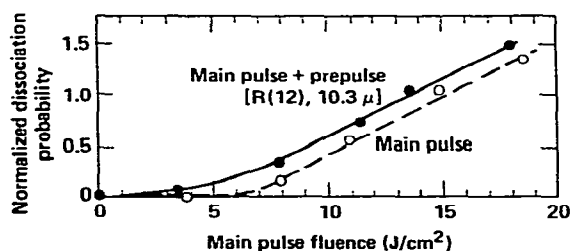


Fig. 2. The dissociation probability normalized to the overlap volume, when either one or two simultaneous R(12), $10.3\ \mu$ laser pulses irradiated the cell. The open circles refer to data with only the main pulse incident, while the solid circle points refer to the cases with a "prepulse" of $3.7\ \text{J}/\text{cm}^2$ fluence also incident. Yield values exceeding unity indicate significant single-laser dissociation outside the two-laser overlap volume (see text).

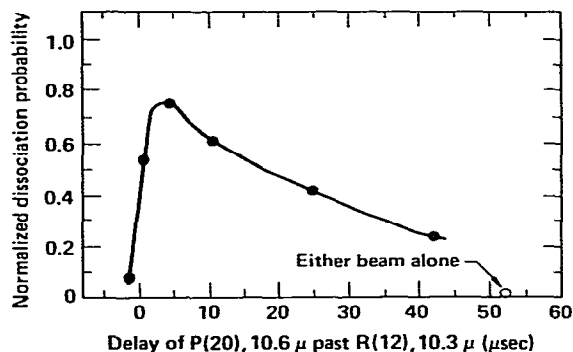


Fig. 3. The 2ν MPD yield with P(20), $10.6\ \mu$, $14\ \text{J}/\text{cm}^2$ delayed after R(12), $10.3\ \mu$, $3\ \text{J}/\text{cm}^2$, as denoted by solid circles. The open circle refers to the 1ν MPD yield with either laser alone and is arbitrarily placed, for presentation purposes, at the $52\ \mu$ s delay abscissa.

was in fact delayed $1.5\ \mu$ s after the main pulse, the yield is still quite small, 0.07. With a small delay of P(20), $10.6\ \mu$ past R(12), $10.3\ \mu$ the dissociation probability attains its maximum value. The yield then monotonically decreases with successively longer delays. Though maximum product formation is expected with the P(20) laser arriving immediately after R(12) with minimal pulse overlap, this figure shows that the measured fractional decomposition is somewhat lower with a nominal main pulse delay of $1.3\ \mu$ s compared to the $4.5\ \mu$ s delay datum point. This unexpectedly low yield with a $1.3\ \mu$ s delay may be due to pulse-to-pulse fluctuations of the laser delay. (Longer, more reliable settings, greater than $1.5\ \mu$ s, were used for the data of figs. 4–6.)

The key finding of this study is the investigation of the 2ν MPD wavelength dependence which is summarized in fig. 4. In these experiments, the prepulse wavelength was fixed at R(12), $10.3\ \mu$ with a fluence of $3.8 \pm 0.4\ \text{J}/\text{cm}^2$. The wavelength of the main pulse was varied and is plotted as the abscissa. The main pulse was delayed by $2.0 \pm 0.3\ \mu$ s past the prepulse, and was maintained at a fixed fluence, $11 \pm 1\ \text{J}/\text{cm}^2$. Single frequency MPD was also examined with only this main pulse incident on the photolysis cell; these data are plotted as the dashed curve in fig. 4, with the ordinate scale labelled on the right side. Since the single and two-frequency MPD raw data con-

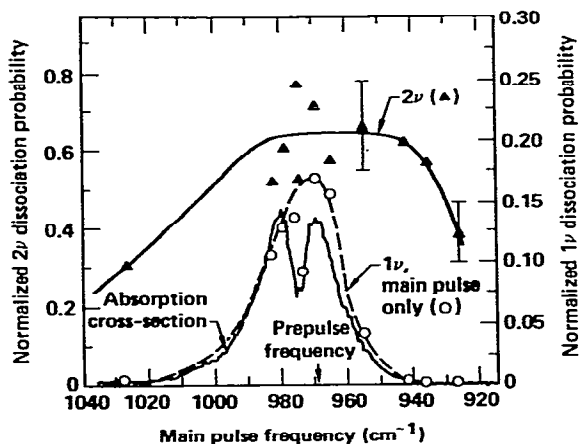


Fig. 4. Normalized 2ν MPD yield (triangles, solid curve, left ordinate scale) plotted versus main pulse frequency (11 J/cm^2 , delayed $2 \mu\text{s}$ past R(12), $10.3 \mu\text{s}$, 3.8 J/cm^2 prepulse). Open circles represent 1ν MPD yield with the main pulse only used (broken curve, right ordinate scale). The CDF_3 absorption spectrum is also plotted (arbitrary ordinate scale).

tain significant contributions from both within and outside the laser overlap region, these data are analyzed and presented in this figure in a manner that best compares the respective contributions in only the overlap volume. This is accomplished by subtracting the single laser MPD yield in the non-overlap volume from the raw data as follows.

In this experimental arrangement the laser fluence is nearly constant along the length of the photolysis cell. Moreover, the net product yield depends linearly on laser pulse energy at fluences well above "threshold" and below saturation, as shown in fig. 2 (and figs. 5 and 6 below). Consequently, in this approximation the 1ν and 2ν MPD data can be corrected for contributions outside the overlap volume by subtracting the product of the respective single frequency dissociation probability per pulse (normalized by the overlap volume) and the ratio of the non-overlap volume to the total volume subtended by the beam within the cell; this ratio is 0.755. It is these corrected two-frequency data that are presented as the bold curve in fig. 4, with the left ordinate scale. The prepulse fluence and corresponding dissociation yield are low enough to ignore the prepulse contribution outside the overlap region. The presented single frequency

data are similarly corrected to reflect only the overlap volume contribution. For reference, the small signal, single-frequency CDF_3 absorption cross section is also plotted, and is presented as the thin solid-line plot with unspecified ordinate scale.

It should be emphasized that for all pairs of photolysis wavelengths the 2ν raw, uncorrected photoproduct yields exceeded the respective 1ν raw yield by at least 70%, as is discernable from the data presented in fig. 4. With only the main pulse incident on the cell, only a small fraction, < 0.17 , of the molecules in the overlap region decompose. Only the data from the final series of runs are presented in the main body of fig. 4; however, all earlier runs exhibited the same high 2ν MPD probability extending from 940 to $\geq 990 \text{ cm}^{-1}$. The 1ν and 2ν MPD data at wavelengths on the wings of the CDF_3 $\nu_3 \leftarrow 0$ absorption curve displayed significantly less run-to-run scatter than when the more strongly absorbed lines were used. The fine structure in both the 1ν and 2ν data (that appears to track with the absorption cross section) is actually within the uncertainty of the wavelength scan.

The variation in the laser beam intersection angle, pulse energy of either laser, focal spot size, and mode quality in the course of the wavelength scan introduces a "random" error to the two-frequency data, estimated to be $\pm 25\%$, which as stated above may account for the observed 2ν MPD structure. The last two parameters are believed to make the most important contributions to this error. The systematic error introduced in the above-described non-overlap volume contribution correction should be much smaller than this "random" error.

Some experiments were conducted with main pulse frequency in the range $1043\text{--}1086 \text{ cm}^{-1}$. These data are not presented in fig. 4 because the two L-602 lasers were used in these experiments: the accompanying unacceptable prepulse/main pulse overlap in the 2ν MPD experiments prevented quantitative analysis. Nonetheless, the qualitative dependence at these shorter wavelengths is clear. The 2ν MPD yield stays above zero ($\approx 0.2\text{--}0.3$) between ν_2 and ν_3 ($1030\text{--}1060 \text{ cm}^{-1}$), where the 1ν MPD probability is zero

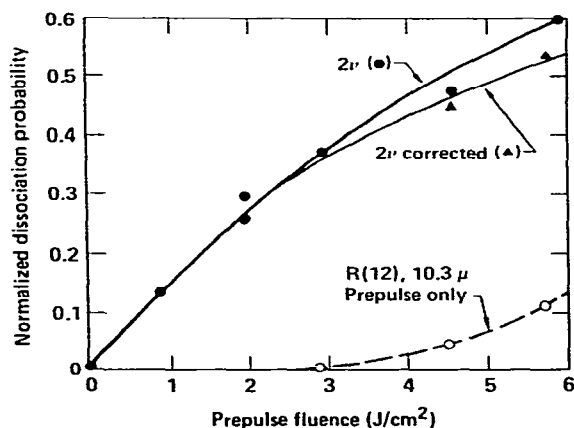


Fig. 5. Two-frequency decomposition cross section with R(12), 10.3 μ prepulse fluence varied (solid circles, solid curve). Main pulse is P(20), 10.6 μ , 11.7 J/cm² delayed by 1.5–2.0 μ s. The 1 ν MPD yield with the prepulse only is shown (open circles, broken curve), along with the 2 ν MPD curve corrected for prepulse 1 ν MPD yield outside overlap volume (triangles).

within detection limit. At higher photon energies near ν_2 (> 1060 cm⁻¹), 2 ν MPD is much larger than the 1 ν MPD contribution (see ref. 6, fig. 6 for ν_2 spectrum).

Further experiments were conducted to study the fluence dependence of 2 ν MPD, with an R(12), 10.3 μ prepulse and a 10.6 μ main pulse, as de-

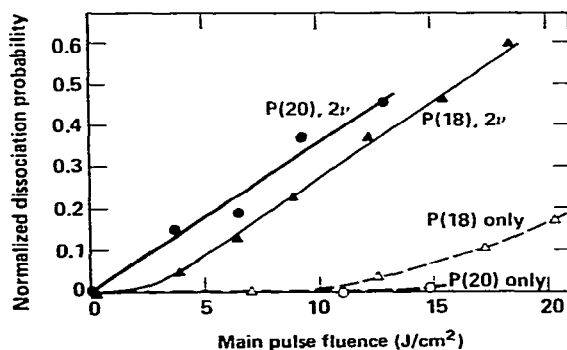


Fig. 6. 2 ν and 1 ν MPD probability with the main pulse fluence varied. Circles represent P(20), 10.6 μ delayed 2 μ s past R(12), 10.3 μ , 3.9 J/cm². Triangles show P(18), 10.6 μ nearly simultaneous with R(12), 10.3 μ , 3.7 J/cm². Solid symbols and solid curves are 2 ν MPD yields; open datum symbols, broken curves are 1 ν MPD results.

picted in figs. 5 and 6. In fig. 5 the P(20) main pulse has fluence $\approx 11.7 \pm 1$ J/cm² and is delayed in the range 1.5–2.0 μ s. The corrected 2 ν MPD curve takes into account the 1 ν MPD due to the prepulse outside the overlapping volume. Note that for prepulse fluences less than 3 J/cm² the photoproduct yield increases nearly linearly with the 10.3 μ fluence; if there is a prepulse threshold, it must be < 1 J/cm². At higher fluences there is evidence of saturation.

In fig. 6, the prepulse fluence is fixed at 3.9 J/cm² with the P(20) main pulse delayed by 2 μ s. The 2 ν MPD fluence dependence using P(18), 10.6 μ was also measured, however, employing dual L-602 operation. In this latter case, the R(12), 10.3 μ fluence was 3.7 J/cm² and there was significant pulse overlap. The respective 1 ν MPD curves are also shown for both cases. Note that the P(18) curve lies below that for P(20) because of this pulse overlap. Both 2 ν curves are linear, with some evidence for a threshold for P(18).

4. Discussion

The frequency dependence of single- and two-wavelength photolysis of CDF₃, depicted in fig. 4, provides important clues to the excited state level structure. The single-frequency MPD probability closely follows the $\nu_3 \leftarrow 0$ (low fluence) absorption cross section, especially in the wings. Notably, for $\lambda > 10.58$ μ the photoproduct yield is nearly zero. No large red shift or significant profile broadening vis-à-vis the absorption spectrum is observed. More precisely, the apparent red shift is at most 5 cm⁻¹. Since the 1 ν MPD spectral profile strongly depends on the absorption spectrum of CDF₃ in the $n_5 = 0-3$ states, the 1 ν MPD red shift is expected to be roughly $-(4 \pm 2)X_{55}$; n_i is the quantum number for the ν_i mode and X_{55} is the spectroscopic constant describing first-order perturbative anharmonicity within the mode of interest. Kirk and Wilt [10] claim that X_{55} is extremely small, -0.25 cm⁻¹, so a small 1 ν MPD red shift is not unexpected. This finding is also consistent with the recent measurement of single-frequency multiple-photon absorption in CDF₃ using short pulse CO₂ lasers (≈ 5 ns fwhm), which showed no red shift

even for fluences up to 20 J/cm² [11].

Within the stated experimental uncertainty, the 2 ν MPD probability is flat from 940 to at least 990 cm⁻¹, when 4 J/cm². R(12) is used as the prepulse. Due to the absence of suitably strong CO₂ laser lines between 985 and 1025 cm⁻¹, some of the details of 2 ν MPD remain uncertain. The data presented in fig. 4 can support 2 ν MPD spectra ranging from one with a red shift of 20 cm⁻¹ and a fwhm broadening of 60 cm⁻¹ (which is much larger than the 25 cm⁻¹ width for 1 ν MPD) to one with a zero red shift, with 100 cm⁻¹ broadening. The curve plotted through the data points in fig. 4 represents a case intermediate between these two extreme scenarios. With a buffer added, the details of the 2 ν MPD spectrum should be insensitive to the frequency of the prepulse, if the number of absorbed prepulse quanta is held constant.

In this set of 2 ν MPD experiments, CDF₃ absorbed roughly 9 ± 2 quanta during prepulse excitation; this is estimated in two ways. In ref. [6] the absorption coefficient of CDF₃/780 Torr Ar mixtures was measured to be $\alpha(\phi) = 2.75 \times 10^{-3} / \phi^{0.28}$ (cm⁻¹ Torr⁻¹) for R(26), 10.21 μ (2 ns pulses with fluence $\phi < 1.2$ J/cm², fluence in J/cm²). Sufficient buffer was added in both this reference and the present study to permit rotational relaxation during the laser pulse and removal of the MPA "bottleneck", so fluence, and not intensity, is the important parameter in both studies. This absorption cross section may therefore be used to estimate the degree of excitation of weak prepulse-irradiated CDF₃ because of the equal absorption strength at R(12) and R(26) [11], leading to ≈ 10.8 quanta absorbed during the prepulse. An alternate estimate may be obtained assuming that MPA cross section decreases as $1/\phi^{1/3}$ [16], and that at a certain saturation fluence, ϕ_{sat} , the molecule can absorb the 28 photons [4] required for dissociation: the number of absorbed photons is then $28(1/\phi_{\text{sat}})^{2/3}$. Here $\phi_{\text{sat}} = 25$ J/cm² [4.6] so ≈ 8.0 quanta are absorbed from the prepulse.

The 1 ν MPD probability dependence on fluence shown in figs. 2, 5 and 6 all exhibit a faster than linear behavior at very low fluences for 20 mTorr CDF₃/20 Torr Ar mixtures. Assuming a ϕ^m power law dissociation probability in this regime, $m \approx 4$ for R(12), 10.3 μ and $m \approx 3$ for P(18), 10.6 μ . At

higher fluences, the 10.3 μ 1 ν MPD yield (fig. 2) varies linearly with fluence. In earlier studies of CDF₃ IR photolysis [4], a cubic fluence dependence was observed with P(26)/P(28), 10.2 μ for low fluences as well as for higher fluences where a more linear dependence is instead observed here with 10.3 μ radiation. Absorption in ground state CDF₃ is far too weak at 10.6 μ to produce much 1 ν MPD (< 0.01) even with 11 J/cm² fluence. However, 10.6 μ absorption must rapidly increase with a small amount of CDF₃ excitation since with only a 1 J/cm² 10.3 μ prepulse ($n_3 \approx 4$) there is significant 2 ν MPD at 10.6 μ (fig. 5).

The diffusion time of prepulse-excited CDF₃ out of the intersection volume is ≈ 10 ms for the 20 mTorr CDF₃/20 Torr Ar mixtures used here [17,18] which is far too slow to account for the dependence portrayed in fig. 3. Clearly, CDF₃/CDF₃ V-V collisions (with a 4.2 μ s average gas kinetic collision time for non-identical molecules) [17] and CDF₃/Ar V-T transfer (4.9 ns collision time) [17,18] are more plausible explanations. (The effects of intramolecular V-V redistribution are assumed to be very rapid and collision-independent.)

Though CDF₃/CDF₃ V-V collisions do not change the average molecular vibrational energy, the vibrational distribution is altered from the more sharply peaked laser excitation profile to the much broader thermal distribution [19,20]. There are more molecules with extremely low and high amounts of vibrational energy in the thermal sample relative to the initial laser-produced medium. In addition, the population distribution peaks at a lower vibrational quantum number for thermal equilibrium. Such thermalization should, in fact, increase the 2 ν MPD yield for small values of the main pulse fluence, and decrease the yield by no more than $\approx 30\%$ at high fluences, contrary to fig. 3. (V-V collisions would greatly affect the MPD probability if the prepulse excited a bimodal distribution. Such a distribution is avoided if the CDF₃ is suitably buffered [4].)

CDF₃/Ar V-T transfer most probably accounts for the pulse delay dependence. An estimate of the V-T reaction rate constant can be obtained by noting that a factor of two decrease in the 2 ν MPD yield is observed when either the

10.3 μ –10.6 μ delay is increased from ≈ 2 to 30 μ s (fig. 3) or the prepulse fluence is decreased from ≈ 3.0 to ≈ 1.5 J/cm² (fig. 5). The above-described methods for estimating absorption in CDF₃, suggest that lowering the prepulse fluence from 3.0 to 1.5 J/cm² decreases the excitation of prepulse-excited CDF₃ by 3400 cm⁻¹ or by 2400 cm⁻¹ respectively. Since the 6000 CDF₃/Ar collisions occurring in the 30 μ s delay also remove this estimated 2900 ± 500 cm⁻¹, $\approx 1/2$ cm⁻¹ is lost per collision or, equivalently, 2000 gas kinetic collisions are needed per V–T relaxation of one ν_5 quantum. This estimate is consistent with the observed quenching of 1 ν MPD in CDF₃ by added argon [4] and the published CHF₃/Ar V–T rate constants[‡].

5. A model of CDF₃ excited state absorption

Excited state CDF₃ absorption profiles are simulated here to better understand the wavelength dependence of 1 ν and 2 ν MPD by extrapolating the first-order perturbative energy level predictions in CDF₃ to higher energy. While the effects of intramolecular relaxation are parametrically included in this model, contributions due to coherent multiquantum transitions are ignored, as are dynamical influences of the rotational level distribution (such as MPA excitation only a fraction of the ground state rotational levels). However, vibrational energy-dependent rotational constants can still modify the employed absorption coefficient contours. The parameterized absorption model presented in this section is essentially a detailed density of states description of excited CDF₃.

The levels involved in MPA are assumed to cluster about the ν_5 anharmonic ladder in CDF₃. The energy of each of these states is given by the

standard expression $E\{n_i\}$ [24]:

$$E\{n_i\} = G\{n_i\} - G\{0\}, \quad (1)$$

where

$$G\{n_i\} = \sum_i \hbar \omega_i (n_i + d_i/2) + \sum_{j \geq i} \sum_i X_{ij} (n_i + d_i/2) (n_j + d_j/2), \quad (2)$$

where $\{n_i\}$ ($i = 1-6$) refers to the quantum numbers of the six distinct normal modes. Modes ν_1 , ν_2 and ν_3 have symmetry A₁ (C_{3v} group) and $d_i = 1$, while ν_4 , ν_5 and ν_6 are doubly degenerate ($d_i = 2$) with symmetry E. ω_i and X_{ij} are the normally defined harmonic frequencies and anharmonic constants [24]. All states within a full width Δ of the n_5 core state are equally populated and randomly phased, due to intramolecular relaxation; Δ will certainly be a function of n_5 but will be treated as a free parameter here. The quantum numbers of the states satisfying this criterion are determined by direct computer counting. Since little spectroscopic data are available detailing the splitting of these multiply-excited degenerate modes in CDF₃, they are assumed to remain degenerate.

Infrared absorption features in the wavelength region of interest may arise from ν_5 fundamental and red shifted ν_2 fundamental transitions. The linecenter of each of these transitions is determined from eq. (2). Contributions due to overtone, difference and combination bands are ignored here. The strength of the infrared transition from each level in the cluster bandwidth is assumed to be proportional to the square of the harmonic oscillator matrix element factor times the degeneracy of the transition. For ν_2 fundamentals this is $(n_2 + 1)(n_4 + 1)(n_5 + 1)(n_6 + 1)$, while for the doubly degenerate ν_5 fundamental the proper factor is $(n_4 + 1)(n_5 + 1)(n_5 + 2)(n_6 + 1)$. The same spectral profile is used to model absorption from each core-cluster state; these are centered about their respective calculated transition frequencies, and are weighted by the above factors. These profiles are then summed and normalized to unity at the maximum cross section, thus arriving at the relative spectral dependence of

[‡] Since the frequencies of the lowest frequency mode in CDF₃ and CHF₃ (ν_6) are nearly equal, V–T transfer rates should be comparable [21]. The collision numbers for CHF₃–Ar V–T transfer are 7430 for low energy [22] and ≈ 330 at very high energy, from thermal unimolecular decomposition experiments at low pressure [25].

absorption from the core-cluster ensemble. The absorption profile of the ground state fundamental (corrected for degeneracy) may be used directly in this model. Alternatively, the details of the rotational structure may be smoothed out, and the profile can be broadened or narrowed to simulate the effects of the excited state rotational constants and intramolecular relaxation.

The available spectroscopic data for CDF_3 compiled and analyzed by Kirk and Wilt [10] are used here. Of the twenty-one anharmonic constants, five come directly from CDF_3 combination, overtone and hot band measurements. The remaining constants were derived from the complete set of X_{ij} for CHF_3 assuming Dennison's rule [25] (which states that $X_{ij}/\omega_i\omega_j$ is invariant to isotopic changes). These constants are listed in table 1.

Kirk and Wilt did not obtain the important constant X_{55} ($= -0.25 \text{ cm}^{-1}$) directly from experiment but instead from the $2\nu_5(\text{E}) \leftarrow 0$ overtone in CHF_3 . However, the 1ν MPD and the MPA spectral dependences do confirm the small magnitude of X_{55} . Furthermore, the less accurate [10] infrared spectra of CDF_3 by Ruoff et al. [26] also suggest that X_{55} is small ($1.1\text{--}1.4 \text{ cm}^{-1}$). Since the cluster states about the core $n_5\nu_5$ states include levels with both ν_4 and ν_5 excitation, the model is not very sensitive to how X_{44} , X_{45} , and X_{55} are

Table 1
 CDF_3 spectroscopic data^{a)}

Harmonic frequencies (cm^{-1})		
$\omega_1 = 2268.0$	$\omega_2 = 1123.3$	$\omega_3 = 704.4$
$\omega_4 = 1235.5$	$\omega_5 = 989.0$	$\omega_6 = 513.7$
Anharmonic constants (cm^{-1})		
$X_{11} = -20.6$	$X_{12} = -4.2$	$X_{13} = 3.6$
$X_{14} = -7.7^{\text{b)}$	$X_{15} = -2.8$	$X_{16} = -1.2^{\text{b)}$
$X_{22} = -0.7$	$X_{23} = -1.5$	$X_{24} = -5.7$
$X_{25} = -0.7$	$X_{26} = -1.9^{\text{b)}$	$X_{33} = -2.4$
$X_{34} = -5.9$	$X_{35} = -0.6$	$X_{36} = 0^{\text{b)}$
$X_{44} = 0.7$	$X_{45} = -10.1$	$X_{46} = -8.1$
$X_{55} = -0.25$	$X_{56} = -0.7$	$X_{66} = -0.5^{\text{b)}$

^{a)} From ref. [10], accuracy $\pm 0.3 \text{ cm}^{-1}$.

^{b)} From spectroscopic measurements in CDF_3 . Other X_{ij} were determined from the CHF_3 anharmonic constants as described in the text.

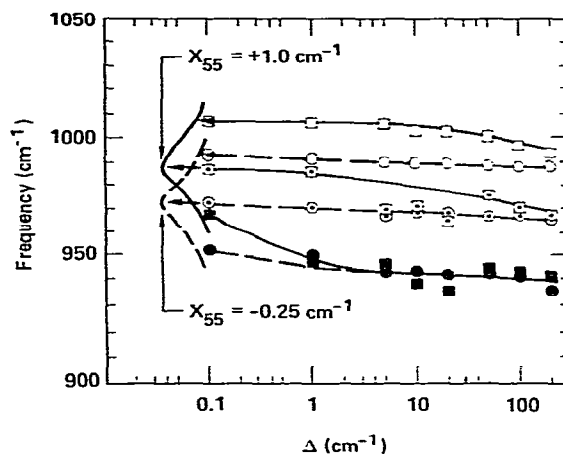


Fig. 7. The peak frequency (dot in open symbol), frequency at 20% peak point on the high (open) and low (solid) frequency wings of the simulated CDF_3 absorption profile for $n_5 = 6$, with $X_{55} = +1.0 \text{ cm}^{-1}$ (squares) or -0.25 cm^{-1} (circles), as a function of the cluster full width, Δ .

transferred from CHF_3 to CDF_3 . In this study a range of values of X_{55} are considered, with detailed examination for $X_{55} = -0.25$ and 1.0 cm^{-1} .

The overall trends of the simulated spectra are summarized in figs. 7 and 8. The ground state ν_5 profiles used in these figures were modified by smoothing away the dip in the P.R. structure. In fig. 7, the frequencies at the peak and 20% peak points are plotted versus the cluster full-width, Δ .

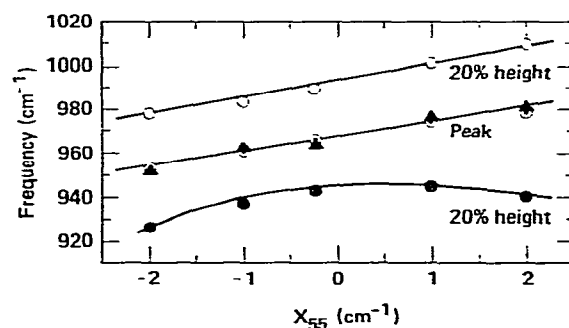


Fig. 8. The peak frequency (dot in circle), 20% point frequency (high, open circle; low, solid circle), of the CDF_3 $n_5 = 6$ profile as a function of X_{55} with $\Delta = 50 \text{ cm}^{-1}$. The triangles represent the peak frequency using the ground state profile of ν_5 with the actual P.R. structure, and not the smoothed version used for the other data.

for either $X_{55} = -0.25$ or 1.0 cm^{-1} , with $n_5 = 6$. (The value of ω_5 was corrected to reproduce the ground state ν_5 fundamental frequency whenever X_{55} was changed from -0.25 cm^{-1} .) As Δ increases, the relative contribution of the core state diminishes and the profile shifts to the red, since, on the average ν_5 is more harmonic than the other CDF_3 modes (table 1). For $X_{55} = -0.25 \text{ cm}^{-1}$ and $\Delta = 0.1 \text{ cm}^{-1}$ only the one core level with a degeneracy of 7 is counted, while for $\Delta = 50 \text{ cm}^{-1}$, there are 27 levels in the cluster width which amount to 258 distinct states when degeneracy is included. For $\Delta \geq 5 \text{ cm}^{-1}$, the important absorption features are only weakly dependent on the cluster width.

In fig. 8, the peak and 20% point frequencies are plotted versus X_{55} for $n_5 = 6$ and $\Delta = 50 \text{ cm}^{-1}$. The frequency of the peak and high-energy 20% peak point increase linearly with X_{55} . In contrast, the red portion of the absorption curve is independent of X_{55} , for $X_{55} > -1 \text{ cm}^{-1}$, since it is predominantly determined by cluster state absorption.

Generally, these absorption profiles are insensitive to the details of the structure of the ν_5 profile used, and to whether the degeneracy factor and the harmonic oscillator contribution to the transition strength are ignored (by making either or both these factors independent of the quantum numbers of each counted level).

Representative examples of simulated excited state absorption spectra are shown in figs. 9 and 10, in which $X_{55} = -0.25$ or 1.0 cm^{-1} respectively. In figs. 9a, 9b and 10a, 10b the core state is $n_5 = 6$, while for figs. 9c and 10c $n_5 = 9$; these conditions are typical of prepulse excited CDF_3 . For figs. 9a and 10a, $\Delta = 0.1 \text{ cm}^{-1}$ and only the core state is populated; $\Delta = 50 \text{ cm}^{-1}$ for figs. 9b, 9c and 10b, 10c. The exact ground state ν_2 and ν_5 absorption profiles were used in both figures. For both $X_{55} = -0.25$ and 1.0 cm^{-1} , increasing the cluster full width from 0.1 to 50 cm^{-1} significantly increases absorption on the low energy wing of ν_5 , particularly at the P(20), $10.6 \mu \text{ CO}_2$ laser frequency of 944 cm^{-1} , while only weakly influencing the high-energy end. Though, increasing the cluster width markedly red shifts the ν_2 contributions near 1080 cm^{-1} , there is still a range of essentially no absorption between ν_2 and ν_5 (near 1030 cm^{-1})

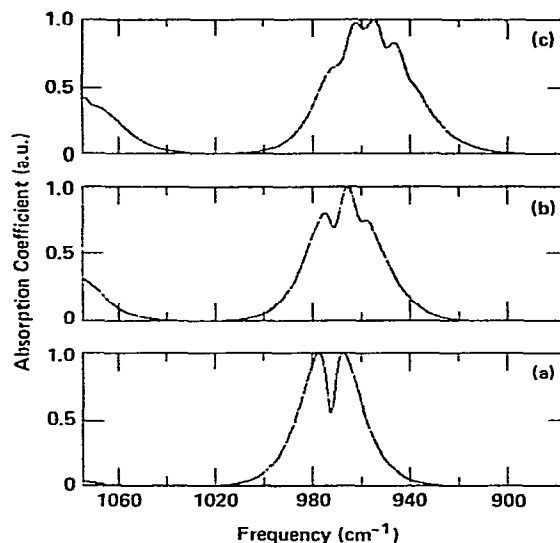


Fig. 9. Simulated CDF_3 excited state absorption spectra with $X_{55} = -0.25 \text{ cm}^{-1}$ (a) $n_5 = 6$, $\Delta = 0.1 \text{ cm}^{-1}$; (b) $n_5 = 6$, $\Delta = 50 \text{ cm}^{-1}$; (c) $n_5 = 9$, $\Delta = 50 \text{ cm}^{-1}$. The main structure near 980 cm^{-1} is the composite ν_5 fundamental, while the wing at 1060 cm^{-1} is due to the ν_2 fundamental. Note that $\nu_5 \leftarrow 0$ is centered at 975 cm^{-1} . The profiles of the ground state ν_2 and ν_5 fundamental transitions were used here.

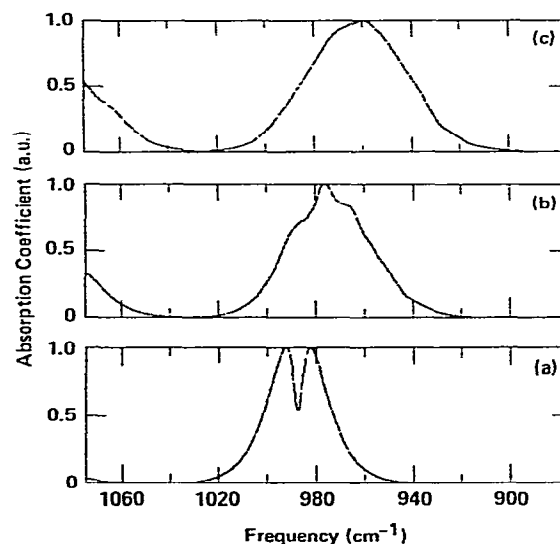


Fig. 10. Simulated CDF_3 excited state absorption profiles with $X_{55} = +1.0 \text{ cm}^{-1}$. (a) $n_5 = 6$, $\Delta = 0.1 \text{ cm}^{-1}$; (b) $n_5 = 6$, $\Delta = 50 \text{ cm}^{-1}$; (c) $n_5 = 9$, $\Delta = 50 \text{ cm}^{-1}$. See caption of fig. 9 for more details.

where, experimentally, there is excited state absorption.

With $n_5 = 9$ (figs. 9c and 10c) the ν_2 contribution increases. The ν_5 blue wing is unchanged for $X_{55} = 1.0 \text{ cm}^{-1}$ but is shifted to slightly lower frequencies for $X_{55} = -0.25 \text{ cm}^{-1}$. In both cases the ν_5 profile broadens and absorption increases on the red wing. For $X_{55} = 1.0 \text{ cm}^{-1}$ there is absorption almost continuously from ν_2 and ν_5 , though not enough to account for the 2ν MPD results.

The cases examined so far with $X_{55} = -0.25$ or 1.0 cm^{-1} can satisfactorily account for excited state absorption on the low energy side of ν_5 , as seen in figs. 3–6; however, the weak, but continuous, excited state absorption from ν_2 to ν_5 is not predicted. Since the absolute value of X_{55} is small, 2ν MPD on the low frequency side of ν_5 depends on the contribution of the state mixing (intramolecular relaxation) term ($\Delta > 0$) or increased red shift in ν_2 . Within the framework of this model, significant absorption between ν_2 and ν_5 can be incorporated by either broadening the employed ground state ν_2 and ν_5 profiles, assuming larger positive values of X_{55} or larger negative values of X_{22} , or by introducing contributions to overtone, combination and difference band transitions which may be strong in excited CDF_3 . For example, broadening the smoothed ν_5 absorption profile by 10 cm^{-1} , while broadening each of the P, Q, and

R features of ν_2 also by 10 cm^{-1} modifies fig. 9b to the spectrum shown in fig. 11a. In fig. 11b ground state ν_2 and ν_5 profiles are again directly used with $n_5 = 6$ and $\Delta = 50 \text{ cm}^{-1}$, but now $X_{55} = 4 \text{ cm}^{-1}$.

6. Implications toward deuterium separation

Previous studies at LLNL and elsewhere have shown that 1ν MPD of $\text{CDF}_3/\text{CHF}_3$ mixtures with $10.2\text{--}10.3 \mu$ radiation is a commercially attractive method of deuterium separation and heavy water production [4–7]. The significant experimental observations of nearly unity dissociation yields of CDF_3 [4,6] with a 20000:1 single-step D/H enrichment factor [5] and $> 1000:1$ isotopic selectivity in absorption [6], bode well for deuterium separation utilizing this technique. Still, an improvement in the absorption selectivity that can at least maintain, and perhaps increase the yield and enrichment factor would be most welcome. 2ν MPD is precisely one such improvement.

The isotopic absorption selectivity in $\text{CDF}_3/\text{CHF}_3$ mixtures is limited by the weak tail absorption in the $2\nu_6 \leftarrow 0$ transition in CHF_3 that is centered at 9.9μ (ref. [4], fig. 1), and also by the decreasing absorption cross section in increasingly vibrationally excited CDF_3 . Cooling the photolysis mixture will decrease the breadth of the absorption wing in ground state CHF_3 . Notably, CHF_3 absorption can be further lessened by 2ν MPD, with a weak prepulse near the 1ν MPD peak at R(12), 10.3μ followed by a much stronger main pulse at a longer wavelength where CHF_3 absorption is much weaker say P(20), 10.6μ . Absorption in vibrationally excited CHF_3 will also be much less at 10.6μ than at 10.3μ . Naturally, prepulse-excited CDF_3 must absorb at 10.6μ at least as strongly as at 10.3μ to maintain, and perhaps increase, the CDF_3 decomposition probability for equal total fluence. The present study has shown that in prepulse excited CDF_3 , 10.3μ and 10.6μ radiations are approximately equally effective in decomposing CDF_3 . Therefore, the average excited state absorption cross section in CDF_3 at both wavelengths are also roughly equal. An additional important benefit of dual 10.3μ , 10.6μ 2ν MPD

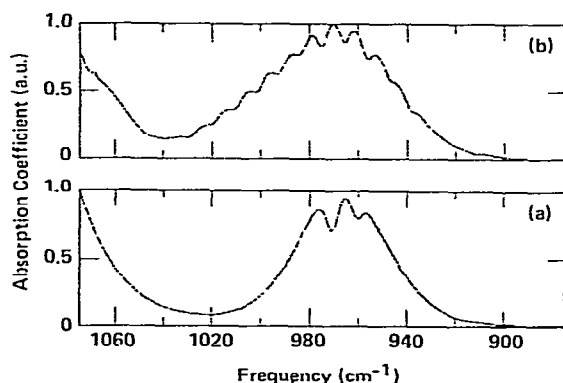


Fig. 11. Composite CDF_3 excited state absorption cross section with (a) $n_5 = 6$, $\Delta = 50 \text{ cm}^{-1}$, $X_{55} = -0.25 \text{ cm}^{-1}$ but ν_2 and ν_5 are broadened by 10 cm^{-1} as outlined in the text; (b) $n_5 = 9$, $\Delta = 50 \text{ cm}^{-1}$, $X_{55} = +4.0 \text{ cm}^{-1}$, no broadening. See caption of fig. 9 for more details.

operation compared to 10.3μ 1ν MPD concerns the superior electrical efficiency, by $\approx 25\%$, of short pulse ($< \approx 5$ ns fwhm) CO_2 laser operation at 10.6μ vis-à-vis 10.3μ [27]; this significantly lowers the electrical operating costs. Based on the present findings, the 10.3μ prepulse may need to contain only ≈ 0.2 of the net two-pulse fluence in D/H separation by 2ν MPD of trifluoromethane. More detailed studies are needed to obtain the fluences required to optimize the process.

7. Concluding remarks

This study has dealt with only a few features of 2ν MPD in CDF_3 . Further examination of excited state absorption in this molecule using 2ν MPD or 2ν MPA, and more detailed conventional spectroscopic measurements of the CDF_3 vibrational energy structure are needed. The model of absorption by vibrationally excited molecules presented here can be further refined, leading to absolute excited state absorption cross sections, and extended to other molecules already examined by MPD and MPA. Finally, a larger base of 2ν MPD data is required for a critical assessment of deuterium separation using two-frequency pumping.

Acknowledgement

The author would like to thank Drs. J.B. Marling, J. Goldhar, and A.H. Weisberg for suggestions regarding dual laser timing, and L. Walkley for expert technical assistance.

References

- [1] M.C. Gower and T.K. Gustafson, *Opt. Commun.* 23 (1977) 69, and references therein.
- [2] R.V. Ambartsumian, V.S. Letokhov, G.N. Makarov and A.A. Puretzky, *Opt. Commun.* 25 (1978) 69, and references therein.
- [3] W.C. Danen and J.C. Jang, in: *Laser-induced chemical processes*, ed. J.I. Steinfeld (Plenum Press, New York, 1981).
- [4] I.P. Herman and J.B. Marling, *Chem. Phys. Letters* 64 (1979) 75.
- [5] I.P. Herman and J.B. Marling, *J. Chem. Phys.* 72 (1980) 516.
- [6] J.B. Marling, I.P. Herman and S.J. Thomas, *J. Chem. Phys.* 72 (1980) 5603.
- [7] S.A. Tuccio and A. Hartford Jr., *Chem. Phys. Letters* 65 (1979) 234.
- [8] I.P. Herman and J.B. Marling, unpublished results.
- [9] V.N. Bagratashvili, Yu.G. Vainer, V.S. Doljikov, V.S. Letokhov, A.A. Makarov, L.P. Malyavkin, E.A. Ryabov and E.G. Silkis, *Opt. Letters* 6 (1981) 148.
- [10] R.W. Kirk and P.M. Wilt, *J. Mol. Spectry*, 58 (1975) 102.
- [11] D.K. Evans, R.D. McAlpine and H.M. Adams, *J. Chem. Phys.* 77 (1982) 3551.
- [12] M. Gauthier, R. Pilon, P.A. Hackett and C. Willis, *Can. J. Chem.* 57 (1979) 3173.
- [13] R.D. McAlpine, D.K. Evans and H.M. Adams, private communication and reported at the 28th Congress of the International Union of Pure and Applied Chemistry, Vancouver, Canada, (1981).
- [14] J. Stone, M.F. Goodman and D.A. Dows, *J. Chem. Phys.* 65 (1976) 5052, 5062; S. Mukamel and J. Jortner, *J. Chem. Phys.* 65 (1976) 5204; M. Quack, *J. Chem. Phys.* 69 (1978) 1282; H.W. Galbraith and J.R. Ackerhalt, in: *Laser-induced chemical processes*, ed. J.I. Steinfeld (Plenum Press, New York, 1981).
- [15] J.C. Stephenson, D.S. King, M.F. Goodman and J. Stone, *J. Chem. Phys.* 70 (1979) 4496.
- [16] O.P. Judd, *J. Chem. Phys.* 71 (1979) 4515.
- [17] G.A. Miller and R.B. Bernstein, *J. Phys. Chem.* 63 (1959) 710.
- [18] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, *Molecular theory of gases and liquids* (Wiley, New York 1954).
- [19] E. Thiele, J. Stone and M.F. Goodman, *Chem. Phys. Letters* 66 (1979) 457.
- [20] E.R. Grant, P.A. Schulz, Aa.S. Subdo, M.J. Coggiola, Y.T. Lee and Y.R. Shen, *Laser spectroscopy*, eds. J.L. Hall and J.L. Carlsten (Springer, Berlin, 1977).
- [21] J.D. Lambert, *J. Chem. Soc. Faraday Trans. II* 68 (1972) 364.
- [22] J.R. Olson and S. Legvold, *J. Chem. Phys.* 39 (1963) 2902.
- [23] A.P. Modica and J.E. LaGraff, *J. Chem. Phys.* 44 (1966) 3375.
- [24] G. Herzberg, *Infrared and Raman spectra of polyatomic molecules* (Van Nostrand, Princeton, 1964).
- [25] B.T. Darling and D.M. Dennison, *Phys. Rev.* 57 (1940) 128.
- [26] A. Ruoff, H. Burger and S. Biedermann, *Spectrochim. Acta* 27A (1971) 1359.
- [27] R. Gibson, private communication.