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Time-resolved infrared-spectroscopic observation of relaxation and reaction processes during and after infrared-multiphoton excitation of ${}^{12}CF_3I$ and ${}^{13}CF_3I$ with shaped nanosecond pulses

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We have produced shaped infrared laser pulses of several kinds ranging from about 2-100 ns duration using a line tuned CO_2 laser combined with intracavity absorbers and a CdTe electrooptical switch. The time-dependent infrared absorption of ¹²CF₃I and ¹³CF₃I during and after infrared-multiphoton excitation with these pulses was followed by means of a line tuned continuous wave- CO_2 laser and a fast HgCdTe infrared detector (time resolution about 1 ns). The effective time-dependent absorption cross section shows fluence-dependent decay at large fluence with an effective exponential decay constant $k_{L\sigma} \simeq 1.12 \text{ cm}^2 \text{ J}^{-1}$. This can be interpreted by first generation and then decay by further radiative pumping of highly excited levels of CF₃I. The results have been analyzed by master equation modeling using a nonlinear case B/C master equation for multiphoton excitation and very simple models for the absorption properties of highly excited molecules. After nanosecond excitation to very high levels, one finds unimolecular decay $CF_3 I \rightarrow CF_3 + I$ with distinct rate constants $(2 \pm 1) \times 10^8$ and $(5 \pm 4) \times 10^6$ s⁻¹, which corresponds to ensembles of molecules differing by one CO₂laser quantum of energy, in agreement with unimolecular rate theory and master equation models. The most striking observation is a slow, collision-free intramolecular rovibrational redistribution process observed by real time spectroscopy on the nanosecond time scale for molecules excited by modest fluence corresponding to typical average energies of five CO_2 laser quanta and somewhat more.

I. INTRODUCTION

The detailed understanding of the photophysical and photochemical primary processes in infrared multiphoton excitation and infrared laser chemistry remains among the challenges in reaction dynamics (for reviews, see Refs. 1-6). Translational energy distributions have been measured by the molecular beam time-of-flight technique^{7,8} and by laserinduced fluorescence experiments.9,10 Internal product energy distributions have been obtained by laser-induced fluorescence techniques,^{9,11,12} IR fluorescence,^{13,14} and time-resolved IR spectroscopy.¹⁵ The dependence of the rate of the excitation process on molecular parameters and laser intensity, predicted by theory,¹⁶⁻¹⁹ has been proven in a number of experiments.²⁰⁻²⁵ The importance of weak vibrational interactions derived from high resolution IR spectroscopy for the understanding of nonlinear intensity effects in multiphoton excitation of CF₃I has been discussed recentlv.6.25-27

Much less is known about the molecular infrared absorption and other spectral properties during the excitation process. Some information can be drawn from experiments with two laser pulses at different frequencies,²⁸ or photoacoustic absorption measurements with a continuously tunable high pressure CO_2 laser.^{29,30} The IR spectra of molecules excited just one photon below reaction threshold,³¹ or considerably above dissociation limit for larger molecules³² have shown moderately broad spectral features somewhat similar to IR spectra of thermally "hot" molecules.³³ Raman techniques do offer a high time resolution to follow the pumping process in multiphoton excitation, but the definite interpretation remains open.^{34,35} Time-resolved infrared and ultraviolet (UV) spectroscopy has been used to follow product formation³⁶ and the evolution of highly excited parent molecules due to unimolecular decay processes and bimolecular collisional deactivation.³⁷

We have developed a time-resolved infrared spectroscopy on the nanosecond time scale in order to elucidate in more detail the excitation process of molecules due to their interaction with a strong IR laser field and to monitor the decay processes after the end or during the laser pulse.¹⁵ This method offers a number of advantages over UV and Raman techniques because usually only one electronic state is involved. In contrast to UV spectroscopy, most molecules absorb in easily accessible spectral ranges and nearly always a spectral region may be found where there is no overlap of the absorption of reactants and products. IR spectroscopy provides furthermore direct insight into the IR absorption properties of highly excited molecules, which are of fundamental interest for the IR-multiphoton excitation process itself.^{3,16} For smaller molecules where the spectroscopy is well understood, it should be possible to monitor for not too high excitation energies the time-dependent population of a clearly defined rovibronic state. In this context, IR spectroscopy has already been used in earlier experiments to monitor the

time evolution of level populations,³⁸ but due to excitation energies in the kW cm⁻² range, only low-lying vibrational levels were probed with a time resolution in the microsecond range. With nitrogen cooled semiconducter detectors, a time resolution of 1 ns is possible today and was achieved in our experiments. Using excitation laser pulses with a duration [full width at half-maximum (FWHM)] of 2 ns (Ref. 39) or longer, we are able, for instance, to determine unimolecular decay constants for highly excited CF₃ I with a cw CO₂ laser used for analysis. Furthermore, infrared spectroscopy gives us direct access to absorption properties relevant for the excitation process, particularly when a tunable IR diode laser¹⁵ is used for the analysis.

In the present paper, we shall address the fast relaxation and reaction processes occurring during and after IR-multiphoton excitation of CF_3I . The infrared laser chemistry of this molecule has been studied early on^{40,41} and has been used repeatedly since that time for fundamental studies of IR-multiphoton absorption, both experimental and theoretical.^{1-6,8,17-21,24,25,31-34,37} We shall report here new observations on a moderately fast intramolecular relaxation process, step function behavior of unimolecular decay rate constants, and the time evolution of the effective infrared absorption cross section of highly excited CF_3I molecules, which can be understood on the basis of model calculations.

II. EXPERIMENT

A transversely excited atmospheric pressure (TEA) CO₂ laser (Lumonics TEA-103) was mode locked by a gaseous, saturable absorber in an intracavity cell, or the spectral structure of the absorber gas was used to force the laser to oscillate on one longitudinal mode only resulting in a smooth temporal pulse profile, as described before.³⁹ The laser pulse was sent to a fast CdTe nonlinear optical switch to select one or two pulses of the mode locked train or a part of the single mode pulse. The switching time of the crystal was shown to be less than 1 ns, the resolution limit of our experimental detection techniques. After passing the switch, the laser pulse was sent six times through a CO₂ laser amplifier (Lumonics TEA-601). For one single 2 ns pulse, a peak intensity of nearly 1 GW could be achieved after amplification. For shorter pulses, the saturation limit for the amplification process was reached, resulting in a reduced fluctuation of the output pulses compared to the input pulses, but due to the saturation effects, there was some asymmetry introduced during the amplification process of rectangular laser pulses. As a consequence, rectangular pulses at higher pulse energies showed a pronounced maximum at the beginning of the output pulse. As the nonlinear optical crystal rotates the polarization of the laser beam by 90°, a combination of two



FIG. 1. Temporal CO₂ laser pulse shapes. The intensity indicated for the different laser pulses corresponds to a fluence F = 1.0 J cm⁻².

mirrors with optical axes perpendicular to each other was used to turn the polarization back to the vertical direction. For more experimental details and for the reliability of the different laser pulses, see Ref. 39. Four examples of different laser pulses used in our experiments are shown in Fig. 1. For each temporal pulse shape, the time-dependent intensity is calculated for an identical fluence of 1.0 J cm^{-2} .

In addition to the laser lines given in Ref. 39, mode locked CO₂ laser pulses were achieved on the 9*P* 26 laser line at 1041.279 cm⁻¹ by using ¹³CF₃I as a saturable absorber. For stable mode locked operation of the laser, a partial pressure of 20 Pa ¹³CF₃I was necessary, diluted in 30 kPa N₂.

The experimental setup for probing the time evolution of the absorption signal is given in Fig. 2 and is rather similar to the one described in Ref. 15. The pulsed CO_2 laser beam is reduced to the appropriate beam diameter of 4-5 mm by a Galilei type telescope consisting of two spherical copper mirrors. At the place of the reaction cell, the pulsed excitation laser beam is crossed almost antiparallel under a small angle of $1^{\circ}-2^{\circ}$ by the probe beam from a cw CO₂ laser (Apollo 550A). Care was taken that the diameter of the probe beam was smaller than the excitation beam by at least a factor of 2 to ensure that only the central part of the excited region was detected. The reaction cell has a length of 240 mm and is equipped with two KCl windows at Brewster's angle. For the experiments with ¹²CF₂ I, we used a flow reactor. Probe and excitation beam were separated by a small hole (diameter = 1 mm) in the copper mirror 0.5 m in front of the reaction cell. The probe beam is focused with an off-axis parabolic mirror (f = 33 mm) onto a fast photovoltaic HgCdTe detector (SAT class C2). To suppress scattered light of the excitation pulse from the windows of the reaction cell, a filter cell was used filled with 15 kPa NH₃ (for excitation with the 9R 16 line at 1075.99 cm⁻¹), or 25 kPa SiF₄ (for excitation with the 9P 30 line at 1037.4 cm⁻¹). Residual stray light was blocked by putting the filter cell, focusing optics, and detector in a covered box.

After amplification, the output of the HgCdTe detector was digitized with a transient recorder (Tektronix 7912AD). The time resolution of the detection system is



FIG. 2. Experimental setup to probe the time-dependent absorption. AP1 and AP2--apertures to reduce the probe laser beam; BS--beam splitter (KCl); M--mirror; OAP--off-axis parabolic mirror; MCT--HgCdTe detector; TEK 7912AD--transient recorder

given by the rise time of the detector, the preamplifier, and the plug-in amplifiers for the transient recorder. The rise time of the photovoltaic HgCdTe detectors depends strongly on the reversed bias voltage applied to the element. For a bias voltage of 0.6 V, an excitation bandwidth of 600 MHz is specified by the supplier. Two different preamplifiers were used in the experiments-an a.c. coupled IR 1200 from SAT (bandwidth 10-1200 MHz) and a d.c. coupled d.c. 3002 A from B&H Electronics Components (bandwidth 3 GHz). The bandwidth for the plug-in amplifiers of the transient recorder is given by 200 (7A26) and 600 MHz (7A19), respectively. This limits the time resolution of the detection system under optimized conditions to a rise time of 0.6 ns. The performance of the detection system was tested by reflecting a small part of a 2 ns pulse from a KCl plate back to the HgCdTe detector. With an applied reverse bias of 0.45 V to the photovoltaic detector, no distortion of the temporal shape of the laser pulse could be detected. This gives an experimental upper limit of 2 ns for the rise time of the detection system.

A small part of the incoming laser pulse was reflected by a KCl beam splitter to a photon drag detector (Rofin 7441) with a rise time of 1 ns and the shape of the excitation pulse was detected for every experiment on a second transient recorder of the same type. Around 50% of the signal from the photon drag detector was split off to trigger the other transient recorder. The delay of the signal from the HgCdTe detector due to different optical path length, different cable length, and due to the time delay produced in the preamplifier was determined by superimposing the signal from the photon drag detector and the signal from HgCdTe detector on the transient recorder. By this method, it was possible to determine the delay between the excitation pulse and the laser-induced kinetics with an accuracy of at least 1 ns.

Probing the excitation and dissociation processes with an antiparallel geometry as described above, one has to take into account that the detected rise time of the probe signal might be distorted due to the finite velocity of light when the transient time of the laser pulse through the reaction cell becomes comparable with the rise time of the signal. A model of a step function with finite rise time traveling in one direction and a probe pulse in the other direction was assumed. A simulation of the deconvolution on the computer showed that for a cell length of 200 mm, the distortions of rise time are less than 10% if the actual rise time (10%– 90%) does not drop below 2 ns. Possible effects from this were thus neglected here.

To determine the laser fluence, the central spot of the excitation beam was selected by a diaphragm (diameter 5 mm) and the total energy within this spot was averaged to determine the fluence $(J \text{ cm}^{-2})$ in the region which was detected by the probe beam. The energy was measured by an integrating pyroelectric detector (Lumonics 50D). For a discussion of details and the limitations of this method, we refer to Ref. 15. To control the laser fluence in each laser shot, a small part of the laser beam was sent to a second pyroelectric detector (Lumonics 20D) calibrated to the first one. The maximum fluence obtained in the experiments was limited by the distruction of the cell windows rather than by

the available energy from the laser system. For 2 ns pulses, this limit was reached at a fluence of ~ 1.5 J cm⁻², whereas for single mode pulses, experiments up to a fluence of 3 J cm⁻² were possible. For higher fluences, a bright flash occurred on the cell windows disturbing the probe signal and leading to a destruction of the windows after a number of laser shots. The fluence range might be extended by a factor of 2 to 3 by reducing the spot size of the excitation pulse, but then IR probing under clearly defined fluence conditions would become difficult.

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CF₃ I in natural isotopic composition was obtained from Fluorochem Ltd. and was outgassed before use by several freeze-pump-thaw cycles. It showed otherwise no important impurities in the IR spectra, which also demonstrated the identity of the substance. ${}^{13}CF_3$ I was synthesized in our laboratory following a scheme developed for a whole set of ${}^{13}C$ enriched compounds, which we use for spectroscopy and laser chemistry, starting out from Ba ${}^{13}CO_3$ (99% ${}^{13}C$, Stohler)

Ba
$${}^{13}CO_3 \xrightarrow{H_2SO_4 (300 \text{ K})} BaSO_4 + {}^{13}CO_2,$$
 (1)

$$^{13}\text{CH}_3\text{OH} \xrightarrow{\text{Cl}_2, hv(UV)} ^{13}\text{CCl}_4,$$
 (3)

$$^{13}\text{CCl}_4 \xrightarrow[315 \text{ K}]{\text{CH}_3\text{CH}_2\text{I/AlCl}_3} ^{13}\text{CI}_4, \qquad (4)$$

$$^{13}\text{CI}_4 \xrightarrow{\text{IF}_5} ^{13}\text{CF}_3\text{I.}$$
 (5)

The yields are 80% [steps (2) and (3) each], 84% [step (4)], and 90% [step (5)]. The raw product had 90% chemical purity and was further purified by preparative gas chromatography to 99.5% CF₃I. The isotopic purity was determined by IR spectroscopy. From two experiments, it was 94% ¹³C in the final product in the first run and 98% in a second run, which was more carefully controlled. The latter product was used for spectroscopy, whereas the former product was used for many of the laser chemical experiments, as the results were not sensitive to a slightly increased ¹²C content, as demonstrated by several tests. A more detailed description of the synthesis procedures will be given elsewhere together with the synthesis of other compounds.⁴²

III. EXPERIMENTAL RESULTS

The two different isotopomers were excited with the $9R \ 16 \ {\rm CO}_2$ laser line at $1075.99 \ {\rm cm}^{-1} \ ({}^{12} \ {\rm CF}_3 \ {\rm I})$ and with the $9P \ 30$ laser line at $1037.43 \ {\rm cm}^{-1} \ ({}^{13} \ {\rm CF}_3 \ {\rm I})$. Both excitation laser lines are situated close to the broad maximum of the frequency-dependent multiphoton dissociation probability for the two different isotopomers.^{20,27,43} The change of the effective absorption cross section due to the excitation process was followed either in the *R* branch of the ground state absorption, or shifted by 30–50 \ {\rm cm}^{-1} to low or high wave numbers with respect to the band center, where only highly



FIG. 3. IR survey spectra of (a) ${}^{12}CF_3I$ and (b) ${}^{13}CF_3I$ in the region of the symmetric CF_3 -stretching vibration (ν_1). The CO_2 laser lines for excitation and probing are indicated. [The resolution used in (b) is lower than in (a), therefore the different fine structure $\Delta(FWHM) = 0.01 \text{ cm}^{-1}$ in (a), 0.02 cm⁻¹ in (b)].

excited molecules would absorb appreciably. For the purpose of quantitatively representing the absorption as a function of time and other parameters, we have defined an effective absorption cross section σ for the ensemble of initially present CF₃I molecules

$$\sigma(t) = \frac{1}{C \cdot l} \ln \left[I_0 / I(t) \right].$$
(6)

Here C is the concentration (as particle density in molecules per unit volume) of the initially present CF₃ I molecules, *l* is the length of the absorption path, I_0 is the incident, and I(t)is the time-dependent transmitted intensity of the probe laser beam. We note that by definition this "cross section" refers to initially present CF₃ I independent of whether this is highly excited or totally dissociated during reaction. σ is a nominal quantity independent of assumptions about the kinetics. The different CO_2 laser lines for excitation and probing are shown in Fig. 3 together with the room temperature spectra of the two isotopomers taken on our Bomem Fourier transform infrared (FTIR) spectrometer. An example for the time-dependent absorption in the two different probing regions is given in Fig. 4 together with a single mode laser pulse at a fluence of 1.85 J cm^{-2} . Even at a fluence above 2.5 $J \text{ cm}^{-2}$, where one would expect a dissociation probability



FIG. 4. Time-dependent absorption signal of ${}^{12}CF_3I$ during excitation (9*R* 16) with a single mode laser pulse ($F = 1.85 \text{ J cm}^{-2}$) at two different probe laser lines.—9*R* 20 (1078.59 cm⁻¹); --- 9*P* 18 (1048.66 cm⁻¹).

of close to unity,^{20,25} the absorption does not disappear completely in the first 2 μ s after the laser pulse. Only on a time scale of 10–20 μ s this remaining absorption decays with a rate constant very close to the one expected for the recombination of CF₃ to give C₂ F₆.^{44–46} This leads to the conclusion that the remaining absorption is due to rotationally excited CF₃. The band center of the symmetric CF-stretching vibration was found at 1090 cm⁻¹.⁴⁷

For a linear dependence of the excitation process on laser intensity (case B), the population of the first molecular levels should decay as a function of *fluence* only. In the experiments, the decay of the effective absorption cross section at the 9R 20 laser line may be fitted very well to an exponential dependence upon laser fluence. For single mode laser pulses, a decay constant of (2.00 ± 0.30) cm² J⁻¹ is obtained independent of the laser pulse energy (and thus intensity) in the measured fluence range of 0.6–2.9 J cm⁻². (For higher fluences, the absorption of the reaction product CF₃ was taken into account.) This result is unexpected for CF₃I, where a nonlinear intensity dependence (case C) had been found by time-resolved detection of the nascent I atoms²⁴ and by yield measurements with CO₂ laser pulses of different temporal shape.²⁵ The decay constant is slightly higher for mode locked laser pulses [$k = (2.40 \pm 0.54)$ J⁻¹ cm²] and for single mode pulses with a pulse length (FWHM) reduced by 10-12 ns which occur randomly due to the amplification process. For ¹³CF₃I, a much more complicated decay of the absorption cross section was found during the pumping process on each of the probe laser lines 9P 10, 9P 12, and 9P 14 around 1053 cm $^{-1}$. This may be explained by the differences in the absorption spectrum of the two isotopomers at lower excitation levels. In order to elucidate this unexpected fluence dependence in more detail, one has to take into account that the effective absorption cross section at a given frequency must not be identified with level populations in a straightforward way. The conclusions which can be drawn from different models are discussed in more detail below.

For the excitation with mode locked laser pulses, the temporal structure of the laser pulse is reflected in the decay



FIG. 5. (a) Time-dependent absorption signal for the excitation of ${}^{12}\text{CF}_3\text{I}$ with a mode-locked pulse at a fluence of $F = 0.17 \text{ J cm}^{-2}$ (---) and F = 1.6 J cm ${}^{-2}$ (---). Excitation 9*R* 16; probing 9*R* 20 (1078.59 cm ${}^{-1}$). (b) Time-dependent absorption signal for the excitation of ${}^{13}\text{CF}_3\text{I}$ with a rectangular laser pulse ($T_p = 23$ ns) and a fluence of $F = 0.20 \text{ J cm}^{-2}$ (---) and $F = 2.12 \text{ J cm}^{-2}$ (---). Excitation 9*P* 30; probing 9*P* 10 (1055.63 cm ${}^{-1}$).

curve for the effective absorption cross section. An example for two different fluences is shown in Fig. 5(a) together with the temporal shape of the laser pulse. During the laser action, a decay of the absorption is detected due to the excitation process. This decay is followed by a recovery of absorption at the end of the laser action. This recovery is less pronounced at higher laser fluences and disappears at the highest fluences. At pressures lower than 200 Pa, intermolecular processes may be ruled out on a time scale on the order of 5 ns or even less. We also did not observe a pressure dependence of the time constant for recovery of absorption (about 3-5 ns, with systematic pressure variation between 15 and 100 Pa and higher pressures under somewhat different conditions). A fast intramolecular process seems to be at the origin of the recovery phenomenon. This explanation would be in agreement with the finding that the recovery phenomenon is absent if higher excited molecular levels are probed at the 9P18 CO₂ laser line at 1048.66 cm⁻¹. The interpretation of the high resolution spectra for the v_1 stretching region of ${}^{12}CF_3I$ leads to an estimate of $\leq 1-2$ ns for the intramolecular decay rate as well.²⁶

A similar recovery effect is detected for the excitation of CF_3 I with a rectangular laser pulse. If ${}^{12}CF_3$ I is excited with

a laser pulse of 23 ns length and probed at the 9*R* 20 laser line the effect is detectable at the end of the laser pulse up to a fluence of 0.4–0.5 J cm⁻². A recovery phenomenon for ¹³CF₃I is shown in Fig. 5(b). The change of the absorption cross section is followed on the 9*P* 10 laser line at 1055.63 cm⁻¹ for an excitation pulse of 23 ns duration and two different fluences. At the end of the pulse with 0.2 J cm⁻², the relaxation time is about 3–5 ns. As mentioned above, the time dependence of the absorption cross section is generally much more complicated for ¹³CF₃I. For a fluence of 2.12 J cm⁻², the absorption at 9*P* 10 decreases during the pulse and there is no (or little) recovery after the pulse.

The time evolution of the population of higher molecular levels may be followed by probing the time-dependent effective absorption cross section far enough outside the room temperature absorption band. For lower laser fluences, only an increase of the absorption is found. Increasing the fluence in the excitation pulse results in a decay of the effective absorption cross section after it has reached some maximum value. In Fig. 6(a), the time-dependent cross section on the 9P 18 laser line is shown for a rectangular (trapezoidal) pulse of 23 ns duration and three different fluences. If the laser pulse is not too short and the laser intensity is not too high, the absorption remains constant after the end of the laser pulse on a time scale of the pulse duration. This behavior can be explained by most of the absorption being due to the population of intermediate levels below or around reaction threshold. Only for laser pulses with very high intensity are levels of more than two quanta above reaction threshold populated appreciably. This is consistent with model calculations based on the master equation approach (see below). The assumption that levels of more than one to two quanta above reaction threshold do not contribute significantly to the absorption cross section was confirmed by exciting the molecules by two 2 ns pulses separated by 18.5 ns which were sliced out of a mode locked pulse train [Fig. 6(b) the absolute fluence being determined only roughly, to within about a factor of two here]. For low intensity pulses, the absorption cross section increases with both laser pulses, whereas it remains constant between the two pulses. Increasing the intensity and fluence results in a decrease of the absorption changes during the second pulse. There are two reasons for the decrease of the absorption step with increasing fluence. First, the molecules have already largely reached the energy range, which contributes to the shifted absorption cross section and further excitation occurs within this energy range or even out of this range, and second there can be dissociation during the laser pulse. The absorption cross section remains constant between the two laser pulses at low fluences. There is unimolecular decay after the second pulse.

Similar to the decay of the absorption cross section at lower excitation levels, the time-dependent probe signal can be normalized to its maximum value. If the decay of absorption is driven by the laser fluence, $\ln \sigma$ as a function of laser fluence provides a meaningful evaluation. An exponential decay should then result in a straight line. The dependence of the natural logarithm of the absorption cross section on laser fluence is shown in Fig. 6(c) for the highest fluence of Fig. 6(a). Here the first part of the signal describes the increase of



FIG. 6. (a) Time-dependent absorption cross section $\sigma(t)$ at 1048.66 cm⁻¹ for the excitation of ¹²CF₃I with a rectangular laser pulse ($T_p = 23$ ns) at a fluence of F = 0.20 J cm⁻² (---), F = 1.93 J cm⁻² (---), and F = 2.97 J cm⁻² (....). Excitation line 9R 16. (b) The same as in (a), but with a double pulse excitation as indicated by the profile given by the dashed lines. The points show an exponential fit for the unimolecular after pulse decay. (c) Logarithm of the normalized absorption cross section for the laser pulses with the highest fluence of (a). A straight line is fitted to the decay of the absorption during the second part of the laser pulse.

TABLE I. Decay constants k_1 (st) for effective absorption.

Excitation*	Probe*	Isotope	Pulse shape ^b	$k_i(st) (cm^2 J^{-1})$
9 <i>R</i> 16	9 <i>P</i> 18	¹² CF ₃ I	23 ns	1.19 ± 0.34°
9 <i>R</i> 16	9 <i>P</i> 18	¹² CF ₃ I	SM	1.12 ± 0.40
9 <i>R</i> 16	9 <i>P</i> 18	¹² CF ₃ I	ML	1.27 ± 0.22
9 <i>P</i> 30	9R 10	¹³ CF ₃ I	SM	1.12 ± 0.81
9 <i>P</i> 30	10R 26	¹³ CF ₃ I	SM	1.29 ± 0.46
9 <i>P</i> 30	10R 26	¹³ CF ₃ I	ML	1.33
9 <i>P</i> 30	9R 10	¹³ CF ₃ I	23 or 15 ns	1.19 ± 0.8

[•]CO₂ laser lines (see Fig. 3).

^bSM for single mode, ML for mode locked (see Fig. 1).

* Errors or scatter are given as 95% confidence intervals only if a sufficiently large number of experiments were

carried out. Otherwise only one number is quoted for one or the average of two experiments.

the absorption during the early part of the laser pulse. For different laser pulse shapes, an exponential fit was performed for the laser-driven decay of the absorption signal for the two isotopomers. For ${}^{13}CF_3I$, the decay was probed as well at a frequency shifted to the high frequency side of the absorption band. The fitted decay constants are summarized for the different excitation and probing conditions in Table I. No important dependence on laser intensity, probe frequency, and isotopomer was found, indicating that the further excitation of the already excited molecules shows a linear intensity dependence, but again, the simplified interpretation has to be confirmed by a simulation of the time evolution for the absorption signal based on reasonable model assumptions (see Sec. IV).

After the end of the laser pulse, the change of the absorption cross section is determined either by unimolecular decay rates or by bimolecular processes. Laser pulses with high enough intensity may lead to a significant population of highly excited molecular levels. For different laser pulses with pulse lengths of 23 ns or less, unimolecular decay rates between 1.3×10^8 and 2.6×10^8 s⁻¹ have been determined on different probe laser lines. The experimental data are summarized in Table II A. We found no significant dependence of the decay rate on excitation conditions and probe laser line. There is no measurable dependence on laser fluence for a given temporal profile over the accessible fluence range. Only the ratio of quickly decaying molecules compared to more stable molecules is influenced by the pulse energy. Figure 7(a) shows the time-dependent effective absorption cross section $\sigma(t)$ for the excitation of ¹³CF₃I with 2 ns pulses of different fluence (probe line 10R 28). Also shown is an exponential decay curve (as a function of time) fitted to

(A)	Probe	Isotope	Pulse shape ^a	Fluence $(J \text{ cm}^{-2})$	$lg(k/s^{-1})$
	9 <i>P</i> 18	¹² CF ₃ I	2 ns	0.21-1.23	8.15 ± 0.39 ^b
	9 <i>P</i> 18	¹² CF ₃ I	11 ns	0.13-1.43	8.18 ± 0.25
	9 <i>P</i> 18	¹² CF, I	DP	0.17-0.30	8.18
	9 <i>P</i> 18	¹² CF ₃ I	23 ns	1.32-2.97	8.11 ± 0.21
	9 R 10	¹³ CF ₃ I	11 ns	0.20-1.65	8.19
	9 <i>R</i> 10	¹³ CF ₃ I	DP	0.36-0.67	8.34
	9 <i>R</i> 10	¹³ CF ₃ I	2 ns	~1.0	8.12
	9R 12	¹³ CF ₃ I	2 ns	~1.0	8.18 ± 0.32
	10 R 28	¹³ CF ₃ I	2 ns	~1.0	8.40
(B)	9 <i>R</i> 10	¹³ CF, I	DP	0.5	6.86
	9R 10	¹³ CF ₃ I	SM	0.96-1.77	6.63
	9 R 10	¹³ CF ₃ I	ML	0.59-1.77	6.92
	9 <i>P</i> 10	¹³ CF ₃ I	23 ns	1.57	6.90
	9 <i>P</i> 10	¹³ CF ₃ I	DP	0.76	~6.4
	10 R 26	¹³ CF ₃ I	SM	0.26-0.49	6.58
	10 <i>R</i> 26	¹³ CF ₄ I	ML	0.280.96	6.25
	10 <i>R</i> 28	¹³ CF,I	2 ns	~1.0	6.32
	9 <i>P</i> 18	¹² CF ₁ I	SM	0.96-1.61	6.24
	9 <i>P</i> 18	¹² CF, I	ML	1.70	6.25

TABLE II. (A) Unimolecular decay rate constants (fast process). (B) Decay constants for the slower process.

• DP stands for double pulse, SM for single mode, MI for mode locked (see Fig. 1). Excitation lines are 9R 16 for ¹²CF₃I and 9P 30 for ¹³CF₃I.

^b Errors or scatters are given as 95% confidence intervals only if a sufficiently large number of experiments were carried out. Otherwise only one number is quoted for one or the average of two experiments.



FIG. 7. (a) Change of the effective absorption cross section of ${}^{13}CF_3I$ probed at 10R 28 (980.91 cm⁻¹) during and after excitation with a 2 ns laser pulse with a fluence at F = 1.25 J cm⁻² (--) and F = 0.98 J cm⁻² (--). Excitation line 9P 30. (b) Slow decay processes of highly excited CF₃I given by $\sigma(t)$. (Upper trace) ${}^{12}CF_3I$ excited with a SM laser pulse [F = 1.92 J cm⁻² (9R 16)] probed at 1048.66 cm⁻¹ (9P 18). (Lower trace) ${}^{13}CF_3I$ excited with a ML laser pulse [F = 0.44 J cm⁻² (9P 30)] probed at 979.71 cm⁻¹ (10R 26). The lowest pointed line shows the single mode laser pulse shape (note the time scale).

the experimental data. This yields a decay constant of 2.54×10^8 s⁻¹ and can clearly be identified as collisionless unimolecular decay of highly excited CF₃ I molecules under our pressure conditions (20–100 Pa).

A second decay process could be detected on the microsecond time scale independent of the shape of the excitation pulse and laser fluence. There seems to be a slight dependence on probe laser frequency. For ¹³CF₃I, a decay rate of $(6.5 \pm 1.5) \times 10^6 \text{ s}^{-1}$ was determined on the 9*R* 10 laser line, whereas probing at 10*R* 26 and 10*R* 28 lines results in decay constants of $(2.8 \pm 1.1) \times 10^6 \text{ s}^{-1}$. When the absorption of ¹²CF₃I after excitation with a single mode or mode locked laser pulse is followed at the 9*P* 18 laser line, an average decay constant of $1.75 \times 10^6 \text{ s}^{-1}$ was found. The constants obtained for the slower decay process are given in Table II B. Two examples for a slow decay process are shown in Fig. 7(b) for excitation with two different fluences and probing the two isotopomers at a frequency shifted to the low fre-

quency side of the absorption band. The increase of the absorption signal in the upper curve is due to absorption of nascent CF₃. Effects from collisions cannot be excluded on this time scale under the experimental conditions (50–100 Pa) and some influence of the pressure on the measured decay rates was, indeed, found. We assume that the slow unimolecular process is influenced by collisions, as is also confirmed by further observations. Nevertheless, the step function behavior for k_1 rising from about 10⁶ to about 10⁸ s⁻¹ is very close to the behavior of k(E) predicted from statistical adiabatic channel model calculations¹⁸ for an ensemble of molecules at threshold and with one more CO₂ laser quantum absorbed.

Processes with intermediate rate constants around $(3.5 \pm 1.5) \times 10^7 \text{ s}^{-1}$ were only found when probing ${}^{13}\text{CF}_3\text{I}$ on the 9P 10 and 9P 14 laser lines. These processes were dominant for fluences below $0.5 \text{ J} \text{ cm}^{-2}$. They lead to an increase of the effective absorption cross section. If these signals were due to a dissociation process, they could only be attributed to an absorption of nascent CF_3 . This seems to be unlikely because even for fluences below 0.3 J cm⁻² in a single mode pulse, this change of the absorption cross section was $\sim 25\%$ of the absorption of unexcited ¹³CF₃I. Taking into account the quite complex change of the absorption cross section on these probe laser lines during the pumping process, a collision-induced bimolecular process seems likely. In comparison to the abovementioned slower processes, which are sensitive only to nonresonant energy transfer, in this spectral region also quasiresonant processes (having much higher collisional cross sections) may lead to a change in the absorption spectrum.

IV. COMPARISON WITH MODEL CALCULATIONS

In order to interpret quantitatively our time-resolved observations, we have carried out model calculations for IRmultiphoton excitation. The time evolution of the level populations was calculated with a model based on a matrix master equation in the transition range between cases B and C,³ as appropriate for CF_3I under the experimental conditions

$$\dot{p} = Kp. \tag{7}$$

Calculations on this basis predicted¹⁹ successfully the subsequent measurements of time- and intensity-dependent unimolecular decay of CF₃I (Ref. 24) and we have taken the model parameters to be the same as in the earlier calculations without further adjustments. This should be sufficient for a semiquantitative description of our present experiments, as we shall confirm below. We shall summarize the main equations from Refs. 16–19, as there are some subtleties in comparison with experiment, which require explicit reference. The rate coefficient $K_{M+1,M}$ for transition by absorption between level M and M + 1 with level populations p_M and p_{M+1} in the matrix equation (7) is given by the general equation (8)

$$K_{M+1,M} = 2\pi |V_{M+1,M}|^2 / \delta_{M+1}.$$
 (8)

 $|V_{M+1,M}|^2$ is the angular frequency mean-square radiative coupling matrix element between all quantum states in level M and all quantum states in level M + 1 and establishes the relation to the full quantum treatment of IR-multiphoton excitation,³ which we shall not discuss here. The quantity δ_{M+1} is the mean angular frequency separation of quantum states in level M + 1, simply related to the average effective density of rovibrational states (respecting relevant selection rules^{48,49}) ρ_{M+1} with Planck's constant h,

$$\rho_{M+1} = 2\pi \delta_{M+1}^{-1} h^{-1}. \tag{9}$$

Equation (8) for absorption is approximately valid both for cases B and C. In the framework of the chromophore model, where the fundamental transition of an infrared chromophore in the excited molecule dominates the contribution to absorption in the frequency range considered, we can parametrize the rate coefficient in a useful way in terms of the vibrational band strength G_v for this fundamental, which is easily available from experiment

$$K_{M+1,M} = C_M \Delta E^{-1} G_v I(\rho_M^{0'} / \rho_M), \qquad (10)$$

$$G_{\nu} = \int_{\text{vibrational band}} \sigma_{10}(\nu) \nu^{-1} d\nu.$$
 (11)

 $\sigma_{10}(\nu)$ is the molecular absorption cross section in the frequency range of the vibrational chromophore fundamental transition (1 – 0 or other). G can be related to the vibrational transition dipole moment and Einstein A and B coefficients (omit $4\pi\epsilon_0$ for the centimeter-gram-second (cgs) system⁵⁰)

$$G = \frac{8\pi^3}{3hc(4\pi\epsilon_0)} |\langle v_f | \mu | v_i \rangle|^2$$
(12a)

$$= 41.624 \left(\frac{|\langle v_f | \mu | v_i \rangle|}{\text{Debye}}\right)^2 pm^2$$
(12b)

$$=\frac{c^2}{8\pi v^3}A=\frac{h}{c}B.$$
 (12c)

For CF₃I, the numerical value for the v_1 (CF₃ symmetric stretching) fundamental is about $G = (9 \pm 1) pm^2$ and thus $M_{10} = |\langle 1|\mu|0\rangle| \approx 0.46$ D. In the simulations, we used $G = 8.5 \ pm^2$, I is the laser intensity (power per unit area), ΔE is a vibrational bandwidth parameter, which can be taken as adjustable (but $\Delta E < h v_{\text{laser}}$), $\rho_M^{0'}$ is the density of vibrational states for all modes except the chromophore, and ρ_M is approximated by the full vibrational state density for all modes using simple calculations. The detailed level and frequency dependence of transition rates are now incorporated in the matrix elements C_{M} , which are only weakly dependent on the level index M and in the simplest case may be taken as a constant $C_M \equiv \overline{C}$.¹⁹ If one has additional information on the absorption properties of highly excited molecules, one may incorporate this into C_M , but at present, such detailed information is lacking and thus $C_M = \text{const.}$ in the following calculations. Furthermore, we have adjusted $\Delta E(hc)^{-1} = 250 \text{ cm}^{-1}$ in order to reproduce the experimental case B steady state rate coefficient k (st) = 1.6×10^8 s⁻¹ at I = 100 MW cm⁻².²⁰ In case B, the effective rate coefficient $K_{M,M+1}$ for stimulated emission is given by the detailed balance relation

$$\frac{K_{M+1,M}}{K_{M,M+1}} = \frac{\rho_{M+1}}{\rho_M}.$$
(13)

The situation is different in case C, where "detailed balance" becomes intensity dependent $(|V_{M+1,M}| \propto \sqrt{I})$,

$$\frac{K_{M+1,M}}{K_{M,M+1}^{C}} = \left(\frac{\rho_{M+1}}{\rho_{M}}\right) \left[\frac{\pi}{2}\sqrt{3}\left(\frac{|V_{M+1,M}|}{\delta_{M+1}}\right)\right].$$
 (14)

In general, the lower levels in the molecule up to level $M_{B,C}^{\text{trans}}$ are described by the rate coefficient in case C and the higher levels by case B. The transition depends on both the density of states ρ_M (and thus the level index M or molecular energy) and intensity. It has been calculated here following the prescription in Ref. 19. Using these expressions for the rate coefficient matrices K, we have solved Eq. (7) by representing the laser pulse by a staircase function with typically ten to 20 steps of variable intensity as shown in Fig. 8. During



FIG. 8. Calculated level population for the excitation of CF_3I with a single mode pulse (a) case C/B; (b) case B; and (c) two 2 ns pulses separated by 15 ns at a fluence of F = 1.0 J cm⁻². The case B calculation for the last case gives almost indistinguishable results.

each time interval, we used as initial population vector $p(t_0)$ the result from the previous time interval and took the general analytical solution for the interval of constant intensity (*K* being independent of time¹⁷ during the interval)

$$p(t) = \exp[K(t - t_0)]p(t_0).$$
(15)

Strictly speaking, K is independent of $p(t_0)$ only in case B, but we have neglected the initial state dependence also in case C for the present purpose, retaining, however, the nonlinear intensity dependence, which is the most important effect. Figure 8 shows the time-dependent population for groups of levels for two typical pulse shapes similar to experiment—Figs. 8(a) and 8(b) for a single mode pulse, and Fig. 8(c) for a double pulse consisting of two short pulses separated by 15 ns. The total fluence is chosen in both cases to be 1 J cm⁻². Level 18 is the first to show unimolecular decay and it is seen that the higher levels are populated appreciably only for the short, intense pulses, after which one can also nicely recognize the after pulse unimolecular (nonradiative) dissociation. Most of the other level populations also show self-explanatory behavior except the relaxation of the population of the lowest levels to higher stationary values at the end of the single mode pulse. This is in part an artifact of the present approximation of not considering the initial state dependence of the case C K matrix. It is a small effect here, which we did not correct for. It does not appear in the simple case B model [Fig. 8(b)]. For simplicity, we also took as the initial average energy one quantum of the CO₂ laser and neglected the ground state altogether, although at room temperature, about 58% of the molecules have less than 300 cm⁻¹ vibrational excitation (86% have less than 850 $(m^{-1})^{51}$. However, in order to describe the detailed population dynamics of the lowest levels, quantum mechanical calculations are necessary which are planned for the future once enough spectroscopic information is available.^{26,51} The high level populations show adequately the possibility of after pulse dissociation in "steps" of rate constants, the slowest processes depending sensitively on the detailed treatment of p(E,J) and k(E,J) which we did not adjust here to experiment. Our calculations indicate, however, that one further rate constant step, with k of the order of $\ge 10^9$ s⁻¹ should be observable, which is masked in our experiments by the limited time resolution, although it might be just barely accessible in the double pulse experiments.

The most interesting observation in our experiments is the time-dependent effective absorption cross section $\sigma(t)$ at the probe frequency (6). At first sight, its simulation would appear to depend in a most sensitive way upon both the assumptions on detailed level structure and population and the absorption properties of excited molecules, but we shall see that some important properties can be derived just from the multiphoton excitation dynamics.

IR-multiphoton excitation generates a density of excited molecules at energy E (and other quantum numbers such as J) as a function of time and coordinates within the probe cell

$$C(E,x,y,z,t) = p(E,x,y,z,t) \cdot C.$$
(16)

The total concentration C of CF_3I is constant throughout the cell, if we include "product states" $CF_3 + I$ in the concentration. The probability distribution p(E,x,y,z,t) can be simplified in several ways. The cell length (in the z direction) of 10 cm corresponds to a beam passage time of 0.33 ns, which is short compared to the time resolution. Furthermore, the excitation pulses are hardly attenuated by the sample in the cell. We thus may set p(...z',t) = p(...z'',t) $\equiv p(...,t)$ for any z at a given t to within our experimental limitations. Furthermore, we consider only the central, probed part of the excitation beam, assuming well-defined fluence at x_0, y_0 (this approximation is somewhat less good and could be relaxed, if desired). Thus we can retain energy dependence only

$$C(E,t) = p(E,t)C.$$
(17)

We next consider the nature of the time-dependent energy distributions p(E,t) generated in the molecules by IR-multiphoton excitation. If initially the molecules were in the ground state (or some other well-defined energy level), after some excitation with fluence, intensity, and time (F,I,t), we would have essentially p(E,t) characterized by a series of δ distributions centered at levels M of multiple laser quanta hv(again including product levels)

$$p(E,t) = \sum_{M} p_{M} \delta(E - M \cdot h\nu).$$
(18)

It is obvious that the δ distributions need not be sharp, but given to within the level width generated by multiphoton excitation. If one allows for an initial (thermal) distribution p_i^0 , one has with energy E_i^0 for the level *i*,

$$p(E,t) = \sum_{i} p_{i}^{0} \sum_{M} p_{M,i} \delta(E - E_{i}^{0} - M \cdot h\nu).$$
(19)

Disregarding overlaps and coincidences, Eq. (19) is simply a superposition of many expressions as given by Eq. (18), and we shall concentrate on the latter, hereafter, for simplicity. The distribution is probed at the probe laser frequency ν_p . The probe laser beam intensity may be amplified by stimulated emission, or reduced by absorption from this molecular distribution. We can now calculate approximately this from two extreme assumptions.

(i) One has strict, narrow δ distributions as given by Eq. (18) and no population at excited levels $M \cdot hv \pm hv_p$. Furthermore, the transitions induced by the probe laser in the very highly excited molecules can be described by case B (obviously not appropriate in a discrete spectrum with few levels at low energy). Between z and dz, the differential change in probe laser intensity is given by Eq. (20)

$$-dI(v_{p},t,z) = I(v_{p},t,z) \cdot \sigma(t) \cdot C \cdot dz, \qquad (20)$$

$$\sigma(t) \equiv hv_{p} \left[\int_{0}^{\infty} K_{E+hv_{p}E}^{(I)} p(E,t) dE - \int_{hv_{p}}^{\infty} K_{E-hv,E}^{(I)} p(E,t) dE \right]. \qquad (21)$$

The expressions result directly as the rate of energy change per unit area and unit time in the probe beam over the length dz (i.e., dI), which is equal to the number of photons absorbed by the molecules in the volume $dz \times$ unit area minus those emitted, multiplied by the energy of the photon. In case B, the rate coefficient for photon absorption (emission) is proportional to intensity

$$K_{E \pm hv_{p}E} = I(v_{p}, t, z) K_{E \pm hv_{p}E}^{(I)}, \qquad (22)$$

where $K^{(I)}$ has dimensions of cm² J⁻¹ as usual,¹⁷ i.e., $K^{(I)} = K/I$. The partial energy change dU per unit volume due to absorption or emission of one photon by molecules at energy E is the product of photon energy and rate processes per unit volume

$$\frac{d^4 U(x,y,z,t)}{dt \, dx \, dy \, dz} = h v_p \int_{\text{level}} K_{E \pm h v_p \cdot E} \cdot p(E,t) \cdot C \, dE.$$
(23)

Multiplication by dz results in the *intensity* change $- dI = d^{3}U/dt dx dy$ [Eqs. (20) and (21)]. These equations can be used for very general calculations of absorption properties of a sample irradiated with some laser beam, but we shall restrict further calculations only to the simplest examples. We assume that neither the probe laser nor collisions or other effects change p(E,t) generated by IR-multiphoton absorption from the ground state [Eq. (18)]. Thus we have from Eqs. (18) and (21) (by integration over the δ distributions)

$$\sigma(t) = h v_p \left(\sum_{M=0}^{\infty} p_M K_{E_M + h v_p, E_M}^{(I)} - \sum_{M=1}^{\infty} p_M K_{E_M - h v_p, E_M}^{(I)} \right).$$
(24)

If we assume now that for some $M > M_{\text{max}}$ and $M < M_{\text{min}}$ we have $p_M \simeq 0$ (or that for the lowest levels $K^{(I)} \simeq 0$ or other calculations are to be performed), we obtain with one summation index

$$\sigma(t) = h \nu_{p} \sum_{M=M_{min}}^{M=M_{max}} p_{M}(t) (\overline{K}_{M+1,M}^{(I)} - \overline{K}_{M-1,M}^{(I)}).$$
(25)

Here we have expressed the difference of $K_{M+1,M} = K_{E+hv,E}$ (for multiphoton excitation) and of $\overline{K}_{M+1,M} = K_{E+hv_p,E}$ by the line (the difference arises obviously from the frequency dependence of the pumping rates at v and v_p). It must therefore be noted that while level "M" arises from labeling steps of IR-multiphoton excitation, levels " $M \pm 1$ " in Eq. (25) arise from the shift by the probe laser photon and we cannot, in general, simplify Eq. (25) by resumming and using detailed balance. However, if the frequency of the probe laser photon is close to the excitation frequency, we can introduce further simplifications using Eq. (10) (or the analog, for a different probe band)

$$\overline{K}_{M+1,M} = C_M \Delta E_p^{-1} G_p I_p(\rho_M^{0'} / \rho_M), \qquad (26)$$

$$\frac{K_{M,M+1}}{\overline{K}_{M+1,M}} \simeq \frac{\rho_M}{\rho_{M+1}}.$$
(27)

We have indicated here by the index p that the "probe" parameters may be different from the excitation parameters, but for CF₃ I, they are approximately the same (except for I_p). It is, however, much more important for off-resonant probing to consider in detail the frequency- (and level-) dependent absorption line shape parameters ($C_M/\Delta E_p$) in the simplified expression

$$\sigma(t) = h v_p G_p \sum_{M=M_{\min}}^{M=M_{\max}} f_M(v - v_{0M}) \left[p_M(\rho_M^{0'}/\rho_M) - p_{M+1}(\rho_M^{0'}/\rho_{M+1}) \right].$$
(28)

This expression results from changing summation indices (assuming p_M to vanish at the limits M_{\min} and M_{\max}) and introducing a line shape function $f_M (v - v_{0M})$, which incorporates explicitly a level-dependent absorption maximum v_{0M} of the relevant band and the width ΔE_M in the shape f_M . We note that contributions from a pair of levels M,M + 1 to $\sigma(t)$ will be positive (i.e., absorption) if $p_M/p_M^{eq} > p_{M+1}/p_{M+1}^{eq}$, with $p_M^{eq} = \operatorname{const} \rho_M$, and negative (stimulated emission) otherwise. Before introducing assumptions on f, we shall consider briefly another set of assumptions on p(E,t).

(ii) We assume that multiphoton excitation generates a broad, continuous distribution, which would result, for instance, if the initial thermal, rovibrational distribution in a large polyatomic molecule is essentially continuous, spreading over several laser quanta.³³ Under these conditions, we may assume that the probe laser (with a frequency close to excitation frequency) sees essentially the contributions from populations p_M , p_{M-1} , and p_{M+1} from the solution of Eq. (7), when we consider absorption and emission from level M, thus

$$\sigma(t) = \frac{1}{2} h \nu_p \sum_{M=M_{\min}}^{M=M_{\max}} \left[(\overline{K}_{M+1,M}^{(I)} - \overline{K}_{M-1,M}^{(I)}) p_M - \overline{K}_{M,M+1}^{(I)} p_{M+1} + \overline{K}_{M,M-1}^{(I)} p_{M-1} \right].$$
(29)

The factor 1/2 arises, because in the explicit sum we count the contribution from each level twice. With the assumptions as in Eq. (27) (i.e., $v_p \simeq v$) and vanishing p_M (or $\overline{K}^{(I)}$) at the limits, we may resum Eq. (29) and obtain exactly the same expressions as before [Eq. (28)]. The reason for this coincidence of results from such different starting points is that contributions from levels with p(E) = 0 vanish and thus do not matter either way with the model (i), but strictly the coincidence is only approximate.

We have calculated $\sigma(t)$ with two ultrasimple models for the off-resonant probing. One model assumes a step function f_{vs} = const between M_{\min} and M_{\max} and zero otherwise. This corresponds to a rectangular absorption band, which is increasingly red shifted as the molecules are excited. The second model $f_{\nu t}$ assumes the band to be trapezoidal. The time-dependent effective cross section $\sigma(t)$ is similar for both assumptions and we show in Fig. 9(a) the result for the rectangular shape with $f_{vs} \neq 0$ from level 10 to 15. The results are presented as $\ln \left[\sigma(t) / \sigma_{max} \right]$ exactly as in the experiments and they show, indeed, a similar shape, as can be seen by comparison with the example in Fig. 9(b). The model calculations from two different fluences yield "rate constants" of 1.6 and 1.7 cm² J⁻¹, compared to 1.23 cm² J⁻¹ from experiment. In the comparison, one must note the extremely crude spectroscopic model, which was not adjusted in any way to experiment. Qualitatively, we can interpret the far off-resonant probing at low wave numbers as measuring the rate of generation and decay of high levels, which absorb



FIG. 9. (a) Normalized calculated absorption cross sections for the excitation of CF₃ I with single mode laser pulses F = 1.5 J cm⁻² (--) and F = 2.5J cm⁻² (----). Assumptions for the model function—levels 10–15 contribute identically to the absorption (step function). A fit to the signal with the higher fluence yields 1.7 cm² J⁻¹, whereas for the lower fluence, a value of 1.6 cm² J⁻¹ is obtained. (b) Experimental normalized absorption cross sections for ¹²CF₃ I probed at 1048.66 cm⁻¹ (9P 18) during the excitation with a single mode laser pulse at a total fluence of F = 2.58 J cm⁻². A straight line is fitted to the decay of the absorption for $F \ge 0.6$ J cm⁻².

at these low wave numbers, by radiative up pumping and finally reaction. At high fluences, a steady state is reached, described by the "steady state rate constant" evaluated from the linear part of the graphs in Fig. 9. The higher the levels are, which we probe by a frequency shifted further and further to low wave numbers compared to cold absorption, in general, the larger is the fluence to reach σ_{max} and this linear part, as is also borne out by experiment (for levels 12 to 20, F > 2 J cm⁻² is needed). A simple case B calculation shifts σ_{max} to occur at somewhat lower fluence, but the rate constants remain essentially unchanged (about 1.7 cm² J⁻¹), as expected.

The model calculations could be easily made much more detailed and it would be computationally easy to evaluate the more general equations (19) and (21) by means of an inhomogeneous master equation (17), if the necessary spectroscopic information on $K^{(I)}$ were available. However, the present model calculations show that the most important

features of the experimental $\sigma(t)$ can be well understood even with much simpler models, making us confident about the basic concepts. The treatment does not include coherent single-photon interaction of the *probe* laser with the molecules (*multiphoton excitation is treated coherently*, in principle), nor does it retain explicitly time-dependent intramolecular processes during the probe time, such as they are evident in our results shown in Fig. 5.

V. DISCUSSION AND CONCLUSIONS

The time-resolved infrared spectroscopy of CF_3 I during and after IR-multiphoton excitation with shaped nanosecond pulses has provided us with several striking observations, from which we shall summarize and discuss the main conclusions:

(i) After high excitation (> 17 photons of the CO₂ laser) with single and double pulses of about 2 ns length, we observe unimolecular decay with rate constants in two quite distinct ranges, the first between 1×10^8 and 3×10^8 s⁻¹ and the second between 1×10^6 and 8×10^6 s⁻¹. Intermediate rate constants contribute much less importantly with excitation lines 9R 16 and 9P 30. The first rate constant is certainly unaffected by collisional processes, whereas the slower one may be influenced by collisions. The step function behavior is expected from statistical theory if the two rate constants correspond to two ensembles of CF₃I molecules with an energy difference corresponding to about one laser photon. The observed rate constants fall exactly in the range predicted by statistical theory for CF₃I.¹⁸ We predict from our model calculations that under our excitation conditions an even faster process ($> 10^9$ s⁻¹) should be observable in experiments with higher time resolution than we could use here. The step function behavior for after pulse decay will arise generally if the thermal initial distribution of energies is sufficiently narrow with respect to the CO_2 laser quantum. With about 300 cm⁻¹ average rotational excitation and a majority of molecules with less than 300 cm⁻¹ vibrational excitation, CF₃ I just about satisfies these conditions at room temperature. For large polyatomic molecules with broad vibrational distributions such as for $C_4 F_9 H$,³³ the decay rate constants after short pulse excitation will be distributed almost continuously. On the other hand, with supersonic jet cooling, very narrow distributions in E and J may be accessible for many molecules, which would result in well-defined $k(E = E_0 + nh\nu, J < J_{\max}).$

(ii) During IR-multiphoton excitation, we observe the effective, time-dependent infrared absorption cross section $\sigma(t)$ at the probe laser wave number, for instance, shifted appreciably to low wave numbers compared to the excitation wave number. This absorption cross section first rises to some maximum value and then decays. A striking observation is that this decay is essentially independent on laser pulse intensity and is fully determined by laser fluence during the pulse. Logarithmic evaluation of this decay as a function of fluence results in effective rate constants $k_{1,\sigma} \simeq 1.2$ cm² J⁻¹, very similar to the corresponding IR-photochemical decay rate constant for CF₃ I.^{20,25} This behavior can be understood as generation by excitation and radiative decay (by further pumping) of highly excited levels of CF₃ I. The

pure fluence dependence of the decay arises from case B¹⁶ being applicable, with intensity proportional rate coefficients, at these high levels of excitation, in contrast to the lower levels of CF₃ I. With pulses of low overall fluence, $\sigma(t)$ just rises to some maximum, corresponding to the generation of absorbing, excited levels without further decay (Fig. 6). The results have been modeled by the simple, detailed master equation model for $\sigma(t)$, which shows qualitatively and semiquantitatively the same behavior for $\sigma(t)$ without being adjusted to experiment. This provides further support to the interpretation of $\sigma(t)$.

(iii) After excitation with short, mode locked or rectangular pulses, we find by probing near the center of the absorption a decrease of absorption by excitation and thus bleaching and a subsequent fast recovery to increasing absorption after the pulse with nanosecond relaxation times [Fig. 5(a)]. This observation is repeated in a series of mode locked nanosecond pulses. Similar relaxation times are also found when inducing first an increase of absorption [Fig. 5(b)]. For excitation with high fluence, the relaxation phenomenon becomes unobservable under our conditions. While for some of these observations coherent radiative phenomena (coherent spontaneous emission and free induction decay) might contribute signal to the phenomena, the only explanation consistent with all our observations seems to be a nanosecond intramolecular rovibrational relaxation process, which occurs under collision-free conditions in our experiments. This relatively slow process happens only at modest excitation of CF_3I [a maximum in the population of levels 5 to 7 is obtained with somewhat less than 0.5 J cm⁻² (Fig. 8)]. It appears to be the first time that such a relatively slow intramolecular rovibrational relaxation process is reported in real time observations after multiphoton excitation under collision-free conditions. Early reports of microsecond relaxations were later interpreted as very fast collisional v-v processes.⁵⁴ The $p\tau$ for rotational relaxation has been determined as 36 ns Torr for SF₆,⁵⁵ although an exceptionally fast collisional process with $p\tau \simeq 2$ ns Torr was also claimed, 56 but never confirmed. Collisionless intramolecular vibrational relaxation in SF6 was estimated to fall in the limits 1-30 ps.⁵⁷ The relatively slow nanosecond redistribution processes contradict a dogma of universally fast (picosecond) rovibrational relaxation in highly excited molecules. They are, however, qualitatively consistent with the interpretation of certain very small rovibrational couplings found in the analysis of high resolution spectra of CF₃I (Ref. 6, 26, and 51) and also agree with recent general considerations on possibilities for both very fast (femtosecond⁵²) and very slow (nanosecond) intramolecular rovibrational redistribution processes.⁵³ The disappearance of the slow process at high excitation fluences is consistent with a much faster (picosecond) relaxation for molecules excited to near the threshold of excitation, which would agree with conventional ideas and many observations on other molecules,¹⁻³ although strictly speaking, we have not directly observed such a fast process. It is, however, the observation of slow, nanosecond relaxation, which opens the way for new experiments on "mode selective" multiphoton excitation of chemical relevance on relatively long time scales.

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