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Vibrationally excited populations from IR-multiphoton absorption. II. Infrared fluorescence measurements^{a)}

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Infrared emission spectra were obtained for 1, 1, 2-trifluoroethane (TFE) excited by infrared multiphoton absorption (1079.85 cm⁻¹). The emission features show that the HF reaction product is formed in vibrational states up to about v = 3. Furthermore, emission attributed to F-C=C-H was observed near 3320 cm⁻¹, indicating that the difluoroethylene primary products of TFE decomposition undergo secondary photolysis; since the difluoroethylene products at room temperature do not absorb laser light, they must be formed vibrationally excited. The emission from the C-H stretch modes of TFE was readily identified near 2980 cm⁻¹ and the emission intensity was obtained as a function of laser fluence. These data are in excellent agreement with predictions based on the theoretical expression for fluorescence intensity and the preceding paper. These results provide additional support for the accuracy of the reconstructed populations and for the theory relating infrared fluorescence intensity to total vibrational energy in polyatomic molecules.

INTRODUCTION

In the preceding paper,¹ results from two experimental techniques were used in conjunction with a Master Equation model² to determine the population distributions produced by infrared multiphoton absorption (MPA). The experimental techniques used were optoacoustic measurement of absorbed laser energy³ and VLP Φ^4 measurement of infrared multiphoton decomposition (IRMPD) yields.⁵ Although these techniques enabled us to reconstruct the apporoximate population distributions produced by MPA, they do not probe directly the population of molecules excited to energies below the decomposition threshold.

In situ experimental techniques that directly monitor the vibrational energies of highly vibrationally excited molecules in their electronic ground states are relatively scarce. For small molecules, laser induced fluorescence⁶ and Raman spectroscopic methods⁷ are appropriate, but for large molecules with high densities of states, UV absorbance⁸⁻¹¹ and infrared fluorescence¹²⁻¹⁴ (IRF) have proved to be effective. Each of these methods requires a calibration curve that relates the observed signal to the vibrational energy.

For the IRF techniques, the calibration curve relating intensity to vibrational energy can be calculated from vibrational spectroscopic theory, or it can be derived from experiments. An important motivation for the present experiments is to test the theoretical predictions of IRF intensity against measurements performed using MPA to produce known populations of excited molecules. Validation of the theoretical expression in the present experiments supports theoretical calculations of infrared emission spectra of highly excited molecules. Such calculations find many uses, including simulations of IRF from interstellar molecules excited by absorption of starlight.¹⁵

The experimental approach in the present work is to obtain time- and wavelength-resolved IFF data as functions of laser fluence and collider-gas pressure. By extrapolating the decay curves to the time origin, the initial IRF intensity can be compared to that predicted by vibrational spectroscopic theory and the Master Equation described in paper I. In the third paper of this series,¹⁶ the calibration curve is used to monitor collisional energy transfer and determine the energy and temperature dependences of the energy transfer step size.

EXPERIMENTAL

Most of the experimental details are described in paper I. Briefly, high power TEA CO₂ lasers operating on the 9.6 μ m R (22) line (1079.85 cm⁻¹) were used to excite 1, 1, 2-trifluoroethane. Laser energy was measured with a volumeabsorbing calorimeter and fluence was calculated from the measured energy and the laser beam cross-sectional area. Gas pressures were measured with a capacitance manometer.

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FIG. 1. Infrared fluorescence decay curve. 20 mTorr TFE and 20 mTorr argon, $\Phi = 1.89$ J cm⁻², 143 laser shots, 3815 cm⁻¹.

The cell used for the IRF experiments was the same as that used for the optoacoustic measurements in paper I. The fluorescence was viewed through a KCl side window by a liquid nitrogen cooled two-color infrared detector (Infrared Associates, Inc.), which consists of an InSb detector overlying a HgCdTe photodiode. Each detector layer is equipped with a separate preamplifier and biasing circuit. The InSb layer is sensitive from 1 to $5.5 \mu m$; at longer wavelengths it is transparent, allowing the HgCdTe detector to respond to wavelengths from $5.5 \text{ to } 16 \mu m$. In the present experiments, only the InSb portion of the detector was used. The original time response of the InSb detector/preamplifier was $1-2 \mu s$, but it was susceptible to electrical interference from the lasers; thus it was modified to give a slower time response (5–6 μ s) and less susceptibility, although there is still some evidence of electrical "ringing". With this modification and due to the ringing, accurate measurements were limited to decay rate constants slower than about 7×10^4 s⁻¹. The signal from the InSb detector/preamplifier was captured using a transient recorder (Biomation 805) and signal averager (Nicolet 1072) interfaced to a laboratory computer (see paper I for details).

Wavelength resolution was achieved using a three-segment circular variable filter (OCLI) mounted in a custom Dewar with the detector and cooled to 77 K. The slits were 1.5 mm, giving a resolution of about 2% of the center wave-



FIG. 2. Infrared fluorescence decay curve. 20 mTorr TFE and 20 mTorr argon, $\Phi = 1.80 \text{ J cm}^{-2}$, 253 laser shots, 3665 cm⁻¹.



FIG. 3. Infrared fluorescence decay curve. 19 mTorr TFE and 19 mTorr argon, $\Phi = 1.95 \text{ J cm}^{-2}$, 121 laser shots, 3020 cm⁻¹.

length. This resolution is sufficient to distinguish C–H stretch emission bands from HF emission and other interferences. The filter bandpass and relative wavelength calibration (wavelength vs rotation angle) were determined using an infrared spectrometer. Absolute positioning of the rotation angle was achieved by observing the CO₂ laser line at 9.26 μ m and fluorescence from CO₂ near 4.2 μ m. We estimate the absolute wavelength calibration to be accurate to within ± 20 cm⁻¹.

from 0.6 to 1.95 J cm⁻². In these experiments, a 1/1 mixture of 1, 1, 2-trifluoroethane (TFE) in argon at a total pressure of 32–40 mTorr flowed slowly through the cell. Argon was added to slow the rates of diffusion and thermal conductivity, and to moderate the temperature excursions. The laser pulse repetition frequency was 0.2–8 Hz, depending on laser fluence, and care was taken not deplete the TFE by more than a few percent. Depending on signal strength, between 50 and 15 000 laser shots were accumulateed for each IRF decay curve to improve the signal/noise ratio.

RESULTS AND DISCUSSION

A survey of the IRF emission was carried out for wavelengths from about 2000 to 4000 cm⁻¹ and laser fluences Fluorescence decay curves were obtained at wavelength intervals of $50-100 \text{ cm}^{-1}$ and a few representative examples are presented in Fig. 1-3. Figure 3 shows a relatively simple exponential decay, while Figs. 1 and 2 show more complicat-



FIG. 4. Time-resolved infrared emission spectrum. 20 mTorr TFE and 20 mTorr argon, $\Phi = 0.59$ J cm⁻², estimated uncertainties are $\pm 10\%$. The top solid line is for 8 μ s following the laser pulse and each successive line is for additional 10 μ s delay times.

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FIG. 5. Time-resolved infrared emission spectrum. 20 mTorr TFE and 20 mTorr argon, $\Phi = 1.17 \text{ J cm}^{-2}$, estimated uncertainties are $\pm 10\%$. Note the different wavelength scale and see Fig. 4 for key.

ed behavior that is evidence for a collisional cascade. All of the decay curves were individually least-squares fitted by sums of exponentials. By combining the fitted results, we obtained the time- and wavelength-resolved spectra presented in Figs. 4–6, which correspond to low, medium, and high laser fluences, respectively.

Inspection of Figs. 4–6 reveals three distinct spectroscopic features at 2980, 3320, and 3500–3800 cm⁻¹; in addition Fig. 5 shows continuum emission between 2100 and 2500 cm^{-1} , which may be due to the so-called "quasicontinuum",¹⁷ which consists of overtone and combination bands.

The intensity of the broad feature near 3800 cm^{-1} in-

creases dramatically with laser fluence. The wavelength corresponds to that of the P branch of HF, which is a primary reaction product¹⁸; the wavelength range of the CVF is not sufficient to observe the Q branch. This feature changes width and center frequency as a function of time, indicating that several vibrational levels of HF are initially formed in the decomposition of TFE and a vibrational cascade ensues. The detailed shapes of the decay curves in Figs. 1 and 2 are explained by the shift and broadening of the 3800 cm⁻¹ feature. Comparisons of the observed spectra and those for excited HF reported, or discussed in the literature¹⁹ indicate that levels up to about v = 3 are significantly populated in



FIG. 6. Time-resolved infrared emission spectrum. 20 mTorr TFE and 20 mTorr argon, $\Phi = 1.95 \text{ J cm}^{-2}$, estimated uncertainties are $\pm 10\%$. See Fig. 4 for key.

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the decomposition reaction. A more detailed analysis is beyond the scope of the present work.

The origin of the feature at 3320 cm^{-1} is uncertain, but it only appears at very high fluences and is about the same frequency as the C-H stretching mode in acetylene.²⁰ Thus, we tentatively conclude that it arises from vibrationally excited F-C=C-H produced by secondary photolysis of difluorethylene products from the primary dissociation:

$$\mathbf{CF}_{2}\mathbf{H}-\mathbf{CFH}_{2}+nh\nu\rightarrow\mathbf{CF}_{2}=\mathbf{CH}_{2}+\mathbf{HF}$$
(A)

$$\rightarrow$$
 cis- or trans-CFH = CFH + HF (B)

 \rightarrow :CF-CFH₂ + HF \rightarrow cis- or trans-CFH = CFH + HF, (C)

Diffuoroethylene(vib.) +
$$mhv \rightarrow F-C \equiv C-H + HF$$
. (D)

The secondary photolysis [process (D)] can only occur with vibrationally excited molecules, because the room temperature difluoroethylene products do not absorb at the laser wavelength, as discussed in paper I. It is interesting to note, then, that both products of the photolysis must contain significant amounts of vibrational energy. Because of the strained three- and four-center cyclic transition state structures, it is expected that vibrationally excited HF and difluoroethylene will be produced, but the extent of excitation and the apportionment of energy varies, depending on the particular reaction channel.¹⁸ For example, the slightly higher energy three-center pathway (C) requires isomerization of the carbene primary product to form difluoroethylene and the difluoroethylene produced by this channel is apportioned more vibrational excitation than the four-center channels.

The spectroscopic feature at 2980 cm^{-1} corresponds to the C-H stretching modes in TFE.²¹ The C-H stretching modes in *cis*- and *trans*-difluoroethylene have frequencies²⁰ near 3100 cm⁻¹ and cannot contribute to the 2980 cm⁻¹ feature. The monotonic decay curves at this frequency (see Fig. 3) indicate relatively simple collisional deactivation of the excited TFE and they can be accurately fitted with a single exponential decay. The empirical fitting on the decay curves is used in the present work only for the purpose of extrapolation to obtain the initial intensity; collisional deactivation of TFE is discussed in paper III.¹⁶ The experimental IRF decay curves for 2980 cm⁻¹ were fitted by a single exponential with the Bevington version of the Marquardt nonlinear least squares algorithm.²² The first 6 μ s of the decay following the laser pulse was neglected (see above) and the least-squares result was extrapolated to t = 0 in order to obtain the initial IRF intensities. The initial intensities were normalized according to the partial pressure of TFE, and the results are presented vs laser fluence in Fig. 7.

For comparison with the experimental results, the IRF intensity was calculated by using the population distributions reconstructed in paper I and the theoretical expression for the microcanonical IRF intensity. The theoretical expression relating IRF intensity to vibrational energy in polyatomic molecules has been discussed elsewhere in detail.^{2,12,13} The expression is written

$$|(E) = N_e \times \sum_{i=1}^{Modes} h\nu_i A_i^{1,0} \sum_{1}^{v_{max}} v \rho_{s-1} (E - v h \nu_i) / \rho_s(E), \quad (1)$$

where N_e is the number of excited molecules, $A_i^{1,0}$ is the Einstein coefficient for emission from the fundamental of the *i*th mode, v is the occupation number of the *i*th mode, v_{\max} is the maximum occupation number for vibrational energy E, $\rho_s(E)$ is the density of vibrational states for all s vibrational modes, and $\rho_{s-1}(E - vhv_i)$ is the density of states for the s-1 modes, not including the emitting mode and the energy contained in it.

Briefly, the theoretical expression is based on the fundamental relationship between IRF intensity and vibrational quantum number,²³ and it incorporates two assumptions: (1) the harmonic oscillator approximation relating Einstein coefficients for higher vibrational levels to that for the fundamental and (2) the ergodic assumption, which states that the vibrational energy is statistically distributed among the vi-



FIG. 7. Infrared fluorescence from TFE C-H modes. Diamond symbols are experimental data points (from extrapolation to time = 0) with estimated uncertainties of $\pm 5\%$; dashed line is theoretical prediction scaled to same magnitude as experiments at $\Phi = 1$ J cm⁻².

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FIG. 8. Microcanonical curve relating IRF from C-H modes to vibrational energy. This curve was calculated using theoretical Eq. (1); see the text for details.

brational modes on the time scale of the fluorescence (microseconds). The accuracy of this expression also relies on the densities of states calculations, which can be carried out using exact-count algorithms.

For the theoretical prediction of IRF intensity vs vibrational energy, the Stein-Rabinovitch method of exact counts²⁴ was used to obtain the densities of states, based on the vibrational assignments for TFE.²¹ The hindered internal rotation was treated as a vibration in these calculations. The Einstein coefficients for the fundamental transitions are not known and they are included in the undetermined scale factor, which also depends on the experiment geometrical configuration, detector sensitivity, amplifier settings, etc. In Fig. 8, the predicted microcanonical dependence of IRF intensity on vibrational energy is presented in arbitrary units.

To compare the predicted IRF intensities with those observed at different laser fluences, the population distributions from paper I were used with the microcanonical IRF intensities to obtain ensemble-averaged IRF intensities vs laser fluence. These theoretical results are shown in Fig. 7 as the dashed line, which has been scaled to match the magnitude of the experimental data at a fluence of 1.0 J cm^{-2} . The agreement between experiment and theory is excellent.

The excellence of the agreement between experiment and theory may be viewed in several ways. If Eq. (1) is accepted as accurate, the agreement provides additional support for the reconstructed population distributions obtained in paper I. This is a legitimate point of view in that Eq. (1) has been successfully tested is several other systems on other molecules,^{12,13} supporting the inference that it should accurately describe IRF in the molecule TFE. The other point of view is that Eq. (1) must be tested by experiment, despite the elegance of its derivation. The reconstructed population distributions are derived from experiments in paper I and therfore the experiments reported here provide an experimental test and demonstration of the accuracy of Eq. (1), when applied to TFE.

Either of these points of view leads to the conclusion

that the Master Equation from paper I and Eq. (1) constitute a self-consistent description of the results from three independent experimental techniques. Considering the highly constrained parametrization of the Master Equation as described in paper I and the fact that Eq. (1) accurately describes IRF in other systems as well as in this one, we conclude that the reconstructed population distributions are good representations of the actual distributions and that IRF can be confidently used to monitor vibrational energy in TFE excited by multiphoton absorption. This technique is used in paper III to determine energy-transfer properties of TFE.

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