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Vibrational energy transfer between DF($v=2$) and CO₂ *

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Rates have been determined for the transfer of vibrational energy between DF($v=2$), DF($v=1$), and CO₂ using a laser-induced fluorescence technique. DF, in DF-CO₂ gas mixtures, was excited to both the $v=1$ and $v=2$ vibrational levels by absorption of radiation from a pulsed DF laser operating simultaneously on $v(1-0)$ and $v(2-1)$ transitions. By monitoring fluorescence intensity at 1.7, 3.5, and 4.4 μ , the temporal behavior of DF($v=2$), DF($v=1$), and CO₂ (001) populations was followed. A computer program was used to solve the differential rate equations and a "best fit" with experimental data determined the rate parameters. Rate constants obtained in this manner from the fluorescence data are $k = 5.1 \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$ for the DF($v=2$)-CO₂ transfer and $k = 1.5 \times 10^4 \text{ sec}^{-1} \text{ torr}^{-1}$ for CO₂ (001) deactivation by DF.

INTRODUCTION

An understanding of the detailed operation of the DF-CO₂ chemical transfer laser requires knowledge of the rates of transfer of vibrational energy between these two molecules. Because the chemical reactions producing vibrationally excited DF have sufficient energy to populate levels up to at least $v=4$, complete information would require transfer rates from DF in each of four vibrational levels in addition to the transfer rate from excited CO₂ (001 level) to ground state DF. The laser induced fluorescence technique, which employs pulsed laser radiation to vibrationally excite molecules and measurement of fluorescence intensity to follow the collisional lifetime of the excited molecules, has been used previously to measure DF-CO₂ transfer rates. Data have been reported for DF ($v=1$)-CO₂ and also for CO₂ (001)-DF transfer from experiments using DF lasers to excite DF/CO₂ mixtures.^{1,2,3} Also, the rate of CO₂ (001)-DF transfer has been measured with a CO₂ laser excitation source.⁴ The method has not previously been used to determine transfer from higher DF vibrational levels, which are relevant to transfer lasers, to CO₂. Information about transfer rates from DF ($v=1$, 2, and 3) has been provided by chemiluminescence studies of DF forming chemical reactions in the presence of CO₂.⁵ That approach has the disadvantage that the method is indirect and the complicated procedure used for evaluating the deactivation by the various atomic and molecular species present may introduce errors in the individual rate constants.

In this report, we describe the results of laser-induced experiments for energy transfer from excited DF ($v=2$) to CO₂ at 295 °K. A DF laser operating on both $v(1-0)$ and $v(2-1)$ laser transitions was used for simultaneous pumping of DF ($v=2$) and ($v=1$) vibrational levels. A similar pumping scheme has been reported in studies of HF ($v=2$) relaxation by ground state HF.⁶ The pulsed DF laser radiation was absorbed by DF in a mixture of DF and CO₂ and fluorescence intensity was monitored at 1.7, 3.7, and 4.4 μ to follow population changes of DF ($v=2$), DF ($v=1$), and CO₂ (001), respectively. A computer simulation of the population decay processes was used to extract specific rate constants.

EXPERIMENTAL

The experimental arrangement for the laser fluorescence measurements is diagrammed in Fig. 1. Radia-

tion from a pulsed transverse excited pin discharge laser absorbed by a gas sample of DF mixed with CO₂ was used to excite DF to the ($v=2$) and ($v=1$) levels and fluorescence intensity was used to monitor changes in the excited molecule populations. The laser employed was an enlarged version of the efficient device described by Pummer and Kompa.⁷ The discharge region, 12 cm \times 1.6 cm \times 1.2 cm, contained 164 pin electrodes in four rows, aligned along the optical axis. The laser gases flowed transverse to this axis. The laser gas mixture consisted of SF₆, He, and D₂ in a ratio of about 5:10:2 at a total pressure of 50 torr. Excitation of the discharge was provided by a four stage Marx bank coupled through a copper sulfate solution to the multipin array; the fast rise time of the low inductance Marx bank configuration and the distributed resistance offered by the copper sulfate solution yield a uniform discharge over the electrode region. Using Irtran IV (Kodak Co.) as an output coupling mirror, the laser produced pulses of 0.3 μ sec duration containing up to 3.3 mJ energy at a repetition rate of 20 pps. About half the energy was contained in the temporal overlapping lines $v(1-0)$, P₅, 6, 7 and $v(2-1)$, P₅, 6, 7, 8 that are useful for the sequential pumping of DF to ($v=1$) and ($v=2$).

The fluorescence intensity used to follow population changes was monitored with two InSb detectors (77 °K) each combined with a matching preamplifier (Perry model 720). Further signal amplification was obtained with a Tektronix 1A7A amplifier. Filters were placed in front of the detectors to pass the fluorescence at 1.7, 3.7, or 4.3 μ and block scattered laser radiation. RF noise pickup in the detector electronics from laser firings was eliminated by isolating the fluorescence part of the apparatus in a screened room. Signal/noise ratio was improved by averaging with a transient recorder (Biomation 610B) in conjunction with a digital signal analyzer (Northern Scientific-NS575). The rise-time of the complete signal processing electronics was about 0.3 μ sec. Signals stored in the analyzer were displayed on an oscilloscope and traced on chart paper.

The gas handling system and fluorescence cell have been described.⁸ The DF was obtained from Ozark-Mahoning Co. and distilled several times (78 °K-300 °K) before each use. CO₂ was supplied by Matheson (Research Grade, 99.995%).

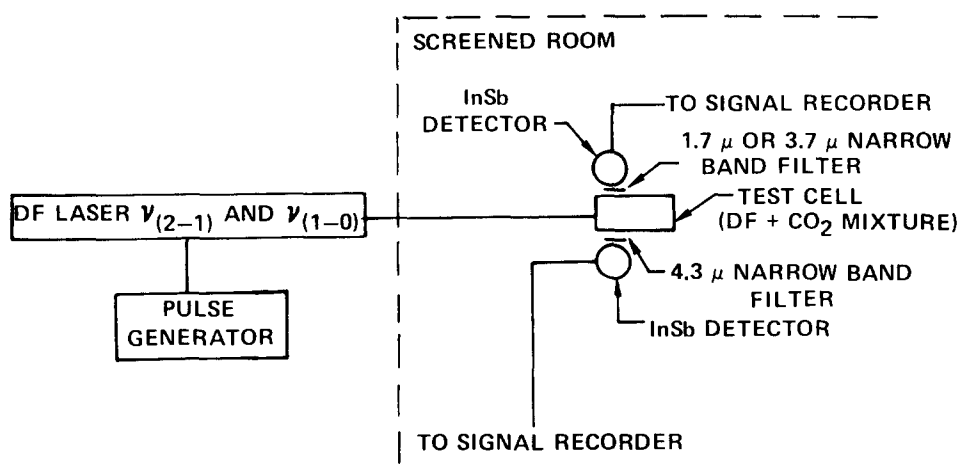
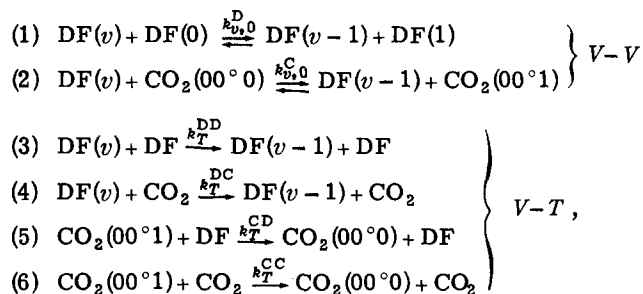


FIG. 1. Experimental arrangement for measuring DF ($\nu=2$) energy transfer to CO₂.

COMPUTER SIMULATION

The relevant transfer processes that are considered in the analysis for mixtures of excited DF and CO₂ are



where (ν) has values of (2) or (1) and only $\Delta\nu=1$ transitions are allowed. Rate constants for the $V-V$ reverse reactions are distinguished by prime notation, e.g., $k_{2,0}'^C$.

The rate equations describing these processes are given by

$$(7) \quad \dot{A} = -A\{(k_{2,0}^D + k_T^{DD})D_0 + (k_{2,0}^C + k_T^{DC})C_0\} + [k_{2,0}'^D(B)^2 + k_{2,0}'^C BC]$$

$$(8) \quad \dot{B} = -B\{k_T^{DD}D_0 + (k_{1,0}^C + k_T^{DC})C_0\} + A\{2k_{2,0}^D D_0 + k_{2,0}^C C_0\} + Ck_{1,0}'^C D_0 + [2k_{2,0}'^D B^2 + k_{2,0}'^C BC]$$

$$(9) \quad \dot{C} = -C\{(k_{1,0}^C + k_T^{CD})D_0 + k_T^{CC}C_0\} + Ak_{2,0}^C C_0 + Bk_{1,0}^C C_0 + [k_{2,0}'^C BC]$$

where

A = DF molecules in $\nu=2$ level,

B = DF molecules in $\nu=1$ level,

C = CO₂ molecules in $00^\circ 1$ level,

D_0 = DF molecules in the ground state (DF pressure),

C_0 = CO₂ molecules in the ground state (CO₂ pressure).

Since only a very small fraction of the ground state DF

molecules will be pumped to the $\nu=1$ and 2 levels, collisions involving only excited molecules of either DF pairs or of DF and CO₂ molecules are highly unlikely. Equations (7)–(9) are then linearized by dropping terms in BC and B^2 for such collisions which are gathered in square brackets on the right side.

These linearized equations were solved for the time behavior of A , B , C as functions of the DF and CO₂ pressure. The solutions were least squares fitted by computer to the experimental data sets from each DF/CO₂ mixture, using the rate coefficient for DF ($\nu=2$)–CO₂ transfer ($k_{2,0}^C$) as one adjustable parameter. The experimental time behavior of the fluorescence was recorded neglecting the absolute scale of the data (i.e., the gain of the amplifiers, efficiencies of the detectors, and transition probabilities were not explicitly included). Since the data at different wavelengths are essentially being measured in different (unknown) amplitude units, a scale factor needs to be included in the coupled equations for simultaneous fits of DF (2) and DF (1) data or of DF (2) and CO₂ data. The best fit values of the rate constant $k_{2,0}^C$ proved to be insensitive to the magnitude of the scale factors between A and B or A and C over a large range of this scale factor (e.g., $A/C \sim 10^{-1}$ to 10^{-6}). This range of scale factors includes the values calculated with our estimates of the amplifier gains, etc. Computer generated displays of the best fit solutions for fluorescence intensity vs time along with the experimental data were made. Values for the rate constants used in these calculations were

$$k_{2,0}^D = 8 \times 10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1} \quad (\text{Ref. 9}),$$

$$k_{2,0}'^D = 1.2 \times 10^6 \text{ sec}^{-1} \cdot \text{torr}^{-1} \quad (\text{Ref. 9}),$$

$$k_T^{DD} = 2.4 \times 10^4 \text{ sec}^{-1} \cdot \text{torr}^{-1} \quad (\text{Ref. 8}),$$

$$k_T^{DC} = 1.25 \times 10^2 \text{ sec}^{-1} \cdot \text{torr}^{-1} \quad (\text{Ref. 10 (note 1)}),$$

$$k_{1,0}^C = 2 \times 10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1} \quad (\text{Refs. 1, 2, 3 (note 2)}),$$

$$k_{1,0}'^C = 1.3 \times 10^4 \text{ sec}^{-1} \cdot \text{torr}^{-1} \quad (\text{note 3}),$$

$$k_T^{CC} = 3.6 \times 10^2 \text{ sec}^{-1} \cdot \text{torr}^{-1} \quad (\text{Ref. 11}),$$

$$k_T^{CD} = 0.2 \times 10^4 \text{ sec}^{-1} \cdot \text{torr}^{-1} \quad (\text{note 4}).$$

Note 1. The rate constant k_T^{DC} is expected to be small compared to $k_{\nu,0}^C$ and was assumed negligible in Refs.

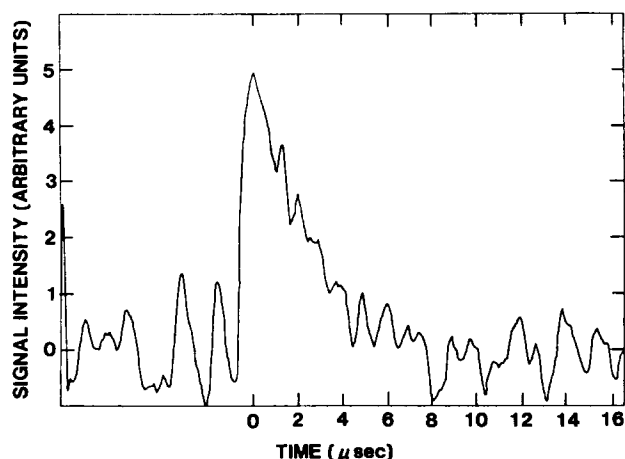


FIG. 2. Fluorescence intensity at 1.7 μ vs time for DF($v=2$) population. Data set 1D, $P_{DF}=0.032$ torr, $P_{CO_2}=0.59$ torr.

1 and 2. For purposes of the calculations here it was assumed that the value of k_T^{DC} is equal to the rate of deactivation of HF by N₂.¹⁰ In the latter system, the deactivation is mainly V-T because of the large energy defect, but, as in the case of DF-CO₂, the polar interactions lead to molecular complex formation in the gas phase.¹² The calculation of $k_{2,0}^C$ is insensitive to the value of k_T^{DC} and a 10^2 increase in its value affected $k_{2,0}^C$ by only a few percent.

Note 2. For $k_{1,0}^C$, an average value of $2 \times 10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1}$ is obtained from Refs. 1-3. This value produced the best fits of calculation with data over a large range of conditions and therefore we regard that the present experiment also confirms this value for $k_{1,0}^C$.

Note 3. The rate $k_{1,0}'^C$ was calculated from $k_{1,0}^C$ using detailed balance.

Note 4. This value was determined from the total rate for deactivation of CO₂ by DF, $K_{CO_2,DF}$, from the present experiment (see below) using $k_T^{CD} = k_{CO_2-DF} - k_{1,0}^C$.

A sensitivity analysis was made for the rate constants used as input to our model by fitting a data set increasing the value of each rate constant ($k_{2,0}^D$, k_T^{DD} , ...) individually by a factor of 3. The best fit values for $k_{2,0}^C$ were found insensitive ($\Delta k_{2,0}^C < 5\%$) for all but $k_{2,0}^D$ and $k_{1,0}^C$, where $\Delta k_{2,0}^C \approx 20\%$.

RESULTS AND DISCUSSIONS

The fluorescence at 1.7 μ was successfully used to track DF ($v=2$) population in DF-CO₂ mixtures, and an example of the data obtained after signal averaging is shown for the 1.7 μ fluorescence in Fig. 2. A fast signal risetime is observed followed by a slower decay which for this particular sample (DF/CO₂ = 1/18) is mainly due to DF ($v=2$) - CO₂ transfer. Similar signals were obtained with DF/CO₂ mixtures ranging from 1/6 to 1/22 with each mixture tested at several pressures. The composition of these gas samples is listed in Table I.

Population change in DF ($v=1$) was followed by mea-

suring fluorescence intensity at 3.7 μ simultaneous with the 1.7 μ fluorescence determination. Data for the 1/18 mixture at 3.7 μ are shown in Fig. 3. The decay to the 1/e value takes about 3 times as long for 3.7 μ as for 1.7 μ fluorescence, reflecting the difference between various rate constants.

With the decay of DF ($v=2$) and DF ($v=1$) there is a concomitant rise in the CO₂ (001) population which was monitored by measuring fluorescence at 4.3 μ . Data for 4.3 μ fluorescence intensity are shown in Fig. 4. On comparing Fig. 4 with Figs. 3 and 2, one can see the rise in 4.3 μ intensity parallels the decay of 1.7 and 3.7 μ intensity as a direct effect of DF (v) - CO₂ transfer. A complete analysis of the fluorescence curves is presented below.

The increase in 4.3 μ intensity is followed by a decay due to the combined deactivation of CO₂ (001) by ground state DF and CO₂. Such long term behavior is shown in Fig. 5. These curves can be described by a single exponential decay and the over-all rate constant is given

TABLE I. Summary of experimental runs and fitting parameters for DF-CO₂ exchange rates.

Data set	DF/CO ₂ ratio	Pressure (torr)	k_{CO_2-DF} (Units of $10^4 \text{ sec}^{-1} \cdot \text{torr}^{-1}$)	$k_{2,0}^C$ (Units of $10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1}$)
1C		0.49		6.96
1D		0.62		5.85
1E		0.74		6.42
1F	1	0.92		6.59
1G	18.5	1.11		6.12
1H		1.34		4.00
1J		1.80	1.7	4.55
1K		2.30	1.8	3.99
2A		2.70	1.2	3.71
2B		1.90	1.6	5.63
2C	1	1.34	2.0	4.00
2D	22	1.14		4.90
2E		0.93		7.07
2F		0.71		8.34
2G		0.53		6.59
3A		0.51		6.40
3B		0.71		4.00
3C	1	1.06		5.38
3D	15.5	1.40		3.73
3E		1.70		3.91
3F		2.30	0.8	3.46
4A		0.46		7.12
4B		0.70		6.71
4C	1	1.10		4.00
4D	10	1.34		5.67
4E		1.70		3.49
4F		2.20	1.1	3.99
5C		0.43		5.95
5D		0.57		6.41
5E	1	0.72		5.54
5F	6	0.87		4.00
5G		1.00	1.4	2.54
5H		1.18	1.9	3.39
5I		1.35	1.6	3.74
Average			1.5 ± 0.2	5.1 ± 1.4

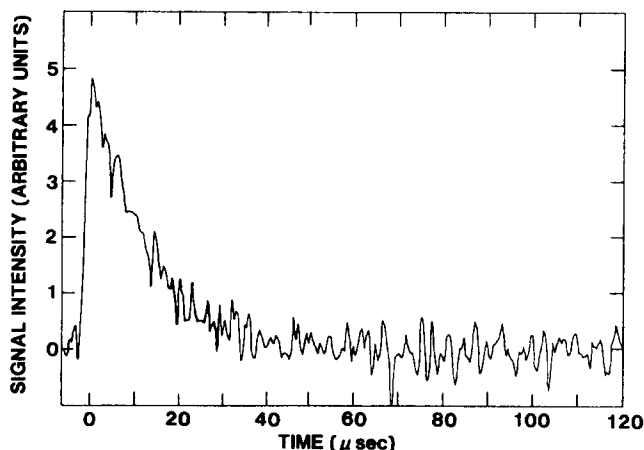


FIG. 3. Fluorescence intensity at 3.7μ vs time for DF($v=1$) population. Data set 1(D), $P_{DF}=0.032$ torr, $P_{CO_2}=0.59$ torr.

by $k = k_T^{CC} C_0 + k_{(CO_2-DF)} D_0$. The value of k_T^{CC} has been determined as $3.6 \times 10^2 \text{ sec}^{-1} \cdot \text{torr}^{-1}$ by Hocker *et al.*,¹¹ and from our fluorescence data for several DF/CO₂ mixtures $k_{(CO_2-DF)}$ was evaluated as $1.5 \times 10^4 \text{ sec}^{-1} \cdot \text{torr}^{-1}$. The data for individual tests are shown in Table I; calculations were made only for mixtures with CO₂ pressure greater than 1 torr because of the significant contribution to the rate from wall deactivation at lower pressures.⁸ The value obtained here is somewhat smaller than the previously reported values $1.9 \times 10^4 \text{ sec}^{-1} \cdot \text{torr}^{-1}$ and $2.4 \times 10^4 \text{ sec}^{-1} \cdot \text{torr}^{-1}$ (see Table II).

Computer solutions of the rate equations along with data from smoothed versions of the experimental curves displayed in Figs. 2–5 are shown in the computer generated plots of Fig. 6. The results of the computer fitting for all of the data sets are shown in Table I. In all cases, fits with the experimental data similar to these shown in Fig. 6 we obtained and gave an average value for the DF ($v=2$)–CO₂ $v-v$ transfer rate constant k_{2-0}^C of $(5.1 \pm 1.4) \times 10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1}$. This value is in reasonable agreement with the only other experimental data of $2.2 \times 10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1}$ ⁵ from chemiluminescence studies.

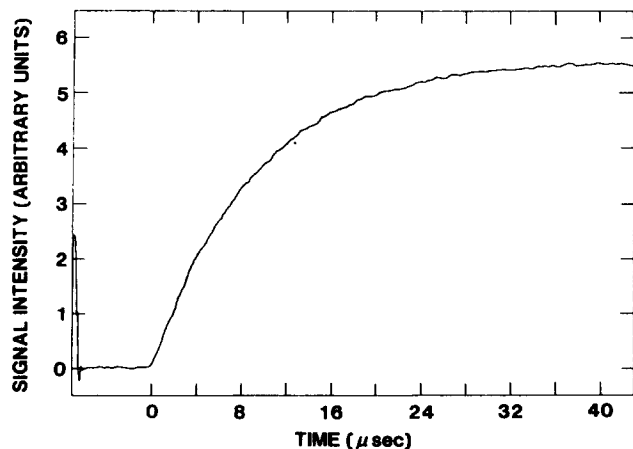


FIG. 4. Fluorescence intensity for CO₂ (001) vs time at 4.4μ as CO₂ (001) as populated by V–V transfer from DF(v). Data set 1D, $P_{DF}=0.032$ torr, $P_{CO_2}=0.59$ torr.

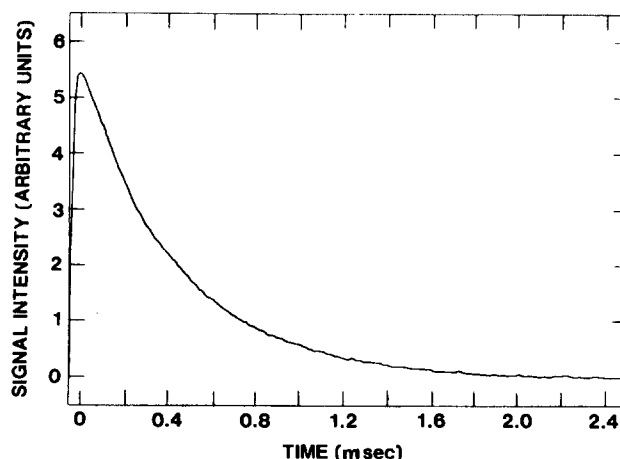


FIG. 5. Fluorescence intensity at 4.4μ for the deactivation of CO₂ (001). Data set 1(D), $P_{DF}=0.032$ torr, $P_{CO_2}=0.59$ torr.

The fit of calculated curves with experimental data, especially for the DF ($v=1$) curves, depends also on the value for DF ($v=1$)–CO₂ exchange rate. Good agreement was obtained using $k_{1,0}^C = 2 \times 10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1}$. A summary of available rate information for the DF/CO₂ system is given in Table III for comparison with values from the present work. The value of $k_{1,0}^C$ compares favorably with those from Refs. 1, 2, and 3. For CO₂ (001) deactivation by DF, the value obtained here for k_{CO_2-DF} of 1.5×10^4 is close to the value from Ref. 4 for direct measurement of this rate but is only about 1/2 the value quoted in Ref. 1.

The extremely fast rates for $v-v$ energy transfer between DF and CO₂ found in this work and in previous studies with DF ($v=1$) can in part be ascribed to strong interactions between molecular polar moments. Burke and Smith¹² have shown evidence for such interactions in spectroscopic studies of complexes formed between DF and CO₂ in the gas phase. However, the energy transfer requires the absorption of significantly large resonance energy differences between vibrational levels in DF and in CO₂ (001–000) levels. For DF $v(1-0)$ and DF $v(2-1)$, this energy defect amounts to 557 cm^{-1} and 465 cm^{-1} , respectively.

TABLE II. Summary of rate constants for DF–CO₂ vibrational energy exchange at $\sim 300^\circ\text{K}$ (units $\text{sec}^{-1} \cdot \text{torr}^{-1}$).

Reaction	DF($v=1$)–CO ₂ $k_{1,0}^C$	DF($v=2$)–CO ₂ $k_{2,0}^C$	DF($v=3$)–CO ₂	CO ₂ (001)–DF k_{CO_2-DF}
Present work	2.0×10^5	5.1×10^5	...	1.5×10^4
Airey and Smith, Ref. 5	1.3×10^5	2.2×10^5	5.2×10^5	...
Bott and Cohen, Ref. 1	1.5×10^5 ^a	2.3×10^4
Stephens and Cool, Ref. 2 (350°K)	1.7×10^5 ^a	1.9×10^4
Lucht and Cool, Ref. 3	2.4×10^5 ^a	2.6×10^4
Chang <i>et al.</i> , Ref. 4	1.8×10^4

^aThese values are actually for $k_{1,0}^C + k_T^{DC}$.

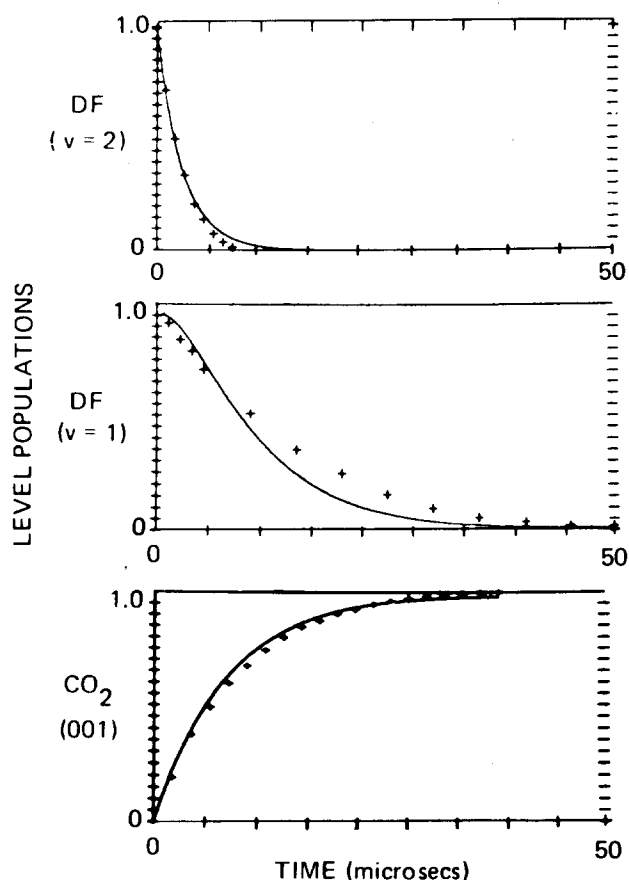


FIG. 6. Computer generated displays of populations vs time. The rate equation calculations are shown along with the experimental fluorescence data designated by +. Data are from set 1D for $P_{DF}=0.032$ torr and $P_{CO_2}=0.59$ torr. The "best fit" calculations give a value for $k_{2 \rightarrow 0}^C$ of $5.8 \times 10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1}$.

Dillon and Stephenson have proposed a theoretical description¹³ of energy transfer between DF ($v=1$) and CO₂ which is in good agreement with experimental data at 300 °K. The theory is a semiclassical, n th order perturbation approach, and the interaction is described as a combination of V-V and R-R transfer where V-V transfer is described by a dipole-dipole moment interaction and R-R by the interaction of an HF dipole with the quadrupole moment of CO₂. Large V-V transfer rates are predicted as a result of the energy defect between vibrational levels being absorbed as rotational excitation in the colliding molecules. Lucht and Cool³ also proposed this mechanism for disposal of the defect energy.

The theoretical calculation applied to DF ($v=2$)-CO₂ transfer by Dillon and Stephenson gave a value for the rate constant $k_{2 \rightarrow 1}^C$ of $3.9 \times 10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1}$ for single quantum exchange. Moreover, they predict a significant double quantum transfer with a rate constant equal to $1.9 \times 10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1}$. The sum of these two values, $5.8 \times 10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1}$, can be compared to the experimental value from the present study of $k_{2 \rightarrow 0}^C$ equal to $(5.1 \pm 1.4) \times 10^5 \text{ sec}^{-1} \cdot \text{torr}^{-1}$. That a double quantum transfer process was not included in the data analysis introduces but a small error as long as $k_{2 \rightarrow 0}^C$ defines the loss of DF ($v=2$) and is considered as a combination rate for $\Delta v=1$ and $\Delta v=2$ transfer. The appearance of excited CO₂ fluorescence would be the same for $\Delta v=1$ and $\Delta v=2$ because the experiment cannot distinguish fluorescence between the CO₂ levels (002-001) and (001-000). The analysis for $\Delta v=1$ would require the fall off of DF ($v=1$) population to be slightly slower [as this level would be fed from DF ($v=2$)] than would be the case if $\Delta v=2$ were included.

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