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Vibrational Relaxation of DF($v = 1-4$)
in D₂, H₂, N₂, HF, and CO₂

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Interim Report

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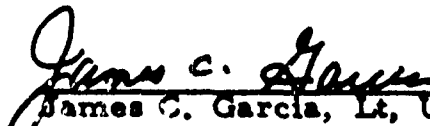
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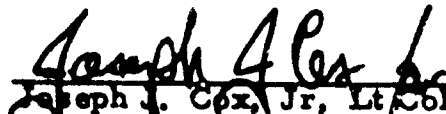
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22. ABSTRACT (Continue on reverse side if necessary and identify by block number) The deactivation of the upper vibrational levels of DF by H_2^+ , D_2^+ , N_2^+ , HF, and CO_2^+ has been studied with the technique of laser-induced fluorescence. The upper vibrational levels were produced by sequential photon absorption in which DF($v = 0$) was pumped first to DF($v = 1$) and subsequently to DF($v = 2$), DF($v = 3$), and DF($v = 4$) by photons from a pulsed multiline DF chemical laser. The deactivation rates (V-V + V-R, T) for all the collision partners except D_2^+ scaled with vibrational levels as v^n with $n = 1.9$ to 2.0 $\rightarrow$ next page			

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for $v = 1$ to 4. Similar studies have indicated the somewhat larger value of $n = 2.7 \pm 0.2$ for HF(v) deactivation by diatomic molecules.

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I. INTRODUCTION

The discovery and development of gas lasers and, in particular, chemical lasers have greatly stimulated studies of vibrational relaxation and energy transfer. Successful modeling of such lasers requires a knowledge of vibrational deactivation rates for the vibrational levels populated by the chemical reaction. In the HF chemical laser, the pumping reaction



directly populates $v = 1, 2$, and 3 . When D_2 is substituted for H_2 , the pumping reaction produces $DF(v)$ with $v = 1$ to 4 .¹ Studies of upper level ($v > 1$) deactivation are complicated by the difficulty of producing the upper vibrational levels under conditions in which specific deactivation processes can be isolated. Several techniques have been developed for studies of the upper vibrational levels: selective laser pumping of $v = 2-4$ of HF,^{2,3} low-pressure combustion with spectroscopic diagnostics,⁴⁻⁶ reactive flows in medium pressure flow tubes,⁷⁻⁹ high-temperature combustion in shock tubes,¹⁰ and laser-induced fluorescence by sequential photon absorption.¹¹⁻¹⁴

In an earlier study,¹³ the latter technique was used to study the room-temperature deactivation of $HF(v = 1, 2, 3)$ by N_2 , H_2 , O_2 , HCl , and CO_2 . The deactivation rates scaled approximately as $k(v) = v^{2.7 \pm 0.2} k(1)$ for N_2 , O_2 , and HCl . The deactivation by H_2 involves an endothermic energy exchange, and its deactivation rate was found to decrease with v . The present study was undertaken to determine if the deactivation rates for $DF(v)$ scale similarly for several diatomic deactivators. The results are compared with those obtained by Poole and Smith^{5,6} in a low-pressure combustion experiment.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The technique of laser-induced fluorescence by sequential photon absorption has been used previously in this laboratory^{13, 14} to study the deactivation of HF($v = 1, 2, 3$). In such experiments, the multiline output of a pulsed HF laser passes through a fluorescence cell that contains HF. A small fraction of the HF is pumped to $v = 1$ by the $1 \rightarrow 0$ laser transitions. Then, a fraction of this HF($v = 1$) is pumped to $v = 2$ and subsequently to $v = 3$ by $2 \rightarrow 1$ and $3 \rightarrow 2$ transitions, respectively. Because all of the pumping occurs during the laser pulse ($\leq 1/2 \mu\text{sec}$), decay times as short as a few microseconds can be measured. The analogous processes occur when a DF laser is used to pump DF, except that DF($v = 4$) can also be produced. The experiments are more difficult to carry out for DF than for HF because of the smaller gain laser, smaller absorption coefficients, weaker fluorescence, and poorer detection capability for comparable vibrational levels. Therefore, several changes were made in the apparatus to make it more adaptable to the DF experiment.

As shown in Fig. 1, the apparatus includes an HF(DF) TEA laser, a fluorescence cell, several detectors, and signal recording and averaging equipment. The laser is constructed of 2.54-cm-diam Plexiglas tubing with calcium fluoride windows at the Brewster angle. Resistors (212 at 1000 Ω) spaced 0.635 cm apart serve as the anodes and generate an active volume that is approximately 1.35 m long. The cathode is a 0.32-cm-diam brass rod positioned 1.25 cm from the resistor wire anodes. The SF₆, H₂ (D₂) gas mixture entered the laser tube at the two ends and was pumped out at the center with a 5 CFM pump throttled such that the gas mixture in the laser tube was exchanged once every second, the operating repetition rate selected for the laser. The flow was regulated to give partial pressures of about 2 to 4 Torr for D₂ and about 30 Torr for SF₆. An energy of 1.6 J

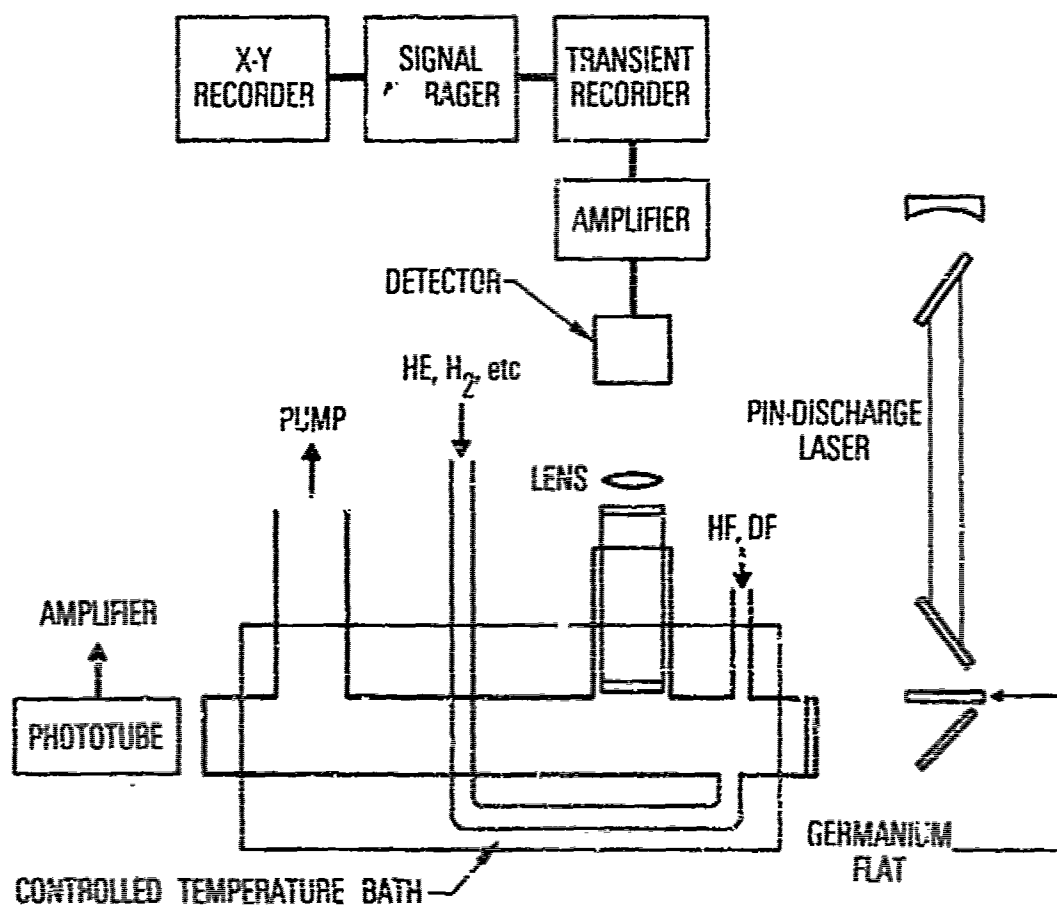


Fig. 1. Schematic of Apparatus

stored in a 10,000-pF capacitor charged to 18,000 V was discharged through the laser with a hydrogen thyratron tube. A silver-coated mirror of 12.5-m radius and a germanium flat formed the optical cavity when the laser was operated on DF. The DF laser produced about 0.03 J in pulses shorter than 0.5 μ sec at a repetition rate of about 1 Hz.

The fluorescence cell was used previously in a study of the deactivation of HF(v) by H atoms.¹⁴ The calorimeter probe for measuring H atoms was removed, but no other changes were made. The Pyrex walls are protected from HF and DF by a coating of halocarbon wax. The DF or HF is injected into the main flow through a small Teflon tube sealed into the connecting s. s. tubing. The cell has sapphire windows that pass the DF laser pulse and the resulting DF fluorescence. The flow rates of the test gases were measured with rotating ball flowmeters calibrated by pressure-rise measurements in a standard volume. The DF flow was regulated with a calibrated vernier needle valve. Partial pressures of the constituent gases were calculated from the flow rates and the total pressure, which was measured with a Baratron model 221 capacitance manometer. The experiments were carried out at DF partial pressures of ~5 m Torr, which yielded a sufficient fluorescence signal and a low self-deactivation rate.

The DF(v = 1) fluorescence was monitored with a Texas Instruments InSb detector and an interference filter that passed the R-branch portion of the v = 1 fluorescence. The signal across a 1 k Ω resistor was amplified 1500 times by Perry amplifiers (models 050 and 070) and recorded with a Biomation 805 transient recorder. The combined response time of the detector and electronics was ≤ 1.4 μ sec. The recorded signals were transferred to a Nicolet signal averager (model 1072), where 64 to 512 experimental signals were stored and averaged before being displayed on an X-Y recorder. The detector was mounted transverse to the laser excitation beam, and the fluorescence focused onto the active element of the detector with 2-in.-diam f/1.5 CaF optics. The 2 $\rightarrow$ 1 fluorescence from DF(v = 2) was monitored with the same infrared detector, except that a 2-cm gas cell filled with

DF at 400 Torr was placed in front of the detector to remove the $1 \rightarrow 0$ fluorescence. Although the gas cell did not remove the $4 \rightarrow 3$ or $3 \rightarrow 2$ fluorescences, their intensities can be expected to be much smaller than the intensity of the $2 \rightarrow 1$ fluorescence because of the smaller concentrations pumped into $v = 3$ and 4. Also, the populations of DF($v = 3$) and DF($v = 4$) decayed on shorter time scales than the DF($v = 2$). The exponential decays of the fluorescence through the gas filter ruled out the possibility that the $4 \rightarrow 3$ and $3 \rightarrow 2$ fluorescences were significant contributions.

The much weaker overtone intensities of DF($v = 4$) at $0.94 \mu\text{m}$ ($4 \rightarrow 0$) DF($v = 3$) at $1.20 \mu\text{m}$ ($3 \rightarrow 0$) were monitored with a photomultiplier mounted at the far end of the cell. The photomultiplier viewed the entire excited volume and collected 5 to 10 times more photons than when mounted in the transverse configuration of the infrared detector. It was protected from the direct DF laser pulse by a 0.63-cm sheet of Plexiglas. No fluorescence signal was measurable without DF flowing in the cell. The DF $3 \rightarrow 0$ overtone fluorescence was monitored with a selected Dumont Type 6911 (S-1 response) photomultiplier with a Corning CS7-56 filter used to block visible fluorescence from the laser discharge. DF $4 \rightarrow 0$ fluorescence was a negligible contribution. The DF $4 \rightarrow 0$ fluorescence was monitored with an RCA GaInAs whose sensitivity decreases abruptly past the $0.94\text{-}\mu\text{m}$ wavelength of the $4 \rightarrow 0$ fluorescence. Again, a CS7-56 filter was used to block any visible fluorescence. A load resistor of 47 k Ω and a Perry 070 amplifier (15X amplification) mounted directly on the end of the photomultiplier provided a response time of $\leq 2 \mu\text{sec}$. The photomultiplier signals were recorded with the Biomation 805 and averaged with the Nicolet 1072 signal averager.

A sample $3 \rightarrow 0$ fluorescence trace for DF($v = 3$) in the presence of 1.69 Torr of D_2 is shown in Fig. 2. The exponential decay time was determined from a semilog plot of the smoothed curve through the fluorescence trace.

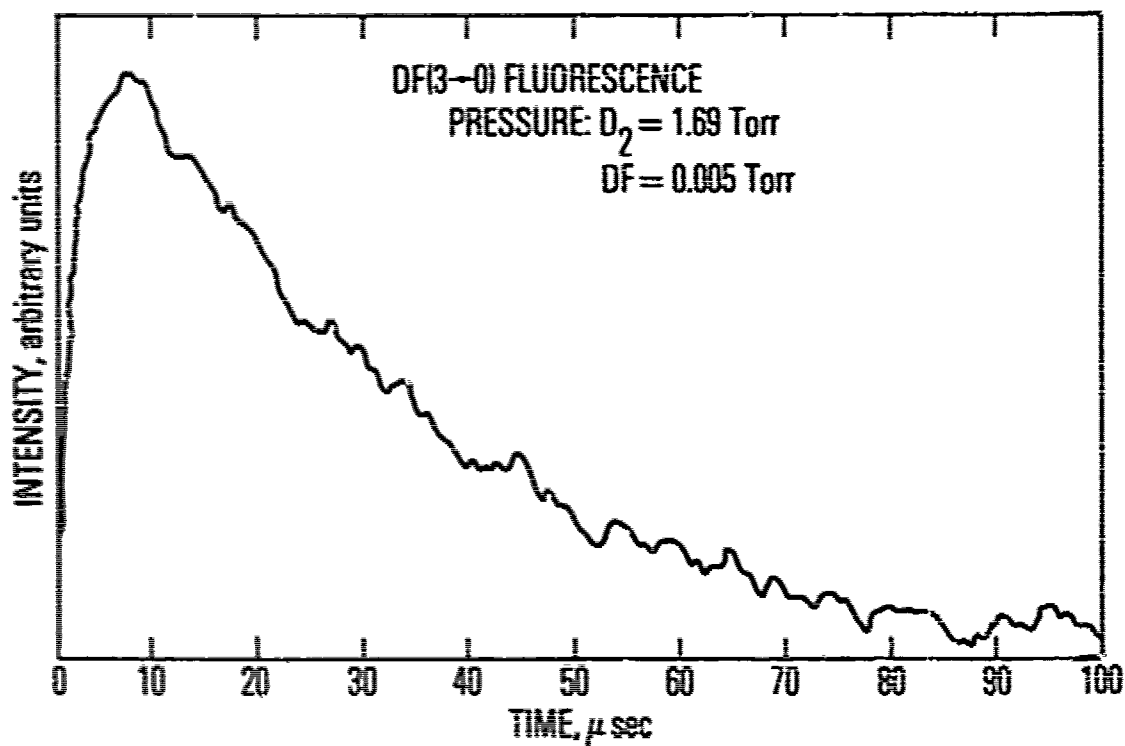


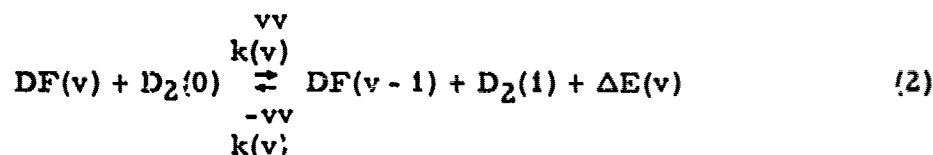
Fig. 2. DF(3) Fluorescence Trace. Pressures: $D_2 = 1.69$ Torr, DF = 0.005 Torr, helium = 12.4 Torr. Average of 512 experiments.

The gases included hydrogen and helium (Air Products 99.995%), nitrogen (Air Products 99.998%), carbon dioxide (Liquid Carbonic 99.99%), deuterium (Oak Ridge > 98%), hydrogen fluoride (Matheson 99% in liquid phase), and deuterium fluoride (Ozark Mahoning 98%). The HF and DF were purified by pumping at 77 K for removal of the noncondensibles before distillation into passivated stainless-steel cylinders.

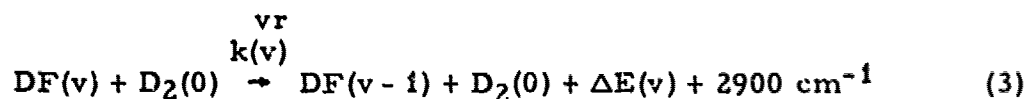
III. RESULTS

A. VIBRATIONAL RELAXATION OF DF(v = 1-4) in D₂

The relaxation times of DF(v) were measured in mixtures of He, DF, and D₂ with the flow rates of He and DF set at 16.5 L-Torr/sec and 0.006 L-Torr/sec, respectively, at a total pressure of 13 Torr and higher. Partial pressures of D₂ were calculated from the relative flow rates and the total pressure. D₂ deactivates DF(v) by both V-V and V-R, T processes, which can be described by



and



We neglect the possibility of multiquantum transfers because the present experiment cannot distinguish between them and single-quantum transfers. Equations describing the relaxation of the v = 1 population are given in Ref. 15. Because of the large concentration of D₂ relative to DF, only single exponential decays were observed. The reciprocal values of the exponential decay times are plotted in Fig. 3 as a function of the partial pressure of D₂. The slopes of the data are equal to the sum of the deactivation rates ($k_{\text{V-V}}(v) + k_{\text{V-R}}(v)$) and are given in Table I. The deactivation rate of $2.1 \times 10^{-2} (\mu\text{sec Torr})^{-1}$ obtained for DF(v = 1) agrees closely with previously reported values¹⁵⁻¹⁷ of 0.0188 ± 0.0020 , 0.0202 ± 0.0033 , and $0.014 \pm 0.006 (\mu\text{sec Torr})^{-1}$.

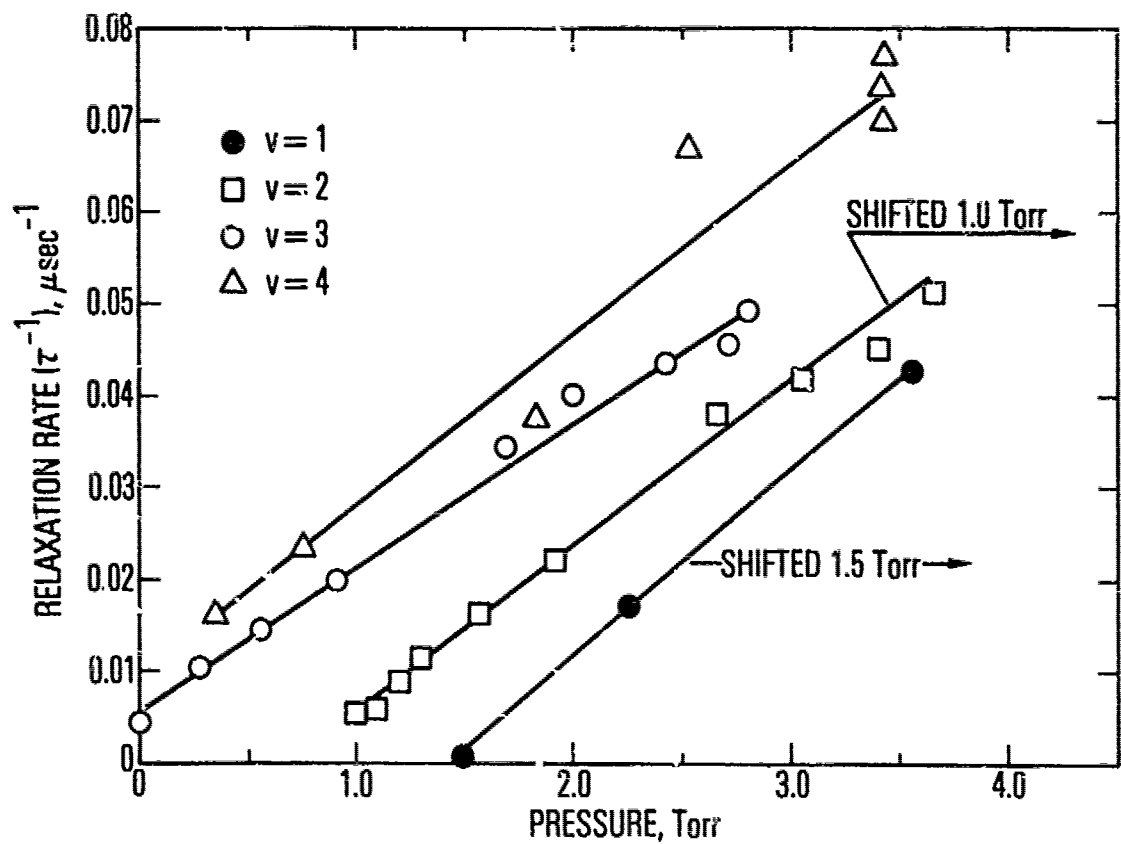


Fig. 3. Relaxation Rates of $\text{DF}(v)$ in D_2

Table i. Vibrational Deactivation Rates for DF(v) in D₂

v	k(v), (μsec Torr) ⁻¹	k(v)/k(1)	^{-vv} k(v), (μsec Torr) ⁻¹	^{-vv} k(v) / k(1)	ΔE(v), cm ⁻¹
1	2.05 × 10 ⁻²	1	3.1 × 10 ⁻²	1	-83.4
2	1.81 × 10 ⁻²	0.88	4.3 × 10 ⁻²	1.4	-175
3	1.55 × 10 ⁻²	0.76	5.6 × 10 ⁻²	1.8	-264
4	1.85 × 10 ⁻²	0.90	10.3 × 10 ⁻²	3.4	-353

The total deactivation rate $k(v) = k(v) + k(v)_{vv} + k(v)_{vr}$ decreases with v , in contrast to the increases with v observed for other molecules in this study. The measured value for $k(4)$ is 20% larger than that for $k(3)$, and $k(v)$ may be starting to increase with v for $v > 4$. However, 20% is the order of the combined experimental uncertainties in the two measurements and may not be significant. Deactivation by D_2 by means of Process (2) is endothermic (the endothermicity increases with v because of the anharmonicity of DF), whereas the other molecules deactivate DF in exothermic V-V or V-R, T processes. In a previous study,¹⁸ $k(1)_{vr}$ was determined to be $\leq 1.0 \times 10^{-4} (\mu\text{sec Torr})^{-1}$, a small contribution to $k(1)_t$. If we estimate $k(v)_{vr} = v^2 k(1)_{vr}$, $k(4)$ is $\leq 10\%$ of the total deactivation rate measured for DF ($v = 4$), which indicates that the V-V energy exchange process, Process (2), is the dominant deactivation process for $v = 1-4$. The endothermicities of these exchanges, $\Delta E(v)$, are given in Table I and were used to calculate the rate coefficients in the exothermic direction from the relation $k(v)_{-vv} = k(v)_{vv} \exp(-\Delta E(v)/RT)$. These rate coefficients (Table I) increase with v .

B. VIBRATIONAL RELAXATION OF DF($v = 1-4$) in H_2 , N_2

The relaxation times of DF(v) were measured in mixtures of DF and H_2 and DF and N_2 . In both cases, the flow rate of DF was fixed at 0.006 L-Torr/sec, and the flow rate of H_2 or N_2 varied to give total pressures up to about 30 Torr. The reciprocal values of the decay times are plotted in Figs. 4 and 5 for H_2 and N_2 , respectively. The deactivation rate coefficients were determined from the slopes of the data and are given in Table II.

The value of $(5.6 \pm 0.6) \times 10^{-4} (\mu\text{sec Torr})^{-1}$ for the deactivation rate of DF($v = 1$) in H_2 compares favorably with the value of $(6.6 \pm 0.7) \times 10^{-4} (\mu\text{sec Torr})^{-1}$ determined previously in this laboratory with different apparatus.¹⁸ A much larger value of $(4.4 \pm 0.8) \times 10^{-3} (\mu\text{sec Torr})^{-1}$ was reported in Ref. 16.

The value of $(7.4 \pm 0.8) \times 10^{-4} (\mu\text{sec Torr})^{-1}$ obtained for the deactivation rate coefficient of DF($v = 1$) in N_2 is somewhat smaller than the value of $(9.1 \pm 0.9) \times 10^{-4} (\mu\text{sec Torr})^{-1}$ obtained with different apparatus in the

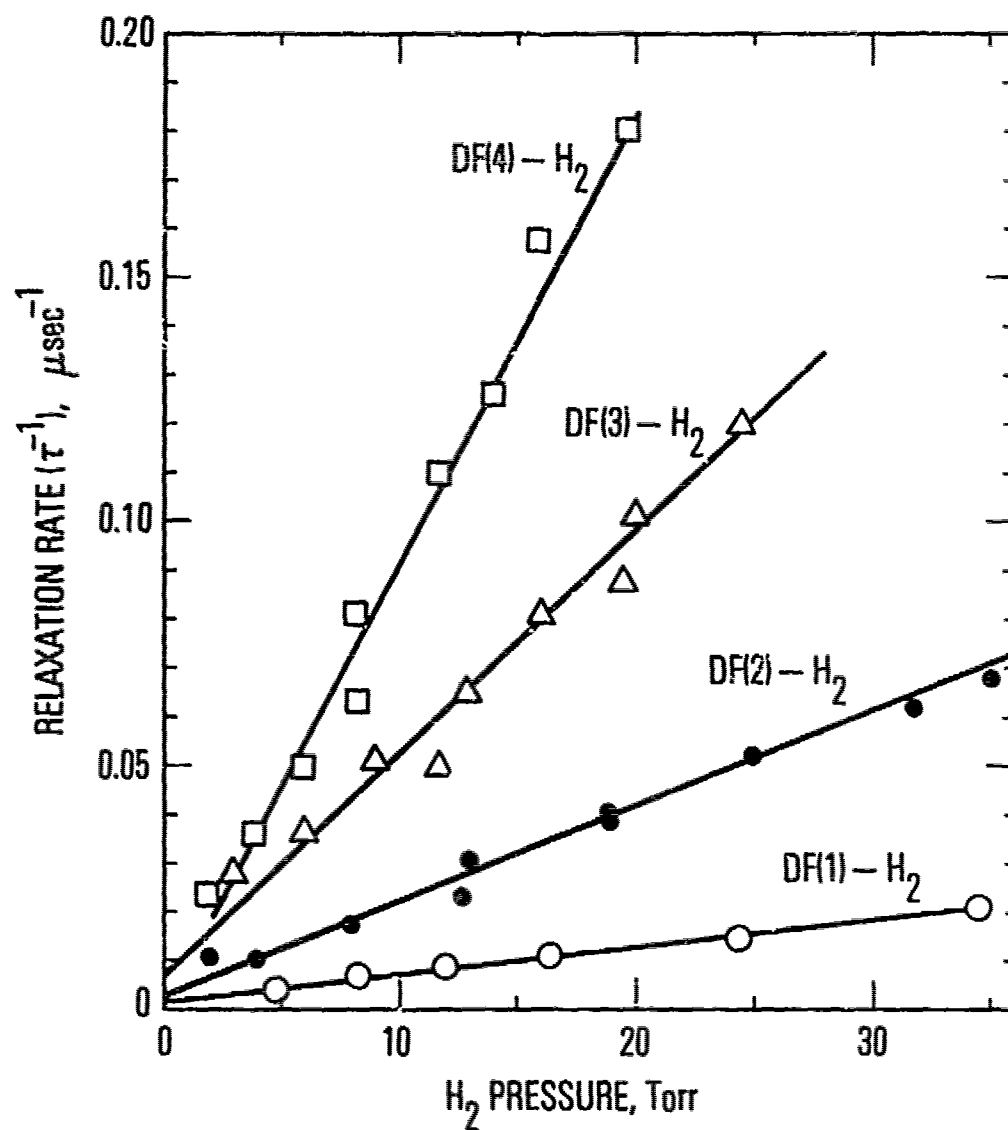


Fig. 4. Relaxation Rates of $\text{DF}(v)$ in H_2

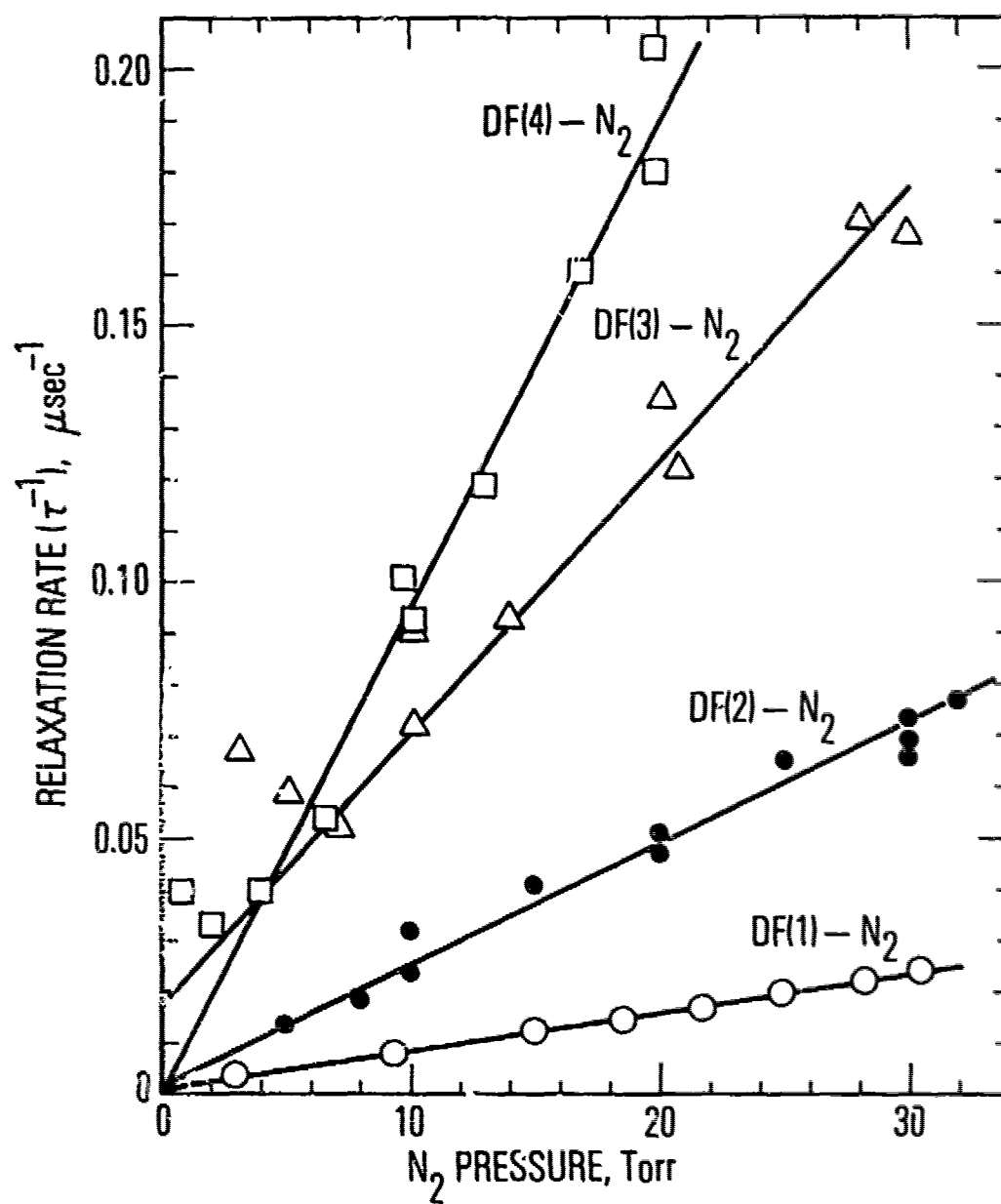


Fig. 5. Relaxation Rates of DF(v) in N₂

Table II. Vibrational Deactivation Rates for DF(v) at 295 K^a

Molecule v	H ₂	N ₂	HF	CO ₂
1	5.6×10^{-4} 1	7.4×10^{-4} 1	3.6×10^{-2} 1	0.154 1
2	1.95×10^{-3} 3.5	2.37×10^{-3} 3.2	1.29×10^{-1} 3.6	0.59 3.8
3	4.5×10^{-3} 8.0	5.3×10^{-3} 7.2	3.0×10^{-1} 8.3	1.5 9.7
4	9.1×10^{-3} 16.3	9.5×10^{-3} 12.8		

^ak, (μsec Torr)⁻¹

same laboratory¹⁸ and much smaller than the value of $(20 \pm 5) \times 10^{-4}$ $(\mu\text{sec Torr})^{-1}$ reported in Ref. 16.

Only V-R, T relaxation processes are possible for single-quantum deactivation of $\text{DF}(v)$ by H_2 . N_2 , however, can deactivate $\text{DF}(v)$ by both V-V and V-R, T processes.

C. VIBRATIONAL RELAXATION OF $\text{DF}(v = 1-3)$ in CO_2

The relaxation times of $\text{DF}(v)$ were measured in mixtures of DF and helium with small amounts of CO_2 . The flow rates of DF and basic helium diluent were maintained at 0.006 L-Torr/sec and 16.5 L-Torr/sec, respectively, and a gas mixture of 10% CO_2 in helium was added to the flow through a calibrated Matheson 610 flowmeter. The total pressure increased from 13 to about 14 Torr at the maximum flow rate of the CO_2 mixture. The reciprocal relaxation times are plotted in Fig. 6 as a function of the calculated CO_2 partial pressure. The deactivation rates obtained from the slopes of the data are given in Table II. The value of $0.154 \pm 0.015 (\mu\text{sec Torr})^{-1}$ for $\text{DF}(v = 1)$ agrees favorably with previously published values.^{4, 12, 19, 20}

D. VIBRATIONAL RELAXATION OF $\text{DF}(v = 1-3)$ in HF

The relaxation times of $\text{DF}(v)$ were measured in mixtures of DF, HF, and helium at a total pressure of about 13 Torr. The calibration of the HF flow rate through the vernier needle valve was not as accurate as the calibrations of the flowmeters. Therefore, the $\text{DF}(v = 1)$ fluorescence decay was recorded along with each $\text{DF}(v = 2)$ and $\text{DF}(v = 3)$ fluorescence trace. The reciprocal decay times for $\text{DF}(v = 2)$ and $\text{DF}(v = 3)$ are plotted in Fig. 7 versus those for $\text{DF}(v = 1)$. The measured slopes of the data in Fig. 7 and a value^{20, 21} of $3.5 \times 10^{-2} (\mu\text{sec Torr})^{-1}$ for the deactivation rate of $\text{DF}(v = 1)$ by HF were used to calculate the rate coefficients for $\text{DF}(v = 2)$ and $\text{DF}(v = 3)$ given in Table II.

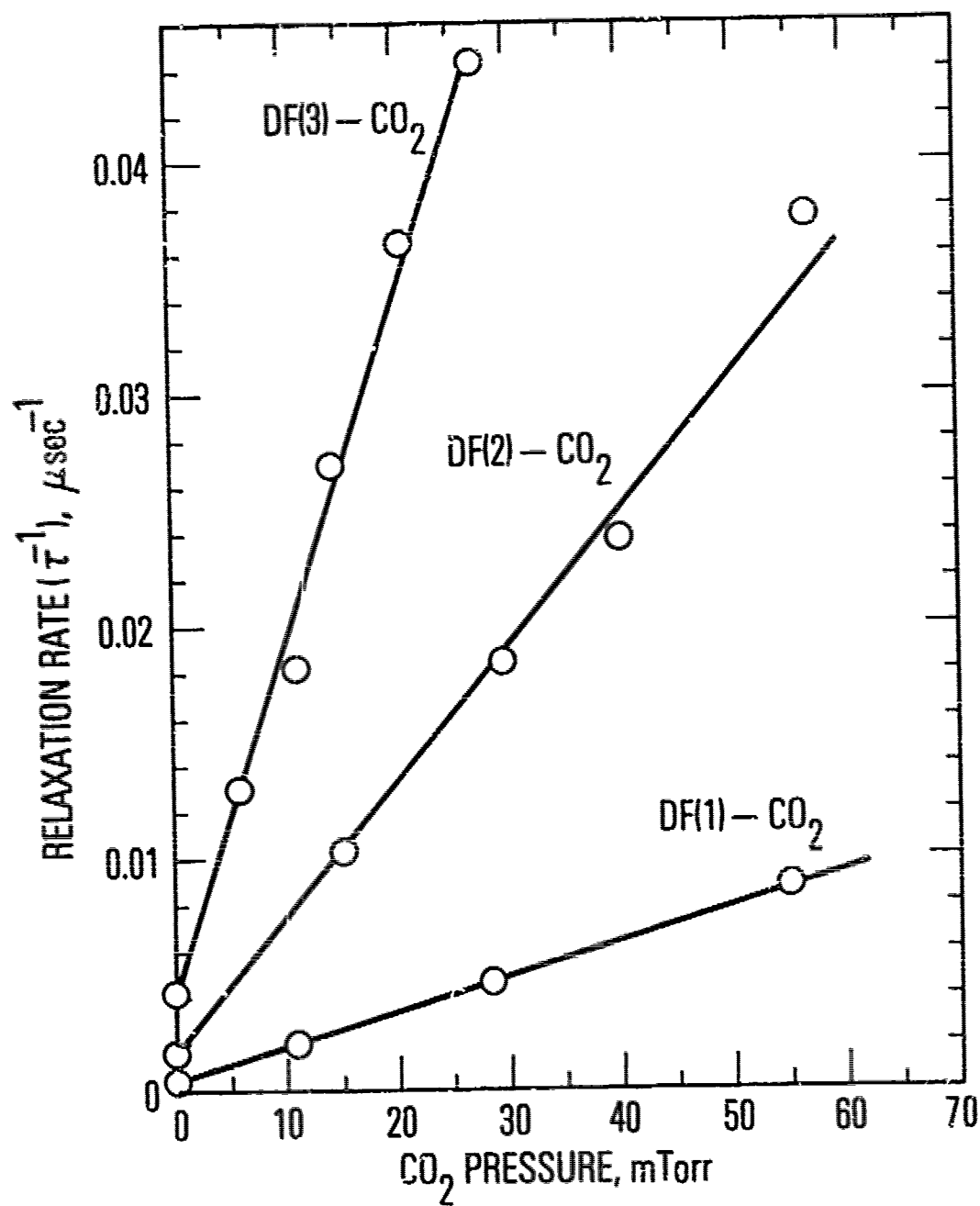


Fig. 6. Relaxation Rates of DF(v) in CO₂

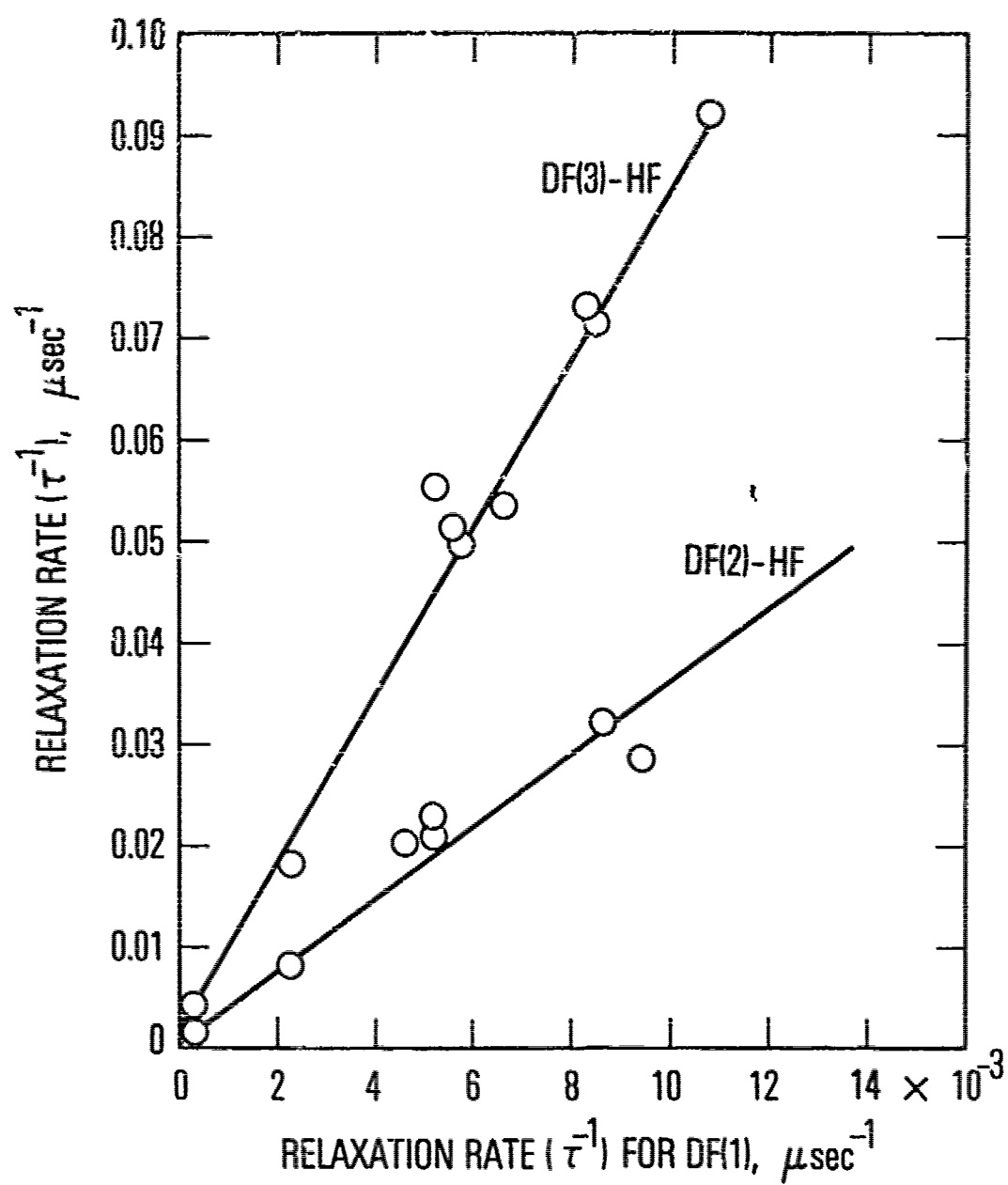


Fig. 7. Relaxation Rates of DF(v) in HF vs Relaxation Rates of DF(1) in HF at Same Pressure

IV. DISCUSSION

The deactivation rates of $DF(v)$ by H_2 , N_2 , HF , and CO_2 are plotted in Fig. 8 as a function of the vibrational level v . Within the accuracy of the experiments, the deactivation rates scale as v^n , where $n = 1.9$ to 2.0 . This v dependence is not as steep as the $v^{2.7 \pm 0.2}$ dependence obtained for the deactivation of HF by several diatomic molecules, but it is steeper than the linear v dependence predicted for harmonic oscillators with no energy defect.²² The v dependence appears to be the same for deactivation rates with V-V contributions as for purely V-R, T deactivation rates. For example, $DF(1)$ relaxes in H_2 and HF only by V-R, T processes because V-V energy exchange is much too endothermic to be significant. On the other hand, $DF(1)$ relaxes in CO_2 and N_2 by both V-V and V-R, T processes. The V-V exchange between DF and CO_2 is the basis of the $DF-CO_2$ chemical transfer laser.^{23,24} Lucht and Cool²⁰ have estimated that V-V energy exchange accounts for as much as two-thirds of the total rate of deactivation of $DF(1)$ by CO_2 . The relative V-V and V-R, T contributions to the total deactivation rate for $DF(1)$ in N_2 have not been established. However, the values of $5.6 \times 10^{-4} (\mu\text{sec Torr})^{-1}$ (Ref. 18), $\leq 1.0 \times 10^{-4} (\mu\text{sec Torr})^{-1}$ (Ref. 18), and $< 3 \times 10^{-5} (\mu\text{sec Torr})^{-1}$ (Ref. 16) for the V-R, T relaxation of $DF(1)$ by H_2 , D_2 , and argon indicate that the V-R, T rate may not be a large contribution to the total deactivation rate of $DF(1)$ in N_2 , which is $7.4 \times 10^{-4} (\mu\text{sec Torr})^{-1}$.

Part of the increase of the deactivation rates with v can be attributed to the decrease with v of the energy defect $\Delta E(v)$. HF and DF are anharmonic—the upper vibrational levels are more closely spaced than the lower ones. Therefore, in both exothermic V-V and V-R, T deactivation processes, a smaller amount of energy must be absorbed by rotational and translational degrees of freedom when $DF(4)$ is deactivated to $DF(3)$ than when $DF(1)$ is deactivated to $DF(0)$. The changes in the energy defect are larger by a factor of 1.85 for $HF(v)$ than for $DF(v)$, which is qualitatively consistent with the faster scaling with v of the measured $HF(v)$ deactivation rates.

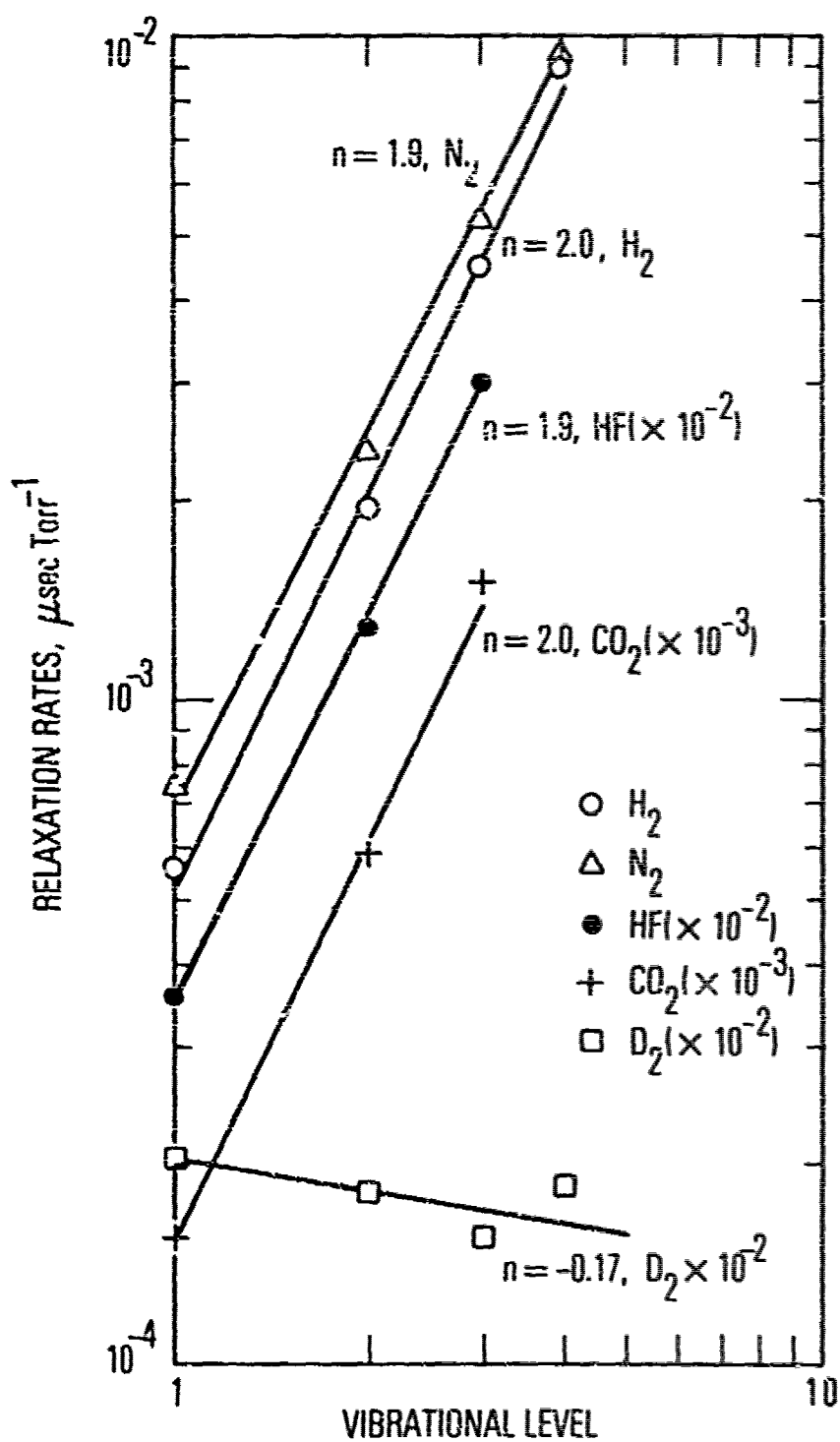


Fig. 8. Relaxation Rates of $\text{DF}(v)$ in N_2 , H_2 , HF , CO_2 , D_2 vs Vibrational Level

The molecular and spectroscopic properties of the collision partner do not affect the v dependence of the deactivation rates, although they may affect the rate coefficients for $DF(v = 1)$. Molecules with similar spectroscopic properties, however, may have deactivation rates with similar v dependencies. $HCl(v)$ and $DF(v)$ have very similar spectroscopic constants, except that $DF(v)$ has a larger radiative transition probability. Although the deactivation rates for $HCl(1)-CO_2$ and $DF(1)-CO_2$ differ by a factor of 1.7, deactivation rates for vibrational levels 1, 2, and 3 scale very similarly.²⁵ Macdonald and Moore²⁶ found the rate for $HCl(2)$ deactivation by O atoms to be four times faster than that for $HCl(1)$; the total removal rate of $HCl(2)$ was more than four times faster but included the contribution of chemical reaction. In another study,²⁷ $HCl(2)$ was removed six times faster than $HCl(1)$ in the presence of Br atoms, but the contributions of chemical reaction and V-E were not ascertained. It appears that deactivation rates for HCl and DF scale with v in a similar manner.

In a study of HCl and DCl relaxation, Chen and Moore²⁸ concluded that the dominant process for the deactivation of $HCl(1)$ by HCl was the conversion of the vibrational energy to rotational energy of the initially excited molecule. For such a deactivation mechanism, the scaling with v could be expected to depend on the anharmonicity of the excited molecule and its rotational spacing and not on the properties of the collision partner. This is in basic agreement with the experimental results for HF and DF .

Poole and Smith^{5,6} have measured deactivation rates for $HF(2 \leq v \leq 7)$ and $DF(3 \leq v \leq 5)$ for a number of collision partners by observing the quenching of the steady-state infrared chemiluminescence of the $HF(v)$ and $DF(v)$ formed in a low-pressure chemical reaction. Their measurements were a continuation of the upper-level deactivation studies of HF initiated by Airey and Smith.⁴ Comparisons of their data and the data obtained with the laser-induced fluorescence technique in the present study of $DF(v)$ and in a previous study of $HF(v)$ ¹³ are given in Figs. 9 and 10. The data obtained by

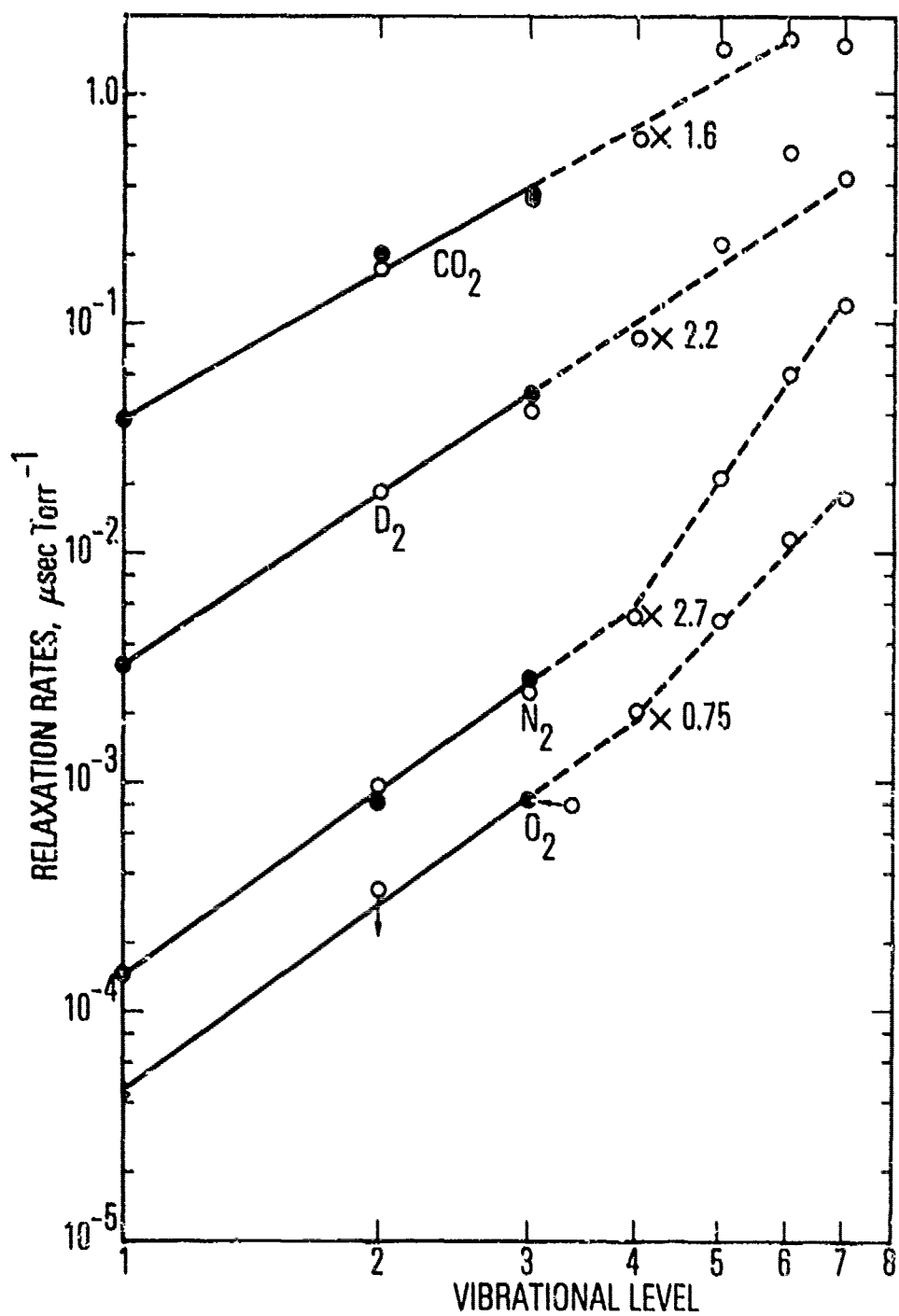


Fig. 9. Relaxation Rates of HF(v) vs Vibrational Level.
 ● Ref. 13. ○ Ref. 5 multiplied by indicated factors.

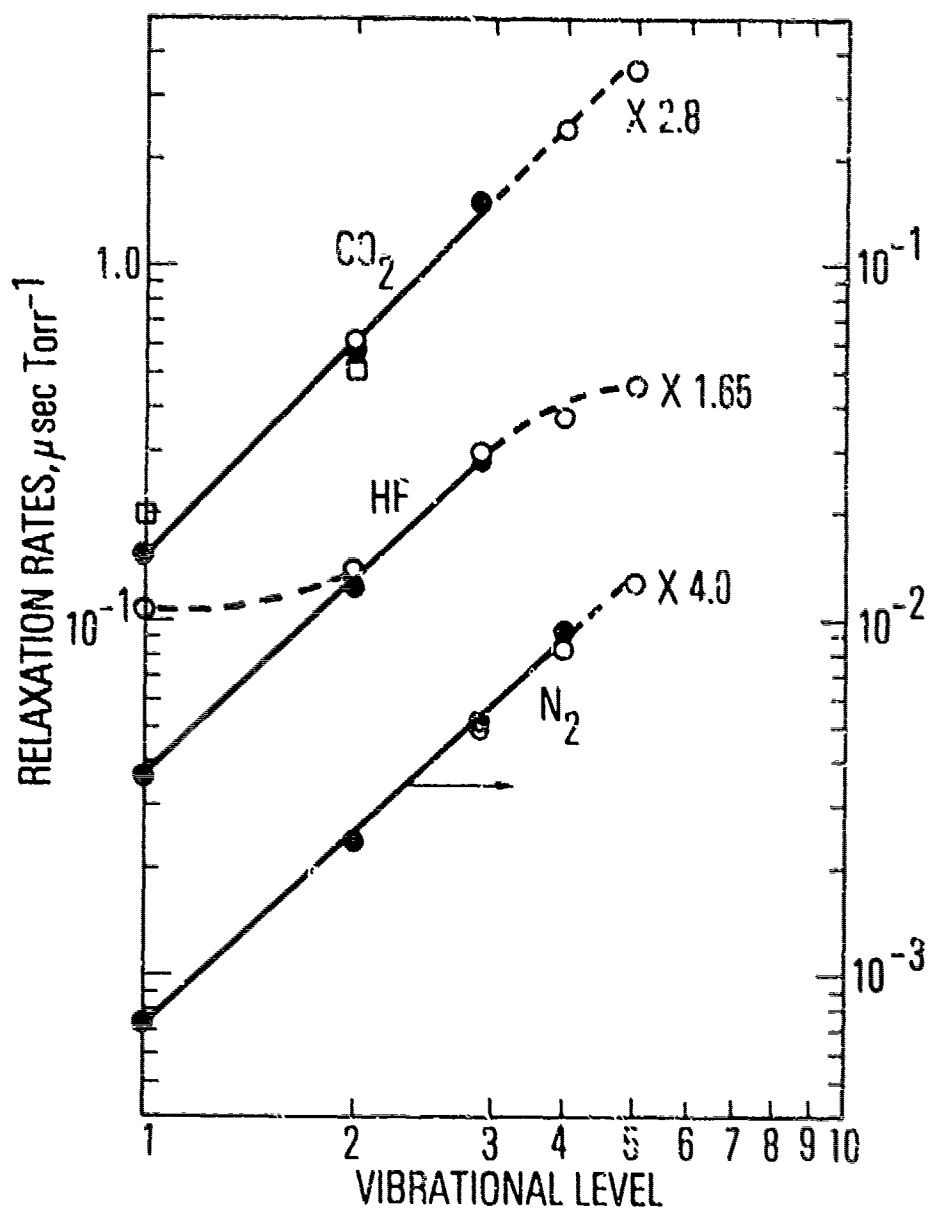


Fig. 10. Relaxation Rates of $DF(v)$ vs Vibrational Level.
 ● Present data, ○ Refs. 5 and 6 multiplied by indicated factors, □ Ref. 12.

Poole and Smith have been multiplied by the factors necessary to bring them into agreement with the deactivation rates for $v = 2$ and 3 of the present study. In five of seven cases, the Poole and Smith deactivation rates had to be multiplied by factors of 1.6 to 2.8 . However, the v dependencies of the data are in very good agreement within the uncertainties of the experiments and the multiplicative factors applied to the data. We have not plotted their data for HF($v = 2,3,4$) deactivation by H_2 , but these data are also a factor of 2 lower than the data of Ref. 13. The rates of Airey and Smith for DF($v = 1,2$)-HF and those of Poole and Smith for DF($v = 3,4,5$)-HF have been increased by the same factor of 1.65 . These data fall along a smooth curve but not a straight line, in contrast to the other data. Poole and Smith^{5,6} tabulated their deactivation data for HF($2 \leq v \leq 7$) and DF($3 \leq v \leq 5$) and other published data for HF($v = 1$) and DF($v = 1$). Comparison of their upper-level deactivation rates to the $v = 1$ deactivation rates of others does not indicate as strong a v dependence as indicated in Figs. 9 and 10.

Kwok and Wilkins¹⁷ have measured the deactivation rates for DF($v = 1-4$) in HF in a medium-pressure, large-diameter flow tube. They obtained rates that increased with v up to $v = 3$; the rate for DF($v = 4$), however, was slower than that for DF($v = 2$). They observed substantial V-V coupling effects at higher ($\times 7$) DF concentrations, and it is possible that some V-V exchanges among the DF vibrational levels served to pump $v = 4$, giving it a slower apparent decay rate.

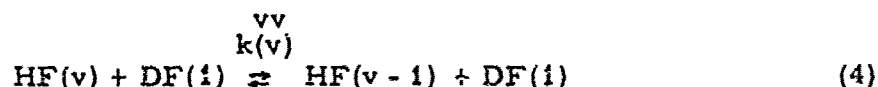
The deactivation rates of DF(v) in D_2 obtained in this study and listed in Table I decrease with v . The deactivation rates for HF(v)- H_2 also decrease with v up to $v = 3$ and increase thereafter.⁵ The deactivation of DF(v) by D_2 by the V-V energy exchange process (2) is endothermic. Because this endothermicity increases with v , the V-V exchange rate coefficients decrease with v . Through the use of state-specific equilibrium constants, we have calculated the exchange rates $k(v)_{-VV}$ for the reverse exothermic exchange (Table I). They increase with v , but do not increase as fast as the v^2 dependence obtained for the other DF(v) deactivation processes in this study. The

other DF(v) deactivation processes, however, have energy defects that decrease with v, whereas DF(v)-D₂ and HF(v)-H₂ have energy defects that increase with v. The total observed deactivation rate is the sum of the rates for processes (2) and (3), $k_{vv}(v) + k_{vr}(v)$. At some v, the total deactivation rate can be expected to increase as a result of the increasing contribution of $k_{vr}(v)$, which, on the basis of this study, can be expected to scale as v². Poole and Smith observed that this increase occurred for HF(v)-H₂ deactivation at v = 4.

Dillon and Stephenson²⁹ calculated exchange rates for HF(v)-CO₂, DF(v)-CO₂, and HCl(v)-CO₂. They performed semiclassical calculations with the use of curved classical trajectories. Excellent agreement with the measured exchange rates was obtained for HCl(v = 1)-CO₂ between 298 and 510 K. Measured rate coefficients of the CO₂ exchanges with DF(v) of the present study, HF(v),¹³ and HCl(v),²⁶ however, have steeper v dependencies than the calculated rate coefficients.

Shin³⁰ performed semiclassical calculations of the energy-exchange rates for DF(v) + DF(0). The molecules were considered to undergo hindered rotational motion and back-and-forth translational motion. The hindered rotational motion was described quantum mechanically, whereas the translational motion was analyzed in terms of classical dynamics. The model is a simplified one, but contains the essential features of hydrogen-bonded systems near the equilibrium configuration. Shin calculated exchange rates for DF(v = 2) through DF(v = 5) colliding with DF(0) that increase approximately as v^{1.53} at 300 K. His calculations included the contributions of a nonrigid dimer model and a rotational model. The rotational model contributes more to the v dependence than the nonrigid model calculation. The present results are in qualitative agreement with his prediction of rate coefficients that increase faster than v, but would be in better agreement if the rotational model contribution were slightly increased. His calculations for DF(v = 2)-DF(0) are in reasonable agreement with experimental data between 295 and 740 K.

Wilkins has performed three-dimensional classical trajectory calculations^{31, 32} of the collision dynamics of HF(v) colliding with HF(0) and DF(0). He found³¹ that the V-V rate coefficients $k_{VV}^{VV}(v)$ for the exothermic exchange



scale approximately as v . This exchange has not been studied with the present technique. The limited experimental data for HF(v) and DF(v) deactivation, however, indicate that the rate coefficients for exchange (4) increase more rapidly with v than those obtained with the trajectory calculations.

Recent measurements³ of HF(3) and HF(4) relaxation rates in HF can be described with a $v^{2.7 \pm 0.2}$ dependence with respect to data for HF(1). Although HF(3) and HF(4) relax in HF by endothermic V-V processes as well as exothermic V-R, T processes, the scaling of the rate coefficients is the same as for HF($v = 1-3$) relaxation in N₂, O₂, and HCl.

In summary, the results of this study and a previous study of HF(v) deactivation¹³ indicate that the deactivation rates scale as $v^{2.0 \pm 0.1}$ for DF($v = 1-4$) and $v^{2.7 \pm 0.2}$ for HF($v = 1-3$) when the deactivator is a diatomic molecule. The exceptions are the rates for DF(v)-D₂ and HF(v)-H₂, which involve endothermic energy exchange rather than the exothermic V-V or V-R, T energy transfer of the other deactivators studied. The deactivation rates for HF($v = 1-3$)-CO₂ and DF($v = 1-3$)-CO₂ were also found to scale as v^2 . The v dependence is the same for several collision partners and, therefore, is qualitatively consistent with a V-R mechanism in which the vibrational energy (or excess vibrational energy in a V-V transfer) is taken up in the rotation of the initially excited molecule.

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