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Vibrational Relaxation of DF ($v = 1$ and 3) in H_2, D_2, N_2, and HF at 200 K

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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The laser-induced fluorescence technique was used to measure the rate coefficients for the deactivation of DF(v = 1) and DF(v = 3) in H_2, D_2, N_2, and HF at 200 ± 5 K. The rate coefficients for deactivation by H_2, N_2, and HF were found to scale with v as $v^{1.9 \pm 0.1}$, essentially the same as the scaling at 295 K. The relaxation rates for DF(v = 1) were compared with data obtained at higher temperatures. At 200 K, the exchange probability of HF(1) + H_2(0) was the same as that of DF(1) + D_2(0) (within 10%) when the endothermicities were considered.

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I. INTRODUCTION

Successful modeling of chemical lasers requires a knowledge of the deactivation rates for the vibrational levels populated by the chemical reactions. In the DF chemical laser, the F + D_2 reaction produces vibrational levels v = 1 through 4. In a previous study[1] of the deactivation of DF (v = 1 through 4) in H_2, D_2, N_2, HF, and CO_2 at room temperature, the deactivation rates for all the collision partners except D_2 scaled with vibrational level as v^n with n = 1.9 to 2.0 for v = 1 through 4. The present study was undertaken to determine how the deactivation rates for DF(v) scale at the low temperature 200 K, which is within the range of temperatures in chemical lasers.

The laser-induced fluorescence technique of sequential photon pumping was used for these studies and for previous studies[2] in which the scaling of HF (v = 1, 2, and 3) deactivation rates with v was insensitive to temperatures between 200 and 295 K. The present results for deactivation rates of DF(v = 1) in D_2, H_2, and N_2 at 200 K are compared with data at higher temperatures.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus and experimental technique are described in detail in Ref. 1 in which room temperature results for DF(v = 1 through 4) deactivation are given. The fluorescence cell and inlet tubes were submerged in a slush bath of ethanol and dry ice and maintained at 200 ± 5 K.[3]

The DF flow was regulated with a calibrated vernier needle valve such that DF partial pressures of approximately 0.015 Torr were obtained. A higher DF partial pressure was required for experiments at 200 K than for experiments at 295 K because of the larger mismatch between the spectral output of the laser and the absorption of the cold DF. The flow rates of the test gases were measured with rotating ball flowmeters calibrated by pressure-rise measurements in a standard volume. 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 gases included hydrogen and helium (Air Products 99.995%), nitrogen (Air Products 99.998%), 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 noncondensables before distillation into passivated stainless steel cylinders.

III. RESULTS

A. VIBRATIONAL RELAXATION OF DF(v = 1 AND 3) IN D_2 AT 200 K

The relaxation times of DF(v) were measured in mixtures of He, DF, and D_2 with the flow rates of He and DF set at 16.5 and 0.006 L-Torr/sec, respectively, at a total pressure of 29 Torr and higher. (The flow rates were calibrated at 295 K.) Partial pressures of D_2 were calculated from the relative flow rates and the total pressures. The reciprocal values of the exponential decay times are plotted in Fig. 1 as a function of the partial pressure of D_2. The slopes of the data are equal to the sum of the V-V and V-R, T deactivation rate coefficients and are given in Table 1. The deactivation rate coefficients for DF(v = 1) are plotted versus temperature in Fig. 2 for comparison with data obtained at higher temperatures.[1,4-6] The rate coefficient at 200 K falls on an extrapolation of the data obtained at higher temperatures. The solid curve through the data fits the expression $(P\tau)^{-1} \propto T^{-1/2} \exp(85/T)$.

The deactivation rate coefficient for DF(v = 3) in D_2 was measured to be 2.0×10^{-2} (μsec Torr)$^{-1}$ at 200 K compared with 2.75×10^{-2} for DF(v = 1). D_2 deactivates DF(v) by the V-V and V-R, T processes,

$$\mathrm{DF}(v) + \mathrm{D}_2(0) \underset{\overset{-vv}{k(v)}}{\overset{\overset{vv}{k(v)}}{\rightleftarrows}} \mathrm{DF}(v - 1) + \mathrm{D}_2(1) \qquad (1)$$

and

$$\mathrm{DF}(v) + \mathrm{D}_2(0) \overset{\overset{vr}{k(v)}}{\rightleftarrows} \mathrm{DF}(v - 1) + \mathrm{D}_2(0) \qquad (2)$$

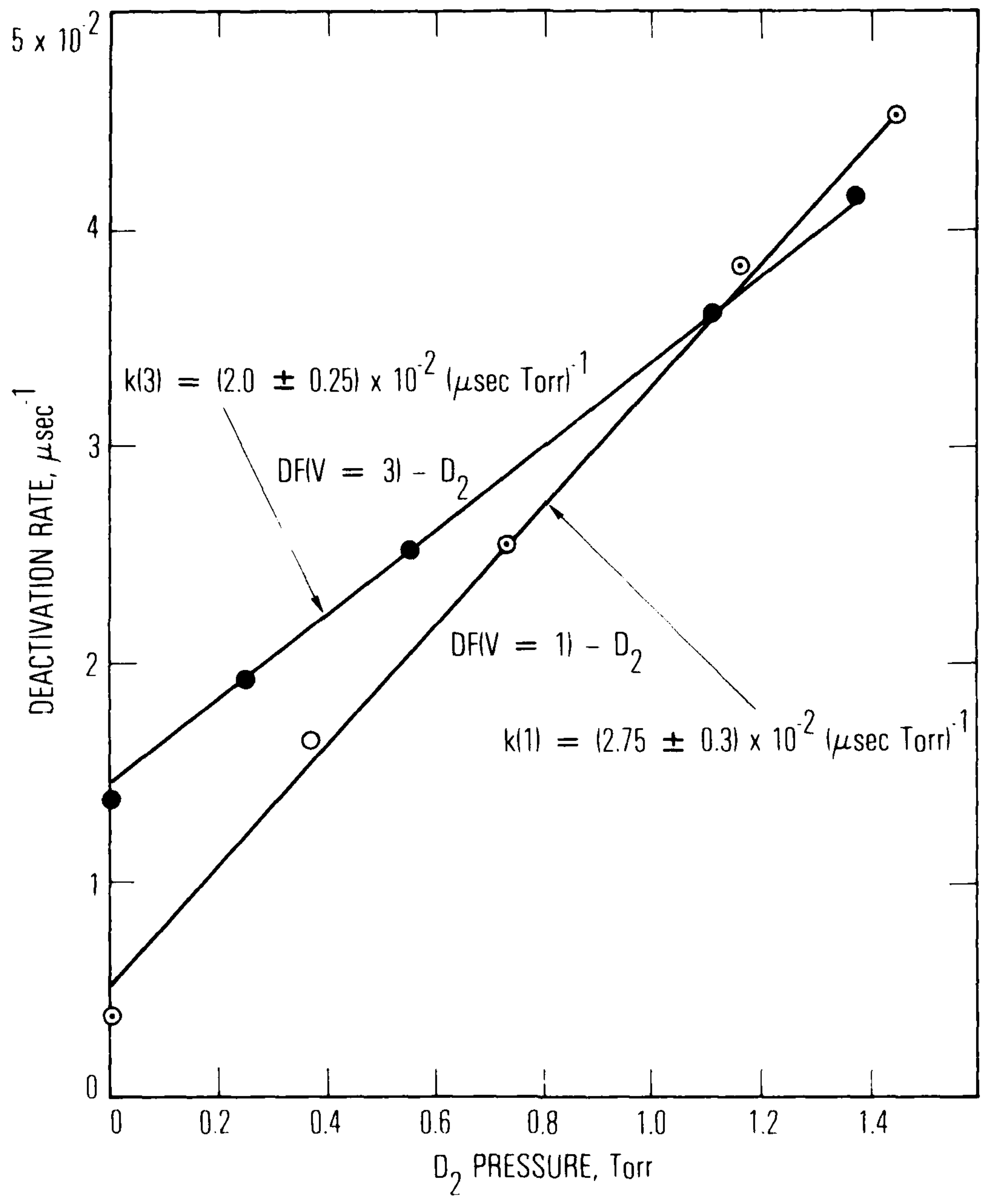

Figure 1. Deactivation Rates of DF(v) vs D_2 Partial Pressure at 200 K

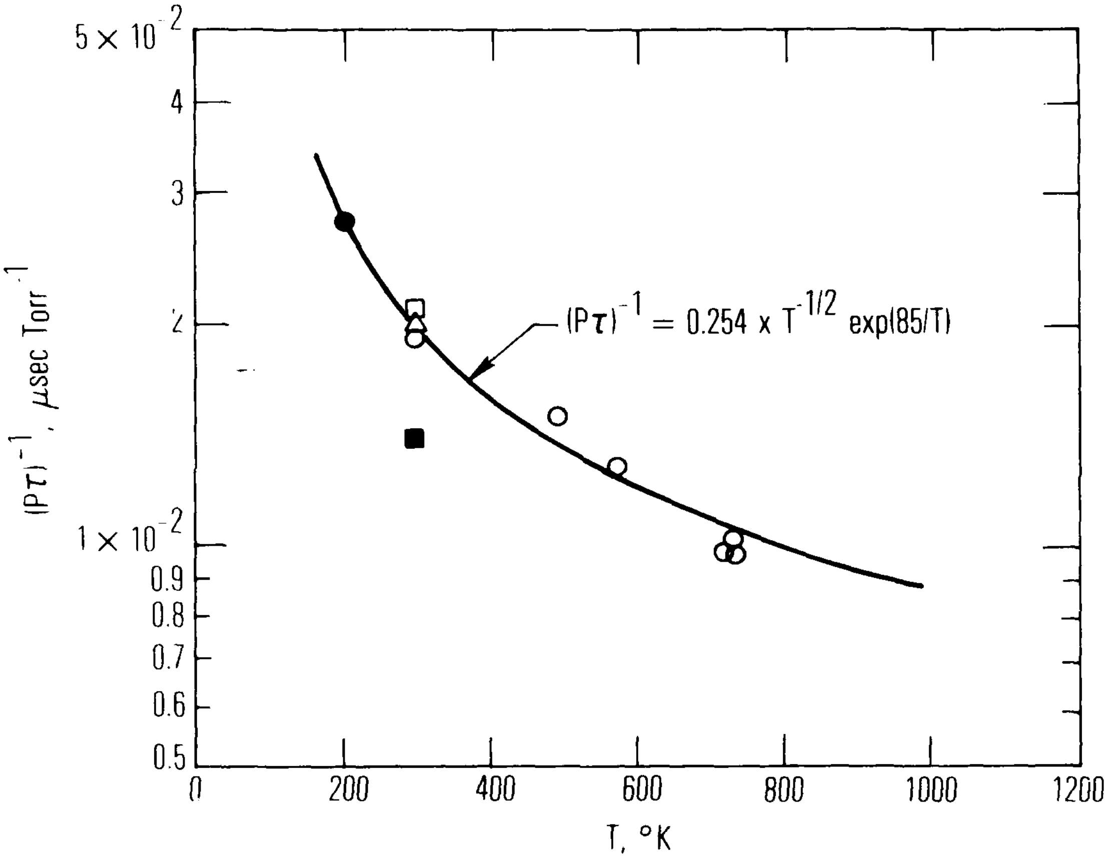

Figure 2. Deactivation Rate Coefficient for DF(v = 1) in D_2 vs Temperature
□ Ref. 1, △ Ref. 4, ■ Ref. 5, ○ Ref. 6, ● present data

We neglect the possibility of multiquantum transfers because in the present experiment we could not distinguish between them and single-quantum transfers. Equations describing the relaxation of the v = 1 population are given in Ref. 6. Deactivation of DF(v) by Process (1) is endothermic with the endothermicity increasing with v. In a previous study,[7] $k^{vr}(1)$ was determined to be $< 1.0 \times 10^{-4}$ $(\mu\text{sec Torr})^{-1}$ at 295 K, a small contribution to the total deactivation rate. In Ref. 1, it was concluded that Process (1) was the dominant process for the deactivation of DF(v = 1 through 4) by D_2. The endothermicities of the exchanges for v = 1 and v = 3 are given in Table 1 and were used to calculate the rate coefficients for the reverse, exothermic exchanges of Process (1), also given in Table 1. Rotational equilibrium was assumed for these calculations.

B. VIBRATIONAL RELAXATION OF DF(v = 1 AND 3) IN H_2 AND N_2

The relaxation times of DF(v = 1 and 3) were measured in mixtures containing H_2 and N_2. In each case, 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. 3 and 4. Deactivation rate coefficients were determined from slopes of the data and are given in Table 2. Rate coefficients for DF(v = 1) deactivation are plotted versus temperature in Figs. 5 and 6 for H_2 and N_2, respectively, for comparison with high-temperature data.

Rate coefficients for DF(v = 3) deactivation are larger than those for DF(v = 1) by factors of 7.4 for both H_2 and N_2. These ratios are essentially unchanged from the room temperature values of 8.0 and 7.2. Larger concentrations of DF required for sufficient fluorescence intensity and larger self-deactivation rates at low temperatures[9,10] resulted in larger V-V pumping of the upper levels. A second and slower decay rate was detectable at long times in the v = 3 fluorescence traces. However, the initial exponential decay rate persisted over a sufficient portion of the trace to allow the rate determination.

Table 1. Vibrational Deactivation Rates for DF(v) in D_2

T (K)	v	k(v) (μsec Torr)$^{-1}$	k(v)/k(1)	$\bar{k}^{vv}(v)$ (μsec Torr)$^{-1}$	$\bar{k}^{vv}(v)/\bar{k}^{vv}(1)$	$\Delta E(v)$ (cm^{-1})
200	1	2.75×10^{-2}	[1]	5.0×10^{-2}	[1]	-83.4
200	3	2.0×10^{-2}	0.73	13.3×10^{-2}	2.66	-264
295	1	2.05×10^{-2}	[1]	3.1×10^{-2}	[1]	-83.4
295	3	1.55×10^{-2}	0.76	5.6×10^{-2}	1.8	-264

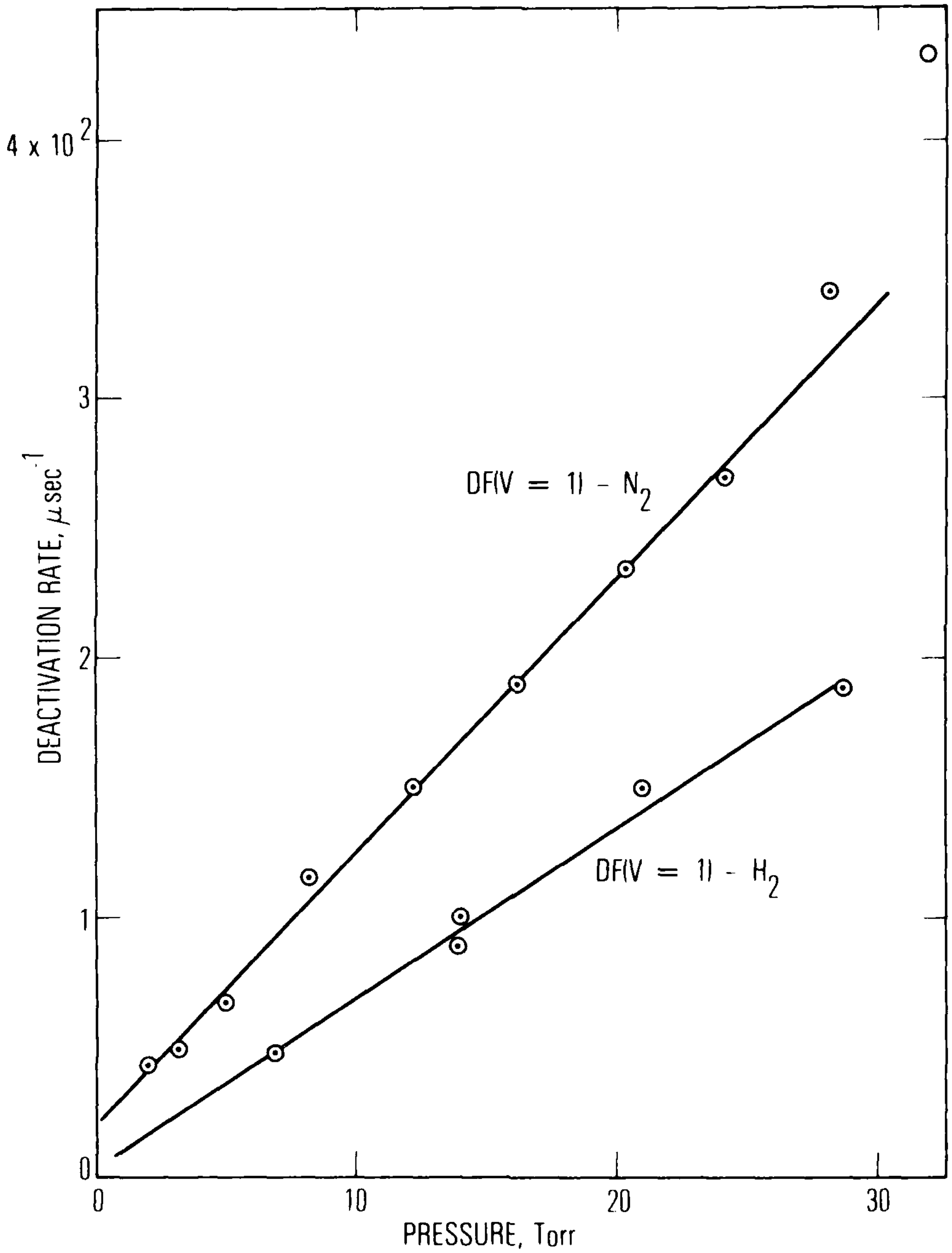

Figure 3. Deactivation Rates of DF(v = 1) in H_2 and N_2 at 200 K

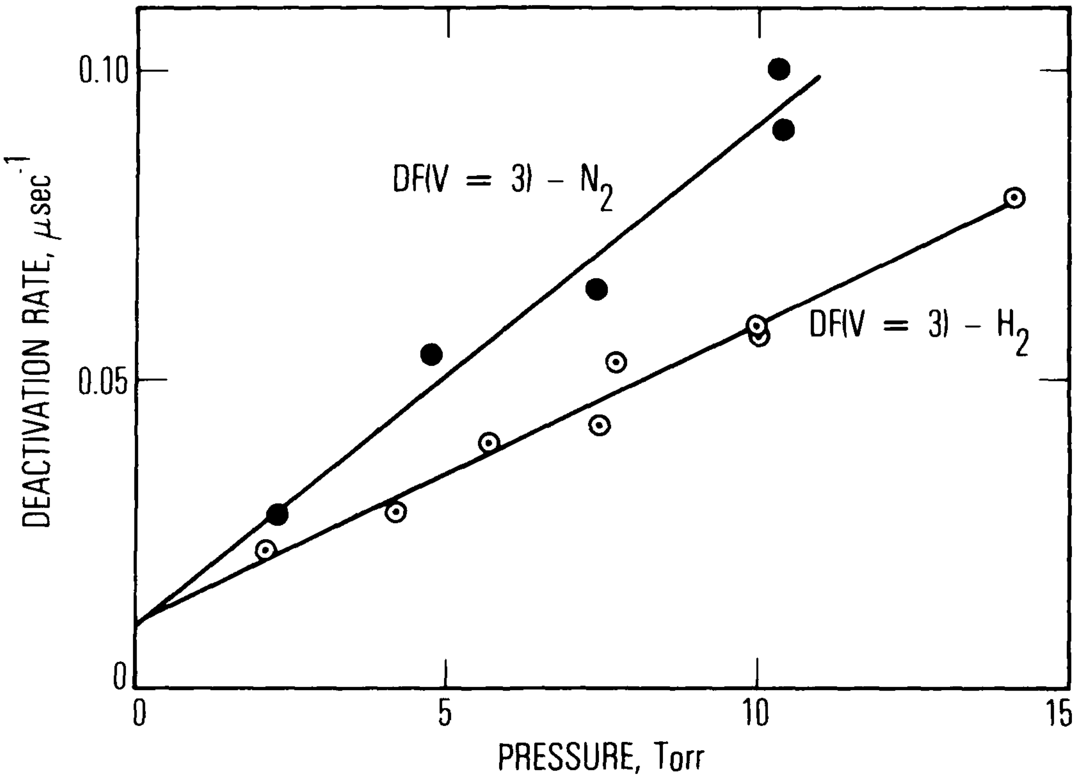

Figure 4. Deactivation Rates of DF(v = 3) in H_2 and N_2 at 200 K

Table 2. Vibrational Deactivation Rates for DF(v) at 200 K[a]

v	Chaperone		
	H_2	N_2	HF
1	$(6.5 \pm 0.9) \times 10^{-4}$	$(1.1 \pm 0.2) \times 10^{-3}$	
3	$(4.8 \pm 0.5) \times 10^{-3}$	$(8.1 \pm 2) \times 10^{-3}$	
k(v = 3)/ k(v = 1)	7.4	7.4	8

[a] k (μsec Torr)$^{-1}$

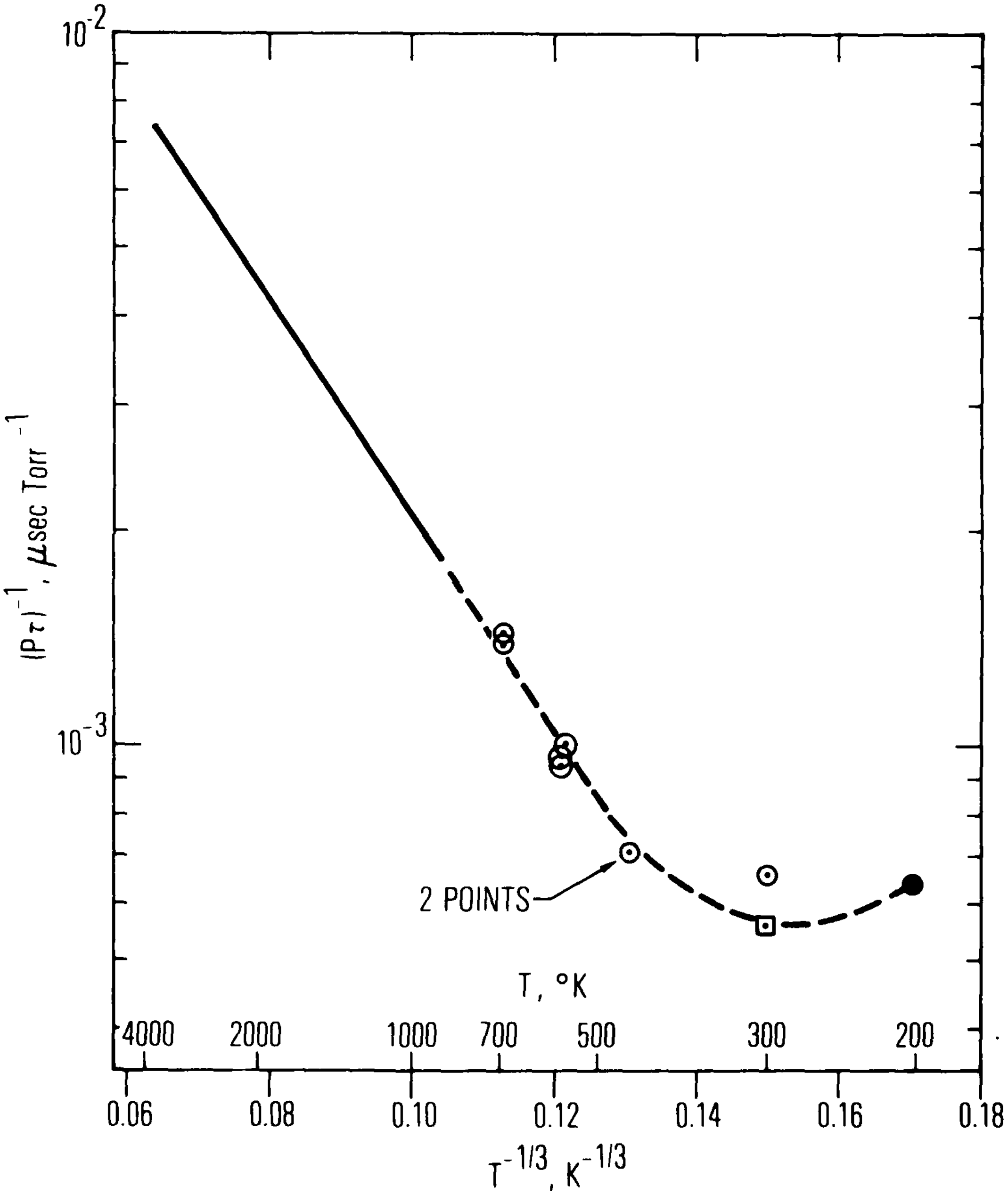

Figure 5. Deactivation Rate Coefficients for DF(v = 1) in H_2 vs Temperature
☐ Ref. 1, ○ Ref. 7, —— Ref. 8, ● present data

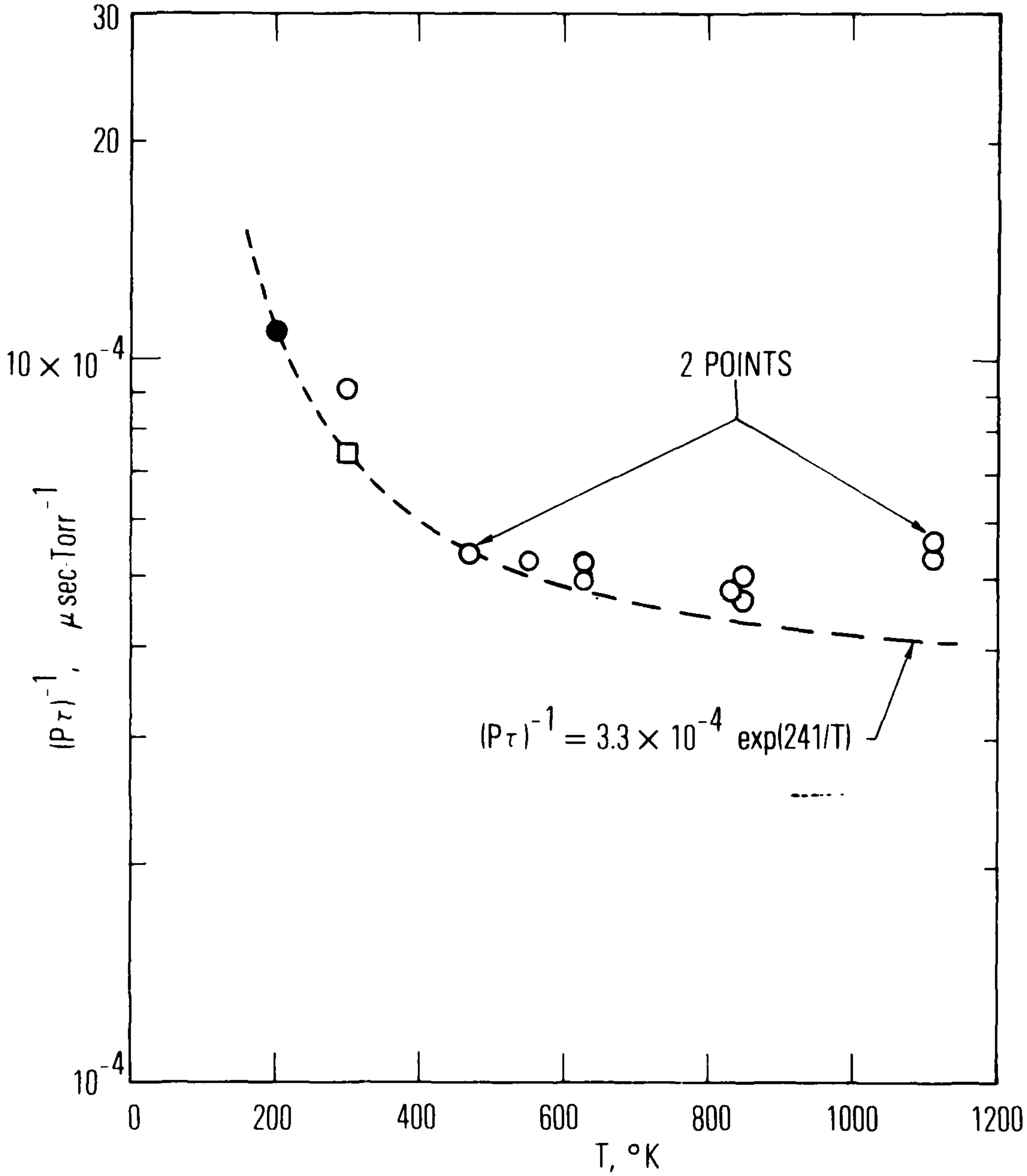

Figure 6. Deactivation Rate Coefficients for DF(v = 1) in N_2 vs Temperature □ Ref. 1, ○ Ref. 6, ● present data. The dashed line is described by $(P\tau)^{-1} = 3.3 \times 10^{-4} \exp(241/T)$ $(\mu\text{sec Torr})^{-1}$

C. VIBRATIONAL RELAXATION OF DF(v = 1 AND 3) IN HF

The relaxation times of DF(v) were measured in mixtures of DF, HF, and He 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 DF(v = 1) fluorescence decay was recorded with each DF(v = 3) fluorescence trace. The reciprocal decay times for DF(v = 3) are plotted in Fig. 7 versus those for DF(v = 1). The data should fall along a straight line, with a slope equal to the ratio of the DF(v = 3) and DF(v = 1) deactivation rates. The data show significant curvature at DF(v = 1) rates above approximately 1×10^{-2} $(\mu\mathrm{sec})^{-1}$. Lucht and Cool[9] and Hancock and Saunders[10] observed pressure effects on DF self-deactivation rates and HF(v = 1)-DF transfer rates at temperatures near 200 K. If the rate of DF(1) relaxation by HF is taken to be 8×10^{-2} $(\mu\mathrm{sec\ Torr})^{-1}$ (Ref. 9), the deactivation rate of 1×10^{-2} $\mu\mathrm{sec}^{-1}$ then corresponds to an HF partial pressure of 0.120 Torr which is within a factor of 2 of the pressures reported in Refs. 9 and 10 for nonlinear effects. These nonlinear effects have been ascribed to quenching by polymers of HF(DF) that form even at low pressures at these low temperatures.

Data in Fig. 7 have a slope of 8.0 ± 1.0 if a straight line is assumed to pass through the origin and the data points for the lowest pressures are weighted most heavily. The ratio of 8.0 is comparable to the value of 8.3 obtained at 295 K.[1]

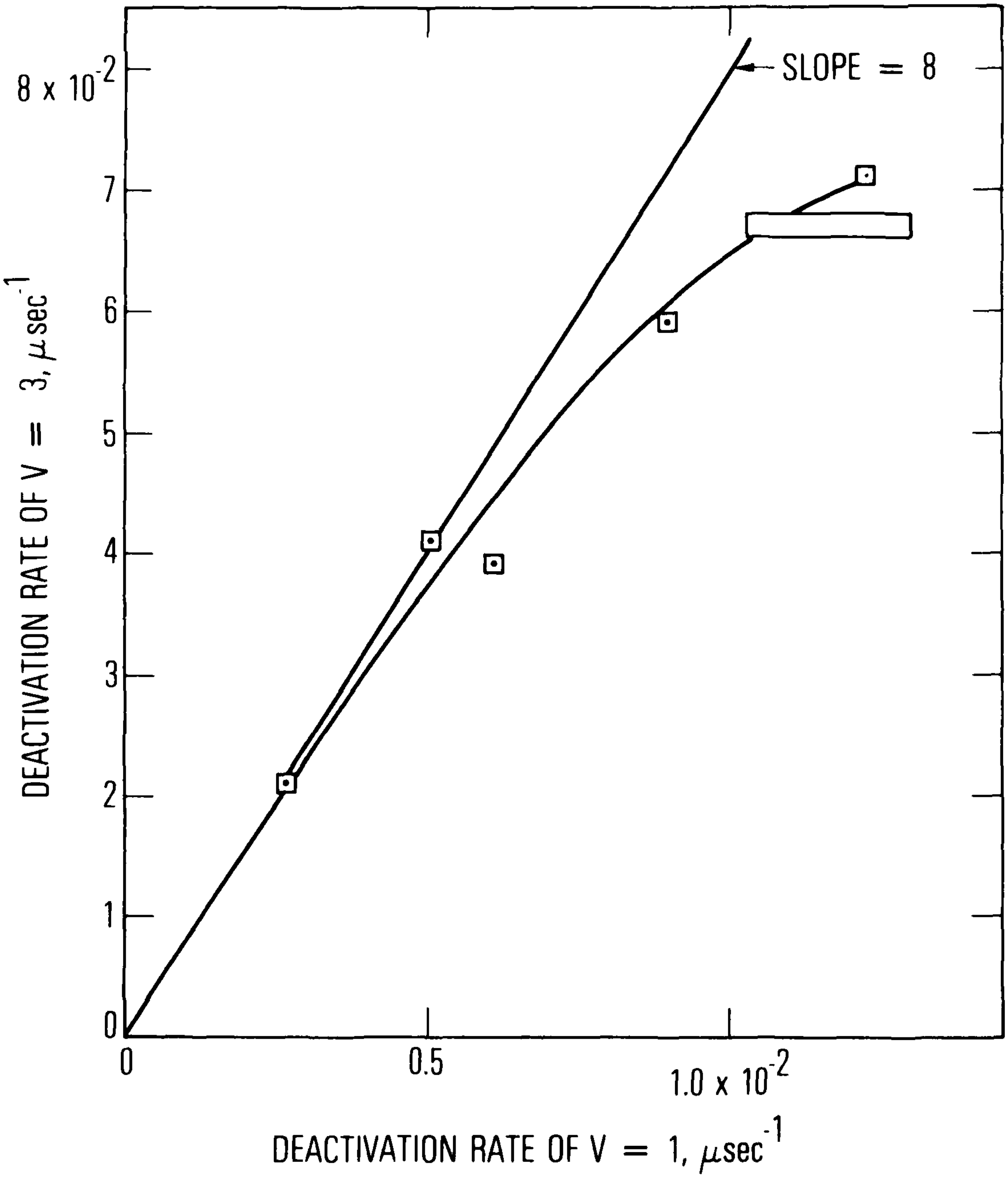

Figure 7. Deactivation Rates of $DF(v = 3)$ by HF vs Deactivation Rates of $DF(v = 1)$ by HF at 200 K

IV. DISCUSSION

The results of the present study show no effect of temperature on the ratio of the deactivation rate for DF(v = 3) to that for DF(v = 1) in H_2, N_2, and HF. Within the experimental uncertainties, the measured ratios at 200 K are the same as the values reported[1] for 295 K. In a previous study,[2] the v-dependence of HF deactivation rates was essentially the same at 200 and 295 K for N_2 and D_2. Ideal harmonic oscillators have deactivation rates that scale linearly with v independently of T for V-T deactivation, as well as for resonant V-V deactivation. However, HF and DF are not harmonic oscillators, and the V-V processes that can contribute to the deactivation have energy mismatches. The deactivation rate coefficients for HF and DF increase more rapidly with v than the linear v-dependence of harmonic oscillators. The rate coefficients for HF(v = 1,2, and 3) deactivation by diatomic molecules were reported to scale as $v^{2.7 \pm 0.2}$ in Refs. 2 and 11. A slightly slower scaling of $v^{2.3}$ was reported by Kwok and Wilkins.[5] Douglas and Moore[12,13] and Lampert[14] performed experiments at room temperature in which HF was pumped directly to HF(v = 4) with a pulsed laser. They obtained rate coefficients from the fluorescence decay of HF(v = 4) that were faster than the HF(v = 3) decay rate by a factor of 2.5 to 2.8 with HF and D_2 collision partners. These rate coefficients scaled with v at least as fast or faster than the $v^{2.7 \pm 0.2}$ reported for v = 1 - 3. The rate coefficients for DF(v) scaled as $v^{1.9 \pm 0.1}$ for v = 1 - 4[1], which was somewhat slower than the HF scaling.

It was concluded in Ref. 2 that the molecular and spectroscopic properties of the collision partner did not affect the v-dependence of the deactivation rates, although they affected the rate coefficients for DF(v = 1). In the study of HCl and DCl relaxation, Chen and Moore[15] concluded that the dominant deactivation process was the conversion of the vibrational energy to rotational energy of the initially excited molecule. For the Chen and Moore model, the scaling with v could be expected to depend on the anharmonicity of the excited molecule and its rotational properties and not on the properties of the collision partner. Rotational populations are shifted toward smaller values of J when DF is cooled to 200 from 295 K. However, this shift did not have a measurable effect on the v-dependence of the deactivation rates, although it may have affected the deactivation rates for DF (v = 1) and DF(v = 3) in the same proportion.

The rates of DF(1) deactivation by D_2 shown in Fig. 2 are fitted with the solid curve described by the expression $(P\tau)^{-1} = 0.254\ T^{-1/2} \exp(85/T)$ (μsec Torr)$^{-1}$. The rate coefficient for the reverse process, $D_2(v = 1) + DF(v = 0)$ can be calculated from this expression and the energy mismatch to be $(P\tau)^{-1} = 0.254\ T^{-1/2} \exp(205/T)$. An exothermic exchange probability of $1.45 \times 10^{-3} \exp(205/T)$ is obtained for collision diameters of 2.9 and 2.5 Å for D_2 and DF, respectively. In Ref. 2, the probability of HF(v = 1) deactivation by H_2 was found to be Probability = $1.57 \times 10^{-3} \exp(-84/T)$ or $1.57 \times 10^{-3} \exp(205/T)$ for the $H_2(v = 1) + HF(v = 0)$ exothermic exchange. (The energy mismatch between HF(1) and $H_2(1)$ in the zero rotational level is 201 cm^{-1}.) Therefore, the exothermic exchange probabilities for $D_2(1) + DF(0)$ and $H_2(1) + HF(0)$ are the same within 10% between 200 and 1000 K. The exp(205/T) temperature dependence of the exothermic probabilities can be explained in a crude way by attractive forces between HF and H_2. (A reasonable assumption for the Lennard-Jones parameter, ε/k, for HF, based on values for other hydrogen halides, leads to an intermolecular force constant for HF-H_2 within 25% of the experimental value of 205 K.)[16]

Hopkins, Chen, and Sharma[17] measured rate coefficients for the deactivation of HCl(v = 1) by D_2 at 196, 296, and 343 K. The probability of the exchange decreased with increasing temperature. An approximate fit to the three data points resulted in a temperature dependence of exp(189 ± 30/T) for the endothermic exchange probability and a temperature dependence of exp(344/T) for the exothermic exchange $D_2(1) + HCl(0)$. This corresponds to a negative activation energy of 680 cal/mole, somewhat larger than the 400 cal/mole for the H_2-HF and D_2-DF exchanges. Hopkins et al. performed first order calculations based on quadrupole-quadrupole and dipole-quadrupole interactions and obtained agreement with the experimental data within about 40%.

H_2 deactivates DF(v = 1) by a V-R, T mechanism with no V-V contributions. Between 500 and 4000 K, the relaxation times (Pτ), can be represented by (Pτ) = 14 exp(35.0 $T^{-1/3}$) μsec Torr. At temperatures near 295 K, the relaxation rate has a minimum and increases at lower temperatures. However, data in Fig. 5 are insufficient to establish a meaningful description of the low-temperature dependence.

N_2 can deactivate DF(v = 1) by both V-V and V-R, T processes. Data in Fig. 6 indicate a minimum in the rate coefficient between 600 and 1000 K. Rate coefficients obtained in shock tube experiments[8] at temperatures above 1300 K increased with temperature. Below 800 K, the probability of DF(v = 1) deactivation by N_2 can be described by Probability = 4.5×10^{-5} $(T/295)^{1/2}$ exp(241/T) or $(P\tau)^{-1}$ = 3.3×10^{-4} exp(241/T)$(\mu\text{sec Torr})^{-1}$.

In summary, the v-dependence of the rate coefficients for DF(v) deactivation by diatomic molecules appears to be the same at 200 and 295 K. A scaling law of $v^{1.9 \pm 0.1}$ brackets the data for N_2, HF, and H_2 at these two temperatures. The probability of DF(v = 1) deactivation in a collision with a diatomic molecule appears to increase with decreasing temperature below approximately 250 to 300 K regardless of whether the deactivation is a V-R, T, or V-V process.

REFERENCES

1. J. F. Bott, J. Chem. Phys. 70, 4123 (1979).
2. J. F. Bott and R. F. Heidner, J. Chem. Phys. 72, 3211 (1980).
3. J. F. Bott and R. F. Heidner, J. Chem. Phys. 68, 1708 (1978).
4. J. J. Hinchen, J. Chem. Phys. 59, 233 (1973).
5. M. A. Kwok and R. L. Wilkins, J. Chem. Phys. 63, 2453 (1975).
6. J. F. Bott, J. Chem. Phys. 60, 427 (1974).
7. J. F. Bott, J. Chem. Phys. 61, 2530 (1974).
8. J. F. Bott and N. Cohen, J. Chem. Phys. 58, 934 (1973).
9. R. A. Lucht and T. A. Cool, J. Chem. Phys. 63, 3962 (1975).
10. J. K. Hancock and A. W. Saunders, J. Chem. Phys. 65, 1275 (1976).
11. J. F. Bott, J. Chem. Phys. 65, 4239 (1976).
12. D. J. Douglas and C. B. Moore, Chem. Phys. Letters 57, 485 (1978).
13. D. J. Douglas and C. B. Moore, J. Chem. Phys. 70, 1769 (1979).
14. J. K. Lampert, G. M. Jurisch, and F. F. Crim, Chem. Phys. Letters 71, 258 (1980).
15. H. L. Chen and C. B. Moore, J. Chem. Phys. 54, 4072 (1971).
16. N. Cohen, The Aerospace Corporation, El Segundo, California, personal communication (June, 1980).
17. B. M. Hopkins, H. L. Chen, and R. D. Sharma, J. Chem. Phys. 59, 5758 (1973).

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