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Publication Date

1978-09-01

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September 1978

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VIBRATIONAL RELAXATION OF HF($v = 3, 4$) by H_2 , D_2 , and CO_2
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(Received)

The vibrational relaxation of HF($v = 3, 4$) in H_2 , D_2 and CO_2 has been studied by pumping HF directly from $v = 0$ to $v = 4$. The relaxation rates at 293 ± 2 K of HF($v = 3$) and HF($v = 4$) were found to be $k_T^3(H_2) = (3.1 \pm 0.6) \times 10^{-13}$ and $k_T^4(H_2) = (4.7 \pm 1.2) \times 10^{-13}$ in H_2 , $k_T^3(D_2) = (1.34 \pm 0.26) \times 10^{-12}$ and $k_T^4(D_2) = (3.34 \pm 0.60) \times 10^{-12}$ in D_2 , and $k_T^3(CO_2) = (1.0 \pm 0.16) \times 10^{-11}$ and $k_T^4(CO_2) = (2.25 \pm 0.43) \times 10^{-11}$ in CO_2 respectively, all in $cm^3 \text{ molec}^{-1} \text{ sec}^{-1}$. The observed relaxation rate for HF($v = 4$) in CO_2 did not depend on the rotational state which was initially excited for $J = 0 - 5$.

I. INTRODUCTION

The vibrational relaxation of HF continues to be of interest for theoretical and practical reasons. Laser-induced fluorescence experiments have given much information on the relaxation of the first excited vibrational level ($v = 1$).^{1 - 7} The relaxation of higher levels has been explored mainly in studies of the quenching of fluorescence from HF($v > 1$) formed in chemical reactions. Poole and Smith have investigated collisions of HF($v = 2 - 7$) and DF($v = 3 - 5$) with a wide range of collision partners in this way.^{8, 9} Kwok and Cohen have studied relaxation of HF($v = 1 - 3$) by several polyatomic molecules in a fast flow tube fluorescence experiment.¹⁰ Brown et al have reported relative rates of relaxation of HF($v = 1 - 6$) and DF($v = 1 - 4$) by CO₂ in chemiluminescence experiments done at much lower pressures than the two earlier studies.¹¹

The application of the laser-induced fluorescence technique to the study of these higher levels has had a slower development. Bott has used sequential pumping to measure the relaxation rates of HF in levels $v = 1 - 3$ by H₂, N₂ and CO₂.¹² Recently we have reported rate constants for the relaxation of pure HF($v = 3, 4$) obtained by pumping HF directly from $v = 0$ to $v = 4$ with a pulsed dye laser.¹³ In this paper we describe the extension of our method to the measurement of the relaxation rate of HF($v = 3, 4$) by H₂, D₂ and CO₂.

II. EXPERIMENTAL

The apparatus has been described previously.¹³ Briefly, a pulsed dye laser (~ 2 mJ pulse, ~ 0.2 cm⁻¹ linewidth) excited HF directly from $v = 0$ to $v = 4$. Second overtone fluorescence ($\Delta v = 3$) from either $v = 3$ or $v = 4$ was detected by a photomultiplier tube. Typically 2000 laser shots were averaged to give a fluorescence decay curve.

Gases used and stated purities were Pacific Oxygen High Purity hydrogen, 99.999%, Matheson prepurified argon 99.998%, Matheson C.P. grade deuterium 99.5% and Matheson bone-dry carbon dioxide 99.8%. The HF handling procedure has been described in ref. 13.

For the experiments to be described here both the HF and the added quencher were flowed through the fluorescence cell (flow speed ~ 10 cm sec⁻¹). The total cell pressure ranged from 0.5 to 10.0 Torr. The flowline for the added quencher M was a standard glass and greaseless stopcock vacuum system. All quenching gases were passed through a glass coil immersed in a cold bath. For the experiments with H₂, D₂ and Ar the coil was held at 77 K and for CO₂ at 195 K. Flows were constant to $\pm 2\%$ while a fluorescence decay curve was recorded. All experiments were performed at room temperature, 293 ± 2 K.

The flows of both HF and added quencher were measured with Hastings-Raydist electronic flowmeters. The flow of added quencher (f_M) was measured with either a 0 - 20

standard cc/min or 0 - 100 standard cc/min meter, and the flow of HF(f_{HF}) with a 0 - 5 standard cc/min monel meter. The mole fraction of HF in the resulting gas mixture was simply given by $X_{\text{HF}} = f_{\text{HF}}/(f_{\text{M}} + f_{\text{HF}})$. This method avoids the necessity of any approximate gas dynamic correction.⁶

The relaxation rate of a vibrational level v ($v = 3$ or 4) is given by $1/\tau = p[k_{\text{T}}^{\text{V}}(\text{M}) + X_{\text{HF}}(k_{\text{T}}^{\text{V}}(\text{HF}) - k_{\text{T}}^{\text{V}}(\text{M}))]$ where τ is the measured lifetime, p is the total pressure, $k_{\text{T}}^{\text{V}}(\text{M})$ is the total rate constant for relaxation of level v by the added quencher M including both V - V and V - T, R processes, and $k_{\text{T}}^{\text{V}}(\text{HF})$ is the total rate constant for relaxation of level v by HF (both V - V and V - T, R). A plot of $1/p\tau$ vs X_{HF} , then, gives a line with intercept $k_{\text{T}}^{\text{V}}(\text{M})$ and slope $k_{\text{T}}^{\text{V}}(\text{HF}) - k_{\text{T}}^{\text{V}}(\text{M})$.

The 0 - 20 standard cc/min and 0 - 100 standard cc/min flowmeters were calibrated by measuring the pressure drop in a known volume. The HF flowmeter was not calibrated in this way. The manufacturer's stated calibration was assumed and the relaxation rate of HF($v = 4$) in HF/Ar mixtures was measured. The resulting plot of $1/p\tau$ vs X_{HF} for HF in Ar is shown in Fig. 1. A least square fit to the data gave $1/p\tau = (1.98 \pm 4.74) \times 10^3 + (2.32 \pm 0.28) \times 10^6 X_{\text{HF}} \text{ sec}^{-1} \text{ Torr}^{-1}$. The corresponding HF self-relaxation rate $k_{\text{T}}^4(\text{HF}) = (7.0 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ is in excellent agreement with our earlier result¹³ of $(7.2 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$, indicating that the assumed HF flowmeter calibration was indeed correct. In fact, for every added quencher this

assumed calibration gave HF - HF rates in agreement with our previous work.

In each case a least square fit to the data was used to calculate $k_T^V(M)$ and the standard deviation in $k_T^V(M)$. The value of $k_T^V(M)$ is very insensitive to the flowmeter calibration since the rate constant is determined by a linear extrapolation to $X_{HF} = 0$. Our error estimates are two standard deviations of the mean plus an additional 2% to account for uncertainty of the pressure.

III. RESULTS

A. HF - H₂

Plots of $1/p\tau$ vs X_{HF} for HF($v = 3$) and HF($v = 4$) in H₂ are shown in Fig. 2. The open circles are the result of one set of experiments. The solid circles, triangles, and squares are the results of experiments each done on separate days. For these latter experiments the flows of HF and H₂ were held constant and 4 or 5 fluorescence decay curves were recorded. The resulting lifetimes in each case were averaged to give the points on the graph. The error bars on the graph are one standard deviation. Least square fits to the data give $1/p\tau = (1.03 \pm 0.16) \times 10^4 + (9.12 \pm 1.32) \times 10^5 X_{HF} \text{ sec}^{-1} \text{ Torr}^{-1}$ for $v = 3$ and $1/p\tau = (1.54 \pm 0.36) \times 10^4 + (2.2 \pm 0.34) \times 10^6 X_{HF} \text{ sec}^{-1} \text{ Torr}^{-1}$ for $v = 4$. This gives $k_T^3(H_2) = (3.1 \pm 0.6) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ and $k_T^4(H_2) = (4.7 \pm 1.2) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$.

Table I compares these rate constants with the work of others. The $v = 3$ rate determined by Bott¹² is in good agreement with our result. Our rates are $\sim 2 \times$ those determined by Poole and Smith.⁸ Both the laser-induced fluorescence experiments and the chemiluminescence data summarized in Table I indicate that the relaxation rate of HF(v) by H_2 at first decreases with vibrational level (to $v = 3$) and then increases. This has been interpreted as reflecting the increasing endothermicity of the V - V process (hence decreasing rate) and an increasing V - T, R rate.⁸

B. HF - D₂
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Figure 3 shows plots of $1/p\tau$ vs X_{HF} for HF($v = 3$) and HF($v = 4$) in D₂. Three separate experiments were done on separate days for each vibrational level (experiments 1 - 6). Some small systematic error is apparent in Fig. 3 in that the results of experiment 2 lie slightly lower than the other data (experiments 1 and 3). To determine a value of $k_T^V(D_2)$ each experiment was least square fit separately and the values of the intercepts averaged to give $k_T^3(D_2) = (1.34 \pm 0.26) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1} ((4.42 \pm 0.76) \times 10^4 \text{ sec}^{-1} \text{ Torr}^{-1})$ and $k_T^4(D_2) = (3.34 \pm 0.60) \times 10^{-12} \text{ cm}^2 \text{ molec}^{-1} \text{ sec}^{-1} ((1.10 \pm 0.16) \times 10^5 \text{ sec}^{-1} \text{ Torr}^{-1})$. The error estimate is two standard deviations of the mean¹⁴ plus the 2% uncertainty for pressure. These uncertainties encompass the values of $k_T^V(D_2)$ determined in each separate experiment. The lines drawn in Fig. 3 have as intercepts these values and were drawn

with a slope which gives an HF self relaxation rate agreeing with our previous work.¹³

Table II compares these HF - D₂ rates with the results of others. No laser-induced fluorescence experiments have been reported for vibrational levels $v > 1$. Again our rate constants are $\sim 2 \times$ those of Poole and Smith. The results of Table I taken together indicate that energy transfer from HF to D₂ increases rapidly with vibrational quantum number. This reflects a V - V process coming increasingly closer into resonance.⁸

It has been suggested¹⁵ that a four-center reaction is possible between HF($v \geq 3$) and D₂ to form DF and HD. We have looked for possible reaction between HF($v = 4$) and H₂, rather than D₂, since the total removal rate (possible reaction + relaxation) is about 7 times less in the case of H₂. Thus any chemical reaction would be a greater fraction of the total removal rate. A four-center reaction between HF and H₂ would produce chemically indistinguishable products. However, chemical reaction would be expected to produce product HF over a range of vibrational states $v = 0 - 4$. Thus chemical reaction would appear as multiquantum energy transfer from HF($v = 4$) in these experiments.

Integrated fluorescence intensities were measured at a mole fraction $X_{\text{HF}} = 0.0052$ to test for multiquantum energy transfer in HF - H₂ relaxation. It was found that the fraction of HF leaving $v = 4$ and becoming $v = 3$ was

1.03 ± 0.43 . After correcting for HF self-relaxation a multiquantum transfer rate (reaction + relaxation) of $(- 0.2 \pm 2.8 \times 10^{-13})$ is calculated. Thus no evidence for reaction is found.

C. HF - CO₂

Two separate experiments were performed for both HF($v = 3$) and HF($v = 4$) in CO₂ (experiments 7 - 10). The results are shown as plots of $1/p\tau$ vs X_{HF} in Fig. 4. The results of both experiments were fit to a single line in each case. For $v = 3$ this gave $1/p\tau = (3.34 \pm 0.48) \times 10^5 + (5.3 \pm 3.2) \times 10^5 \text{ sec}^{-1} \text{ Torr}^{-1}$ and for $v = 4$ $1/p\tau = (7.4 \pm 1.3) \times 10^5 + (2.1 \pm 0.7) \times 10^6 \text{ sec}^{-1} \text{ Torr}^{-1}$, and hence $k_T^3(\text{CO}_2) = (1.01 \pm 0.16) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ and $k_T^4(\text{CO}_2) = (2.25 \pm 0.43) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$.

The chemiluminescence experiments of Brown et al.¹¹ indicate that for high vibrational levels ($v = 6$ in their experiment) the vibrational relaxation rate may begin to compete with the rotational relaxation rate in HF - CO₂ collisions. We have pumped each of the rotational levels $J = 0 - 5$ in $v = 4$ in an HF - CO₂ mixture with $X_{\text{HF}} = 0.085$. The same relaxation rate was observed to within the $\pm 20\%$ uncertainty of this experiment. No systematic trend of rate with initial J was apparent. We conclude that rotational disequilibrium did not affect our rate. This is a consequence of the lower vibrational relaxation rate of $v = 4$ compared

to $v = 6$ (Table II) and the higher mole fraction of HF in our experiments. The rotational relaxation rate of HF by HF is ~ 10 x faster than that by CO_2 (Ref. 16 and references therein). Thus for our mixture at $X_{\text{HF}} = 0.085$ we estimate that the rotational relaxation rate is > 10 x the vibrational relaxation rate.

Table II compares these results with the work of others. The rate determined by Bott¹² for $v = 3$ is in good agreement with this work. The rate of Kwok and Cohen¹⁰ is not in good agreement and reflects the difficulty of modelling fast flow tube experiments. The relative rates for $v = 3$ and $v = 4$ measured by Brown et al.¹¹ ($k_T^4/k_T^3 = 1.8$) are in fairly good agreement with this work ($k_T^4/k_T^3 = 2.2 \pm 0.70$).

The chemiluminescence work of Airey and Smith⁷ and Poole and Smith^{8, 9} again give rates which are significantly less than ours. For every collision partner the rate constants determined in our laser-induced fluorescence experiments and in the laser-induced fluorescence work of Bott are roughly twice those obtained by Poole and Smith. As discussed in Ref. 13, this may be a consequence of some additional undetected relaxation in the absence of quencher in the work of Poole and Smith. This would lead to calculated absolute rates which are too small. Both H_2 and D_2 alter the chemistry of the chemiluminescent reaction adding a further complication to the determination of the rate of HF relaxation by these molecules. Nevertheless the trend of relaxation rate with

vibrational level obtained from the experiments of Poole and Smith is in good agreement with both the laser-induced fluorescence experiments and the much lower pressure chemiluminescence work of Brown et al. in every case. Thus the data of Poole and Smith are likely to give a fair description of the relative rates of relaxation of HF in a wide range of vibrational levels and with a wide range of collision partners.

Dillon and Stephenson¹⁶ have performed extensive theoretical calculations of the HF and DF - CO₂ relaxation rates. The absolute rate constants calculated for $v = 3$ and $v = 4$ are in reasonable agreement with our measured rates. However, the theory predicts approximately equal relaxation rates for $v = 4$ and $v = 5$. The experiments of Brown et al. and Poole and Smith both indicate that $v = 5$ relaxes significantly faster than $v = 4$ (Table II). Thus the success of the theory for the $v = 3$ and 4 rates may be somewhat fortuitous.

The relatively small number of electrons in the HF-H₂ system makes an ab initio calculation of a realistic potential energy surface possible. Billing and coworkers have developed a scattering theory which appears to provide a good description of HF vibrational relaxation.¹⁷ This method could reasonably be applied to HF - H₂ and HF - D₂ collisions. The experiments reported here, combined with those of Poole and Smith,^{8, 9} would supply a good test of such a calculation.

ACKNOWLEDGMENTS

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We thank the Division of Advanced Systems Materials Production, Office of Advanced Isotope Separation, U.S. Department of Energy and the U.S. Army Research Office, Triangle Park, NC for support of this work. D.J.D. thanks the National Research Council of Canada for a postdoctoral fellowship and the Royal Society of Canada for a scholarship.

REFERENCES

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- ¹J.K. Hancock and W.H. Green, J. Chem. Phys. 57, 4515 (1972).
- ²J.F. Bott and N. Cohen, J. Chem. Phys. 58, 4539 (1973).
- ³J.J. Hinchey, J. Chem. Phys. 59, 233 (1973).
- ⁴R.A. Lucht and T.A. Cool, J. Chem. Phys. 60, 1026 (1974).
- ⁵R.A. Lucht and T.A. Cool, J. Chem. Phys. 63, 3962 (1975).
- ⁶J.F. Bott, J. Chem. Phys. 61, 3414 (1974) and references therein.
- ⁷J.R. Airey and I.W.M. Smith, J. Chem. Phys. 57, 1669 (1972).
- ⁸P.R. Poole and I.W.M. Smith, J. Chem. Soc. Faraday II, 73, 1434 (1977).
- ⁹P.R. Poole and I.W.M. Smith, J. Chem. Soc. Faraday II, 73, 1447 (1977).
- ¹⁰M.A. Kwok and N. Cohen, J. Chem. Phys. 61, 5221 (1974).
- ¹¹R.D.H. Brown, D.J. Douglas, and J.C. Polanyi, J. Chem. Soc. Faraday II, in press (1978).
- ¹²J.F. Bott, J. Chem. Phys. 65, 4239 (1976).
- ¹³D.J. Douglas and C.B. Moore, Chem. Phys. Lett., in press (1978).
- ¹⁴i.e. $\sigma = 1/3(\sigma_1^2 + \sigma_2^2 + \sigma_3^2)^{1/2}$ where $\sigma_1, \sigma_2, \sigma_3$ are the standard deviations of the individual intercepts.
- ¹⁵R.S. Chang and G.J. Wolga, I.E.E.E. J. Quant. Electronics QE-10, 702 (1974).

- ¹⁶T.A. Dillon and J.C. Stephenson, J. Chem. Phys. 58. 2056
(1973).
- ¹⁷G.D. Billing and L.L. Poulsen, J. Chem. Phys. 68. 5128
(1978).

TABLE I. Comparison of HF - H₂ and HF - D₂ relaxation rates
(cm³ molec⁻¹ sec⁻¹ x 10¹³).

Reference	v=1	v=2	v=3	v=4	v=5	v=6	v=7
<u>H₂</u>							
Poole and Smith ⁸	-	2.1	1.5	2.1	4.9	9.9	16
Bott ¹²	4.32±0.45						
Hancock and Green ¹	7.3 ±0.9						
Hinchen ³	8.5 ±2.2						
Bott and Cohen ²	5.16± .30						
This work			3.1±0.6	4.7±1.2			
<u>D₂</u>							
Poole and Smith ⁸	-	2.6	5.9	12	31	82	~61
Hancock and Green ¹	1.12±0.11						
Bott and Cohen	0.94±0.18						
This work			13.4±2.6	33.4±6.0			

TABLE II. Comparison of HF - CO₂ rates (cm³ molec⁻¹ sec⁻¹ x 10¹²).

Reference	v=1	v=2	v=3	v=4	v=5	v=6	v=7
Poole and Smith ⁸	-	3.4	7.0	12.5	27	35	32
Airey and Smith ⁷	1.1	4.4	6.4	12.0	≥20		
Bott and Cohen ²	(1.1±.06)						
Kwok and Cohen ¹⁰	0.77	2.9	3.1				
Lucht and Cool ⁴	2.1±.15						
Hancock and Green	1.8±.1						
Bott ¹²	1.2±.1						
This work			10.1±1.6	22.5±4.3			
Brown et al. ^{11, a}		8	10	18	27	31	
Dillon and Stephenson ^{17, b}	2.7	8.8	13.5	20.2	20.2		

^arelative rates only.

^btheoretical rates.

Figure 1. $1/p\tau$ vs $X_{\text{HF}}(v = 4)$ in argon.

Figure 2. $1/p\tau$ vs X_{HF} for $\text{HF}(v = 3)$ and $\text{HF}(v = 4)$ in H_2O ; average of four points $\bigcirc$; average of 5 points Δ ; average of 5 points $\square$.

Figure 3. $1/p\tau$ vs X_{HF} for $\text{HF}(v = 3)$ and $\text{HF}(v = 4)$ in D_2 . Experiment 1 Δ ; experiment 2 $\square$; experiment 3 $\square$; experiment 4 Δ ; experiment 5 $\bigcirc$; experiment 6 $\bigcirc$.

Figure 4. $1/p\tau$ vs X_{HF} for $\text{HF}(v = 3)$ and $\text{HF}(v = 4)$ in CO_2 . Experiment 7 Δ ; experiment 8 $\bigcirc$; experiment 9 Δ ; experiment 10 $\bigcirc$.

XBL 789-10846

XBL 789-10847

XBL 789-10848

XBL 789-10849

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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