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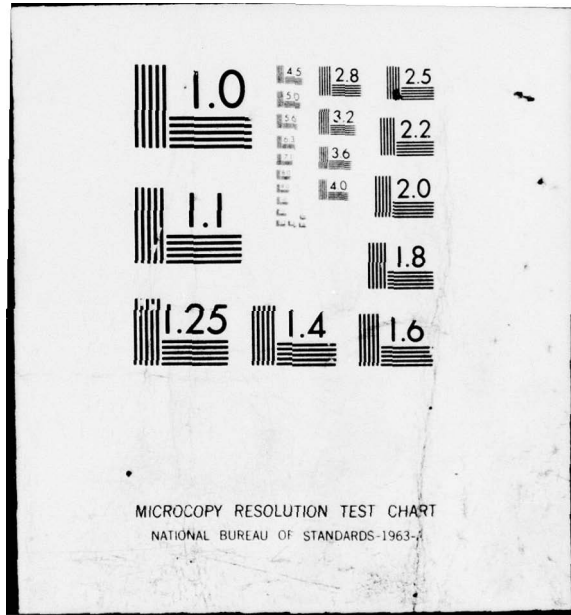
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Progress in the Study of Collisional Quenching of DF ($v \leq 8$) by Use of a Large Flow Tube

Aerophysics Laboratory
The Ivan A. Getting Laboratories
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El Segundo, Calif. 90245

18 August 1977

Interim Report

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Prepared for
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) An approach to studying collisional quenching rate coefficients $K_M(v)$ of very high vibrational levels of DF(v) for several chaperones M is reported. Typically, M = HF, DF, CO ₂ . Some of the physics represented by $K_M(v)$ are discussed by relating $k_M(v)$ to a summation involving the cross sections of energy transfer. <i>K sub M (v)</i> 409 944 <i>James</i>		

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I. INTRODUCTION

By means of the experimental approach used in determining the quenching of HF(v) with HF, DF, or CO₂, studies were attempted with DF(v) for the same chaperones. In this work-in-progress report, the DF(v) and HF(v) experiments are compared, and the difficulties encountered in studying DF(v) are noted. Also discussed are the physical implications of deduced quenching coefficients $K_M(v)$ for processes HF(v) + M or DF(v) + M, determined with these or laser-induced fluorescence experiments.

II. EXPERIMENT

The experiment was identical to that previously reported by Kwok and Cohen¹ with the following exceptions. For achievement of very high v levels such as DF($v = 7, 8$), the very exoergic reaction $F + DI$ was employed. Approximately 65 kcal/mol of energy are available in the reaction, and, analogously to the reaction $F + HI$, virtually all of this excess energy was converted into the vibrational energy of DF. The flow-tube method was the same as that used previously; the reactive flow was placed in the large-diameter, fast-flow, 1-Torr tube in the so-called steady state, and steady-state analysis was performed for deduction of the collisional quenching coefficients.

A second major difference between the two experiments was the method used to detect the chemiluminescence. Success with the steady-state method demands minimal concentrations in the species to be observed. In the DF(v) experiment, a very sensitive cooled Ge detector system was used for the 1.2- to 1.7- μm region; a cooled PbS PV detector was used for the 1.7- to 2.1- μm region.

In the study of DF(v), four types of problems arose: those associated with the detector, the DF spectroscopy, the DF versus HF spectroscopy, and the chemistry.

From Table 1, it can be seen that for DF fundamental and first overtone bands, an optimized detector with good D^* is not available. InSb peaks at 5 μm ; PbS, at 3 μm . For the second overtone, the Ge detector system performs well at equivalent D^* of $5 \times 10^{13} \text{ cm Hz}^{1/2} \text{ watt}^{-1}$, but interference from impurity HF emissions limits the detector's usefulness.

Generally, DF bands are more overlapping, and the A-coefficients are below those of HF by a factor of 5. For very high DF levels, however, there is some recovery, as shown in Table 2.

¹M. A. Kwok and N. Cohen, Quenching of Upper Vibrational Levels of HF($v \leq 6$), The Aerospace Corporation, El Segundo, Calif. (to be published).

Table 1. DF Emission Wavelength Positions

DF emissions		Detector
$\Delta v = 1$	3.5-4.2 μm	Cooled InSb
$\Delta v = 2$	1.8-2.1 μm	Cooled PbS
$\Delta v = 3$	1.2-1.4 μm	Ge system

Table 2. Radiative Decay Rates

Band	Δv	DF	HF
3-2	1	129	398
3-1	2	14	68
3-0	3	0.16	1.2
8-5	3	8.6	
8-6	2	109	

As detection improves for the DF(v) higher overtone emissions, any impurity HF(v) present tends to neutralize this advantage. At the 1.2- to 1.4- μm region, or DF second overtone positions, the excellent detector is not usable for DF(6, 7, 8), as shown in Fig. 1, because of HF first overtone emissions. From calibrations and spectral data, it is estimated that 2% to 10% HF(v) impurity densities are being observed compared to DF(v). Therefore, extraordinary purities of $\lesssim 0.1\%$ H-impurity are demanded in the deuterated fuel for successful studies. These impurities affect emission signals but not the kinetics, because species densities are usually very low. Such a situation led to the decision to use the PbS detector.

The fourth difficulty encountered in DF studies is the production chemistry. Because of isotopic effects, the overall rate for F + DI is expected to be smaller than that for F + HI. Moreover, the initial distribution involves more v levels in DF and is not favorable for observation of strong DF(6, 7, 8) signals.

In summary, with the use of a PbS detector, and with equivalent flows of F and HI or DI, one can expect approximately 100 times less signal at the detector from a DF(8) level than from, for example, an HF(6). A solution is to increase the F and DI reagents to a degree consistent with the maintenance of the steady-state condition and to avoid V-V coupling in DF levels.

With the PbS detector, the DF spectra for F + DI can be observed (Fig. 2). States up to $v = 8$ are chemically produced, and an approximate estimate of the initial distribution is given in Fig. 3 by use of the P(1) lines of each band and approximate spectral data. No $v = 2$ or $v = 9$ is observed. For the purpose of comparison, the approximate initial distribution for F + HI is also given. The peaks in the distribution are slightly shifted. For reference, 65 kcal corresponds to $2.3 \times 10^4 \text{ cm}^{-1}$. Zero-point energies are subtracted out. $N_{\nu} A_{\nu \text{ tot}}$ is exactly the steady-state initial distribution if coupling between DF levels (collisional and radiative cascades) is completely negligible. The corrections are not made. It is concluded that, with improvements in detection, F + DI should provide adequate DF(8, 7, 6) for quenching studies.

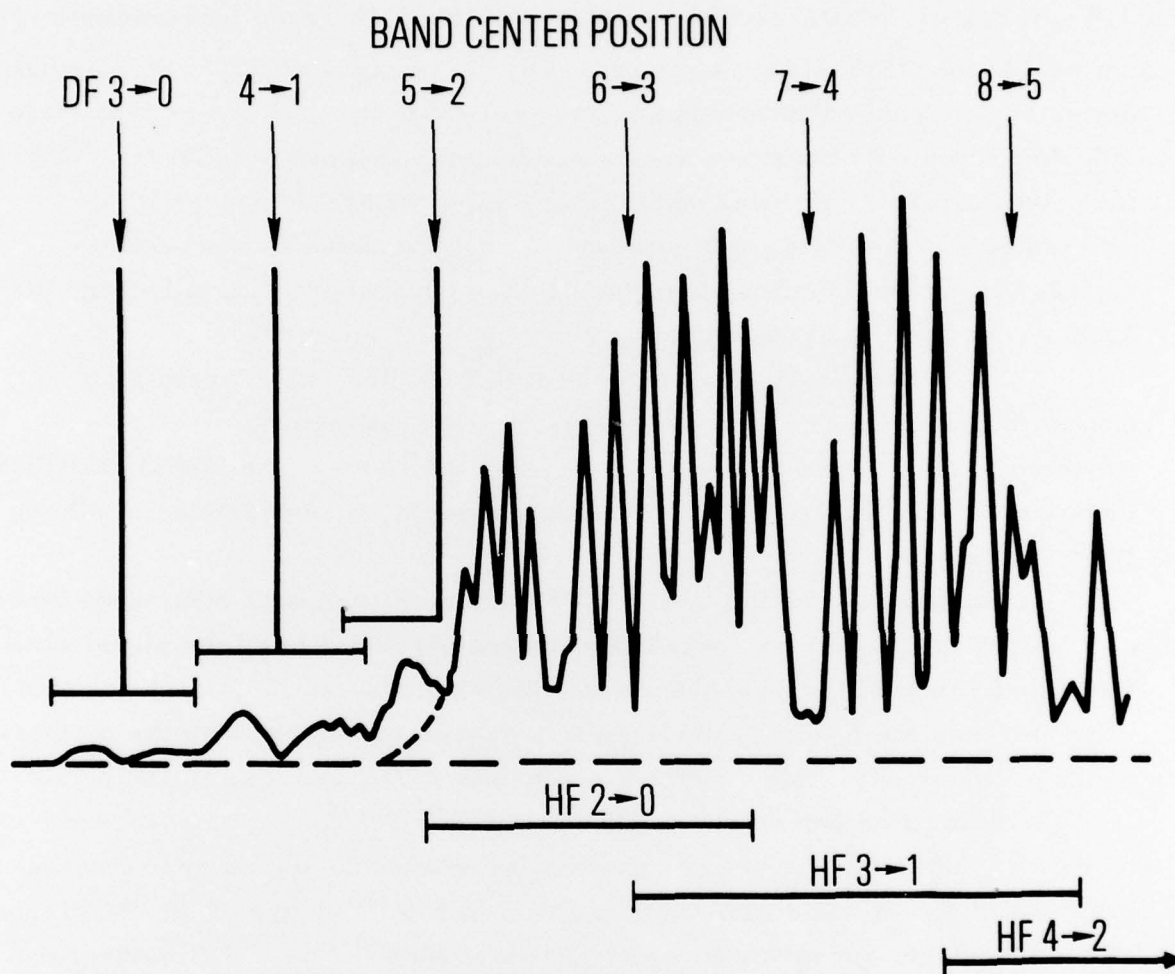


Fig. 1. DF Spectra at 1.2 to 1.4 μm . F + DI reaction.
Cooled Ge detector, 500- μm slits.

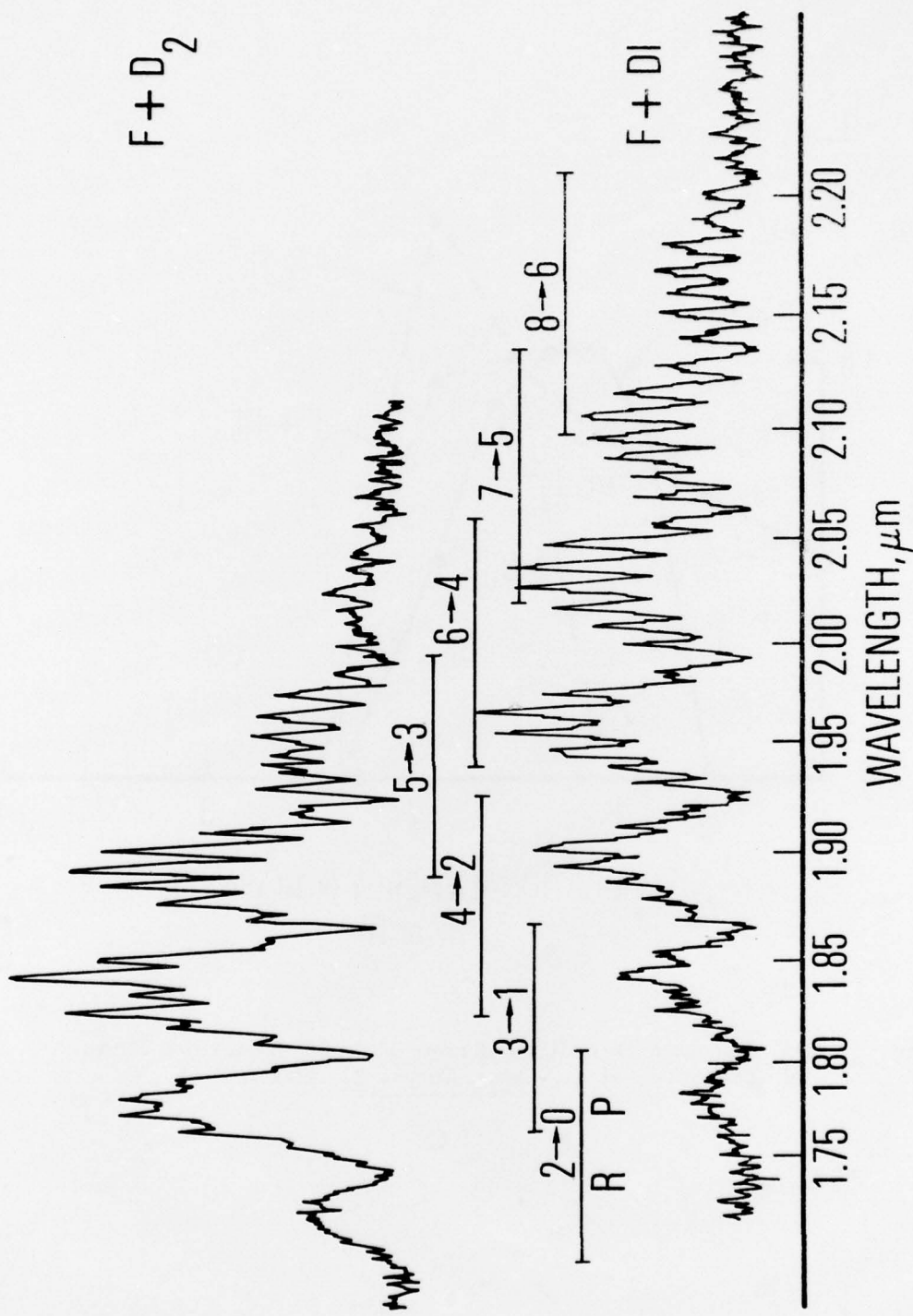


Fig. 2. DF Spectra at 1.7 to 2.1 μm . F + D₂ and F + DI reactions. Cooled PbS detector, 1000- μm slits.

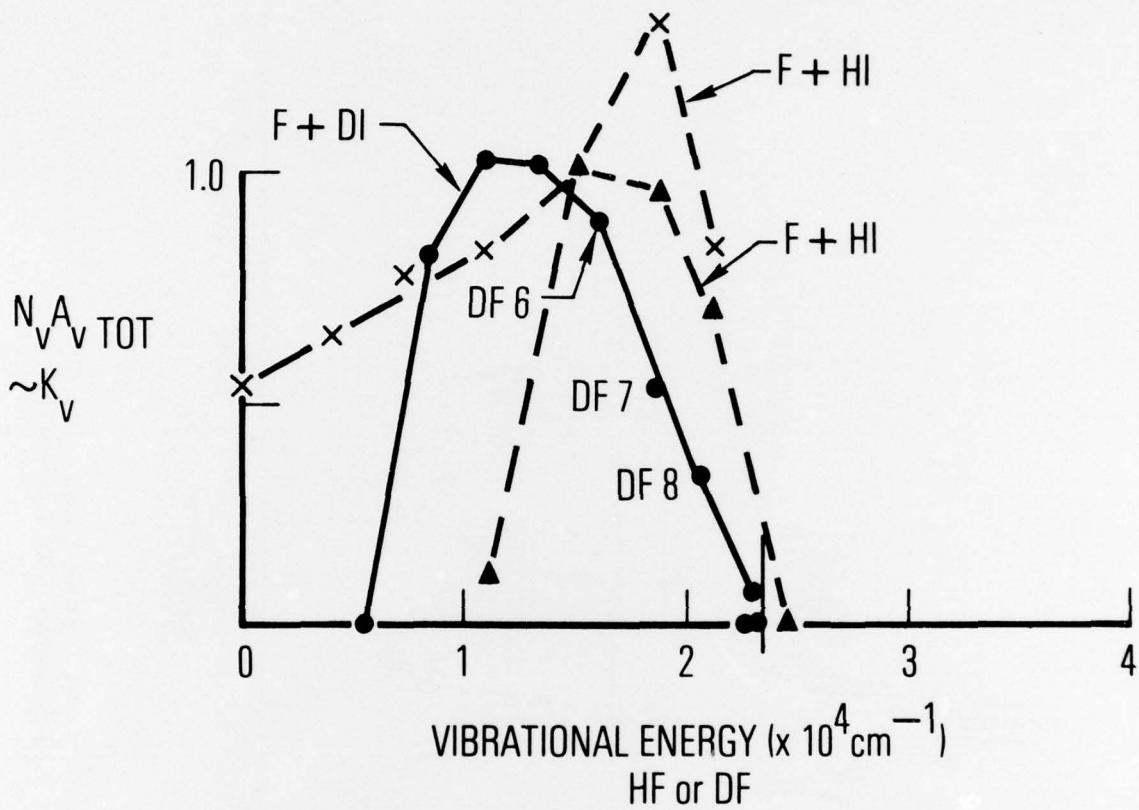
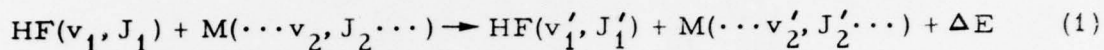


Fig. 3. DF Number Densities From F + DI Reaction. From N. Jonathan, et al., Mol. Phys. **22**, 561 (1971).

III. DISCUSSION

In an internal energy transfer collision process involving DF($v_1 J_1$) or HF(v_1, J_1) with chaperone M, the change in state in the collisional system can be expressed by



$$k_f(v_1 J_1 v_2 J_2; v_1' J_1' v_2' J_2')$$

with the cross section for the process given by $k_f(v_1 J_1 v_2 J_2; v_1' J_1' v_2' J_2')$. Writing the kinetic equations on a (v, J) and then a (v) basis and grouping appropriate terms yield the following expression for relating the observed quenching coefficient to the cross sections

$$K_M(v_1) = K_M^{VR}(v_1) + K_M^{VV}(v_1) - K_M^{-VV}(v_1) - K_M^{RV}(v_1) \quad (2)$$

where, for V-R processes

$$K_M^{VR}(v_1) = \sum_{\substack{v_1 J_1 v_2 J_2 \\ v_1' J_1' v_2' J_2'}} k_f(v_1 J_1 v_2 J_2; v_1' J_1' v_2' J_2') \frac{N(v_1 J_1)}{N(v_1)} \frac{N(v_2 J_2)}{N(v_2)} \quad (3)$$

$$v_1 + v_2 \neq v_1' + v_2'$$

$$v_1 - v_1' = 1, 2, \dots, v_1$$

$$J_1 \neq J_1'$$

$$J_2 \neq J_2'$$

with $N(v_1 J_1)$ the species number density and $N(v_1)$ the number density sum of all $N(v_1 J_1)$. Generally, $v_2 = v_2' = 0$ in these experiments. For the V-V processes

$$K_M^{VV}(v_1) = \sum_{\substack{J_1 v_2 J_2 \\ v_1' J_1' v_2' J_2'}} k_f(v_1 J_1 v_2 J_2; v_1' J_1' v_2' J_2') \frac{N(v_1 J_1)}{N(v_1)} \frac{N(v_2 J_2)}{N(v_2)} \quad (4)$$

$$v_1 \neq v_1'$$

$$J_1 \neq J_1'$$

$$v_2 \neq v_2'$$

$$J_2 \neq J_2'$$

$$v_1 - v_1' = v_2' - v_2$$

Usually, $v_1 - v_1' = 1$, according to Wilkins'² results. The reverse V-V process is

$$K_M^{-VV}(v_1) = \sum_{v_1' v_2'} \frac{N(v_1') N(v_2')}{N(v_1) N(v_2)} \sum_{\substack{J_1 v_2 J_2 \\ J_1' J_2'}} k_b(v_1 J_1 v_2 J_2; v_1' J_1' v_2' J_2') \frac{N(v_1' J_1')}{N(v_1')} \frac{N(v_2' J_2')}{N(v_2')} \quad (5)$$

The $K_M^{-VV}(v_1)$ can be controlled or minimized by the experimental conditions used. The k_b are determined by detailed balancing.

Because some of the terms in the V-R processes are nearly resonant, the reverse or R-V terms may not be negligible. Then

²R. L. Wilkins, Mechanisms of Energy Transfer in Hydrogen Fluoride Systems, TR-0077(2603)-5, The Aerospace Corporation, El Segundo, Calif. (to be published).

$$K_M^{RV}(v_1) = \sum_{v_1' v_2'} \frac{N(v_1') N(v_2')}{N(v_1) N(v_2)} \sum_{\substack{J_1 v_2 J_2 \\ J_1' J_2'}} k_b(v_1^{J_1} v_2^{J_2}; v_1'^{J_1'} v_2'^{J_2'}) \frac{N(v_1'^{J_1'}) N(v_2'^{J_2'})}{N(v_1') N(v_2')} \quad (6)$$

From the forms of Eqs. (2) through (5), the following statements are evident:

1. $K_M(v_1)$ can be considerably larger (or smaller) than any individual $k_f(v_1^{J_1} v_2^{J_2}; v_1'^{J_1'} v_2'^{J_2'})$.
2. $K_M(v_1)$ is usually pressure and temperature dependent.
3. The temperature dependence of $K_M(v_1)$ may be significantly different from that of individual $k_f(v_1^{J_1} v_2^{J_2}; v_1'^{J_1'} v_2'^{J_2'})$.
4. In general, one should avoid making determinations of reverse rates $K_{Mr}(v_1)$ by detail balancing, using quenching coefficients $K_M(v_1)$ and rotationless energy defects for process $HF(v_1) + M(v_2) \rightarrow HF(v_1') + M(v_2')$.

When colliding species are immersed in a bath and characteristic times are sufficiently long for processes other than rotational relaxation, certain density ratios of type $N(v_1^{J_1})/N(v_1)$, especially at low J_1 , become Boltzmann factors. Observed $K_M(v_1)$ becomes pressure independent if terms K_M^{-VV} and K_M^{RV} can be suppressed experimentally. It is not clear at this time whether it is possible to suppress K_M^{RV} . Because most quenching coefficients are measured in flow tube, flow cell, or laser-induced fluorescence experiments under such experimental conditions, care must be exercised when the $K_M(v_1)$ is used in describing situations that depart significantly from "rotational-translational equilibrium."

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