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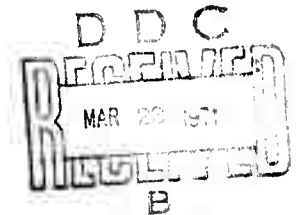
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THE VIBRATIONAL EXCITATION OF HF BEHIND INCIDENT SHOCK WAVES

W. C. SOLOMON, J. A. BLAUER,
T. W. OWENS AND J. G. HNAT, CAPT, USAF

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FOREWORD

The work described in this report was accomplished as part of the Air Force Rocket Propulsion Laboratory's in-house project 314803BCB, Propellant Kinetics, and funded in part by AFWL, Fund PD 71-1-999001, during the period July 1970 to November 1970.

The vibrational excitation of HF behind incident shock waves is discussed. The effect of fluorine atoms upon the subsequent relaxation process is considered.

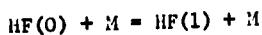
The authors gratefully acknowledge the significant contribution of Mr. M. A. Abrego in the experimental phase of the work.

This report has been reviewed and approved.

ALFRED D. BROWN, JR., Lt. Col, USAF
Chief, Technology Division
Air Force Rocket Propulsion Laboratory

ABSTRACT

The vibrational excitation of HF occurring behind incident shock waves has been studied in the temperature range of 1400°K to 4100°K. The extent of excitation was determined as a function of time by continuously monitoring the emission intensity from the 1-0 band of HF centered at 2.5 μ . The data were interpreted in terms of the process



and gave a value of

$$(\tau p)_{\text{HF}}^{-1} = 10^{9.2 \pm 0.1} \exp\left(\frac{-64 \pm 4}{T^{1/3}}\right) \text{ atm}^{-1} \text{ sec}^{-1}$$

for M = HF. The corresponding result for $(\tau p)_{\text{Ar}}^{-1}$ was found to be insignificant in comparison to this result. Data were also obtained for the effect of F atoms upon the relaxation rate, i.e., it was found that

$$(\tau p)_{\text{HF}} / (\tau p)_{\text{F}} \sim 18 \pm 1$$

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SECTION I

INTRODUCTION

The current interest in chemical lasers^{1,2,3} has generated a need for kinetic information concerning energy exchange processes that govern excited state lifetimes. We report here some results for one such process, i.e., that concerning the vibrational relaxation of HF. The only data currently available for this molecule are the indirect result of Talrose⁴ concerning its deactivation by H₂ and some preliminary results of Airey⁵ concerning its self-catalyzed de-excitation.

SECTION II

EXPERIMENTAL PROCEDURE

The shock tube was of conventional design and has been described adequately elsewhere.⁶ Shock detection was by means of ionization gauges. The shock tube and gas handling system were found to have a leak rate of less than 10^{-3} torr per minute. Absorbed water was removed from the walls by repeated treatment of the shock tube and gas handling system with fluorine gas.

The relaxation process was followed by monitoring the infrared emission intensity as a function of time. Spectral isolation was accomplished by use of a NaCl prism monochromator (Perkin-Elmer Model 98). Detection of radiation at 2.5μ was by means of an InSb photovoltaic detector coupled to a low noise broadband (10 MHz) amplifier. The detection system was found to have a risetime of less than 0.4μ s.

The slit function for the spectrometer system was determined by monitoring the emission intensity from the spin reversal reaction, $^2P_{1/2} + ^2P_{3/2}$, of Br atoms (at 3680 cm^{-1}) which had been shock heated to $4500 \pm 50\text{K}$. The latter measurement gave a half width of 300 cm^{-1} .

Argon and hydrogen fluoride having stated purities of 99.998% and 99.9%, respectively, were purchased from Mathieson. The Ar was used without further purification. However, the HF was further purified by evacuation to 1 torr at -75°C followed by warming at 0°C at which temperature the HF was slowly distilled from the container. Fluorine for this study having a measured purity of 99.9% was prepared at Stanford Research Institute⁷.

Mixes of Ar, HF, and F_2 containing 0.9% HF, and 0-3% F_2 were prepared and stored in stainless steel tanks. Immediately before using a gaseous mixture its HF and F_2 contents were determined by reading its optical densities at 2.5 and 0.285μ , respectively, on a Beckman DK-2 spectrophotometer equipped with a stainless steel absorption cell having sapphire windows.

A calibration of the spectrophotometer for HF was affected by titration of a standard base solution with binary mixtures of HF and Ar. A corresponding calibration for F₂ was obtained by measuring absorption coefficients of freshly prepared mixes. All pressures were measured with Wallace and Tiernan gauges with a precision of ±1%.

SECTION III

CALCULATIONS

The emission intensity, E , behind the incident shock wave increases exponentially with time and was treated in a manner analogous to that given in reference 8. For those data having a relaxation time under 30 sec, a correction for the presence of the detector was made by means of a solution of the equations

$$\frac{dO}{dt} = \frac{1}{\tau_s} (E - O) \quad \text{and} \quad \frac{dE}{dt} = \frac{1}{\tau} (E_\infty - E) \quad (1)$$

where τ is the molecular relaxation time, τ_s is the relaxation time of the monitoring system, and O is the observed voltage. Decius⁹ has shown that, $\Delta v = \pm 1$ transitions, the emission intensity summed over several states is a correct measure of the total vibrational energy of the molecule. In the temperature range of the present study, only contributions from $v=1$ states are of major consequence.

SECTION IV

RESULTS AND DISCUSSION

Values for the vibrational relaxation time at one atmosphere pressure, τ_p , are presented as a function of temperature in Figure 1. In an attempt to separate the effects of HF and Ar as collision partners, the following expression was fitted to the data:

$$\frac{1}{\tau_p} = \frac{X}{(\tau_p)_{\text{HF}}} + \frac{1-X}{(\tau_p)_{\text{Ar}}} \quad (2)$$

where X is the mole fraction for HF in the mix. The results show that $(\tau_p)_{\text{Ar}} \gg (\tau_p)_{\text{HF}}$, disallowing an accurate measure for $(\tau_p)_{\text{Ar}}$. Indeed, the data can all be treated as though Ar were not present. The result of this assumption is illustrated in Figure 1. The relaxation data for all binary mixes of HF and Ar can be described by means of the following equation:

$$\frac{1}{(\tau_p)_{\text{HF}}} = 10^{9.2 \pm 0.1} \exp\left(\frac{-64+4}{T^{1/3}}\right) \text{ atm}^{-1} \text{ sec}^{-1} \quad (3)$$

The experimental results described by equation (3) have been compared to the theory of Schwartz, Slawsky, and Herzfeld (SSH)¹⁰ and the rotation-vibration theory of Moore¹¹. Method B was used for the SSH calculation with the parameters $\epsilon/k = 360^\circ\text{K}$ and $\sigma = 3.3\text{\AA}$ for the Lennard-Jones potential. The latter values correspond to those tabulated for HCl by Hirschfelder et al¹². The comparison is shown in Table I.

Although the theory of Moore more closely approximates the experimental data, both theories give relaxation times that are too long by more than an order of magnitude. Furthermore, neither theory gives a good

description of the observed temperature dependence of the relaxation process. The very large discrepancy between the SSH theory and the data may be due in part to an underestimate of the potential parameter, ϵ/k . Nevertheless, this theory is also in error when compared to the analogous data for HCl¹³.

Finally, the effect of added fluorine upon the relaxation rate is illustrated in Figure 2. Calculations based upon the results of Diesen¹⁴ give a half life for F₂ ranging from 1 to 100 usec under the conditions of our experiments. Consequently, the effects illustrated in Figure 2 suggest that the catalyst in the present instance is the F atom. In an attempt to evaluate the efficiency of F atoms relative to that of HF in relaxing the HF molecule, entire relaxation profiles have been reproduced by means of a nonequilibrium computer program¹⁵ which solves the rate equations simultaneously with the conservation equations. The following mechanism is assumed:



the rate constant for equation (4) was estimated initially from equation (3), and k_5 was taken from Diesen¹⁴.

The occurrence of reaction (5) causes the temperature to drop by as much as 200°K during a typical test. Consequently, account must also be made of the temperature dependence of the process



Values for the quantity $E_{00}/[\text{HF}(1)]$ have been computed from the experimental data and are found to have the following temperature dependence:

$$10^{-8} \cdot E_{\infty} / [\text{HF}(1)] = 0.6 \pm 0.1 + (0.11 \pm 0.04) \times 10^{-3} (T) \quad (8)$$

Although $[\text{HF}(1)]$ varied by a factor of 20, no concentration dependence of these apparent radiantcies could be detected. Reference to equation (8) shows that for a temperature change of 200°K there is no significant change in $E_{\infty} / [\text{HF}(1)]$. Consequently, the true voltage, E , is a direct measure of $[\text{HF}(1)]$. Finally, equation (1) is used to compute E from the observed voltage, 0 .

Computed relaxation profiles and experimental data are shown in comparison in Figure 3 for several tests. The best fit of the experimental data resulted when the following rate constants were employed:

$$k_4 = 0.7 \times 10^9 \text{Te}^{-10870/RT} \text{ cc/mole/sec} \quad (9)$$

and

$$k_6 = 18k_4 \quad (10)$$

The mathematical form of k_4 is dictated by the input required for the computer program.

At 2000°K, k_4 is 1.6×10^{12} cc/mole/sec. Mayer and Schieler¹⁶ have used the hard-sphere collision theory coupled to the Johnston-Parr¹⁷ method of estimating activation energies to obtain a rate constant

$$k = 0.35 \times 10^{11} (T) e^{-1100/RT} \text{ cc/mole/sec}$$

for the rate of the H-atom-abstraction reaction



At 2000°L, the rate constant, $k_{11} = 5.3 \times 10^{13}$ cc/mole/sec, is indicated.

Therefore, if vibrational energy transfer occurs by H-atom-abstraction, approximately 3% of all collisions between F atoms and HF molecules must be effective. This compares favorably to the fraction of such collisions (ca. 6%) which have sufficient energy to cause a vibrational transition in HF. Accordingly, it is reasonable to assume that reaction (6) proceeds by H-atom-abstraction.

SECTION V

CONCLUSIONS

The vibrational relaxation of HF in a binary mix of HF and Ar proceeds predominantly by collisions between HF molecules. The current theories of vibrational energy transfer were unable to describe the data with satisfactory precision; however, the assumption of rotation - vibration interaction does give an order-of-magnitude estimate.

The high efficiency of F atoms in vibrationally relaxing HF can be plausibly explained on the basis of H-atom-abstraction by translationally "hot" F atoms.

Table I

Comparison of Theory with Experiment

for HF - HF Collisions

Vibrational Relaxation Times ($\mu\text{sec.atm}$)

T°K	Moore (V-R)	SSH(V-T)	Obs.
1500	2.2	690	0.18
2000	0.8	140	0.11
2500	0.4	44	0.08
3000	0.2	18	0.08

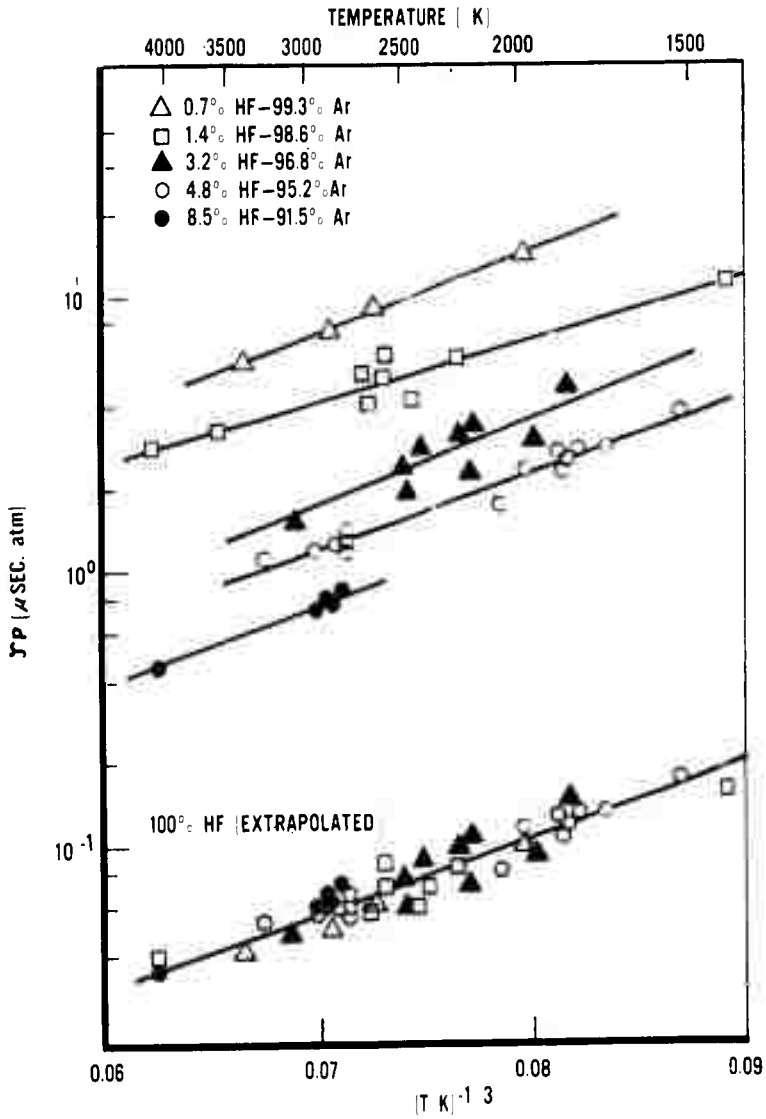


Figure 1. Relaxation Data for HF in an Ar Bath as a Function of Temperature

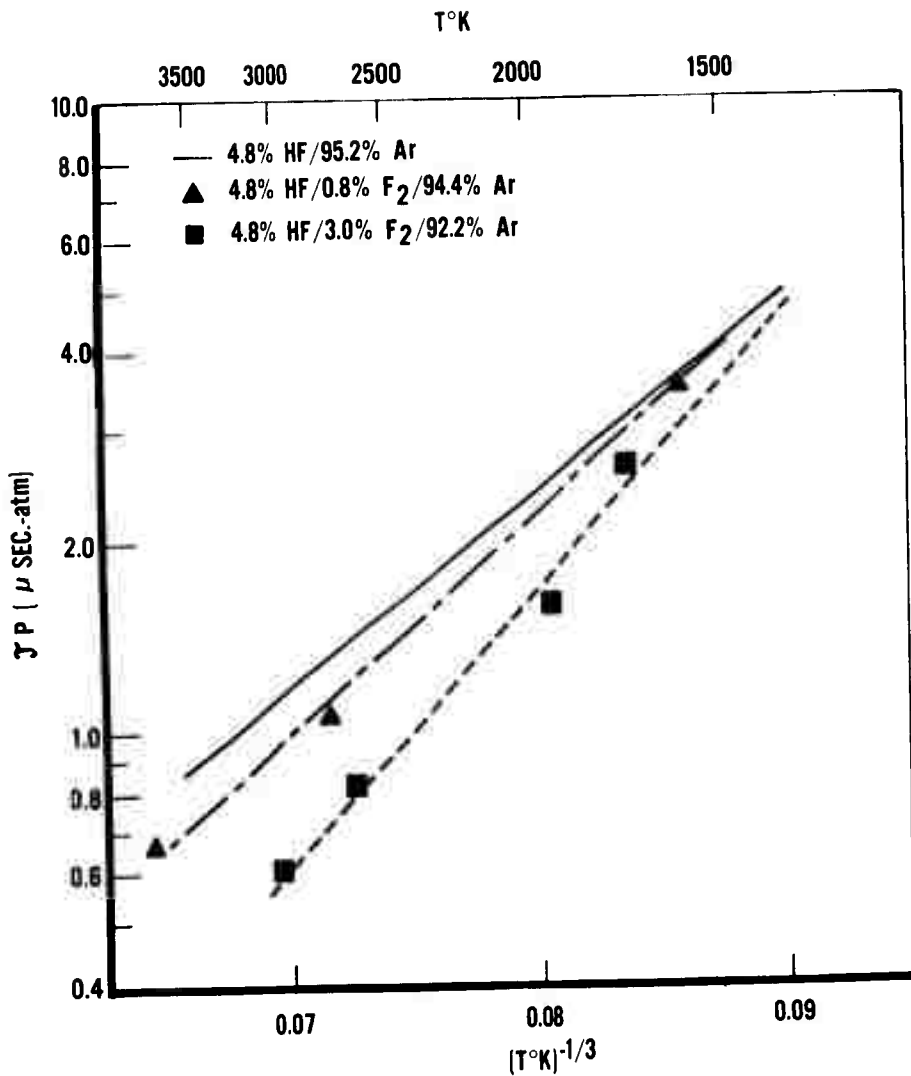


Figure 2. Vibrational Relaxation of HF in the Presence of Added F₂

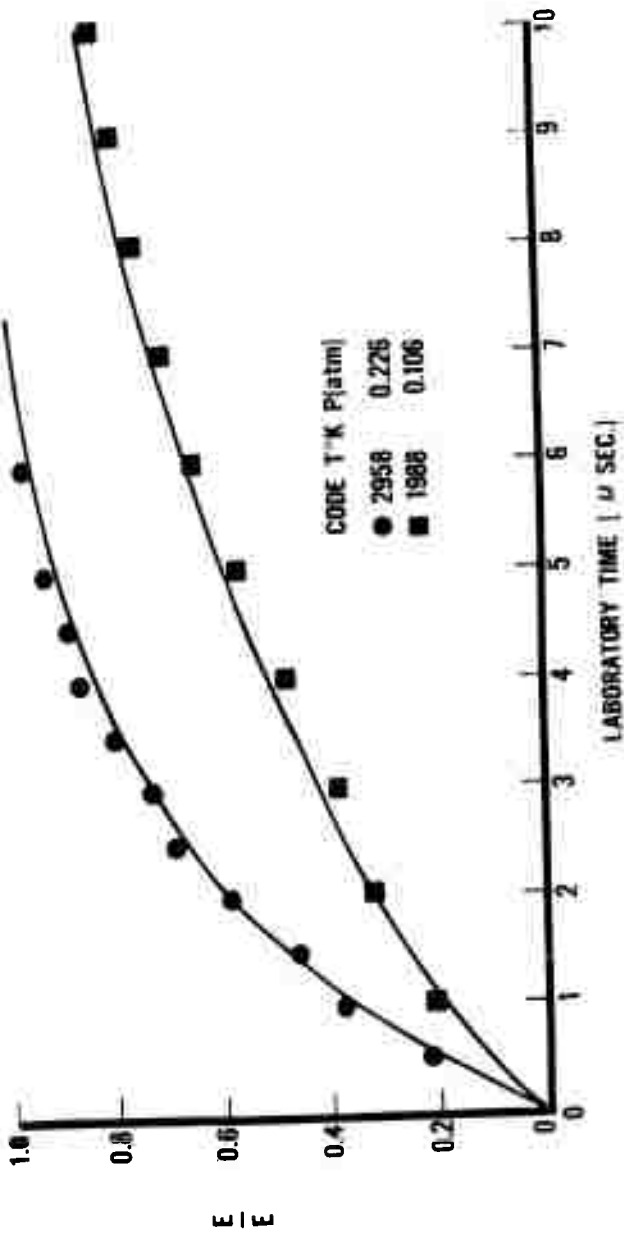


Figure 3a. Comparison of Computed and Observed Relaxation Profiles for Mixes Containing No Added F₂ and 4.8 Percent HF

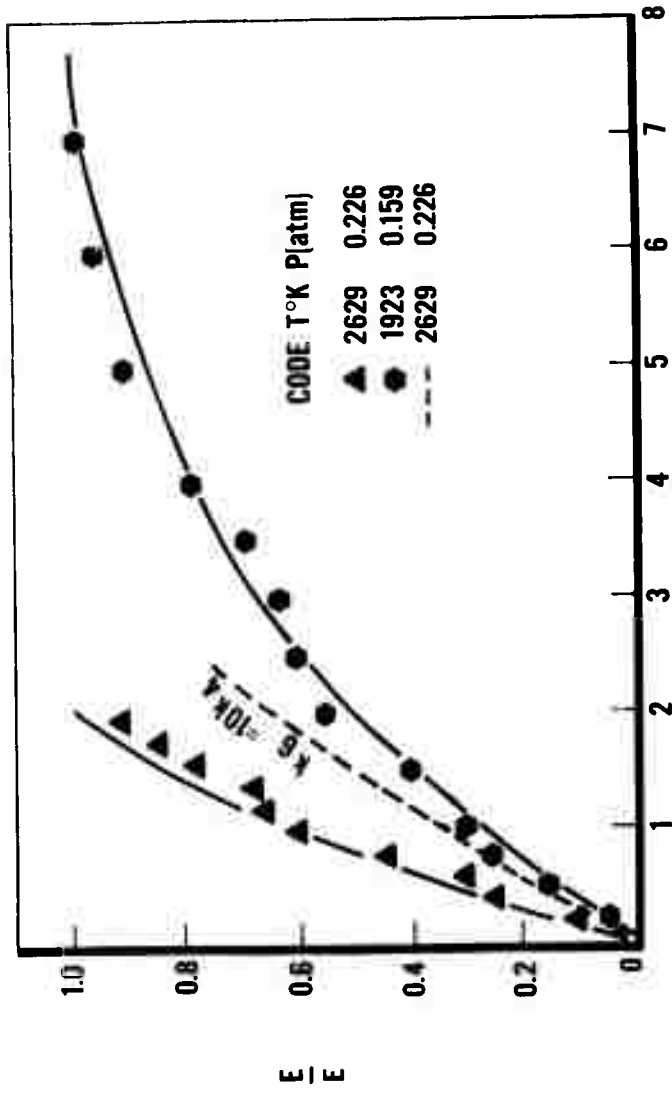


Figure 3b. Comparison of Computed and Observed Relaxation Profiles for Mixes Containing 3.0 Percent Added F₂ and 4.8 Percent HF

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Development Chemist, Shell Chemical 1955-1958 analysis of bio-active organic materials and process development.

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