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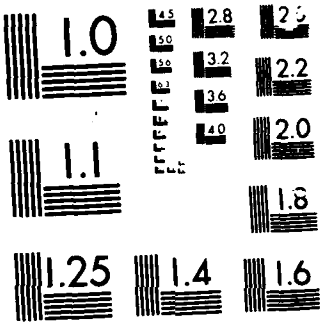

MICROCOPY RESOLUTION TEST CHART

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The Deactivation of HF ($v = 3$) by Water

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The room temperature (T = 295 K) deactivation rate of HF(v = 3) by H_2O has been measured to be faster than the deactivation rate of HF(v = 1) by H_2O by a factor of 3.9. On the basis of a previously reported measurement of the HF(v = 1) - H_2O rate coefficient, the deactivation rate coefficient of HF(v = 3) by H_2O is estimated to be 16 $(\mu sec\ Torr)^{-1}$, which is a factor of 3 faster than the hard sphere collision rate. The theoretical implications of this fast-rate coefficient are reviewed.

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CONTENTS

I. INTRODUCTION

Water is often present as an impurity in HF chemical laser systems and can affect laser performance because of the large HF(1) - H_2O deactivation rate coefficient.[1] Diatomic molecules have been found[2-4] to deactivate the higher vibrational levels of HF(v) with rate coefficients that scale with v as v^n where n = 2.7 when the deactivation process is exothermic. This scaling does not hold for HF(v) - H_2 collisions in which the primary deactivation process is an endothermic V-V transfer with the endothermicity increasing with v.

The very fast deactivation rate coefficients for HF(1) deactivation by H_2O and D_2O have been discussed by Hancock and Green.[1] Because two vibrational energy levels of H_2O (3652 and 3756 cm^{-1}) fall close to the fundamental vibrational level of HF at 3962 cm^{-1}, two possible V-V transfer processes are

$$\mathrm{HF}(v = 1) + \mathrm{H_2O}(000) \rightarrow \mathrm{HF}(v = 0) + \mathrm{H_2O}(001) \quad (\Delta E = 206\ \mathrm{cm^{-1}}) \tag{1}$$

and

$$\mathrm{HF}(v = 1) + \mathrm{H_2O}(000) \rightarrow \mathrm{HF}(v = 0) + \mathrm{H_2O}(100) \quad (\Delta E = 310\ \mathrm{cm^{-1}}) \tag{2}$$

where ΔE is based on band center energy differences. The corresponding processes for HF(v = 3) are

$$\mathrm{HF}(v = 3) + \mathrm{H_2O}(000) \rightarrow \mathrm{HF}(v = 2) + \mathrm{H_2O}(001) \quad (\Delta E = -134\ \mathrm{cm^{-1}}) \tag{3}$$

and

$$HF(v = 3) + H_2O(000) \rightarrow HF(v = 2) + H_2O(100) \quad (\Delta E = -30 \text{ cm}^{-1}) \tag{4}$$

Whereas the V-V processes involving HF(v = 1) are exothermic, the V-V processes involving HF(v = 3) are endothermic (the HF vibrational levels are more closely spaced at the higher vibrational levels).

The present study was undertaken to determine the relative rates of HF(v = 3) and HF(v = 1) deactivation by H_2O. The studies were performed in a laser-induced fluorescence cell by means of sequential photon pumping.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The technique of laser-induced fluorescence by sequential photon absorption has been used previously[2,5] 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 → 0 laser transitions. Then, a fraction of this HF(v = 1) is pumped to v = 2 and subsequently to v = 3 by 2 → 1 and 3 → 2 laser transitions, respectively.

The HF(v = 1) fluorescence was monitored with a Texas Instruments InSb detector. The signal across a 1-kΩ 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 approximately 1.4 μsec. 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 was focused onto the active element of the detector by means of 2 in.-diam f/1.5 CaF optics.

The (3 → 0) overtone emission from HF(v = 3) was monitored with an RCA GaAs 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 it was mounted in the transverse configuration of the infrared detector. It was protected from the direct HF laser pulse by a 0.63-cm sheet of Plexiglas. No fluorescence signal was measurable without HF flowing in the cell.

A load resistor of 47 kΩ and a Perry 070 amplifier (15X amplification) mounted directly on the end of the photomultiplier provided a response time of 2 μsec. The photomultiplier signals were recorded with the Biomation 805 and averaged with the Nicolet 1072 signal averager.

The flow rate of the He gas was measured with a rotating ball flowmeter calibrated by pressure-rise measurements in a standard volume. HF was injected into the main flow through a small Teflon tube sealed into a stainless steel coupling and regulated with a vernier needle valve. Water was introduced into the main flow by passing a small fraction of the He over H_2O at room temperature before injecting it into the main flow. The experiments were performed at a total pressure of about 5 Torr, which was measured with a Baratron Model 221 capacitance manometer.

A flow rate of He-H_2O was set, and the fluorescence traces of HF(v = 1) and HF(v = 3) were recorded, one after the other, which permitted the exponential decay rates of HF(v = 1) and HF(v = 3) to be determined under the same conditions, i.e., at the same partial pressure of H_2O.

III. RESULTS

The exponential decay rates of HF(v = 3) are plotted versus those of HF(v = 1) in Fig. 1. The decay rates are the reciprocal exponential decay times, and the two sets of data were obtained with slightly different HF flow rates. The slope of the data is 3.9 ± 0.4, indicating that H_2O deactivates HF(v = 3) faster than it deactivates HF(v = 1) by a factor of 3.9.

As a rough check of the rate coefficient for the deactivation of HF(v = 1) by H_2O, several decay rates of HF(v = 1) were calculated from the estimated partial pressures of H_2O in the flow. The partial pressure of the H_2O was estimated from the total pressure, the fraction of He passing over the H_2O, and the vapor pressure of H_2O at the room temperature (assuming saturation of the He carrier). The rough checks agreed with the value of 4.1 $(\mu\text{sec Torr})^{-1}$ obtained by Green and Hancock[1] within the uncertainties (±40%) of the H_2O pressure estimates.

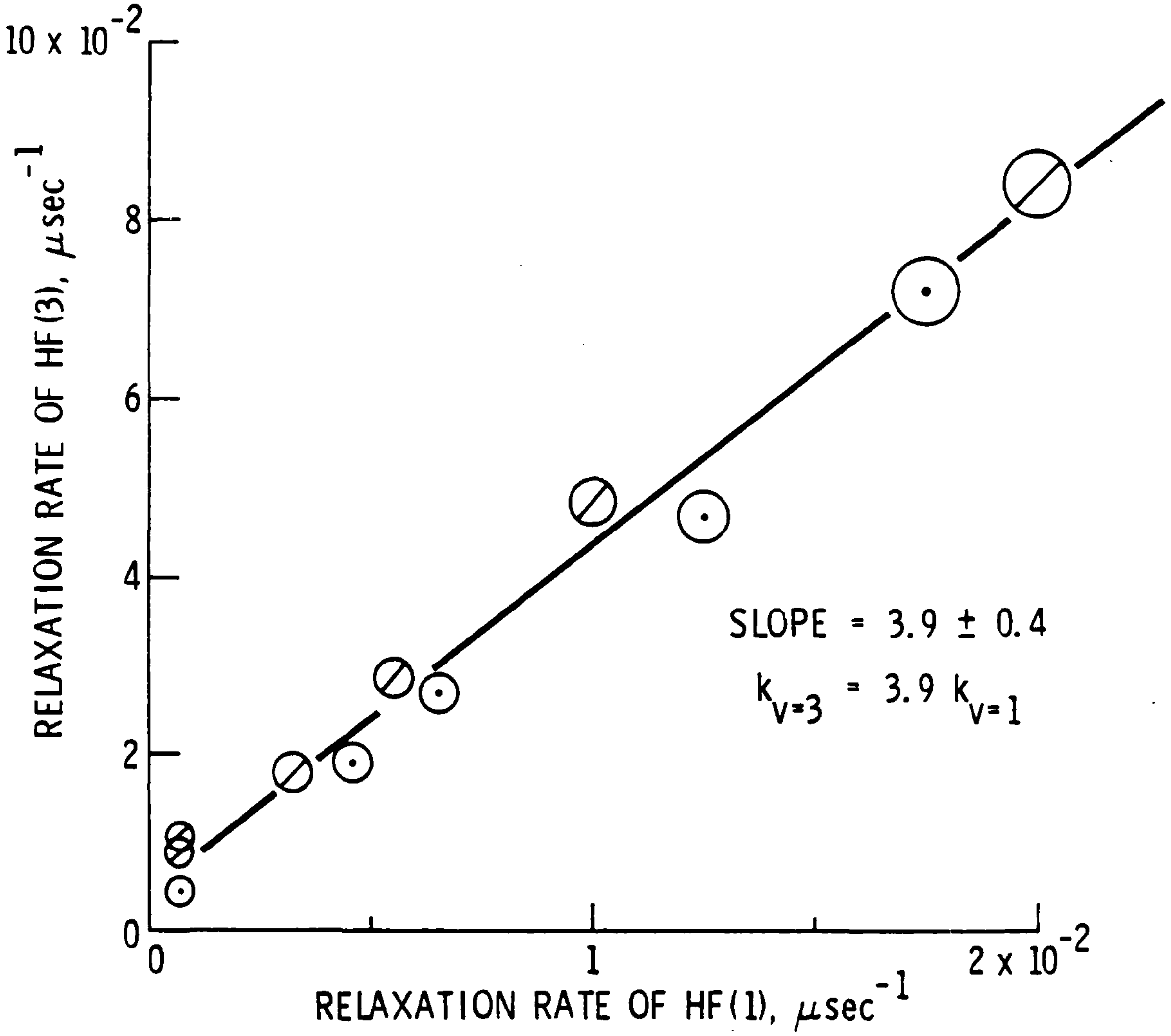

Fig. 1. Relaxation Rate of HF(v = 3) versus that of HF(v = 1) at various partial pressures of H_2O. Results are shown for experiments performed at two different concentrations of HF.

IV. DISCUSSION

Hancock and Green[1] estimated that the probability of HF(v = 1) deactivation by H_2O was 0.77 per collision on the basis of their measured rate coefficients and a hard sphere collision diameter of 2.5 Å for HF. The present measurements indicate that the deactivation of HF(v = 3) by H_2O is 3.9 times faster than that of HF(v = 1), implying a value of 16 $(\mu\text{sec Torr})^{-1}$ for the deactivation rate coefficient of HF(v = 3), which is a factor of 3.0 faster than the hard sphere collision rate. Rate coefficients that are faster than gas kinetic collision rates have been reported for rotational relaxation processes in HF[6] but not for vibrational relaxation.

In previous studies[2-4] of HF(v) deactivation by diatomic molecules the measured rate coefficients have been found to scale as v^n for V-R,T deactivation processes and exothermic V-V exchanges. A $v^{2.7}$ scaling results in a value of 19 for the ratio of deactivation rate coefficients for v = 3 and v = 1. The rate coefficient for HF(v = 3) deactivation by H_2 is only 0.70 times the rate coefficient for HF(v = 1) deactivation by H_2.[2] However, the deactivation of HF(v = 1) by V-V exchange with H_2 is endothermic by 201 cm^{-1} with the endothermicity increasing to 541 cm^{-1} for HF(v = 3) deactivation. The rate coefficients for the deactivation of HF(v = 3) and HF(v = 1) by the triatomic molecule CO_2 have a ratio[7] of 10. HF(v) is probably deactivated by CO_2 by means of an exothermic V-V energy exchange.[1] The V-V energy exchanges that could occur in the deactivation of HF(v) by H_2O differ from the previous examples in that the V-V exchange for HF(v = 1) - H_2O is exothermic and that for HF(v = 3) - H_2O is endothermic.

Hancock and Green considered whether conventional "hard-collision" V-V, V → R,T processes or a "chemical affinity" process could be responsible for HF(v) - H_2O deactivation, and concluded that the chemical affinity case qualitatively explained their measurements of the equal and nearly gas kinetic rate coefficients for the deactivation of HF(v = 1) by H_2O and D_2O. In the chemical affinity argument, the large bond strength (~10 kcal/mole) for the HF - H_2O collision complex results in "sticky" collisions in which the complex stays together during a number of vibrations permitting time for the transfer of energy out of HF(v = 1). It is not clear whether sticky collisions could account for the faster rate coefficients obtained for HF(v = 3). On the other hand, the factor of 3.9 can be rationalized on the basis of V-V processes analogous to those for other molecules. For instance, the deactivation rate coefficient for HF(v = 2) - CO_2 was found to be 5 times faster than that for HF(v = 1) so that an estimate of 5 to 6 for the ratio of rate coefficients for HF(v = 2) and HF(v = 1) deactivation by H_2O seems appropriate. (A factor of 6.5 would be predicted for a $v^{2.7}$ scaling.) The deactivation of HF(v = 2) by a V-V exchange with H_2O is only slightly exothermic. By analogy with the data[2] for HF(v) deactivation by H_2, we would expect the rate coefficient for the endothermic V-V deactivation of HF(v = 3) by H_2O to be slower by 10 to 20% than the deactivation of HF(v = 2). Therefore, one might predict a factor of 4 to 5 compared to the present measured value of 3.9. The present data, therefore, do not prove or disprove either mechanism and both may actually be required to explain all of the evidence.

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