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Temperature Dependence of $HF(v_1 = 1) + HF(v_2 = 0)$ Vibrational Relaxation

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15 August 1978

Interim Report

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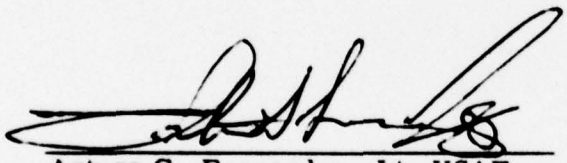

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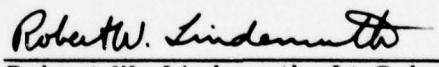

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A kinetics model of infrared laser-induced fluorescence experiments has been used to simulate the experimental quenching rate coefficients reported between 300 and 4000 K for the vibrational relaxation of HF(v_1 = 1) by HF. This rotational nonequilibrium model is based on the predicted energy-transfer mechanisms in hydrogen fluoride systems reported in a trajectory study by Wilkins. This model includes v → R, R → v, R → (R′, T′), and (R′, T′) → R energy-transfer processes. A key process is nonresonant vibrational-to-rotational intramolecular energy transfer in which

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HF($v_1' = 1$, J_1') terminates on high J_1' states of $v_1' = 0$. The calculated temperature-dependent quenching rate coefficient for self-relaxation of HF($v_1 = 1$) at temperatures between 300 to 2000 K is dependent on $v \rightarrow R$ and $R \rightarrow v$ energy-transfer processes, and beyond 2000 K only on $v \rightarrow R$ processes. The puzzling temperature dependence observed for HF($v_1 = 1$) vibrational relaxation by HF($v_2 = 0$) is explained by this model. For the high rotational states in the $v_1' = 0$ manifold, this model predicts incomplete rotational thermalization at low temperatures and complete rotational thermalization at high temperatures. No mechanisms involving dimerization appear to be necessary in understanding the inverse temperature dependence of the reported quenching rate coefficients.

LEVEL II

PREFACE

The authors gratefully acknowledge Drs. J. F. Bott and J. J. T. Hough for many helpful discussions on several aspects of this study, and Ms. K. L. Foster for her invaluable assistance with the calculations.

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FIGURES

TABLE

I. INTRODUCTION

The understanding of the temperature dependence generated by the large set of experimental rate coefficients[1-14] for HF(v_1 = 1) relaxation by HF between 300 and 4000 K hitherto has been incomplete. Bott and Cohen[2] and Hinchen[9] compared these experimental rate coefficients with rate coefficients calculated by means of several theoretical models.[15-18] They concluded that neither the temperature dependence nor the magnitude of the rate coefficient for HF vibrational relaxation is predicted adequately by means of these models.

The experimental rate coefficient for HF(v = 1) relaxation by HF decreases with increasing temperature from 300 to about 1400 K and increases with increasing temperature beyond 1400 K. This anomalous temperature dependence has been observed in other hydrogen halides and is a basis for speculation that vibrational-to-rotational (v → R) energy transfer is involved in these interactions. A comparison of isotopic relaxation rates for HCl-HCl and DCl-DCl collisions by Chen and Moore[19] and HBr-HBr and DBr-DBr collisions by Chen and Chen[20] provides convincing evidence that the relaxation of hydrogen halide molecules in the v_1 = 1 vibrational state occurs by a v → R energy-transfer process. Experimental analyses are based on the assumption that the rotational states of HF are equilibrated in about 0.2 μsec for a typical pressure of 20 Torr;[8] therefore, rotational equilibrium is assumed in the analyses.[1-10, 12, 13] The possibility of formation of highly excited rotational states of HF by a v → R mechanism in HF(v_1 = 1) +

$HF(v_2 = 0)$ collisions and of rotational relaxation from these high rotational states with considerably longer characteristic times has not been considered. This possibility of formation of high rotational states of HF by a $v \rightarrow R$ mechanism has been suggested, however, by several authors[8, 21, 22] on the basis that the $HF(v_1 = 1)$ self-relaxation rates observed in pure HF were 30% slower than the similar rates with HF diluted in argon. It was predicted in a previous trajectory study[23] that in $HF(v_1 = 1) + HF(v_2 = 0)$ collisions, the vibrationally excited HF rotor removes the energy mismatch ΔE that corresponds to rotationless HF molecules by means of a $v \rightarrow R$ energy-transfer process. This process, which corresponds to nonresonant $v \rightarrow R$ intramolecular energy transfer, accounts for the formation of highly excited rotational states ($J_1' = 10$ through 16) of HF. These high rotational states of HF are slowly relaxed by $R \rightarrow (T', R')$ energy-transfer processes.

The trajectory study provided temperature-dependent rate coefficients for the formation of HF in high rotational states. These calculated temperature-dependent rate coefficients cannot be compared directly with the experimental temperature-dependent rate coefficient for the vibrational deactivation of $HF(v_1 = 1)$ in pure HF. The latter should be called an "empirical quenching coefficient" since it represents the net removal rate of $HF(v_1 = 1)$ through a number of energy transfer channels. The previous analyses used to deduce the experimental results did not consider $v \rightarrow R$ and $R \rightarrow v$ energy-transfer processes, which are believed to be important in the vibrational deactivation of $HF(v_1 = 1)$. In fact, the experimental methods to date are not capable of

measuring directly the actual rate coefficients for the energy-transfer processes predicted by the trajectory study.

The rate coefficients were incorporated for $v \rightarrow R$, $R \rightarrow v$, $R \rightarrow (T', R')$, and $(R', T') \rightarrow R$ energy-transfer processes obtained from the trajectory study into a nonequilibrium kinetic computer program that models the shock tube laser-induced fluorescence technique. This study is designed to determine if this rotational nonequilibrium model can reproduce the experimental temperature-dependent quenching rate coefficients for the vibrational deactivation of $HF(v_1 = 1)$ by HF.

II. MODEL

A computer code was developed in order to calculate the time-dependent $HF(v_1, J_1)$ concentrations in defined vibrational v_1 and rotational J_1 states for specific kinetics experiments relevant to energy transfer in HF. This code is an extension of the nonequilibrium chemistry and gasdynamics code[24] (or NEST code) to consider rotational nonequilibrium effects. Until now, in NEST, it was assumed that HF species were in rotational-translational equilibrium at all times, whereas the kinetics between vibrational levels only could be represented. The relation of Wilkins'[2,3] predicted rate coefficients with experiments can only be understood with a more sophisticated model. As a test of this model, an attempt was made to duplicate the anomalous results of the experimental rate coefficient for $HF(v = 1)$ self-relaxation, with its pronounced minimum at about 1400 K. Since the principal method of experimental study has been laser-induced fluorescence,[1, 4-10, 12] often coupled with a shock tube[6, 21] or heated cell,[4, 8-10] model initial conditions have been defined to replicate these approaches.

The generation of time-dependent $HF(v_1, J_1)$ densities by the model is required for comparison with actual experiments. These computer number densities can be summed over J_1, and the sum then analyzed in the same manner as in actual experiments in order to deduce those empirical quenching coefficients reported by experimentalists. The relationship between these empirical quenching coefficients and rate coefficients for different modes of energy transfer is discussed.

The mechanisms of importance for $HF(v_1 = 1)$ + HF quenching are described by v → R energy-transfer processes

$$HF(v_1 = 1, J_1) + HF(v_2 = 0, J_2) \underset{k_b^{R \to v}(J_1, J_2, J_1', J_2')}{\overset{k_f^{v \to R}(J_1, J_2, J_1', J_2')}{\rightleftharpoons}} HF(v_1' = 0, J_1') + HF(v_2' = 0, J_2') + \Delta E_{v, J}^{v \to R} \quad (1)$$

and rotational-to-rotational-translation energy-transfer process

$$HF(v_1, J_1) + HF(v_2 = 0, J_2) \underset{k_b^{(R', T') \to R}(J_1, J_2, J_1', J_2'; v_1)}{\overset{k_f^{(R \to R', T')}(J_1, J_2, J_1', J_2'; v_1)}{\rightleftharpoons}} HF(v_1', J_1') + HF(v_2 = 0, J_2') + \Delta E_{v, J}^{R \to (R', T')} \quad (2)$$

The v → R processes in Eq. (1) reflect the main results of a recent trajectory study,[23] which predicted that in one out of three $HF(v_1 = 1, J_1) + HF(v_2 = 0, J_2)$ collisions, one quantum of vibrational energy of $HF(v_1 = 1, J_1)$ is transferred to rotational energy of the same molecule with almost no change in the distribution of internal energy of the $HF(v_2 = 0, J_2)$ molecule. For the range of study $10 \lesssim J_1' \lesssim 16$, the energy defects for the v → R processes in Eq. (1) are much smaller than would be predicted if both reagent and product HF species were assumed to be rotationless. The rotationally excited HF molecules in the $v_1' = 0$ vibrational state are relaxed by collisions with other HF molecules by way of the R → (R′, T′) energy-transfer processes given in Eq. (2).

The $R \rightarrow (R', T')$ mechanisms with $\Delta J = -1$ are the main processes for deexcitation of rotationally excited HF species. The $HF(v_1' = 0, J_1')$ species at low temperatures will have a nonequilibrium distribution of the high rotational states because, at high values of J, spacing between the rotational levels is so large that a few collisions will not cause rotational relaxation by $\Delta J = -1$ transitions. In trajectory study,[23] it was predicted that rotational relaxation from the high J levels to the low J levels with multiple quantum J-transitions is a very inefficient process. A transition from J = 3 to J = 2 occurs about one in three collisions, whereas a multiquantum transition from J = 15 to J = 12 occurs about 1 in 1000 collisions, or a transition from J = 3 to J = 0 occurs about 1 in 50 collisions. Even at low J levels, the probability of multiquantum transitions are at least one order of magnitude smaller than the probability of a single-quantum transition. In this study, only single-quantum deactivation processes are used for the $R \rightarrow (R', T')$ mechanisms for relaxing the rotationally excited states of HF.

The generalized rate equations for the $v \rightarrow R$ and $R \rightarrow (T', R')$ energy transfer processes in Eqs. (1) and (2) are given as

$$\frac{d[HF(v_1 = 1, J_1)]}{dt} = -\sum_{J_2}\sum_{J_2'}\sum_{J_1'=10}^{16} k_f^{v \rightarrow R}(J_1, J_2, J_1', J_2')[HF(v_1 = 1, J_1)] \times [HF(v_2 = 0, J_2)]$$

(cont.)

$$+ \sum_{J_2} \sum_{J_2'} \sum_{J_1'=10}^{16} k_b^{R \to v}(J_1, J_2, J_1', J_2')[HF(v_1' = 0, J_1')]$$

$$\times [HF(v_2' = 0, J_2')]$$

$$- \sum_{J_2} \sum_{J_2'} \sum_{J_1'} k_f^{R \to (R', T')}(J_1, J_2, J_1', J_2'; v_1 = 1)$$

$$\times [HF(v_1 = 1, J_1)][HF(v_2 = 0, J_2)]$$

$$+ \sum_{J_2} \sum_{J_2'} \sum_{J_1'} k_b^{(T', R') \to R}(J_1, J_2, J_1', J_2'; v_1 = 1)$$

$$\times [HF(v_1' = 1, J_1')][HF(v_2' = 0, J_2')] \qquad (3)$$

$$\frac{d[HF(v_1' = 0, J_1' \geq 10)]}{dt} = \sum_{J_1} \sum_{J_2} \sum_{J_2'} k_f^{v \to R}(J_1, J_2, J_1', J_2')[HF(v_1 = 1, J_1)]$$

$$\times [HF(v_2 = 0, J_2)]$$

$$- \sum_{J_1} \sum_{J_2} \sum_{J_2'} k_b^{R \to v}(J_1, J_2, J_1', J_2')[HF(v_1' = 0, J_1')]$$

$$\times [HF(v_2' = 0, J_2')]$$

$$- \sum_{J_1''} \sum_{J_2} \sum_{J_2'} k_f^{R \to (R', T')}(J_1, J_2, J_1'', J_2'; v_1 = 0)$$

$$\times [HF(v_1' = 0, J_1')][HF(v_2 = 0, J_2')]$$

(cont.)

$$+ \sum_{J_1''} \sum_{J_2} \sum_{J_2'} k_b^{(R', T') \rightarrow R}(J_1', J_2, J_1'', J_2'; v_1 = 0)$$

$$\times [HF(v_1' = 0, J_1'')][HF(v_2' = 0, J_2')] \qquad (4)$$

and

$$\frac{d[HF(v_1' = 0, J_1' < 10)]}{dt} = - \sum_{J_1'} \sum_{J_2} \sum_{J_2'} k_f^{R \rightarrow (R', T')}(J_1, J_2, J_1', J_2'; v_1 = 0)$$

$$\times [HF(v_1 = 0, J_1)][HF(v_2 = 0, J_2)]$$

$$+ \sum_{J_1'} \sum_{J_2} \sum_{J_2'} k_b^{(R', T') \rightarrow R}(J_1, J_2, J_1', J_2'; v_1 = 0)$$

$$\times [HF(v_1' = 0, J_1')][HF(v_2' = 0, J_2')] \qquad (5)$$

Equations (3), (4), and (5) provide a coupled set of first-order differential equations solvable by the use of NEST.[24] The rate coefficients $k_f^{v \rightarrow R}$ and $k_f^{R \rightarrow (T', R')}$ depend on the eight quantum numbers (v_1, J_1, v_2, J_2, v_1', J_1', v_2', and J_2'). In Table 1 are given the $k_f^{v \rightarrow R}$ and $k_f^{R \rightarrow (T', R')}$ rate coefficients used to calculate the quenching rate coefficient for self-relaxation of $HF(v_1 = 1)$ at 300 K.

The initial conditions for the computation simulate a laser-induced fluorescence experiment. At a given temperature, pressures of $[HF(v_2 = 0)] = \sum_{J_2} [HF(v_2 = 0, J_2)]$ up to 0.5 Torr were used. The initial amount of rotationally equilibrated $HF(v_1 = 1) = \sum_{J_1} [HF(v_1 = 1, J_1)]$ is taken to be 0.01 of $[HF(v_2 = 0)]$

Table 1. Rate coefficients[a] for $v \rightarrow R$ and $R \rightarrow (R', T')$ energy transfer in $HF(v_1 = 1) + HF(v_2 = 0)$ collisions at T = 300 K

$v \rightarrow R$ Rates	$10^{-11} k_f^{v \rightarrow R}$, $cm^3/mol\text{-}sec$
$HF(1, 0) + HF(0, J_2) \rightarrow HF(0, J_1') + HF(0, J_2)$	1.3
$HF(1, 1) + HF(0, J_2) \rightarrow HF(0, J_1') + HF(0, J_2)$	6.4
$HF(1, 2) + HF(0, J_2) \rightarrow HF(0, J_1') + HF(0, J_2)$	13.0
$HF(1, 3) + HF(0, J_2) \rightarrow HF(0, J_1') + HF(0, J_2)$	9.1
$HF(1, 4) + HF(0, J_2) \rightarrow HF(0, J_1') + HF(0, J_2)$	5.1
$HF(1, 5) + HF(0, J_2) \rightarrow HF(0, J_1') + HF(0, J_2)$	5.1
$R \rightarrow (R', T')$ Rates	$10^{-11} k_f^{R \rightarrow (R', T')}$, $cm^3/mol\text{-}sec$
$HF(0, 16) + M \rightleftarrows HF(0, 15) + M$	3.3
$HF(0, J_1') + M \rightleftarrows HF(0, J_1' - 1) + M$, $J_1' = 15, \ldots, 11$	6.6
$HF(0, J_1') + M \rightleftarrows HF(0, J_1' - 1) + M$, $J_1' = 10, \ldots, 6$	11.
$HF(0, J_1') + M \rightleftarrows HF(0, J_1' - 1) + M$, $J_1' = 5, \ldots, 1$	21.

[a] $J_1' = 16, 15, \ldots, 10$. $J_2 = 0, 1, \ldots, 5$. To obtain rate coefficient for $v \rightarrow R$ relaxation of $HF(v_1 = 1, J_1)$ by $HF(v_2 = 0, J_2)$, multiply $k_f^{v \rightarrow R}$ by $(2J_2 + 1) \cdot \exp[-E(v_2 = 0, J_2)/kT]/Q_R(v_2, J_2)$, where $Q_R(v_2, J_2)$ is the total rotational partition function.

at temperatures from 300 to 1000 K, 0.1 from 1000 to 1500 K and 0.2 from 1600 to 2400 K. Since the $[HF(v_1 = 1)]$ concentration is generally much less than that for $[HF(v_1 = 0)]$, in Eq. (3) $v \rightarrow v$ pumping processes that involve collisions of two $HF(v_1 = 1)$ molecules have been neglected.

The Landau-Teller theory[25] for an harmonic oscillator gives the relationship for the time rate of change of number density $n_1(t)$ at the instantaneous translational temperature

$$\frac{1}{\tau} = \frac{1}{[n_1(t) - n_1(t = \infty)]}\left(-\frac{dn_1}{dt}\right) \tag{6}$$

where $n_1(t = \infty)$ is the equilibrium number density of the $v = 1$ vibrational state and τ is the relaxation time of the bimolecular collisional deactivation mechanism. The empirical quenching rate coefficient k_{emp} obtained from Eq. (6) can be written as

$$k_{emp} = \frac{1}{[HF(v = 0)]} \cdot \frac{1}{\{[HF(v = 1)] - [HF(v = 1)]_{eq}\}} \cdot \left(-\frac{d[HF(v = 1)]}{dt}\right) \tag{7}$$

From Eq. (3) with application of Eq. (7), the empirical quenching rate coefficients depend on the $v \rightarrow R$ and $R \rightarrow v$ energy-transfer processes.

III. RESULTS AND DISCUSSION

Typical results from the calculation are shown in Figs. 1 through 3. The logarithmic densities of HF(v = 1, J) and HF(v = 0, J) are plotted as a function of time. An essentially exponential decay is computed for $HF(v_1 = 1, J_1)$. As with the actual experiments, the empirical quenching coefficient k_{emp} is deduced through Eq. (7). The calculation is performed at several HF densities in order to verify that k_{emp} is indeed the result of HF quenching. The slope of the inverse characteristic decay times versus HF(v = 0) densities yields the same computed value of k_{emp}. This procedure has been used by experimentalists to ensure that the deduced observed quenching coefficient is not effected by competing or secondary processes. Thus, the analytical techniques of the experimental workers have been duplicated exactly.

Vibrational-to-rotational processes predominately cause the high J states of HF(v = 0, J), corresponding to the J_1' states of Eq. (1), to depart significantly from equilibrium in Figs. 2 and 3. For example, at t = 50 μsec, HF(v = 0, J = 13) is four orders of magnitude greater than its equilibrium density. In this model, rotational inversions are also computed for some J in limited time domains.

In Figs. 1 through 3, the initial amount of rotational equilibrated $HF(v_1 = 1)$ is taken to be 0.01 of $HF(v_2 = 0)$. For this case, the densities of the $HF(v_1' = 0, J_1' = 10, \ldots, 14)$ after 50 μsec are equivalent to those of the initial

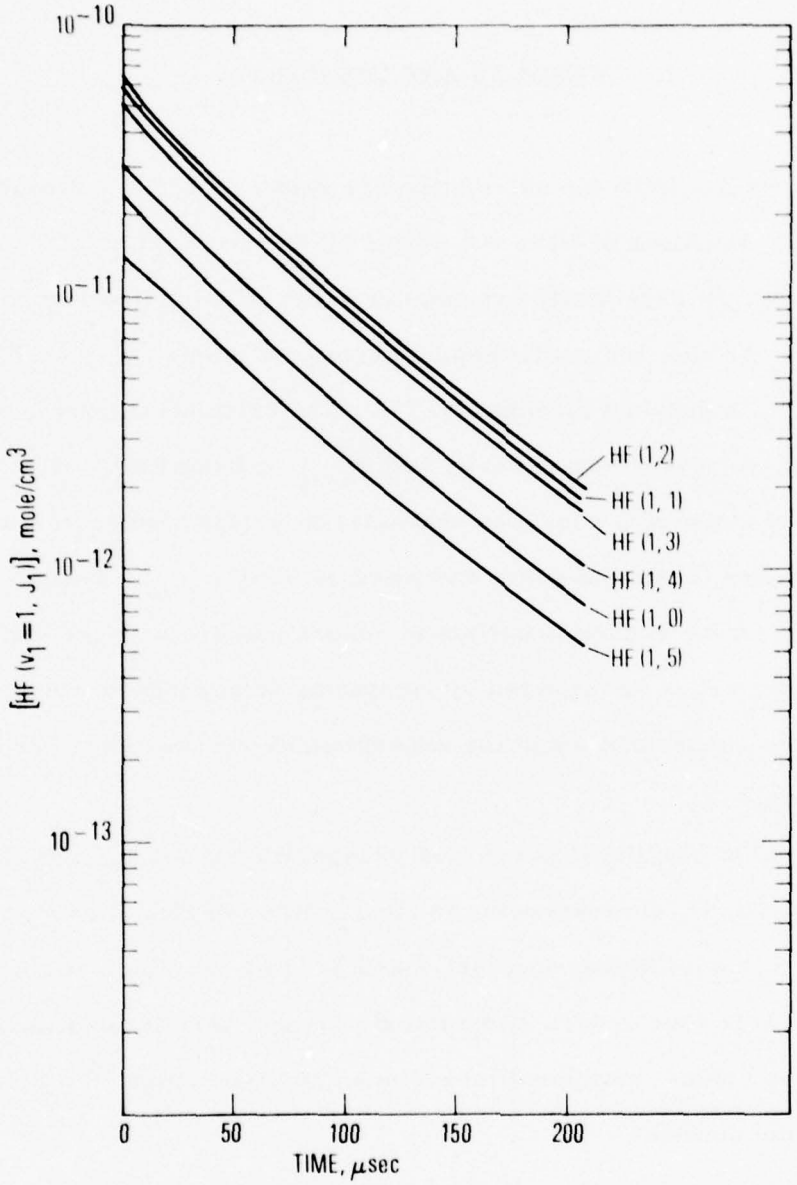

Fig. 1. Typical computer-generated number-density curves of a laser-induced fluorescence study of HF(v_1 = 1) + HF(v_2 = 0) molar concentrations of HF(v_1 = 1, J = 1 through 5) versus t(μsec). T = 300 K, P = 0.47 Torr.

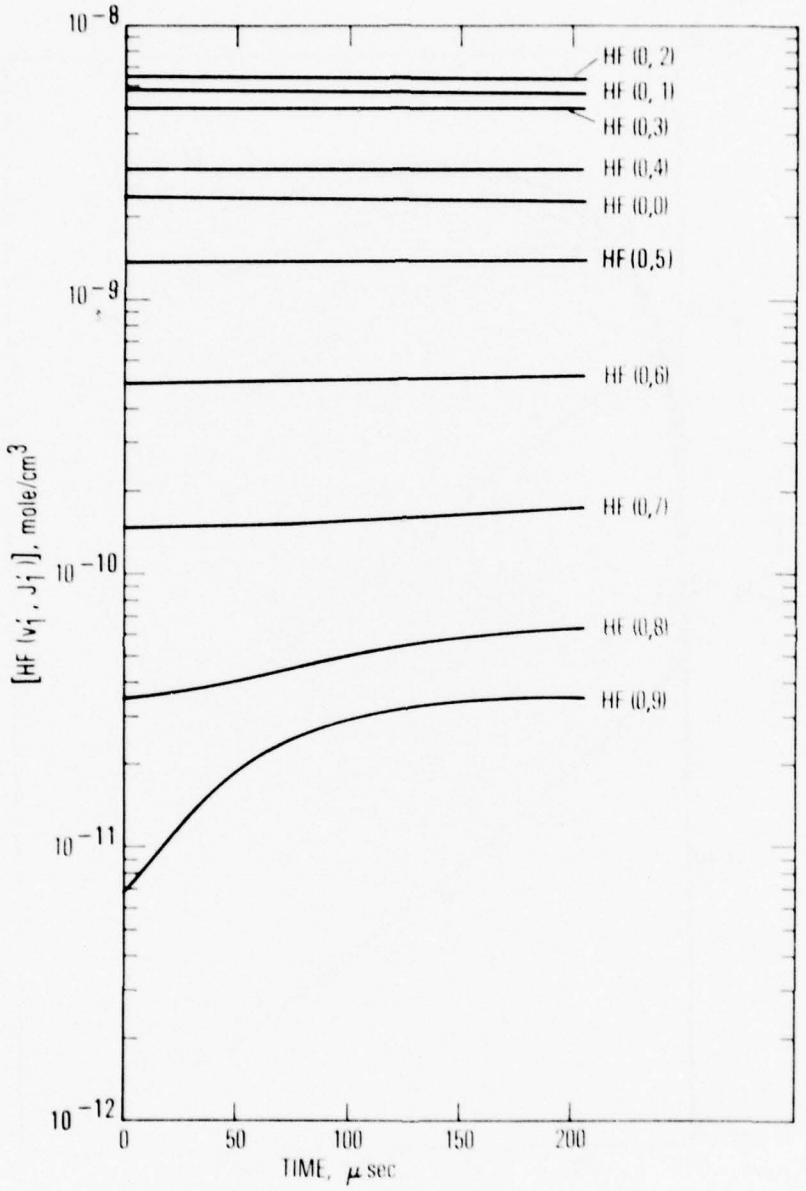

Fig. 2. Molar concentrations of HF(v_2 = 0, J_2 = 0 through 9) versus t(μsec). T = 300 K, P = 0.47 Torr.

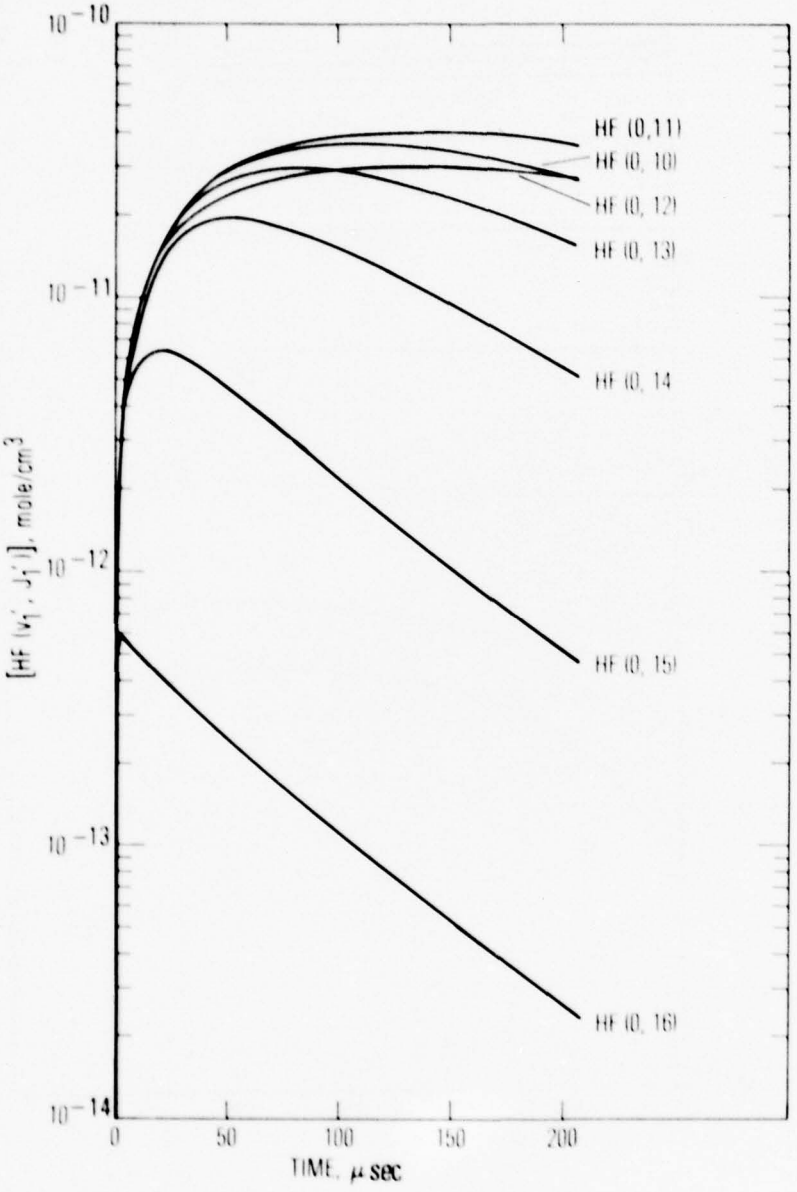

Fig. 3. Molar concentrations of HF(v_2 = 0, J_2 = 10 through 16) versus t(μsec). T = 300 K, P = 0.47 Torr.

$HF(v_1 = 1, J_1)$ states. If only 0.1% of the $HF(v_2 = 0)$ molecules are pumped into $HF(v_1 = 1)$ state, similar calculations indicate that the densities of the $HF(v_1' = 0, J_1' = 10, \ldots, 14)$ after 50 μsec are down by almost an order of magnitude from those of the 1.0% pumped case. These computed results mean that the presence of the J_1' states would be difficult to detect and that the magnitude of these J_1' state densities are quite sensitive to initially excited vibrational-rotational states.

The inverse of the quenching rate coefficient is shown on a traditional Landau-Teller plot in Fig. 4, where P_T is plotted as a function of $T^{-1/3}$. The calculated quenching coefficient P_T, depicted for pedagogical purposes by large open circles, is in quite good agreement with the available experimental data. It increases with increasing temperature up to 1371 K, levels off at about 1400 K, and then begins to decrease. The range of study is 300 to 2400 K. Thus, the model is able to replicate the behavior of the empirical quenching coefficient for HF(v = 1) + HF relaxation.

The agreement of k_{emp} is within 5% of Bott[6] and Osgood[7] results at 300 K but 34% smaller than that of Stephen.[4] At 1000 K, the agreement with Bott[6] and Hinchen[9] is excellent, whereas k_{emp} is 30% smaller than the quenching coefficient of Blair.[12] At 2400 K, agreement within 10% of the results of Bott,[2] Vasil'ev,[11] and Just[13] is still achieved; but this computed k_{emp} is 43% smaller than the number of Solomon[3] or Blair.[12] When it is considered that our model is constructed from theoretical cross sections (Table 1) without adjustment of parameters, the general agreement over the entire temperature range with experiments is quite satisfactory.

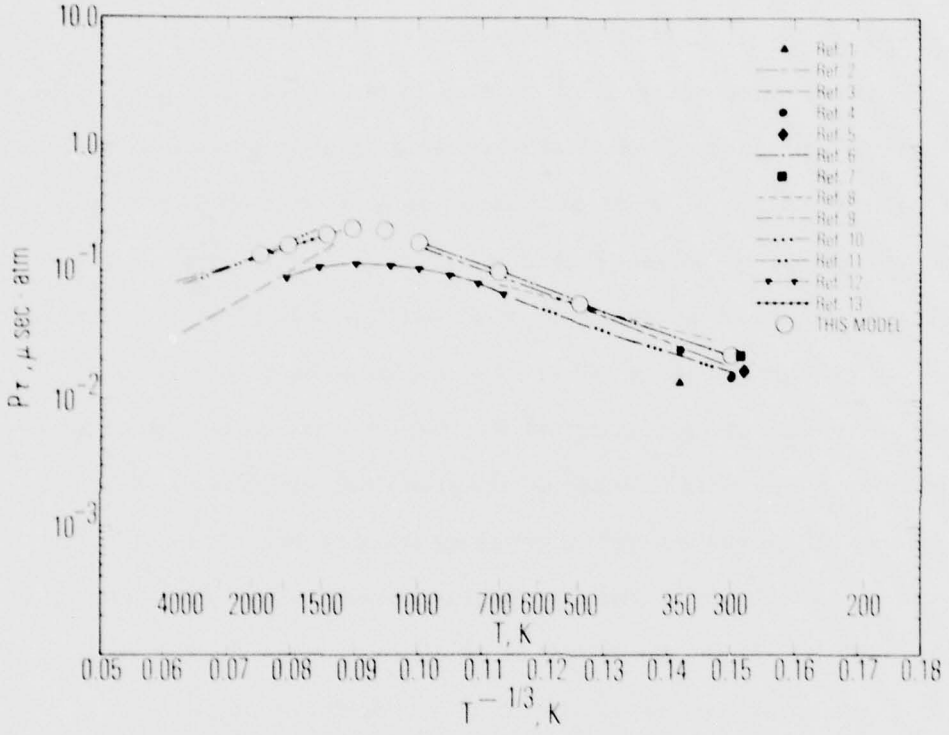

Fig. 4. Comparison of computer model deduced quenching rate coefficients k_{emp} with experimental results. Vibrational relaxation times for deactivation HF(v = 1) by HF. P_T values are plotted versus $T^{-1/3}$.

This model provides a satisfactory description of HF relaxation without invoking the formation of collision complexes. The formation of HF dimers has been proposed by several authors[1,26,29] in order to explain the temperature dependence in vibrational relaxation of HF($v_1 = 1$) by HF. Trajectory calculations by Wilkins[23] indicate that collision complexes are not formed in HF + HF collisions in the temperature range at or above 300 K. The trajectory calculations indicate that the HF($v_1 = 1$) + HF($v_2 = 0$) collisions, the vibrational energy of the vibrationally excited HF molecule is transferred into rotational energy of the same molecule. The energy defects are much smaller in these $v \rightarrow R$ processes than what would have been predicted if both reagent and product HF species were assumed to be rotationless. The long-range attractive forces in HF-HF collisions reduce the steepness of the short-range repulsive forces in HF-HF collisions and thereby permit more conversion of vibrational energy. The near-resonant $v \rightarrow R$ transitions are not important in explaining HF($v_1 = 1$) vibrational relaxation in pure HF.

The experimental or empirical quenching coefficient k_{emp} represents not one unique rate coefficient but a complex sum of a number of rate terms for several energy transfer channels available. Regions of temperature in Fig. 4 can now be delineated as to which particular processes contribute to k_{emp}; these are discussed later in this work.

The calculated time-dependent HF($v = 0, J$) concentrations at temperatures of 300, 500, 700, and 1000 K are presented as a function of the rotational

quantum number J' in Figs. 5 through 8. At low temperatures, the low rotational states ($J' < 8$) have a Boltzmann distribution; the high rotational states ($J' > 8$) exhibit a non-Boltzmann distribution. At high temperatures ($T > 700$ K), all of the rotational states exhibit a Boltzmann distribution. In Fig. 5 is shown the incomplete thermalization of the high rotational J-levels during vibrational relaxation of $HF(v_1 = 1)$ in pure HF. The maximum rotational nonequilibrium in the high rotational states at about $t = 50$ μsec. As t increases from 50 to 800 μsec, the high rotational states tend to relax rotationally toward the Boltzmann distribution indicated at $t = 0$ μsec. In Fig. 5, inverted behavior of some of the high J or J_1' states with time can be observed.

From Eq. (7), k_{emp} can be written as

$$k_{emp} = \frac{1}{[HF(v_2 = 0)]} \frac{1}{\{[HF(v_1 = 1)] - [HF(v_1 = 1)]_{eq}\}} (L_f - L_b) \qquad (8)$$

The L_f and L_b terms represent the total rate contributions to $(-dn_1/dt)$ from $v \rightarrow R$ and $R \rightarrow v$ processes, respectively. In Fig. 9, are curves representing the temperature dependency of the four parts of the expression for k_{emp}: L_f, L_b, $[HF(v_2 = 0)]^{-1}$, and $\{[HF(v_1 = 1)] - [HF(v_1 = 1)]_{eq}\}^{-1}$. The initial amount of $HF(v_1 = 1)$ is 0.01 that of $HF(v_2 = 0)$. In Fig. 10, another four curves are exhibited for the high-temperature conditions; initial $HF(v_1 = 1)$ is 0.1 of initial $HF(v_2 = 0)$. From the curves given in Figs. 9 and 10, both $v \rightarrow R$ and $R \rightarrow v$ processes are important from 300 to 2000 K

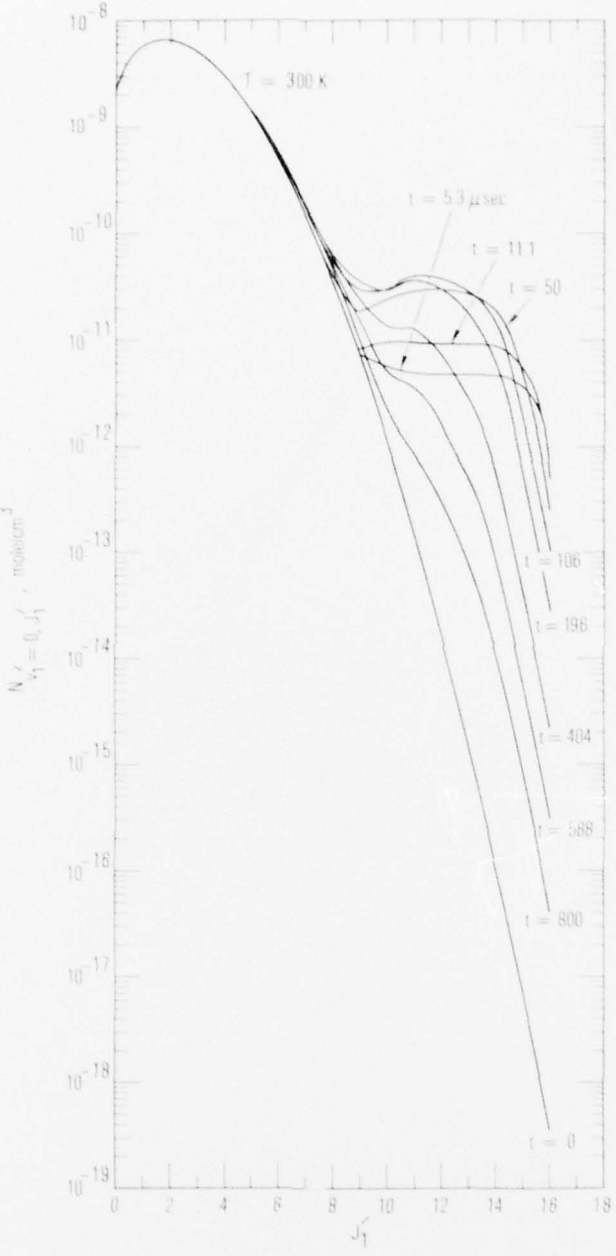

Fig. 5. Molar concentration of $HF(v_1' = 0, J_1')$ versus rotational quantum number J_1' at various times. T = 300 K, P = 0.47 Torr.

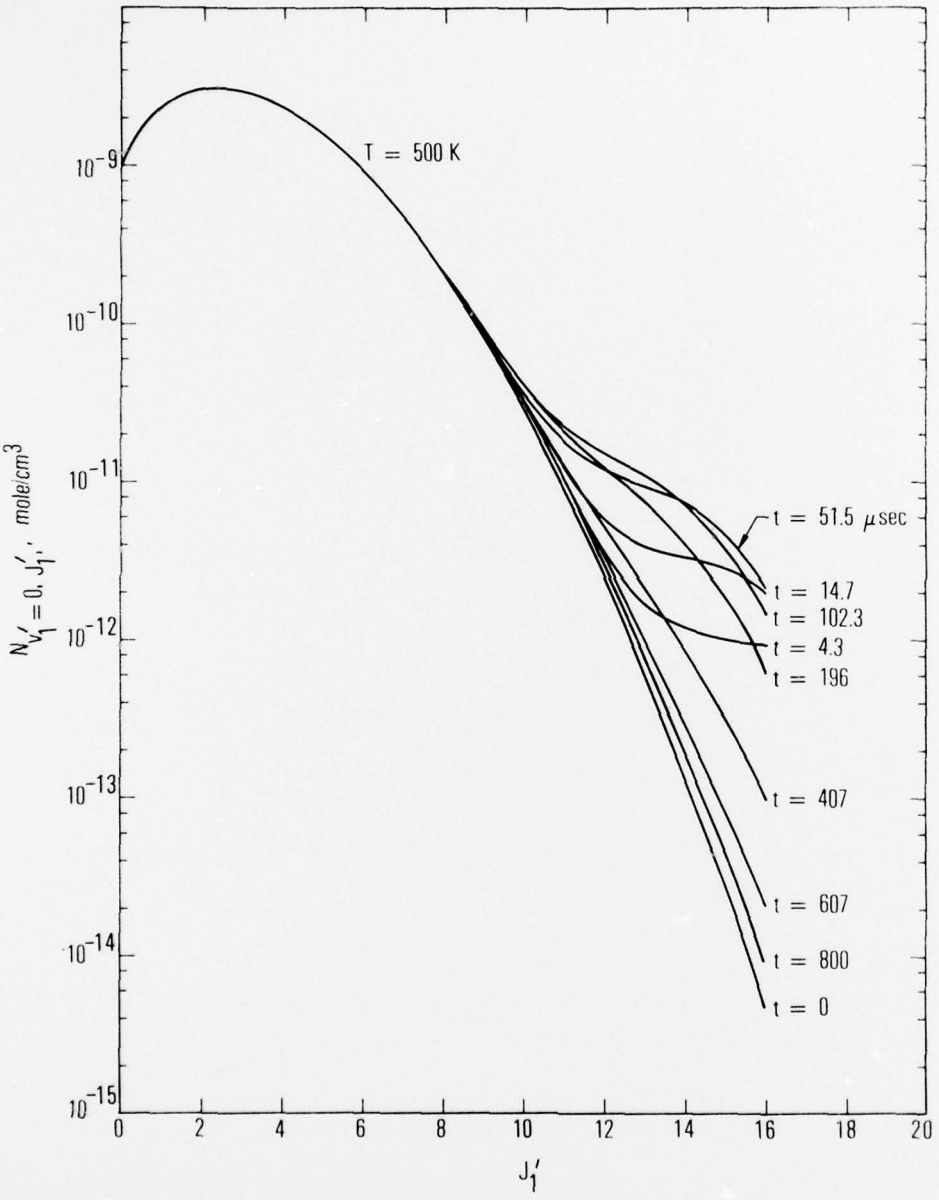

Fig. 6. Molar concentrations of $HF(v_1' = 0, J_1')$ versus rotational quantum number J_1' at various times. T = 500 K, P ≈ 0.47 Torr.

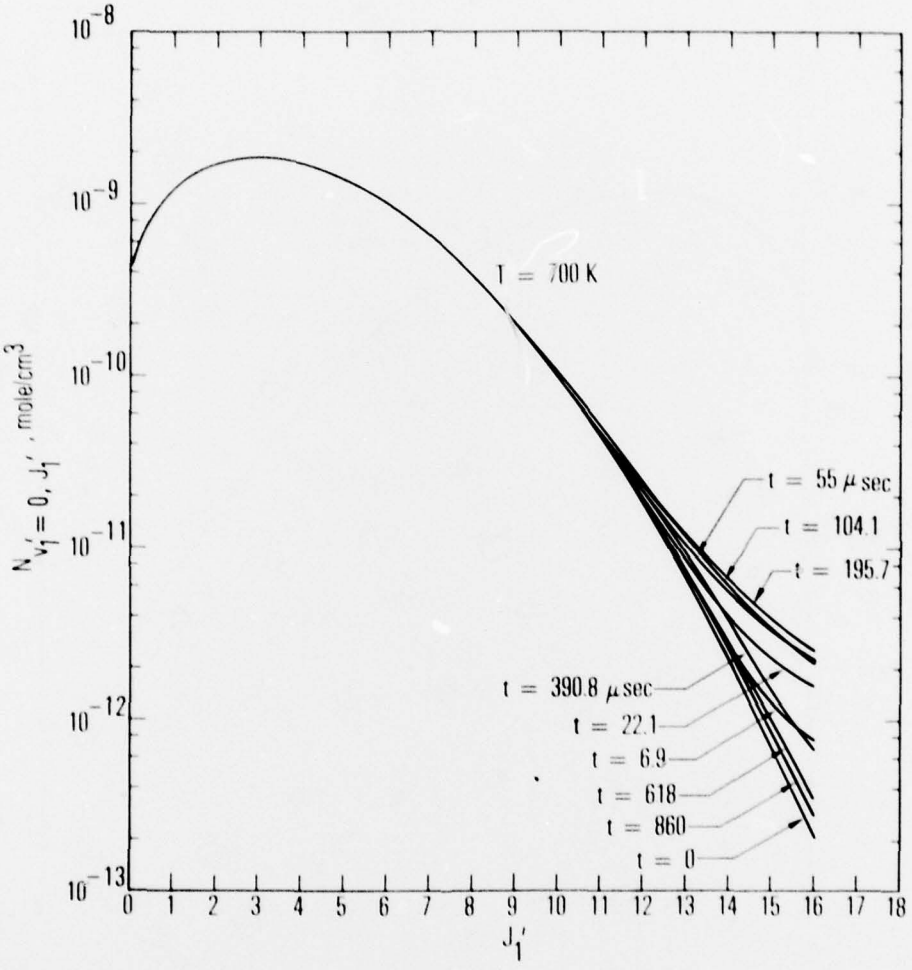

Fig. 7. Molar concentrations of $HF(v_1' = 0, J_1')$ versus rotational quantum number J_1' at various times. T = 700 K, P = 0.47 Torr.

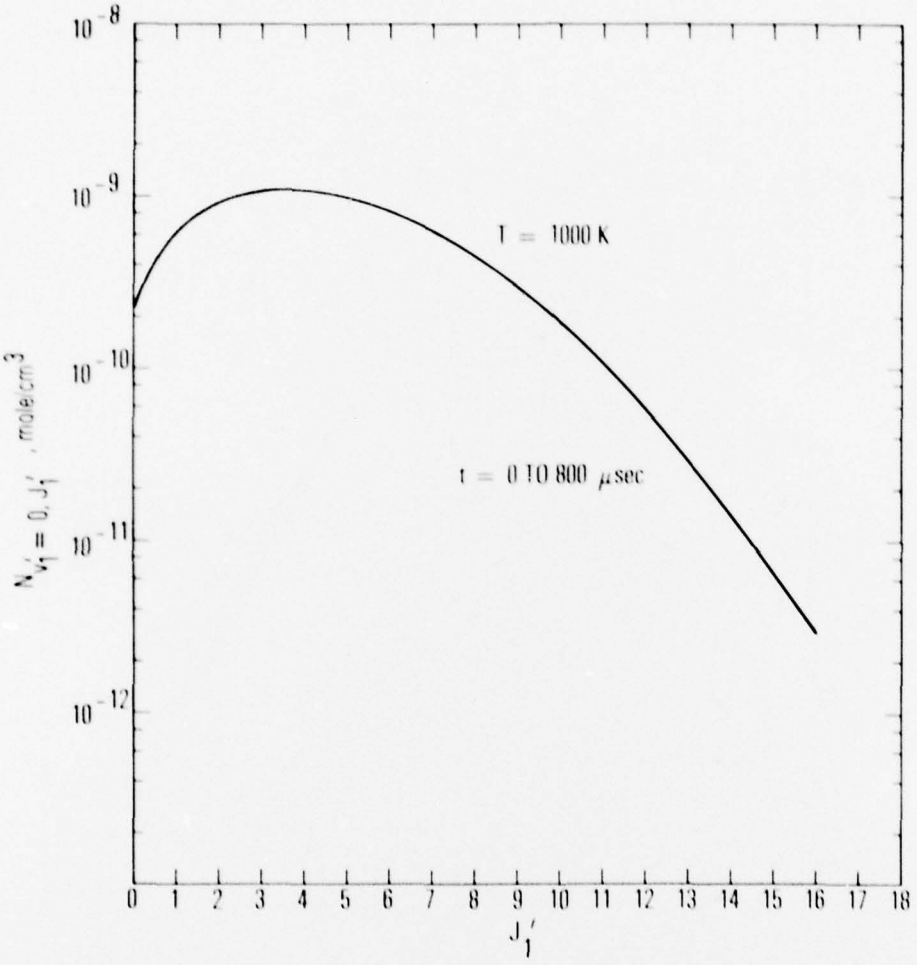

Fig. 8. Molar concentrations of $HF(v_1' = 0, J_1')$ versus rotational quantum number J_1' at various times. T = 1000 K, P = 0.47 Torr.

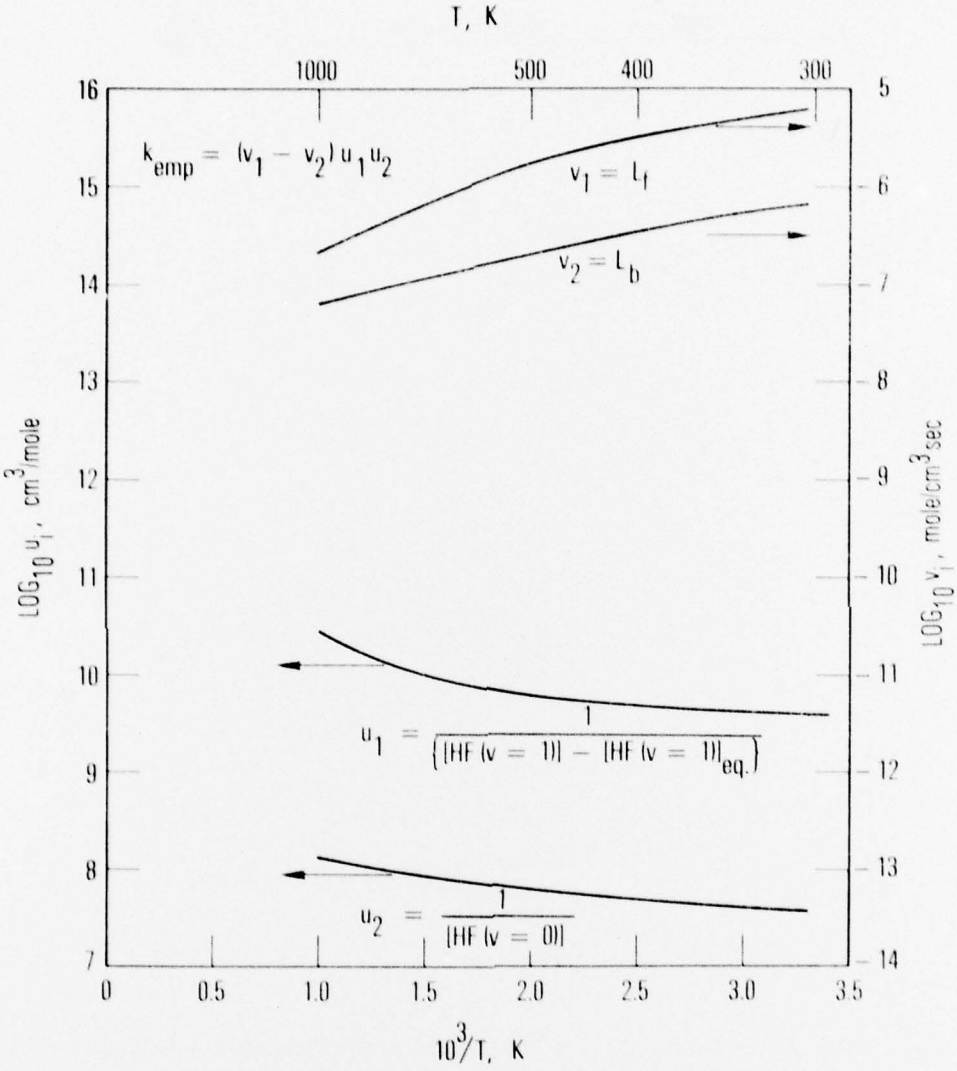

Fig. 9. The four terms in Eq. (8) required to calculate k_{emp} versus $10^3/T$ (K). $HF(v_1 = 1)$ was taken to be 0.01 of $HF(v_2 = 0)$. L_f is the rate of $v \rightarrow R$ processes affecting $d[HF(v = 1)]/dt$. L_b is the rate of $R \rightarrow v$ processes. t = 10 μsec, P = 0.47 Torr.

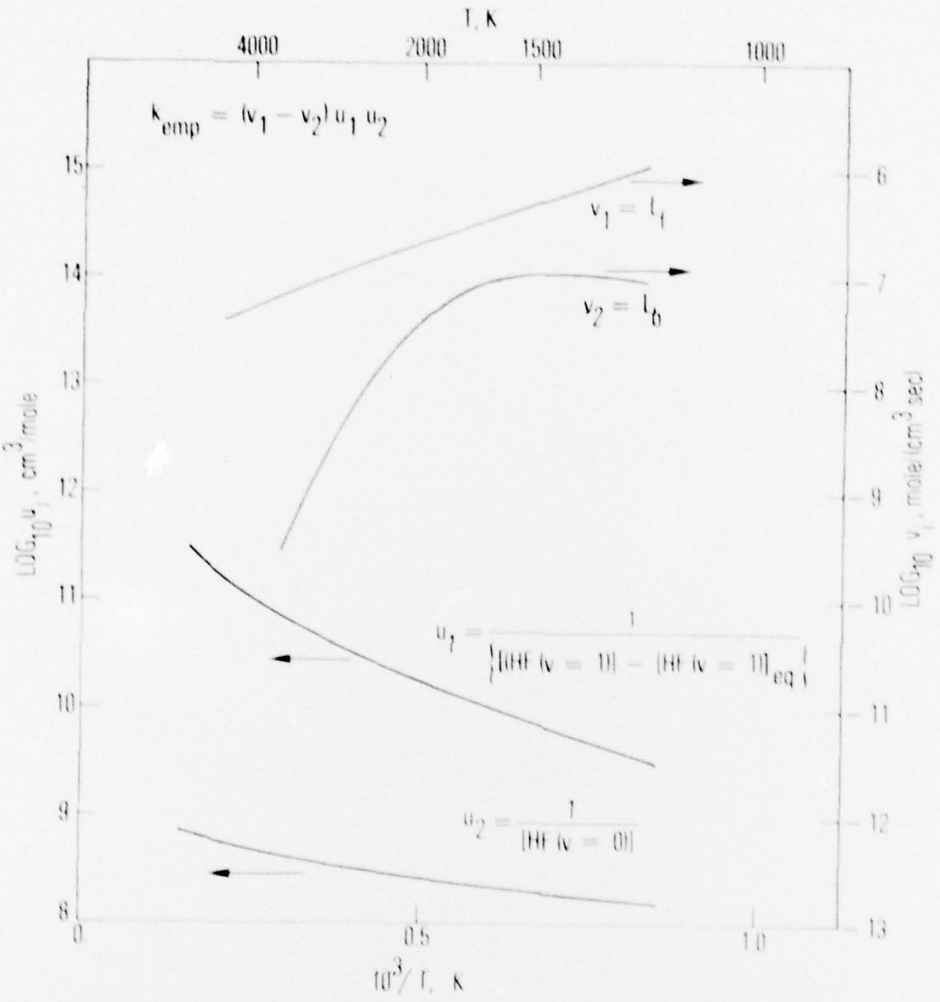

Fig. 10. Four terms in Eq. (8) required to calculate k_{emp} versus $10^3/T$ (K). $HF(v_1 = 1)$ was taken to be 0.1 of $HF(v_2 = 0)$. t = 10 μsec, P = 0.47 Torr.

and beyond 2000 K, only the $v \rightarrow R$ processes are important. The contributions from $v \rightarrow R$ processes decrease monatonically with increasing temperature. The contributions from $R \rightarrow v$ processes decrease with increasing temperature. The expression $L_f - L_b$, therefore, exhibits a decreasing slope with increasing temperature or a concave-up behavior for k_{emp}. The ascending high-temperature leg of k_{emp} (or descending leg of Pr) depends very much on the Landau-Teller analytical interpretation used by experimentalists[2, 12] and the fact that $\{[HF(v = 1)] - [HF(v = 1)]_{eq}\}$ becomes much smaller at higher temperatures, which gives the "normal" appearance of a rate coefficient with a $T^{-1/3}$ dependence. Without this interpretation and division by the difference of two densities, the high-temperature leg of k_{emp} cannot be reproduced by the model. The model also indicates that even though a Boltzmann distribution of J states is maintained at all times above 1000 K (Fig. 8), the functional behavior of L_f, L_b, and $\{[HF(v = 1)] - [HF(v = 1)]_{eq}\}$ generates the minimum and increasing leg of k_{emp}.

It appears that k_{emp} is a net summation of a series of rate terms representing available channels for $v \rightarrow R$ and $R \rightarrow v$ mechanisms. Each rate term is essentially a collision frequency consisting of a product of rate coefficients and densities of colliding molecules, Eqs. (3), (4), and (5). In general, k_{emp} can have significantly larger or smaller values than the individual $k_f^{v \rightarrow R}(J_1, J_2, J'_1, J'_2)$ terms. Moreover, the temperature dependence of k_{emp} need not have the same behavior as the individual $k_f^{v \rightarrow R}(J_1, J_2, J'_1, J'_2)$ terms. It follows then that the rotationless energy defect, definable from experiments on k_{emp} as 3961 cm^{-1}, also has no meaning when determining a

"backward" quenching rate coefficient. The individual energy defects $\Delta E_{v,J}$, as defined by Eq. (1), are much smaller.

Evidence of high J_1' states in significant rotational nonequilibrium conditions is crucial evidence in establishing validity for the v → R processes and this model. The densities in Fig. 3 indicate some rotational population inversions, which means that laser action on pure rotational transitions of HF might be possible. For example, Deutsch[30] observed laser action on pure rotational transitions of HF formed by the F + H_2 chemical reaction. He observed rotational transitions in HF from energy levels corresponding to very high J values, which indicates a rotational nonequilibrium distribution of HF(v, J_{high}) states. The rotational states responsible for the laser action observed by Deutsch could not have been formed from the F + H_2 reactions.[23] It would appear that the high J states observed may have been formed by energy-transfer processes involving vibrational relaxation from high (v, J) levels of HF where multiquantum v → R energy-transfer processes are important. This is believed to provide a plausible explanation for the high J-states observed by Deutsch. Krough[31] has reported lasing in flash-photolysis-initiated HF chemical lasers involving exceptionally high J states and has invoked versions of the v → R mechanism to explain the results.

Some indication of rotational nonequilibrium has been given by Green, Sanders, and Hancock,[21, 22, 32] who measured HF(v = 1) self-relaxation rates in pure HF in HF highly diluted with argon by means of the laser-excited vibrational fluorescence technique. They found that HF(v_1 = 1) self-relaxation rate observed in pure HF was 30% slower than the similar rate with HF diluted

in argon. They speculated that this behavior was a result of incomplete thermalization of the high rotational states during vibrational relaxation in pure HF. If it is assumed that a quantum of vibrational energy of the $HF(v_1 = 1)$ molecule goes mostly into rotational energy of the same molecule upon an $HF(v_1 = 1) + HF(v_2 = 0)$ collision, the $v \rightarrow R$ mechanism would give a large ΔJ change with a very small energy defect. In Fig. 5, the incomplete thermalization of the rotational levels speculated on by Green, Sanders, and Hancock is shown. Such evidence is considered to be indirect, however, and an unambiguous experiment, which reveals very high J states out of equilibrium as a result of the $v \rightarrow R$ processes in HF, is still to be performed.

IV. CONCLUSIONS

The empirical quenching coefficient for $HF(v_1 = 1)$ + HF vibrational relaxation has been successfully duplicated with good agreement over the entire temperature range with the use of a rotational nonequilibrium model and rate coefficients computed by Wilkins.[23] The key processes are $v \rightarrow R$ and $R \rightarrow v$ mechanisms, which give the problem a multiple-channel nature. The puzzling temperature dependence[33] observed for $HF(v_1 = 1)$ vibrational relaxation by $HF(v_2 = 0)$ is explained by this model. This model should be equally applicable to vibrational relaxation of other hydrogen halide molecules. This theoretical study is the first in which $HF(v_1 = 1)$ vibrational relaxation by $HF(v_2 = 0)$ has been fully described over the entire temperature range. It also confirms previous high (>1400 K) and low (<1000 K) temperature experimental studies. No mechanisms involving dimerization appear to be necessary to an understanding of the inverse temperature dependence of the reported quenching rate coefficients.

Significant high rotational state nonequilibria are predicted by Wilkins and this kinetic model at the low temperatures. An attempt by us to experimentally observe these high J states is in progress.

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