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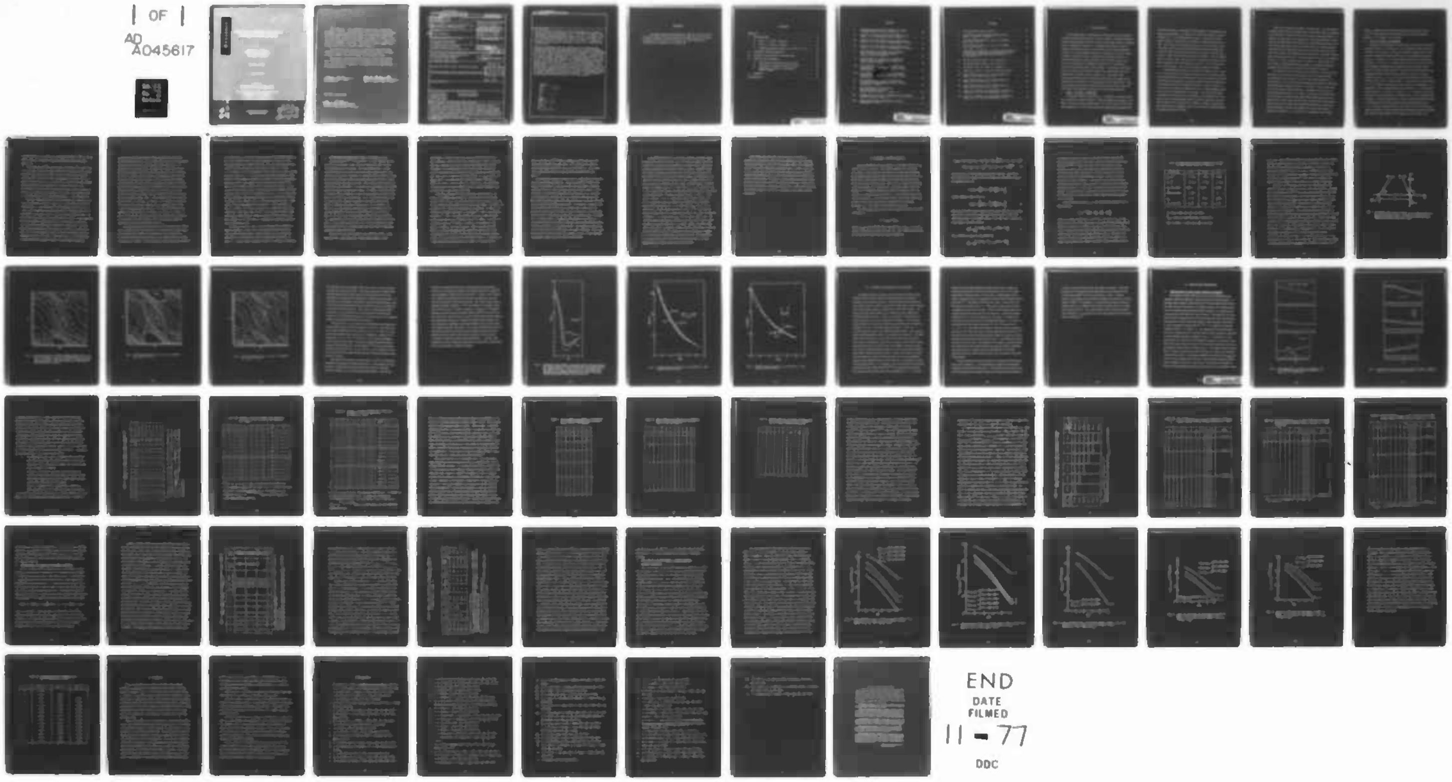

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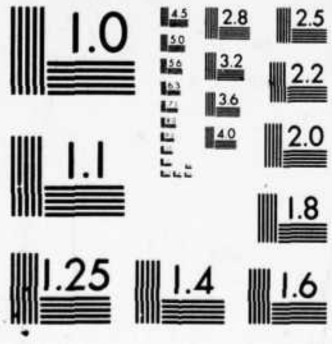

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Rate coefficients are calculated for the energy-transfer processes that occur when HF(v_1, J_1) molecules collide with HF(v_2, J_2) molecules. Three-dimensional classical trajectories of the collision dynamics of these energy-transfer processes were calculated by means of a potential energy surface, which consists of a London-Eyring-Polanyi-Sato (LEPS) potential function for the short-range interactions and a partial-point-charge, dipole-dipole function for the long-range interactions. This energy surface was used to predict an equilibrium geometry of the HF dimer.

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From the trajectory calculations, it was predicted that the v → v energy-transfer processes occur by means of $\Delta v = \pm 1$ transitions and that the rate coefficients for the processes $HF(v) + HF(v = 0) \rightarrow HF(v - 1) + HF(v = 1)$ decrease with increasing vibrational quantum number v. A calculation of the v → v rate for the reaction $HF(v = 1) + HF(v = 1) \rightarrow HF(v = 0) + HF(v = 2)$ indicates a value of 1.2×10^{13} cm^3 mole^{-1} sec^{-1} at 300 K. This process corresponds to near-resonant vibration-to-vibration (v → v) intermolecular energy transfer.

The major contribution to the rate coefficients for the energy-transfer mechanisms comes from the rotating HF molecules. The vibrationally excited HF rotor takes the energy mismatch ΔE, corresponding to rotationless HF molecules, away by means of a vibration-to-rotation (v → R) energy transfer process. This process corresponds to a nonresonant v → R intramolecular energy transfer. Multiquantum v → R processes are predicted. At low v, it is predicted that one in three HF-HF collisions produces v → R energy transfer. For many of the important v → R energy-transfer processes, the energy defect is less than 200 cm^{-1}. The trajectory calculations indicate that the number of v → R open channels increases with increasing v. The multiquantum v → R transitions provide more ways to distribute the vibration energy of the vibrationally excited HF molecules into rotational energy; i.e., into very high rotational quantum states. The high rotational quantum states are quickly relaxed by R → v processes and by fast v → R processes in which even higher rotational quantum states are produced. The high rotational quantum states are relaxed slowly by R → (R', T) processes.

PREFACE

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[redacted]

FIGURES

I. INTRODUCTION

The energy-transfer mechanisms for self-deactivation of vibrationally excited hydrogen fluoride molecules are quite complex. Possible mechanisms include energy-transfer processes in which (1) vibrational energy is exchanged between colliding HF molecules (v → v) through intermolecular energy exchange; (2) vibrational energy is converted into rotational and translational energy (v → R, T) through intermolecular or intramolecular energy exchange, or both; (3) rotational energy is converted into vibrational energy (R → v) through intramolecular energy exchange; and (4) rotational energy is converted into rotational and translational energy (R → R, T) through intermolecular and intramolecular energy exchange. It is difficult, if not impossible, to determine experimentally detailed rate coefficients for these four possible types of energy-transfer mechanisms. A knowledge of the temperature-dependent rate coefficients for these types of energy-transfer mechanisms is important for an understanding of HF chemical lasers. Some of the problems associated with interpretation of previous work on the self-deactivation of vibrationally excited HF are briefly summarized here.

A. $HF(v_1 = 1) + HF(v_2 = 0)$ SYSTEM

Vibrational relaxation rates of $HF(v_1 = 1)$ by $HF(v_2 = 0)$ molecules have been measured by several techniques.[1] The deactivation rate of $HF(v_1 = 1)$ by $HF(v_2 = 0)$ has an average measured value of 1.2×10^{12} cm^3 mole^{-1} sec^{-1} at room temperature.[2] In the interpretation of the experiments reported in the published literature, it is assumed by most authors[1] in reducing their data that the reaction $HF(v_1 = 1) + HF(v_2 = 0) \rightarrow HF(v_1' = 0) + HF(v_2' = 0)$ occurs through a v → T, R energy-transfer process, which has an energy defect of 3962 cm^{-1}; this energy is assumed to be given up to the thermal bath. Airey and Fried[3] postulated that these fast self-relaxation rates of HF are the result of a strong attraction potential that exists between HF molecules, which results in the formation of HF dimers, and that they, perhaps, could be caused by monomer-dimer collisions. Airey and Fried[3] point out, however, that, at the pressures and temperature of their experiment, less than 0.001% of the HF exists as dimers, so that the measured rate, in their opinion, is the result of monomer-monomer collisions.

Thompson[4] points out that Airey and Fried' s point of view is correct if it is assumed that the vibrational relaxation occurs by collisions between the excited HF molecule and the HF dimer, but it is not necessarily correct if the effective intermediate is a long-lived complex formed by collision of an excited HF molecule with another HF molecule. Under the latter circumstances, the vibrational relaxation rates are critically dependent on the rate of formation and dissociation of the dimer. The long-lived complex corresponds to two HF molecules held together by an attractive well. The complex can be stabilized temporarily by transfer of collision energy into several modes of the complex such as rotation. Transfer of energy from these modes back to translation results in an equilibrium condition between the monomers and dimers of HF.

Shin[5] used a vibration-to-rotation, energy-transfer, one-dimensional analytical model, which included the effects of the dipole-dipole and hydrogen-bond interactions to explain the efficient vibrational relaxation of HF($v_1 = 1$) by HF($v_2 = 0$) molecules at low temperatures. Shin speculated that, because of the strong dipole-dipole attractive forces, the HF molecules attract each other at large separations even when each HF molecule is rotating rapidly. The addition of the dipole-dipole interaction term to the short-range interaction term enhances the probability of energy transfer. In HF-HF collisions, Shin's model predicts that the $v \rightarrow T$ energy-transfer process is less efficient than the $v \rightarrow R$ energy-transfer process. In the Shin analytical model, the dipole-dipole and hydrogen-bond interactions are considered as separate, important interactions in the relaxation of vibrationally excited HF.

One objective of this research was to investigate the requirement that HF dimers be formed at room temperature in order to explain the fast self-relaxation rates measured by various experimental techniques.[1] A second objective was to calculate the temperature-dependent rate coefficient for the vibrational relaxation of HF($v_1 = 1$) by HF($v_2 = 0$) and compare the result with available experimental data. A potential energy surface for the collisions between HF(v_1, J_1) + HF(v_2, J_2) molecules was constructed, which consists of a London-Eyring-Polanyi-Sato (LEPS) potential-energy function for the short-range interactions and a partial-point charge, dipole-dipole function for the long-range interactions between the four particles. Three-dimensional trajectory calculations were made of the collision dynamics of the HF($v_1 = 1$, J_1) + HF($v_2 = 0$, J_2) systems on this energy surface. Temperature-dependent rate coefficients are reported for the v → R, T energy-transfer processes that occur in collisions involving $HF(v_1 = 1, J_1) + HF(v_2 = 0, J_2)$ systems.

B. $HF(v_1 \geq 1) + HF(v_2 = 0)$ SYSTEMS

Knowledge of the temperature-dependent rate coefficient for vibrational relaxation of $HF(v_1 = 1)$ by $HF(v_2 = 0)$ is not sufficient to model the HF chemical laser. It is necessary to know also temperature-dependent rate coefficients for vibrational relaxation of HF species from the higher vibrational levels ($v_1 = 2$ through $v_1 = 6$). Rate coefficients that include contributions from both v → v and v → R, T energy-transfer processes for the deactivation from the higher vibrational levels of HF have been reported by several authors.[6-8] Some of these authors[6,7] estimated the contribution to the rate coefficients for the energy-transfer processes by means of a harmonic oscillator model $k_{v,v-1} = vk_{1,0}$ to predict the contribution to the total rate coefficient from v → R, T energy transfer. In the harmonic oscillator model, the v → R, T energy-transfer processes do not involve multiquantum v → R, T transitions. The rate coefficients for the endothermic v → v energy-transfer processes $HF(v_1 > 1) + HF(v_2 = 0) \rightarrow HF(v_1' = v_1 - 1) + HF(v_2' = 1)$ can be calculated if the rate coefficients are available for the v → R, T energy-transfer processes. Flowtube measurements reported by Kwok and Wilkins[8] indicate a v^2 dependence for the rate coefficients that represent the sum of all v → R, T energy processes that occur from a given v level for the $DF(v_1) + HF(v_2 = 0)$ system. Since the dipole-dipole interactions between the colliding HF + HF, DF + DF, and the HF + DF systems are quite similar, it is probable that the v → R, T total rate coefficients for $DF(v_1) + DF(v_2 = 0)$, and $HF(v_1) + HF(v_2 = 0)$ exhibit a v dependence similar to that for $DF(v_1) + HF(v_2 = 0)$.

It has not been possible to separate the contributions from the v → v and v → R, T energy-transfer processes obtained in experimental measurements. In an $HF^* + HF$ system, where HF^* represents vibrationally excited HF species, the HF^* vibrational levels may relax at the same time. If the v → v rates are faster than the v → R, T rates, the v → v rates would couple together all the vibrational levels so that the rate coefficients for the v → R, T energy-transfer processes could not be separated from the rate coefficients for the v → v energy-transfer processes. Only the $k_{1,0}$ rate coefficient for v → R energy transfer can be obtained without this v → v coupling difficulty.

There is a definite need for both the temperature and v dependences of the rate coefficients for both v → v and v → R, T energy-transfer processes. Experimental v → v rate coefficients can be deduced from measured (v → v + v → R, T) rate coefficients only when information is available on the v → R, T rate behavior of the upper v levels. A v^2 or greater dependence in the v → R rate coefficients would result in a further decrease in the v → v rate coefficients and would probably eliminate the problem of predicting from experiment v → v rate coefficients that exceed the gaskinetic collision rate. The computer modeling of flowtube results of $HF(v_1 > 1) + HF(v_2 = 0)$ systems provides indirect evidence that such large v → v rate coefficients for the upper vibrational levels are not correct. When such large v → v rate coefficients are used to model the flowtube results, it is not possible to obtain any agreement with the measured decay slopes. Additional experimental evidence[9] that such large v → v rate coefficients are not correct involves the measurement of the time-resolved spectral behavior for the v → v - 1 transitions at room temperature. Too much laser energy output is predicted from the upper vibrational levels when such large rate coefficients for the v → v rates are used in pulsed or continuous-wave chemical-laser computer codes. The effect of fast v → v rates is to pump-up the higher vibrational levels more than would be predicted on the basis of the initial product distributions measured for the pumping reactions used to generate the lasing species. It would seem, therefore, that the v → R, T rate coefficients must have a greater than the v dependence predicted from the harmonic oscillator model. The v → v rate coefficients for the exothermic processes $HF(v_1 \geq 1) + HF(v_2 = 1) \rightarrow HF(v_1' = v_1 + 1) + HF(v_2' = 0)$ would not be larger than the gaskinetic collision rates, as predicted from recent experimental measurements, if (1) the v → R, T rate coefficients for the endothermic processes $HF(v_1 \geq 1) + HF(v_2 = 2) \rightarrow HF(v_1 - 1) + HF(v_2' = 1)$ have a v^2 or greater v dependence and (2) if the energy mismatch ΔE used to calculate the rate in the exothermic direction includes the effect of rotational motion of the colliding HF molecules.

A one-dimensional theory of vibrational-to-vibrational energy transfer was developed by Shin.[10] In this theory, it is assumed that energy transfer occurs through the formation of nonrigid dimers at low temperatures ($T \leq 300$ K) and through rotational motion of the colliding molecules at high temperatures ($T > 300$ K). In the nonrigid dimer model, the energy mismatch is transferred to the restricted translation motion of the colliding molecules, and, in the rotational model, the energy mismatch is transferred to the rotational motion of the colliding molecules. The rate coefficients predicted by Shin[10] for the deactivation processes $HF(v_1) + HF(v_2 = 0) \rightarrow HF(v_1' = v_1 - 1) + HF(v_2' = 1)$ at room temperature increase with v_1, but, after reaching a maximum value at $v_1 = 4$, they decrease sharply with increasing v_1. Shin and Kim[11] extended Shin's one-dimensional model[10] to study the temperature dependence of the energy-transfer rates in the temperature range 200 to 2000 K. They found that; at 200 K, the rate coefficients for those $v \rightarrow v$ processes decrease with increasing v because of the dimer mechanism; at 200 K, a maximum value in these rate coefficients occurs at $v_1 = 3$; and, above 300 K the rate coefficients increase with increasing v_1 as a result of the rotational contribution of the rotational motion to the energy-transfer processes. Shin and Kim's model, when applied to two-quantum $v \rightarrow v$ processes $HF(v_1) + HF(v_2 = 0) \rightarrow HF(v_1' - 2) + HF(v_2' = 2)$, predicts very small values of the rate coefficients. Their theory does not indicate the mechanism by which vibrational energy is converted into rotational energy in HF-HF collisions, nor does it predict, for HF· HF collisions, multiquantum vibrational-rotational energy exchange processes.

One objective of this research was to investigate the mechanism by which the vibrational energy of the vibrationally excited HF molecule is converted into rotational energy. Another objective was to calculate the temperature and v dependences of the rate coefficients for both the $v \rightarrow v$ and $v \rightarrow R, T$ energy-transfer processes in $HF(v_1 > 1) + HF(v_2 = 0)$ collisions.

C. ROTATIONAL RELAXATION OF $HF(v_1, J_1)$ BY $HF(v_2 = 0, J_2)$

Green and Hancock[12, 13] measured $HF(v = 1)$ self-relaxation rates in pure HF and in HF highly diluted with Ar by means of the laser-excited vibrational fluorescence technique. They found that the $HF(v = 1)$ self-relaxation rate observed in pure HF was 30% slower than the similar rate with the HF diluted in Ar. They gave one explanation of this behavior as being the result of incomplete rotational thermalization of high rotational J levels during vibrational relaxation in pure HF. With it assumed that a quantum of vibrational energy of the $HF(v = 1)$ molecule goes preferentially into rotational energy of the same molecule upon an $HF(v_1 = 1) + HF(v_2 = 0)$ collision, such an energy mechanism would give a large ΔJ change with a very small energy defect. The rotationally excited $HF(v_1' = 0, J_1' = 14)$ molecule produced can be expected to have a lifetime comparable to the vibrationally excited $HF(v_1 = 1)$ molecule vibrational-relaxation time. If, for example, the $HF(v_1' = 0, J_1' = 14)$ molecules produced by the $v \rightarrow R$ mechanism are not removed immediately, it is then possible for them to transfer back to $HF(v_1 = 1, J = 2)$ by an $R \rightarrow v$ process (the result of small energy defects, i.e., less than 200 cm^{-1}) and consequently decrease the apparent measured $HF(v_1 = 1)$ self-relaxation rate by the $v \rightarrow R, T$ energy-transfer processes. This mechanism[14] is not as effective when Ar is used, since Ar efficiently rotationally quenches HF and DF.

Hancock and Saunders[14] studied the self-relaxation of $DF(v = 1)$ and found that their room-temperature results clearly indicate a 50%

slower DF($v = 1$) self-quenching rate in pure DF than when measured in DF-Ar mixtures. This decrease in the relaxation time of DF($v = 1$) in pure DF can be explained if it is assumed that the vibrational and rotational relaxation occur on similar time scales in undiluted DF. Hancock and Green[13] speculated that Ar efficiently quenches rotationally excited HF and DF. This means of rotational deactivation of HF($v = 0$, J_{high}) or DF($v = 0$, J_{high}) with Ar is not applicable when studying vibrational relaxation of HF($v = 1$) or DF($v = 1$) in pure HF or DF, respectively. The complicated situation that the vibrational relaxation and the rotational relaxation occur on similar time scales must be dealt with.

Hancock and Saunders[14] reported that their measured HF($v_1 = 1$) - DF($v_2 = 0$) quenching rates indicated no discrepancy between the diluent versus no diluent cases. The argument used for pure HF or DF can be used also to explain the lack of difference observed in their HF($v_1 = 1$) + DF($v_2 = 0$) quenching rates. Most of the vibrational energy in HF($v_1 = 1$) + DF($v_2 = 0$) collisions is transferred through v → v exchange,[15, 1] with an energy defect of 1055 cm^{-1}. The v → R energy-transfer processes are still important, but the energy that must be absorbed [1055 cm^{-1} for HF($v_1 = 1$) + DF($v = 0$) compared to 3962 cm^{-1} for HF($v_1 = 1$) + HF($v_2 = 0$) and 2907 cm^{-1} for HF($v_1 = 1$) + DF($v_2 = 0$)] is much smaller. Lower rotational states of DF($v_1 = 0$) would be populated and the rotational energy transfer would proceed faster because of the close spacings of the low rotational energy levels. The rate coefficient for the deactivation of DF($v_1 = 1$) by DF($v_2 = 0$) is approximately less than half the rate coefficient for deactivation of

HF(v = 1) by HF(v = 0),[14,16] which is additional evidence that nearly all of the initial vibrational energy of HF(v = 1) is converted into rotational energy rather than translational energy of the colliding pair. This result concurs with earlier results for HCl and DCl presented by Chen and Moore.[17]

The rotational relaxation of highly rotational excited HF molecules has only been investigated qualitatively. Polanyi and Woodall[18] and Ding and Polanyi[19] showed that, for hydrogen halides, the probability of rotational deactivation decreases with increasing rotational quantum number J. The vibrational energy of vibrationally excited HF molecules can be converted almost entirely into rotational energy by a mechanism that populates the high rotational quantum states of the same vibrationally excited HF molecules (large ΔJ change) with small energy defects. It is expected, therefore, that the rate coefficients for deactivation from these high J states by R → T processes decrease with increasing J because an increase in J is associated with an increase in the energy spacings between rotational levels. In addition to R → T energy transfer, it is expected that collisions with resonance transfer of rotational energy play an important role in rotational deactivation. This type of collision is R → R energy transfer. The rotational energy given up by one HF molecule is transferred to its partner in collision. The R → R,T energy-transfer processes provide the drainage necessary for the rotational nonequilibrium states to relax to a thermal distribution.

Deutsch[20] observed laser action on pure rotational transitions of HF formed by the chemical reaction $F + H_2$. He observed rotational transitions in HF from energy levels corresponding to very high J values, indicating a rotational nonequilibrium distribution of HF(v, J) states. Polanyi[21] points out that this rotational nonequilibrium can exist when the spacing between the rotational levels becomes large enough such that a few collisions are not sufficient to induce rotational relaxation by $\Delta J = 1$ rotational jumps, as is the case when the rotational spacing is small. Deutsch[20] reports rotational lasing, for example, from $v = 0$, $J = 28$, from $v = 2$, $J = 20$, and from $v = 3$, $J = 28$. Theoretical trajectory calculations by Wilkins[22] for the $F + H_2$ reaction predict that the $HF(v', J')$ states are populated up to $J' = 17$ for $v' = 1$ and up to $J' = 12$ for $v' = 2$ or 3. Polanyi and Tardy,[23] in their study of the $F + H_2$ reaction by means of an infrared chemiluminescence technique, observed HF emission from $v' = 1$, 2, and 3, with $J'_{max} = 12$, 12, and 4, respectively. No HF emission was observed from $v' = 4$. From thermodynamic considerations, the reaction energy of the $F + H_2$ system is sufficient to populate $v' = 1$, 2, and 3 up to $J'_{max} = 20$, 14, and 5, respectively. The rotational states responsible for the laser action observed by Deutsch could not have been formed from the $F + H_2$ reaction. Another objective of this study was to attempt to determine whether or not the high J states are formed by energy-transfer processes involving vibrational relaxation from higher (v, J) levels where multiquantum v → R processes occur. If multiquantum v → R energy-transfer processes occur, they would provide a plausible explanation for the high J states observed by Deutsch.

Still another objective of this report is to give the results of calculations of temperature-dependent rate coefficients for the rotational relaxation of HF species from both low and high J states. In a subsequent report,[24] these rate coefficients calculated for the v → v and v → R, T and R → R, T energy-transfer processes will be incorporated into a model for rotational nonequilibrium to see if the constructed model can explain some of the HF laser kinetics. In Section II, the semiempirical treatment of the potential energy surface for HF-HF collisions is described. In Section III, the classical trajectory calculations are discussed. Results and discussions of this study are given in Section IV. A summary of the results is given in Section V.

II. POTENTIAL ENERGY SURFACE

Before modeling the collision dynamics, a reasonable potential energy surface must be constructed. The potential employed here for HF-HF interactions is constructed from two functions, a London-Eyring-Polanyi-Sato (LEPS) potential energy function for the short-range interactions and a point-charge, dipole-dipole potential energy function for the long-range interactions between the four atoms. This surface is capable of supporting a quasi-bound state, i.e., the HF dimer. It has been proposed by some authors[4,5,27-29] that the formation of quasi-bound complexes in HF-HF collisions is responsible for the efficient v → v energy transfer observed in several experiments. It is hoped that the surface used in this analysis will be able to uncover the role of dimer formation in HF-HF collisions involving v → v, v → R, and R → R energy-transfer processes.

The total potential energy E for a given configuration of the four atoms is defined by

$$E = E_{LEPS} + E_{d-d} \tag{1}$$

where E_{LEPS} is the LEPS potential energy function, and E_{d-d} is the point-charge, dipole-dipole potential energy function. The LEPS potential function for the interaction between the four atoms is defined by

$$E_{LEPS} = Q_{12} + Q_{34} + Q_{13} + Q_{14} + Q_{23} + Q_{24} - \left\{\frac{1}{2}\left[(J_{12} + J_{34} - J_{23} - J_{24})^2 + (J_{23} + J_{24} - J_{13} - J_{24})^2 + (J_{13} + J_{24} - J_{12} - J_{34})^2\right]\right\}^{1/2} \quad (2)$$

where Q_{ij} and J_{ij} are the Coulomb and exchange integrals, respectively. The Q_{ij}s and J_{ij}s are written in terms of bonding and antibonding energies. The Coulomb terms are

$$Q_{ij}(R_{ij}) = \frac{1}{2}\left[E^b_{ij}(R_{ij}) + \left(\frac{1 - K_{ij}}{1 + K_{ij}}\right) E^a_{ij}(R_{ij})\right] \quad (3)$$

and the exchange integral terms are

$$J_{ij}(R_{ij}) = \frac{1}{2}\left[E^b_{ij}(R_{ij}) - \left(\frac{1 - K_{ij}}{1 + K_{ij}}\right) E^a_{ij}(R_{ij})\right] \quad (4)$$

where R_{ij} is the internuclear distance between atom i and atom j, K_{ij} is the square of the overlap integral, E^b_{ij} is the bonding energy, and E^a_{ij} is the antibonding energy. The bonding energies or the single-state energies are represented by the Morse function

$$E^b_{ij} = D_{ij}\left[e^{-2a_{ij}(R_{ij} - R^{\circ}_{ij})} - 2e^{-a_{ij}(R_{ij} - R^{\circ}_{ij})}\right] \quad (5)$$

The antibonding energies are represented by

$$E^a_{ij} = A_{ij}\left[e^{-2a_{ij}(R_{ij} - R_{ij})} + 2e^{-a_{ij}(R_{ij} - R^{\circ}_{ij})}\right] \quad (6)$$

The diatomic parameters required to calculate an LEPS surface for the systems $F + H_2$, $H + F_2$, $H + HF$, and $F + HF$ were evaluated previously by Wilkins.[22,26,30,31] These parameters were determined in previous trajectory studies in which each surface was constructed for a specific reaction to match either experimental activation energy for the overall reaction or product energy distributions, or both. The values of these parameters are given in Table I. In this study, it was assumed that the diatomic potential energy surface parameters used in the dynamical studies involving the species, H, and F were transferable to the four-atom HF-HF system. Previous trajectory calculations by White and Thompson[32] support the validity of the assumption that the LEPS equation diatomic parameters are transferable.

The long-range potential E_{d-d} is represented by the Coulomb electrostatic function

$$E_{d-d} = \delta^2 \left[\frac{1}{R_{13}} + \frac{1}{R_{24}} - \frac{1}{R_{14}} - \frac{1}{R_{23}} \right] \tag{7}$$

where δ is assigned a value of 2.0×10^{-10} esu. The function E_{d-d} is constructed as the sum of four electrostatic atom-atom potential $\pm \delta^2/R_{ij}$ terms; each term represents a nonbonded atom pair in the HF-HF system. The term $\pm \delta^2/R_{ij}$ is consistent with the classical model in which the HF dipole is considered to consist of two opposite charges, δ and $-\delta$. The value to be used for δ was taken from Berend and Thommarson,[33] who reported on a planar classical trajectory study of vibrational relaxation of HF and DF by

Table I. Parameters Used to Construct Surface for Energy Transfer Between HF(v_1,J_1) + HF(v_2,J_2)

Parameters	H-F	H-H	F-F
β_{ij}, Å^{-1}	2.232	1.942	2.902
r_e, Å	0.9171	0.7419	1.4170
D_e, kcal/mole	140.7	109.2	38.02
Dipole Moment	1.82[a]	0	0
K_{ij}	0.15	0.15	0.05
A_{ij}, kcal/mole	70.4[b]	54.6[b]	46.0[c]

[a] R. Weiss, Phys. Rev. 131, 659 (1963).

[b] A_{ij} = 1/2 D_e for antibonding states of HF and H_2.

[c] R. L. Wilkins, J. Chem. Phys. 58, 2326 (1973).

HF and DF. These authors determined δ for the potential E_{d-d} by assuming that the equilibrium geometry for the dimer corresponds to a linear configuration that has an HF hydrogen-bond energy of 6.7 kcal/mole, as suggested by Coulson,[34] and by use of the F-F distance in the HF dimer the value 2.55 Å predicted from an ab initio self-consistent field (SCF) study carried out by Del Bene and Pople.[35] Their value of δ reproduces the known experimental dipole moment of HF at the equilibrium separation.

Yarkony et al.[36] calculated the interaction potential between two rigid HF molecules by means of the Hartree-Fock approximation. Ab initio SCF computational studies[35-39] have indicated that the single-configuration SCF theory provides a qualitative correct description of hydrogen bonding. The uncertainty in the HF dimer bond energy makes it impossible to determine if the SCF theory provides a quantitative description of hydrogen bonding.[36] Yarkony et al.[36] published total energies for planar and nonplanar HF-HF configurations. The coordinate system chosen by them to describe two rigid HF molecules with an internuclear separation of 1.723 bohr is shown in Fig. 1. This coordinate system was used in this study to make it much easier to compare parts of this surface with those of Yarkony et al.[36] for R = 5, 6, and 8 bohr. The resulting contour maps are shown in Figs. 2 through 4. For the planar surface calculations at R = 5, 6, and 8 bohr, the least-square deviations σ, from the results reported by Yarkony et al.,[36] are as follows: $R = 5a_0$, $\sigma = \pm 2.1$ kcal/mole; $R = 6a_0$, $\sigma = \pm 1.3$ kcal/mole; and $R = 8\ a_0$, $\sigma = \pm 0.25$ kcal/mole. This semiempirical surface compares favorably with the ab initio SCF calculation by Yarkony et al.[36]

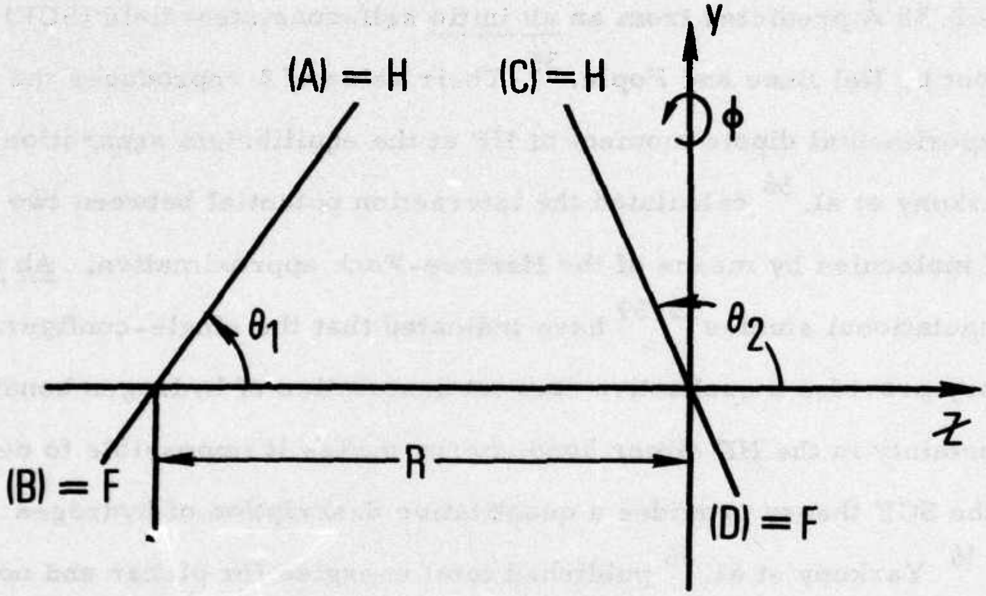

Fig. 1. Coordinate system used for HF-HF. R is the distance between the two HF centers of mass. The angle θ is defined with respect to the indicated z axis. ϕ is the angle of rotation of the right-hand HF molecule about the y-axis.

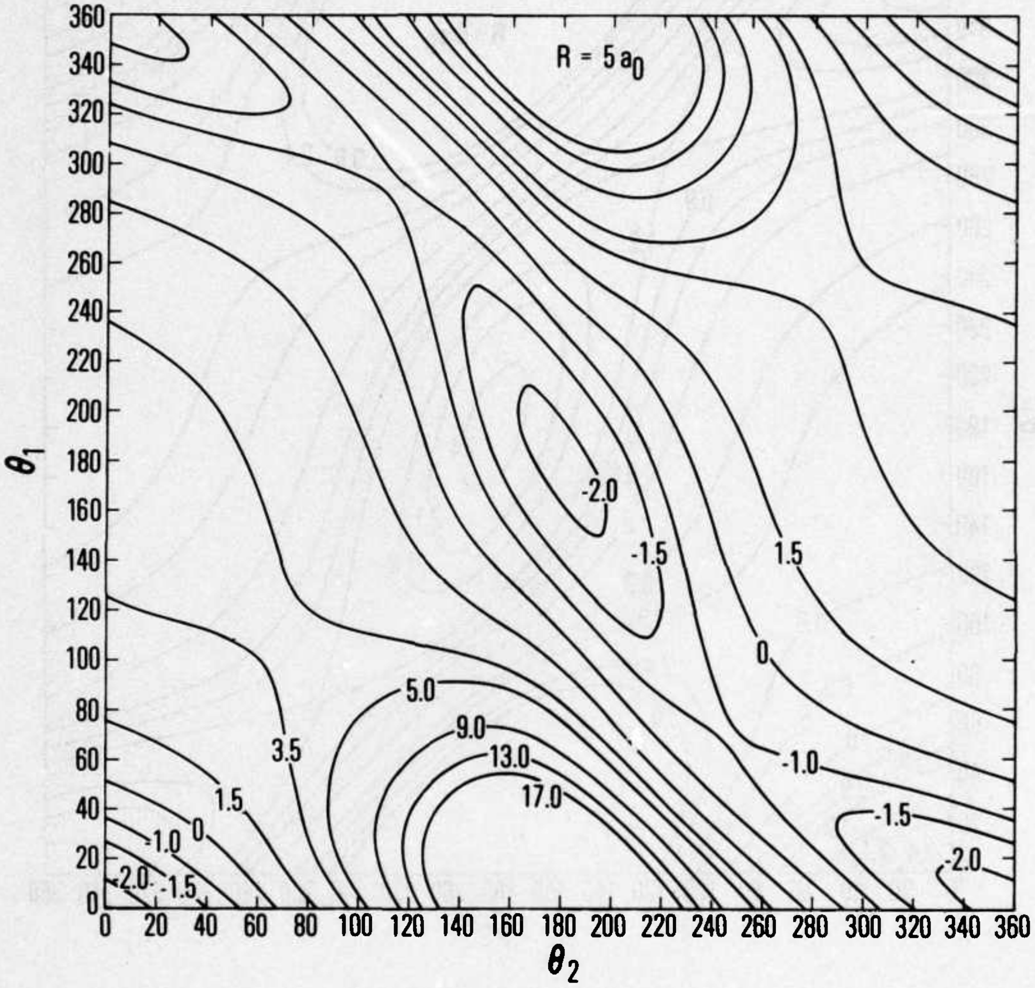

Fig. 2. Contour map for part of HF-HF potential surface with $R = 5\ a_o$ and $\phi = 0^\circ$ (planar). θ_1 and θ_2 are defined in Fig. 1. The contours are in units of kcal/mole, relative to two infinitely separated HF molecules. Each HF molecule has a fixed internuclear separation of $1.737\ a_o$.

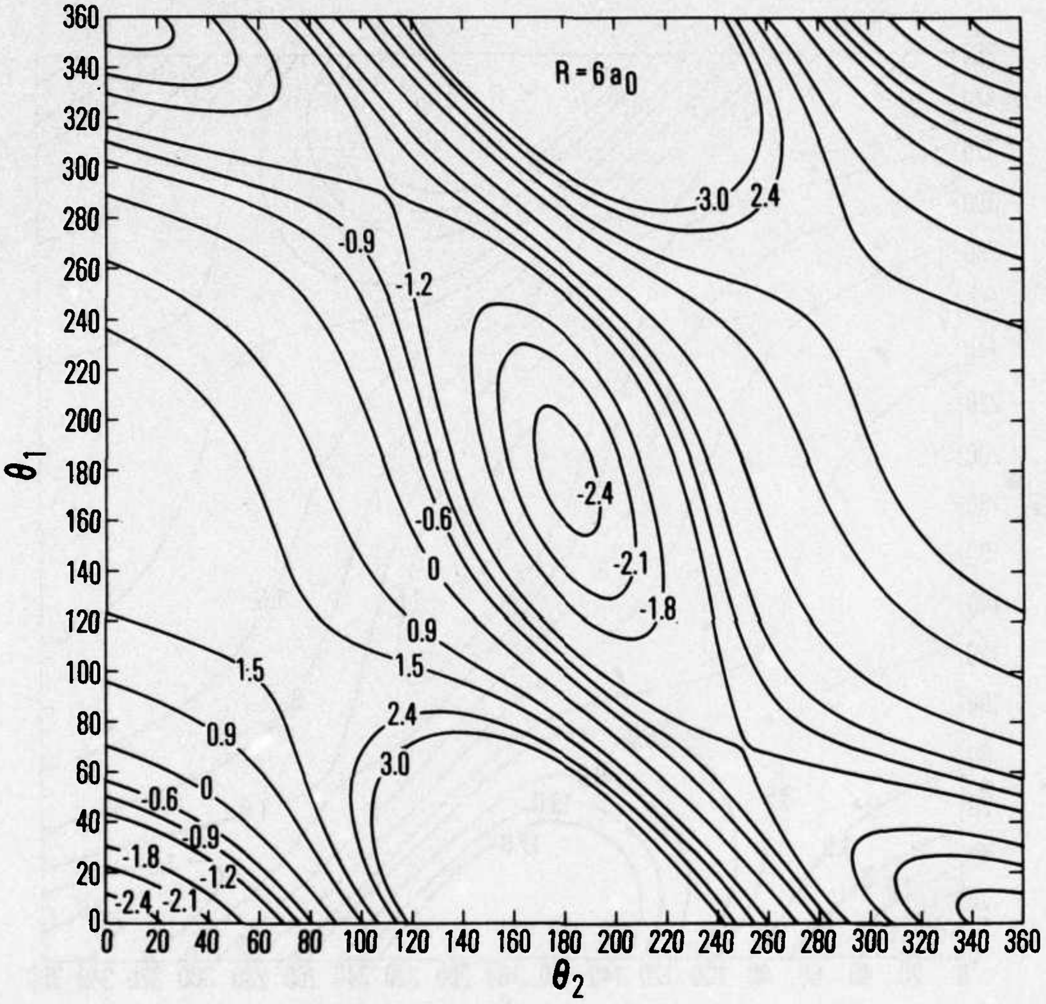

Fig. 3. HF-HF potential surface, $R = 6\ a_o$, $\phi = 0°$ (planar), $R_{12} = R_{34} = 1.737\ a_o$.

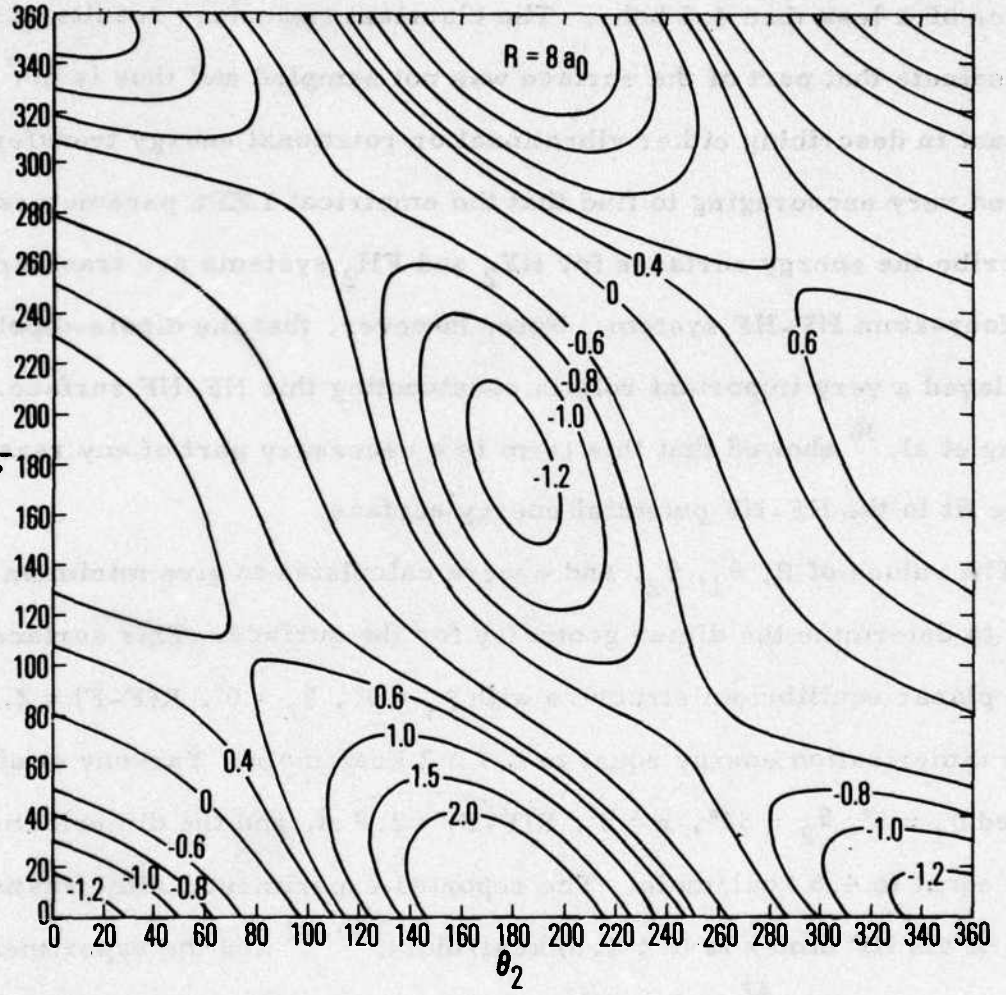

Fig. 4. HF-HF potential surface, R = 8 a_o, $\phi = 0°$ (planar), $R_{12} = R_{34} = 1.737\ a_o$.

This HF-HF surface and the SCF surface were found to be quite repulsive at values of R less than 4.5 bohr. The classical trajectory results of this study indicate that part of the surface was not sampled and thus is not important in describing either vibrational or rotational energy transfer. It is indeed very encouraging to find that the empirical LEPS parameters used to describe the energy surfaces for HF_2 and FH_2 systems are transferable to the four-atom HF-HF system. Note, however, that the dipole-dipole term played a very important role in constructing this HF-HF surface. Yarkony et al.[36] showed that this term is a necessary part of any reasonable analytic fit to the HF-HF potential energy surface.

The values of R, θ_1, θ_2, and ϕ were calculated to give minimum total energy to determine the dimer geometry for the surface. This surface predicts a planar equilibrium structure with $\theta_1 = 0°$, $\theta_2 = 0°$, R(F-F) = 2.9 Å, and the dimerization energy equal to 2.7 ± 2 kcal/mole. Yarkony et al.[36] reported $\theta_1 = 5°$, $\theta_2 = 52°$, $\phi = 0°$, R(F-F) = 2.8 Å, and the dimerization energy equal to 4.5 kcal/mole. The reported experimental dimerization energy of the HF dimer is (6 ± 1.5) kcal/mole,[40-41] and the experimental equilibrium geometry[42] is $\theta_1 = 0°$, $\theta_2 = 60\text{-}70°$, $\phi = 0°$, and R(F-F) = 2.8 Å. The results of all these studies indicate that the equilibrium geometry of the HF dimer is planar.

The electron-gas method was used by Parker et al.[43] to calculate the intermolecular potential for HF-HF interactions. In this method, the intermolecular energy between closed shell systems is the sum of kinetic, Coulomb, exchange, and correlation energy contributions. The detailed method for calculating intermolecular potentials between closed-shell systems was developed by Gaydaenko and Nikulin[44] and Gordon and Kim[45] and was modified by Rae[46] and Cohen and Pack.[47] Parker et al.[43] applied their method for calculating the intermolecular potentials for molecule-molecule interactions to HF-HF interactions. The results of this study are compared with those of Parker et al.[43] and with the accurate SCF calculations of Yarkony et al.[36] in Figs. 5 through 7. Parker et al.[43] added the leading term of the long-range induction (IND) energy[48] to the SCF part of the electron-gas results since the true SCF results contain induction effects. The method described here to calculate the intermolecular potential compares favorably at all distances and angles with the results of the electron-gas method and the SCF calculations. The present method and the electron-gas plus IND method do not contain all the induction and charge transfer effects present in the SCF calculation and, therefore, fail to describe accurately the hydrogen bonding region shown in Fig. 5. However, this method does produce enough of the attractive well to provide a valid calculation for energy transfer in HF-HF collisions.

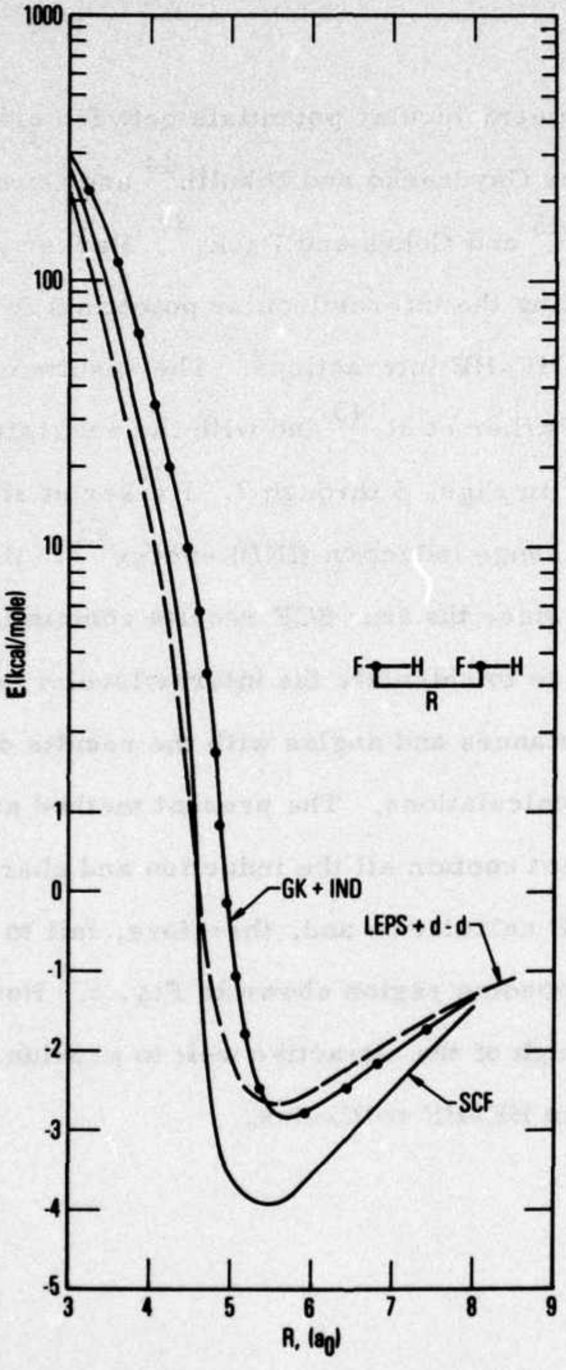

Fig. 5. **Comparison of the (LEPS + d-d) method with the SCF and (electron-gas + IND) results for the interaction energy E in kcal/mole of two HF molecules with $\theta_1 = 0$, $\theta_2 = 0$, and $\phi = 0$. The dashed line is the (LEPS + d-d) results of this report, the solid-dot line is the electron-gas plus induction results of Parker et al.,[43] and the solid line is the SCF results of Yarkony et al.[43]**

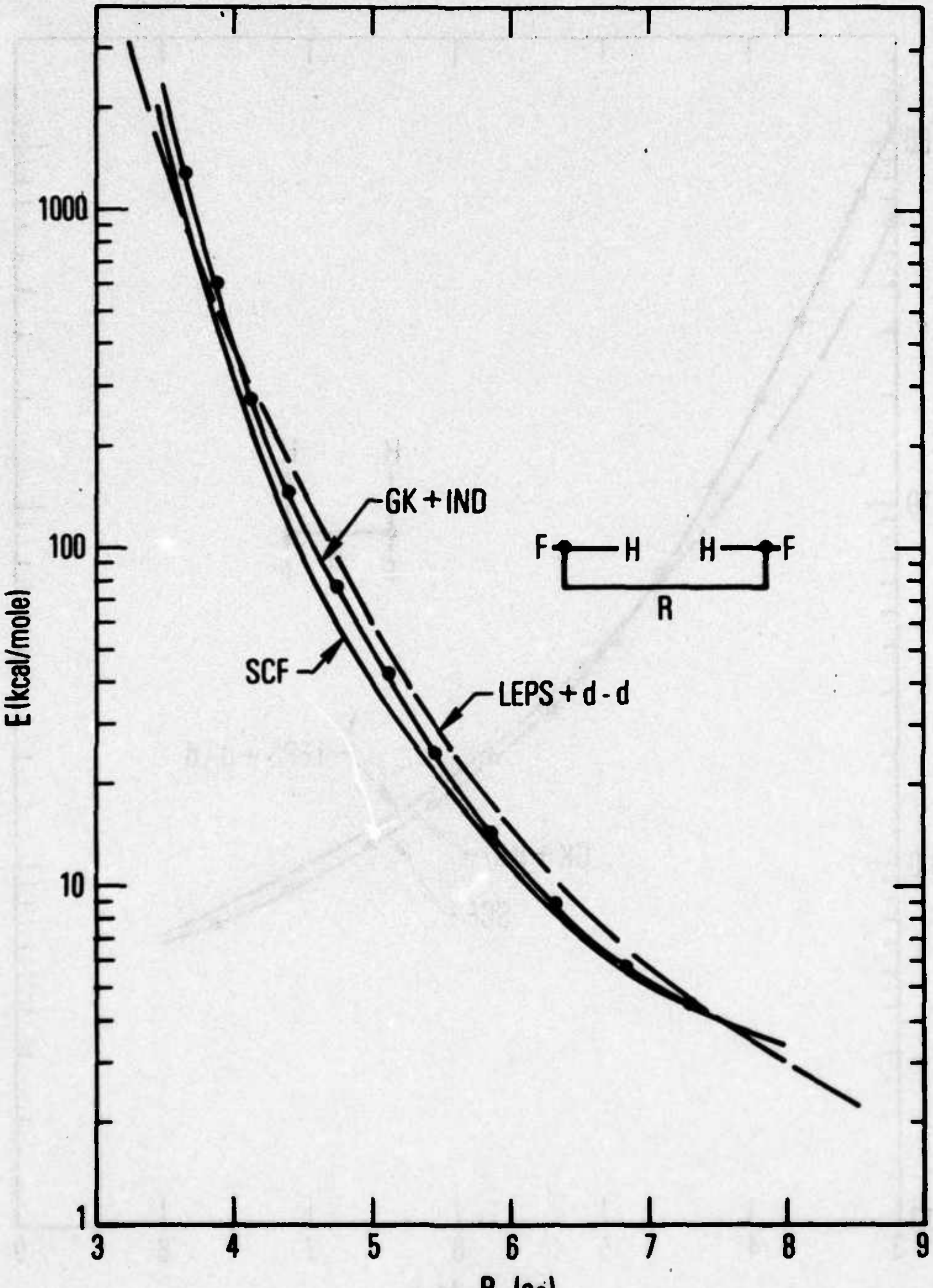

Fig. 6. HF-HF interactions with $\theta_1 = \theta_2 = \Pi/2$ and $\phi = 0$. The notation is given in Fig. 5.

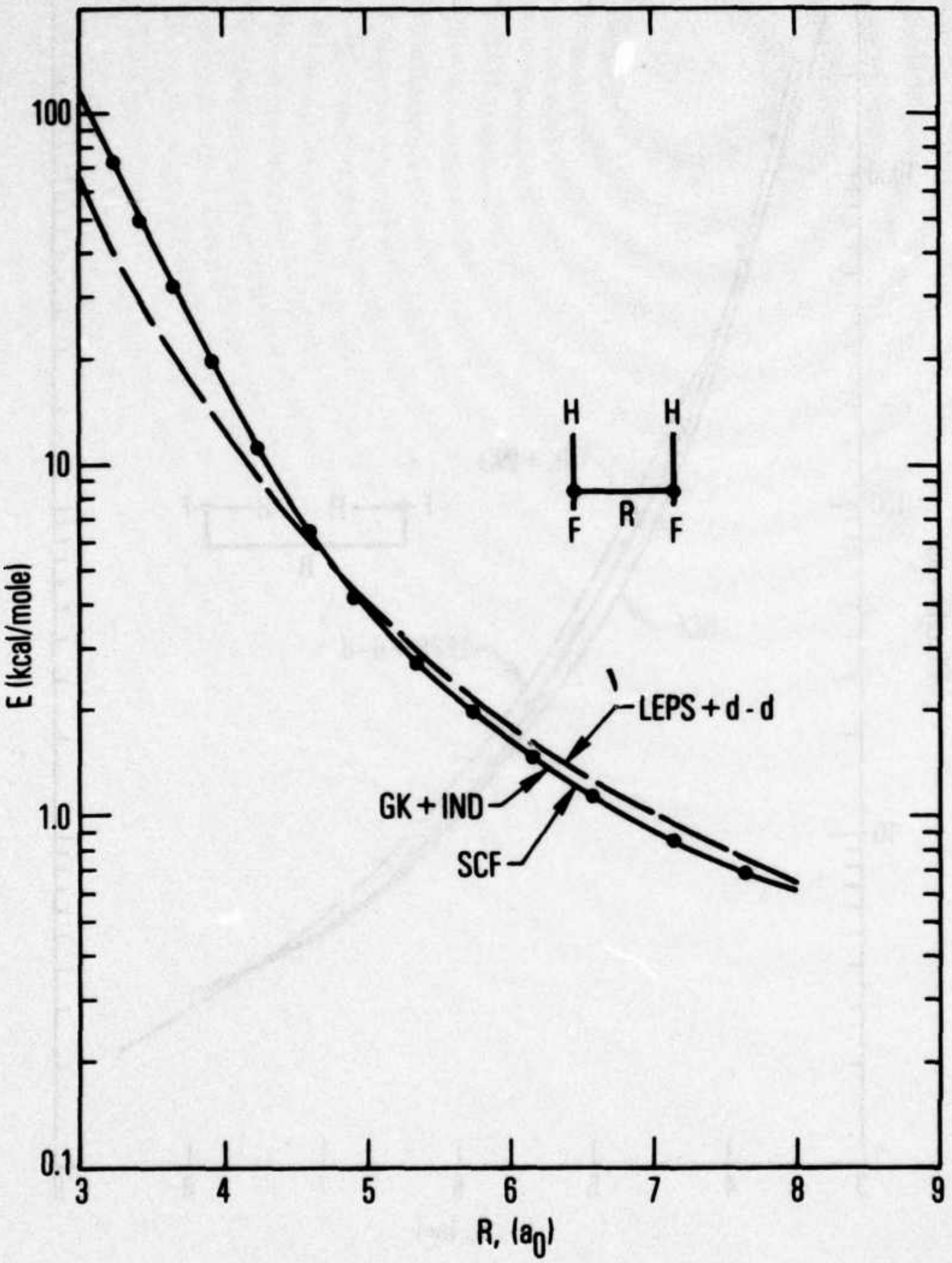

Fig. 7. HF-HF interactions with $\theta_1 = \theta_2 = \Pi/2$ and $\phi = 0$. The notation is given in Fig. 5.

III. CLASSICAL TRAJECTORY CALCULATIONS

The quasi-classical procedure described by Raff, Thompson, Sims, and Porter[49] was used to examine the collision dynamics of diatomic-diatomic energy-transfer processes. The Hamiltonian that describes the four-particle system is written in generalized coordinates, and the resulting set of 18 Hamilton equations is integrated on a CDC 7600 computer. The initial vibrational states of $HF(v_1, J_1)$ and $HF(v_2, J_2)$ were assigned the vibrational quantum numbers v_1 and v_2, respectively. Calculations were made with values of v_1 and v_2 varying from 0 through 6. The rotational quantum numbers J_1 and J_2 were Monte Carlo selected for the calculations involving $v \rightarrow v$ and $v \rightarrow R$ energy-transfer processes. For $R \rightarrow R$, T energy-transfer processes, the rotational quantum number J_1 was assigned, and the rotational quantum number J_2 was Monte Carlo selected. The initial values of the coordinates in each collision are determined by means of a fixed relative translational energy of the reactants, a chosen initial relative separation between the centers of mass of the diatomic molecules; chosen values of the vibrational quantum numbers v_1 and v_2; and randomly selected values of the rotational quantum numbers J_1 and J_2, the impact parameter, the vibrational phase angles of both molecules, two sets of orientational angles, and the rotational planes of both moelcules. Averaging over initial internal states of $HF(v_1, J_1)$ and $HF(v_2, J_2)$ was carried out by the technique described by Porter, Raff, and Miller.[50] For excited vibrational states, the calculation of the initial values of the momenta $P_i (i = 1, \ldots, 9)$ is more difficult since the initial amplitudes of both molecules are no longer the classical turning points and the internal momentum vectors are no longer perpendicular to the bond axis. For this case, a method based on Euler angles was used and that was adequately described by Raff, Thompson, Sims, and Porter.[49] The distance R between the center of mass of the two HF molecules was taken to be 8 a.u. This value is large enough to ensure a negligible initial interaction energy. Relative translational energies were assigned values that ranged from 0.5 to 6 kcal/mole. Approximately 200 trajectories were run for each initial set of parameters. A uniform distribution was used for the square of the impact parameter b. All runs were made with a maximum impact parameter of 2.5 Å. The step size was 5.7×10^{-17} sec. The integration technique, which has not been reported in the literature,[51] proved to be faster than the Runge-Kutta-Gill procedure,[52] with the accuracy of the integration tested by changes in the step size and by integration backwards along selected trajectories. As an additional verification of numerical accuracy, each trajectory was checked at each point along the trajectory for conservation of total energy and total angular momentum. Computation time for a single trajectory was dependent on the initial parameters but was, on the average, about 9 sec per trajectory on the CDC 7600 computer.

The final properties of each trajectory were analyzed to determine the nature of the collision, i.e., the total angular momentum and vibrational-rotational energy of both HF molecules. The partition of the internal energy between vibrational and rotational energy was determined from the internal energy of each HF molecule and its total angular momentum. The actual technique for calculating the partitioning of the internal energy has been described previously[53] and is not repeated here. The v → v energy-transfer cross sections were calculated by Method 2 described in a previous paper by Wilkins.[54] In Method 2, it is assumed that vibrational energy is transferred in every collision and that only one quantum state is accessible in the transfer process. The energy-transfer cross sections and specific rate coefficients were calculated by means of the equations given by Karplus, Porter, and Sharma.[55]

IV. RESULTS AND DISCUSSIONS

A. VIBRATIONAL-TO-ROTATIONAL ENERGY TRANSFER

The question of which molecular forces cause vibrational energy exchange in HF-HF collisions, in general, has not yet been answered. In hydrogen halide mixtures, Chen and Moore[17] demonstrated in HCl-HCl and DCl-DCl collisions the transfer of vibrational energy into rotational energy of the vibrationally excited hydrogen halide molecules. In analyzing their relaxation data on HCl and DCl, Chen and Moore[17] speculated on the importance of such strong interactions as the deep attractive well in the potential energy surface caused by hydrogen bonding. The formation of HF dimers has been proposed by several authors[3-5,10,11] to explain the vibrational relaxation of HF(v = 1) by HF(v = 0). The dynamics for 27,000 HF-HF collisions were examined for the potential energy surface described in Section II. A typical HF-HF bond plot is displayed in Fig. 8. A bond plot for a four-atom system is a plot of the six interparticle distances as a function of time. The motion of the centers of mass of the four-particle system as it moves on the potential energy surface is shown in Fig. 9. The typical HF-HF collision (Fig. 7) indicates that the two F atoms approach one another until repulsion reverses their course. If a collision complex were formed, then $R_{ABCD}(t)$ in Fig. 9 would oscillate back and forth, which provides additional evidence that a complex is not formed. Since there are six degrees of freedom involved in constructing the potential energy surface, it is not possible to show

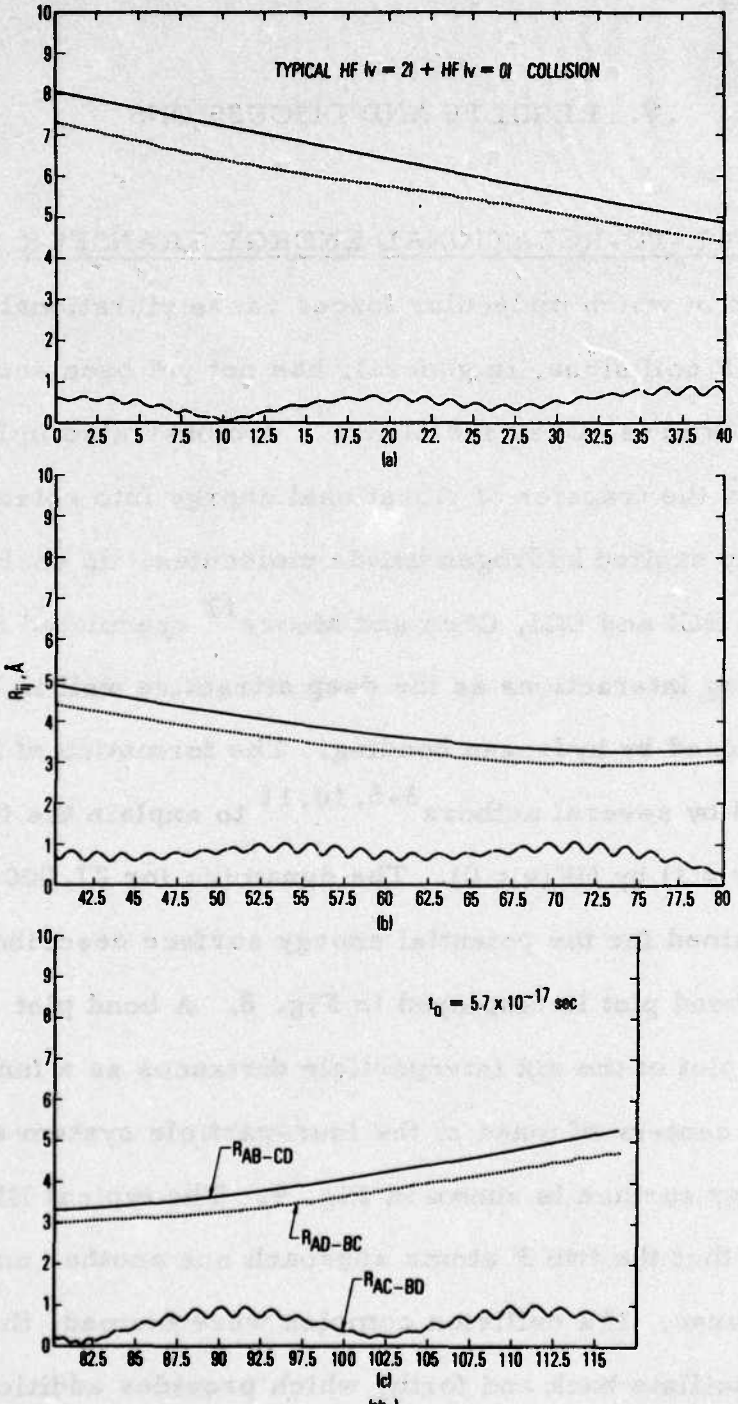

Fig. 8. Bond plot of HF(v = 2) + HF(v = 0) collisions. R_{ij} is the distance between the ith and the jth particle. $t_o = 5.7 \times 10^{-17}$ sec.

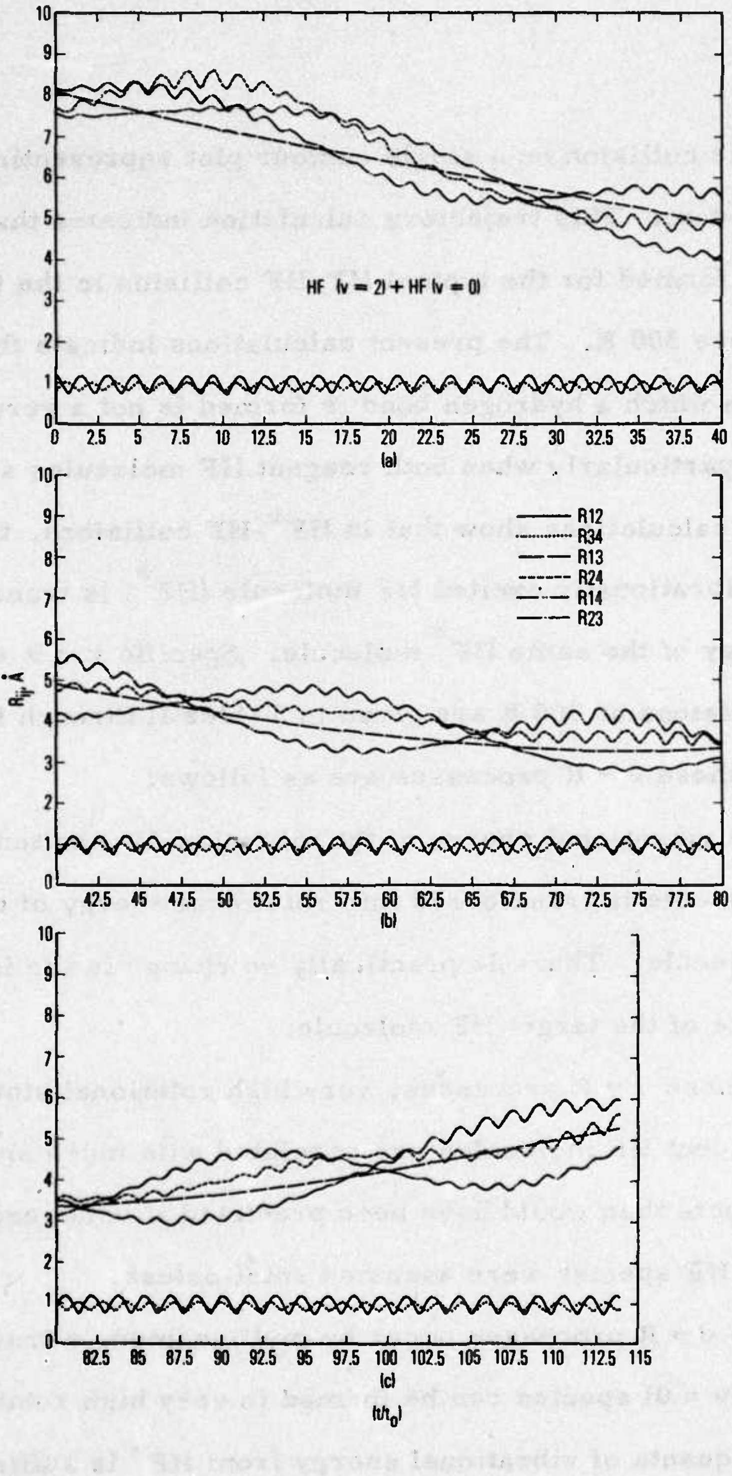

Fig. 9. Bond plot of centers of mass of four-particle system. The symbols A, B, C, and D are defined in Fig. 1. $t_o = 5.7 \times 10^{-17}$ sec.

the nature of the collision on a single contour plot representing only two degrees of freedom. This trajectory calculation indicates that a collision complex is not formed for the typical HF-HF collision in the temperature range at or above 300 K. The present calculations indicate that the HF-HF configuration in which a hydrogen bond is formed is not a very favorable configuration, particularly when both reagent HF molecules are rotating. The trajectory calculations show that in HF^*-HF collisions, the vibrational energy of the vibrationally excited HF molecule (HF^*) is transferred into rotational energy of the same HF^* molecule. Specific $v \rightarrow R$ rate coefficients for HF-HF collisions at 300 K are given in Tables II through IV. The qualitative results of these $v \rightarrow R$ processes are as follows:

1. The vibrational energy of the vibrationally excited incident HF molecule is transferred into rotational energy of the same HF molecule. There is practically no change in the internal energy state of the target HF molecule.
2. In these $v \rightarrow R$ processes, very high rotational states of the incident HF molecules are populated with much smaller energy defects than would have been predicted if both reagent and product HF species were assumed rotationless.
3. The $v \rightarrow R$ processes occur by multiquantum v transitions. $HF(v = 0)$ species can be formed in very high rotational states.

A loss of three quanta of vibrational energy from HF^* is sufficient to form an $HF(v = 0, J = 24)$ molecule, with an energy defect of 125 cm^{-1} (Table IV).

Table II. Vibration-to-Rotation Detailed Rate Coefficients for HF ($v_1 = 1$, $J_1 = 2$) + HF ($v_2 = 0$) at T = 300 K

v_1	J_1	v_2	J_2	v_1'	J_1'	v_2'	J_2'	ΔE cm^{-1}	k_λ [a]
1	2	0	J_2	0	16	0	J_2	1357	5.0 ± 1.5
1	2	0	J_2	0	15	0	J_2	733	3.2 ± 1.2
1	2	0	J_2	0	14	0	J_2	144	3.6 ± 1.2
1	2	0	J_2	0	13	0	J_2	- 409	3.6 ± 1.3
1	2	0	J_2	0	12	0	J_2	- 925	4.1 ± 1.3
1	2	0	J_2	0	11	0	J_2	-1404	2.3 ± 1.0
1	2	0	J_2	0	10	0	J_2	-1844	4.5 ± 1.4

[a] $\lambda \equiv (v_1, J_1, v_2, v_1', J_1', v_2', J_2')$. k_λ is the total rate coefficient for v → R relaxation in units of 10^{12} cm^3 $mole^{-1}$ sec^{-1}. To obtain rate coefficient for v → R relaxation of HF($v_1 = 1$, $J_1 = 2$) by HF($v_2 = 0$, J_2), multiply k_λ by $(2J_2 + 1)\, e^{-E_{v_2 = 0, J_2}/kT} / Q_R(v_2, J_2)$, where $Q_R(v_2, J_2)$ is the rotational partition function.

Table III. Vibration-to-Rotation Detailed Rate Coefficients for HF (v_1 = 2, J_1 = 2) + HF (v_2 = 0) Collisions at T = 300 K.

v_1	J_1	v_2	J_2	v_1'	J_1'	v_2'	J_2'	ΔE, cm^{-1}	k_λ [a]
2	2	0	J_2	1	16	0	J_2	1328.0	0.9 ± 0.6
2	2	0	J_2	1	15	0	J_2	728.0	2.8 ± 1.1
2	2	0	J_2	1	14	0	J_2	161.0	3.3 ± 1.2
2	2	0	J_2	1	13	0	J_2	-370.0	2.8 ± 1.1
2	2	0	J_2	1	12	0	J_2	-667.0	1.4 ± 0.8
2	2	0	J_2	1	11	0	J_2	-1328.0	3.3 ± 1.2
2	2	0	J_2	1	10	0	J_2	-1752.0	2.3 ± 1.0
2	2	0	J_2	0	21	0	J_2	1197.0	1.4 ± 0.8
2	2	0	J_2	0	20	0	J_2	406.0	4.7 ± 1.5
2	2	0	J_2	0	19	0	J_2	-352.0	3.3 ± 1.2
2	2	0	J_2	0	18	0	J_2	-1075.0	2.3 ± 1.0
2	2	0	J_2	0	17	0	J_2	-1770.0	3.3 ± 1.2
2	2	0	J_2	0	16	0	J_2	-2427.0	2.3 ± 1.0

[a] $\lambda \equiv (v_1, J_1, v_2, v_1', J_1', v_2', J_2')$. k_λ is the total rate coefficient for v → R relaxation in units of 10^{12} cm^3 $mole^{-1}$ $sec.^{-1}$ To obtain rate coefficient for v → R relaxation of HF(v_1 = 2. J_1 = 2) by HF(v_2 = 0, J_2), multiply k_λ by $(2J_2 + 1) e^{-E_{v_2 = 0, J_2}/kT} / Q_R(v_2, J_2)$, where $Q_R(v_2, J_2)$ is the rotational partition function.

Table IV. Vibration-to-Rotation Detailed Rate Coefficients for HF ($v_1 = 3$, $J_1 = 2$) + HF ($v_2 = 0$) Collisions at T = 300 K

v_1	J_1	v_2	J_2	v_1'	J_1'	v_2'	J_2'	ΔE, cm^{-1}	k_λ [a]
3	2	0	J_2	2	15	0	J_2	722.0	2.3 ± 1.0
3	2	0	J_2	2	14	0	J_2	178.0	1.4 ± 0.8
3	2	0	J_2	2	13	0	J_2	-333.0	2.7 ± 1.1
3	2	0	J_2	2	12	0	J_2	-811.0	3.2 ± 1.2
3	2	0	J_2	2	11	0	J_2	-1254.0	2.7 ± 1.1
3	2	0	J_2	2	10	0	J_2	-1662.0	6.3 ± 1.6
3	2	0	J_2	1	20	0	J_2	437.0	3.2 ± 1.2
3	2	0	J_2	1	19	0	J_2	-291.0	0.9 ± 0.6
3	2	0	J_2	1	18	0	J_2	-989.0	1.8 ± 0.9
3	2	0	J_2	1	17	0	J_2	-1655.0	2.7 ± 1.1
3	2	0	J_2	1	16	0	J_2	-2289.0	2.7 ± 1.1
3	2	0	J_2	0	26	0	J_2	1962.0	1.4 ± 0.8
3	2	0	J_2	0	25	0	J_2	1030.0	4.5 ± 1.4
3	2	0	J_2	0	24	0	J_2	125.0	2.7 ± 1.1
3	2	0	J_2	0	23	0	J_2	-752.0	2.3 ± 1.0
3	2	0	J_2	0	22	0	J_2	-1602.0	2.3 ± 1.0
3	2	0	J_2	0	21	0	J_2	-2421.0	1.8 ± 0.9

[a] $\lambda \equiv (v_1, J_1, v_2, v_1', J_1', v_2', J_2')$. The total rate coefficient for v → R relaxation is in units of 10^{12} cm^3 $mole^{-1}$ sec^{-1}. To obtain rate coefficient for v → R relaxation of HF($v_1 = 3, J_1 = 2$) by HF($v_2 = 0, J_2$), multiply k_λ by $(2J_2 + 1)\, e^{-E_{v_2 = 0, J_2}/kT} / Q_R(v_2, J_2)$, where $Q_R(v_2, J_2)$ is the rotational partition function.

The (v′, J′) states with the smallest energy defects to be populated by v → R processes in HF-HF collisions are listed in Tables V and VI. The v → R processes are quite complex (Tables V and VI). When an HF(v = 3) molecule collides with an HF(v = 0) molecule, the HF(v = 3) molecule can transfer one, two, or three quanta of vibrational energy into rotational energy of the same HF molecule by an intramolecular energy-transfer mechanism (Table V). When both HF molecules are vibrationally excited, either or both HF^* molecules are capable of converting one or more quanta of vibrational energy of either or both HF^* molecules by intramolecular energy transfer (Table VI). It is probable that v → R processes are required to explain the high J states observed in the pure rotation laser described by Deutsch.[20]

This is the first time, to our knowledge, that v → R processes have been predicted by a three-dimensional trajectory calculation to be very important in HF-HF collisions. It is not the first time, however, that the role of v → R mechanisms in atom-diatomic collisions or diatomic-diatomic collisions have been recognized. Kelley[56] investigated the role of rotational motion in the de-excitation of vibrationally excited diatomic molecules with an atom. Application of his impulsive collision theory indicates that intramolecular v → R processes should be very important in HF-HF collisions. Dillon and Stephenson[57] reported that multiquantum rotational transitions play an important role in vibrational energy exchange involving diatomic-diatomic collisions by allowing large vibrational energy defects to be absorbed by the rotational degrees of freedom. McGuire and Toennies[58] used the couple-state approximation to calculate vibrational de-excitation cross

Table V. Most Probable (v_1', J_1') States to be Populated by Vibration-to-Rotation Energy Transfer in $HF(v_1) + HF(v_2 = 0)$ Collisions

v_1	v_2	v_1'	J_1'
1	0	0	14
2	0	1	14
2	0	0	20
3	0	2	14
3	0	1	20
3	0	0	24
4	0	3	14
4	0	2	20
4	0	1	24
4	0	0	28
5	0	4	14
5	0	3	20
5	0	2	24
5	0	1	28
5	0	0	32
6	0	5	14
6	0	4	20
6	0	3	24
6	0	2	28
6	0	1	32
6	0	0	36

Table VI. Most Probable (v', J') States to be Populated by Vibrational-to-Rotational Energy Transfer in HF (v_1) + HF (v_2) Collisions

v_1	v_2	v'_1	J'_1	v'_2	J'_2
1	1	0	14	0	14
2	2	1	14	1	14
2	2	0	20	1	14
2	2	0	20	0	20
3	3	2	14	2	14
3	3	1	20	2	14
3	3	1	20	1	20
3	3	0	24	2	14
3	3	0	24	1	20
3	3	0	24	0	24
4	4	3	14	3	14
4	4	2	20	3	14
4	4	2	20	2	20
4	4	1	24	3	14
4	4	1	24	2	20
4	4	1	24	1	24
4	4	0	28	3	14
4	4	0	28	2	20
4	4	0	28	1	24
4	4	0	28	0	28

Table VI. Most Probable (v', J') States to be Populated by Vibrational-to-Rotational Energy Transfer in HF (v_1) + HF (v_2) Collisions (Continued)

v_1	v_2	v'_1	J'_1	v'_2	J'_2
5	5	4	14	4	14
5	5	3	20	4	14
5	5	3	20	3	20
5	5	2	24	4	14
5	5	2	24	3	20
5	5	2	24	2	24
5	5	1	28	4	14
5	5	1	28	3	20
5	5	1	28	2	24
5	5	1	28	1	28
5	5	0	32	4	14
5	5	0	32	3	20
5	5	0	32	2	24
5	5	0	32	1	28
5	5	0	32	0	32

sections for the He-H_2 system. They found that v → R energy transfer plays a major role in H_2 relaxation by Ar. The role of v → R transitions has been discussed in connection with experimental observations for the He-H_2 system[59-61] and He-D_2 systems.[62-63] Nazar et al.[64] postulated that highly rotationally excited hydrides can relax by cascading. This process involves rapid vibrational exchange in which the vibrationally excited hydride (the donor molecule) is de-excited by a single quantum of vibrational energy with retention of its initial rotational quantum number. Although the Nazar et al.[64] observation does not concur with our v → R prediction that a large change in ΔJ occurs by an intramolecular energy mechanism in the donor molecule, their experiment indicates that this rapid energy exchange is indicative of a resonant v → R energy-transfer process. The theory of Dillon and Stephenson,[57] however, does concur with finding of this study that there are efficient v → R processes in which large vibrational energy defects are absorbed by multi-quantum changes in the rotational degree of freedom. Streit and Johnston[65] in their work on the quenching of vibrationally excited OH by several chaperones suggested that in such collision processes a considerable amount of vibrational energy is absorbed into rotation in order to reduce the energy defect. This idea, according to Streit and Johnston,[65] requires a theory in which ΔJ transitions are responsible for the very efficient vibrational relaxation of HF($v \leq 9$). Downey et al.[67] found intramolecular v → R energy-transfer mechanisms to be important in the relaxation of vibrationally excited OH molecules by Ar atoms. This intramolecular v → R transfer, according to

Downey et al.,[67] must be the dominant channel for relaxation in experiments involving a light rotor and Ar, or a light rotor and Krypton.

In Tables VII through IX are listed detailed rate coefficients at T = 300 K for the v → R energy-transfer processes $HF(v_1) + HF(v_2) \rightarrow HF(v_1') + HF(v_2')$. The v → R rate coefficients $k_{v_1, v_2; v_1', v_2'}$ are easily converted to probabilities $P_{v_1, v_2; v_1', v_2'}$ by dividing $k_{v_1, v_2; v_1', v_2'}$ by the gaskinetic rate 9×10^{13} cm^3 mole^{-1} sec^{-1} at room temperature. There is a probability of 0.2 for most single-quantum transitions and a probability of 0.1 for most multiquantum transitions from any vibrational level v (Table VII). The overall rate coefficients tabulated in Tables VII through IX indicate a slight increase with increasing vibrational quantum number v. These overall rate coefficients are not comparable to the effective rate coefficients measured in the laboratory. The rate coefficients listed in Tables VII through IX are for all v → R processes from a given v_1 level to a final v_1' level, regardless of the final J_1' state. The rate coefficients for v → R transfer processes in which the final J_1' states are given in Tables II through IV. When the detailed v → R rate coefficients listed in Tables II through IV are used in a rotational nonequilibrium model along with R → R', T rate coefficients presented here, temperature-dependent rate coefficients are calculated for HF(v = 1) + HF(v = 0) collisions that concur with measured temperature-dependent effective v → R rate coefficients. The actual calculations will be described by Kwok and Wilkins[24] at a later time. There is an increase in the number of v → R channels, and a decrease in the specific rate coefficients for v → R processes with increasing v (Tables VIII and IX). The multiquantum v → R

Table VII. Rate Coefficients $k_{v_1,v_2:\,v_1',v_2'}$ for Vibrational-to-Rotational Energy Transfer in $HF(v_1) + HF(v_2)$ Collisions at T = 300 K

$v_1' + v_2'$ $v_1 + v_2$	5 + 0	4 + 0	3 + 0	2 + 0	1 + 0	0 + 0	Overall Rate Coefficients[a, b]
6 + 0	18.0 ± 2.6	8.9 ± 1.9	7.5 ± 1.7	8.5 ± 1.9	5.6 ± 1.6	8.5 ± 1.9	58.0 ± 3.0
5 + 0		19.0 ± 2.6	7.1 ± 1.7	11.0 ± 2.1	7.1 ± 1.7	9.4 ± 1.9	53.6 ± 3.2
4 + 0			17.0 ± 2.5	14.0 ± 2.3	8.9 ± 1.9	9.9 ± 2.0	49.8 ± 3.2
3 + 0				15.0 ± 2.4	17.0 ± 2.5	11.0 ± 2.1	43.0 ± 3.2
2 + 0					24.0 ± 2.8	15.0 ± 2.4	39.0 ± 3.1
1 + 0						30.0 ± 3.0	30.0 ± 3.0

[a] $k_{v_1 v_2;\,v_1', v_2'}$ in units of 10^{12} cm^3 $mole^{-1}$ sec^{-1}.

[b] The overall rate coefficient is the summation of $k_{v_1 v_2;\,v_1', v_2'}$ over the v_1' levels.

Table VIII. Rate Coefficients $k_{v_1,v_2,v_1',v_2'}$ for Vibrational-to-Rotational Energy Transfer in HF(v_1) + HF(v_2) Collisions at T = 300 K

v_1	v_2	v_1'	v_2'	$k_{v_1,v_2,v_1',v_2'}$	k_{vR} [a]
1	1	1	0	4.1 ± 1.3	
1	1	0	0	1.5 ± 0.9	5.6 ± 0.3
2	2	2	1	2.8 ± 1.1	
2	2	2	0	2.0 ± 1.0	
2	2	1	1	0.7 ± 0.2	
2	2	1	0	0.5 ± 0.1	
2	2	0	0	1.0 ± 0.2	7.0 ± 0.3
3	3	3	2	1.7 ± 0.2	
3	3	3	1	1.5 ± 0.2	
3	3	3	0	1.5 ± 0.2	
3	3	2	2	0.7 ± 0.2	
3	3	2	1	0.5 ± 0.1	
3	3	2	0	0.3 ± 0.1	
3	3	1	1	0.1 ± 0.1	
3	3	1	0	0.6 ± 0.1	
3	3	0	0	0.6 ± 0.1	7.4 ± 0.3
4	4	3	4	1.7 ± 0.2	
4	4	2	4	0.9 ± 0.2	
4	4	1	4	0.7 ± 0.2	
4	4	0	4	1.1 ± 0.2	
4	4	3	3	0.2 ± 0.1	
4	4	2	3	0.6 ± 0.1	
4	4	1	3	0.4 ± 0.1	
4	4	0	3	0.2 ± 0.1	
4	4	2	2	0.1 ± 0.1	
4	4	1	2	0.2 ± 0.1	
4	4	0	2	0.5 ± 0.1	

Table VIII. Rate Coefficients $k_{v_1,v_2,v_1',v_2'}$ for Vibrational-to-Rotational Energy Transfer in $HF(v_1) + HF(v_2)$ Collisions at T = 300K (Continued)

v_1	v_2	v_1'	v_2'	$k_{v_1,v_2,v_1',v_2'}$	$k_{vR}{}^a$
4	4	1	1	0.3 ± 0.1	
4	4	0	1	0.3 ± 0.1	
4	4	0	0	0.4 ± 0.1	7.6 ± 0.3
5	5	4	5	1.5 ± 0.2	
5	5	3	5	0.7 ± 0.2	
5	5	2	5	0.6 ± 0.1	
5	5	1	5	0.7 ± 0.2	
5	5	0	5	0.7 ± 0.2	
5	5	4	4	0.3 ± 0.1	
5	5	3	4	0.4 ± 0.1	
5	5	2	4	0.3 ± 0.1	
5	5	1	4	0.4 ± 0.1	
5	5	0	4	0.3 ± 0.1	
5	5	3	3	0.2 ± 0.1	
5	5	2	3	0.2 ± 0.1	
5	5	1	3	0.1 ± 0.1	
5	5	0	3	0.2 ± 0.1	
5	5	2	2	0.1 ± 0.1	
5	5	1	2	0.6 ± 0.2	
5	5	0	2	0.3 ± 0.1	
5	5	1	1	0.2 ± 0.1	
5	5	0	1	0.3 ± 0.1	
5	5	0	0	0.3 ± 0.1	7.8 ± 0.3

[a] $k_{v_1,v_2;v_1',v_2'}$ is in units of 10^{13} cm^3 $mole^{-1}$ sec^{-1}.

Table IX. **Rate Coefficient $k_{v_1,v_2;v_1',v_2'}$ for Vibrational-to-Rotational Energy Transfer in $HF(v_1) + HF(v_2)$ Collisions at T = 300 K**

v_1	v_2	v_1'	v_2'	$k_{v_1,v_2,v_1',v_2'}$	k_{vR}[a]
2	1	1	1	1.6 ± 0.2	
2	1	0	1	1.7 ± 0.2	
2	1	2	0	2.0 ± 0.2	
2	1	0	0	1.1 ± 0.2	6.4 ± 0.3
3	1	2	1	1.2 ± 0.2	
3	1	1	1	0.5 ± 0.2	
3	1	0	1	1.4 ± 0.2	
3	1	3	0	1.8 ± 0.2	
3	1	2	0	0.7 ± 0.2	
3	1	0	0	0.8 ± 0.2	6.5 ± 0.3
4	1	3	1	1.0 ± 0.2	
4	1	2	1	0.6 ± 0.2	
4	1	1	1	0.4 ± 0.1	
4	1	0	1	1.3 ± 0.2	
4	1	4	0	1.5 ± 0.2	
4	1	3	0	0.8 ± 0.2	
4	1	2	0	0.6 ± 0.2	
4	1	0	0	0.6 ± 0.2	6.7 ± 0.3
5	1	4	1	1.0 ± 0.2	
5	1	3	1	0.6 ± 0.2	
5	1	2	1	0.3 ± 0.1	
5	1	1	1	0.3 ± 0.1	
5	1	0	1	1.0 ± 0.2	
5	1	5	0	1.4 ± 0.2	
5	1	4	0	0.8 ± 0.2	
5	1	3	0	0.5 ± 0.1	
5	1	2	0	0.5 ± 0.2	
5	1	0	0	0.6 ± 0.2	6.9 ± 0.3

[a] $k_{v_1,v_2;v_1',v_2'}$ is in units of 10^{13} cm^3 $mole^{-1}$ sec^{-1}.

energy-transfer processes are slightly less probable than the single-quantum processes. Chen and Moore's[17] model of their measurement for vibrational relaxation of HCl by HCl and DCl by DCl support our prediction that rotational up-pumping occurs as the vibrational energy is reduced by deactivation in HF-HF collisions.

B. VIBRATIONAL-TO-VIBRATIONAL ENERGY TRANSFER

The v → v energy-transfer processes are one of the kinds of energy-transfer processes that are responsible for the excitation and de-excitation of vibrationally excited HF species in HF chemical lasers. It is important in evaluating the performance of HF chemical lasers to have temperature-dependent rate coefficients for the v → v energy-transfer processes. Since the energy mismatch ΔE is small for these collisions, there has been speculation that the energy-transfer rates for the v → v processes are very fast. Rate coefficients for room temperature have been provided by several experimental studies[1,6-8] for endothermic processes (reading from left to right)

$$HF(v_1, J_1) + HF(v_2 = 0, J_2) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HF(v_1' = v_1 - 1, J_1') + HF(v_2' = 1, J_2') \quad (1)$$

with $v_1 = 2$ through 5. If it is assumed, as it commonly is, that the net change in rotational energy across the endothermic processes is zero and, if equilibrium constants are used to calculate the rate coefficients in the exothermic direction, then rate coefficients for some of these processes as high as 10^8 Torr^{-1} sec^{-1} at room temperature are obtained.

Another problem associated with the experimental measurements is that in the measurements it has not been possible to separate the contributions from the v → v and v → R, T energy-transfer processes. In addition to this problem, there is the problem of not knowing experimentally the actual energy defects ΔE for the endothermic processes given in Eq. (1). The main advantage of this trajectory study is that the rate coefficients for both the endothermic and exothermic v → v energy-transfer processes can be calculated. Rate coefficients for room temperature v → v energy-transfer processes obtained from this trajectory study are given in Table X. In column 6, of Table X, is given the energy mismatch ΔE obtained from the relationship between the rate coefficients for the endothermic and exothermic processes, i.e., $k_{-1} = k_1 \exp(\Delta E/RT)$. The trend of ΔE is not apparent from this calculation since there is a 25% uncertainty in these calculated rate coefficients. However, it is clear that the v → v processes are very much near resonant. In column 7 are listed the energy defects obtained under the assumption that both reagent and product HF species have zero rotational energy. The large rate coefficients predicted experimentally for the exothermic processes can be explained only by application of these large energy defects. The trajectory calculations indicate that such large energy defects are not correct and that the rotational states of reagent and product HF species must be considered to calculate a realistic energy defect ΔE. On the basis of the energy defects tabulated in column 7, the rate coefficients for v → v energy-transfer processes would be expected to decrease with increasing v. The trajectory calculations predict (column 5) that the rate

Table X. Rate Coefficients for Vibrational-to-Vibrational Energy Transfer[a] $HF(v_1) + HF(v_2) \rightarrow HF(v_1 - 1) + HF(v_2 + 1)$

v_1	v_2	$v_1 - 1$	$v_2 + 1$	$k_{v_1, v_2 : v_1 - 1, v_2 + 1}$, $10^{12} cm^3 mole^{-1} sec^{-1}$	ΔE,[b] cm^{-1}	ΔE,[c] cm^{-1}
2	0	1	1	8.5 ± 1.9	72	175
3	0	2	1	5.2 ± 1.4	87	343
4	0	3	1	3.3 ± 1.2	88	504
5	0	4	1	1.9 ± 0.9	81	665
6	0	5	1	1.2 ± 0.7	81	822
1	1	0	2	12.0 ± 2.1	-72	-175
1	2	0	3	7.8 ± 1.8	-87	-343
1	3	0	4	5.0 ± 1.4	-88	-504
1	4	0	5	2.8 ± 1.2	-81	-665
1	5	0	6	1.7 ± 0.9	-81	-822
2	2	1	3	6.6 ± 1.8	-13	-168
3	3	2	4	3.9 ± 1.2		-161
4	4	3	5	2.3 ± 1.1		-161
5	5	4	6	1.2 ± 0.7		-157
6	6	5	7	0.7 ± 0.2		-154
3	1	2	2	6.2 ± 1.4	+13	168

[a] T = 300 K. The value in the table must be multiplied by $(T/300)^{0.5}$ to obtain rate coefficient at any other temperature.

[b] Trajectory calculations.

[c] Change in rotational energy across reaction is assumed to be zero. Both reagent and product HF species are assumed to have zero rotational energy.

coefficients decrease with v for both the endothermic and the exothermic v → v energy-transfer processes. From this trajectory calculation, it is predicted that only single-quantum processes are important in the v → v intermolecular energy-transfer processes and that the v dependence in the endothermic direction is approximately given by $k_{v,0;v-1,1} = 2^{2-v} k_{2,0;1,1}$ for $v \geq 2$. In the exothermic direction, the v dependence is $k_{v,v;v-1,v+1} = 2^{1-v} k_{1,1;0,2}$ for $v \geq 1$. Trajectory calculations were performed for T = 300, 500, 1000, and 1500 K. Analysis of the results indicates a temperature dependence of $T^{0.5}$ for both the v → v and v → R energy-transfer processes.

In Table XI are given the measured (v → v + v → R) rate coefficients, the v → R rate coefficients for an assumed v dependence, the reduced endothermic v → v rate coefficients, v → v rate coefficients obtained from this trajectory study, and v → v rate coefficients calculated by Shin[10] with his one-dimensional analytical model. In columns 2 through 4 are listed the measured rate coefficients for the (v → v + v → R) energy-transfer processes. In column 5 are listed the v → R rate coefficients with $k_v^{v\to R} = v^{2.3} k_{1\to 0}^{v\to R}$ assumed. The 2.3 power of v was recommended by Kwok as a result of his flowtube studies on the HF + HF system. In columns 6 through 8 are listed the v → v rate coefficients obtained from the measured (v → v + v → R) rate coefficients by subtracting from the sum the value given in column 5 for the assumed v → R rate coefficient. Although the measurements for the (v → v + v → R) rate coefficients agree within a factor of two, the uncertainty in all of the measured (v → v + v → R) rate coefficients is too large (in excess of 25%) to deduce the correct v dependence for the v → v energy-transfer processes.

Table XI. Endothermic Vibrational-to-Vibrational Rate Coefficients $k(v_1, v_2 = 0; v_1' = v - 1, v_2' = 1)$, 10^{12} cm^3 mole^{-1} sec^{-1}, at 300 K for $HF(v_1) + HF(v_2 = 0)$

v_1	Ref. 2[a]	Ref. 6[a]	Ref. 7[a]	$v^{2.3}k_{1\to 0}^{-v\to R}$	Ref. 2[b]	Ref. 6[b]	Ref. 7[b]	This Study	Ref. 10
2	9.9 ± 3.0	11.0	16.0	4.9	5.0	6.1	11.0	8.5 ± 1.9	8.5
3	15.7 ± 6.0	12.0	31.0	12.5	3.2	d	18.4	5.2 ± 1.4	9.8
4	16.3 ± 6.0	>32	28.0	24.3	d	>7.7	3.7	3.3 ± 1.2	10.0
5	35.0[c]	>48		40.5	d	>7.5	e	1.9 ± 0.9	2.3
6	61.0[c]	e		61.6	d	e	e	1.2 ± 0.7	e

[a] Measured ($v \to v + v \to R$) rate coefficients.

[b] The $v \to v$ rate coefficient is obtained from the measured ($v \to v + v \to R$) rate coefficient by subtracting the HF-HF $v \to R$ rate coefficient listed in column 5. These $v \to R$ rate coefficients are assumed to vary as $1.0\, v^{2.3}$. The 2.3 power of v dependence was recommended by Kwok (personal communication).

[c] From M. A. Kwok and N. Cohen, personal communication.

[d] The subtraction of $k_v^{v \to R}$ from the sum $(k^{v \to R} + k^{v \to v})$ produces a negative value.

[e] The measured or theoretical data are not available.

If the v → v rate decreases with increasing v, as predicted from this trajectory study (column 9), then the (v → v + v → R) measured rates at the high v levels (v greater than 4) must reflect only v → R energy-transfer processes. The slow v → v pumping rates and the fast v → R de-excitation rates with increasing v could account for the large decrease in measured excited HF species concentrations in the higher vibrational levels (v greater than 6). The v → v rate coefficients obtained from this trajectory study (column 9) can be compared with those reported by Shin[10] (column 10) with his one-dimensional analytical model. The v → v rates reported by Shin[10] indicate a slight increase from $v = 2$ to $v = 4$, then a decrease from $v = 4$ to $v = 5$; this increase from $v = 2$ to $v = 4$ is not seen in results obtained from the trajectory study. The arrested rotational model used by Shin in which the mechanism for v → v energy transfer in HF-HF collisions is the result of strong hydrogen-bond attraction was not observed in the 27,000 trajectories analyzed in this study. These trajectories show that most of the energy mismatch, corresponding to rotationless reagent and product HF molecules, enters rotational motion of the colliding HF molecules. This study indicates that dimer formation at temperatures at and above room temperature will not occur if both reagent HF molecules have initial rotational energy, since the dipole-dipole forces are strongly attractive only when the HF molecules are oriented in an unfavorable configuration. If HF dimers were to form, then the v → v rates would increase with increasing v because the density of states in the $(HF)_2$ transition complex would increase with increasing vibrational excitation. This trajectory study and the reduced v → v rate coefficients obtained from the measured (v → v + v → R) rate coefficients do not seem to reflect this increase.

C. ROTATIONAL-TO-ROTATIONAL, TRANSLATIONAL ENERGY TRANSFER

In a recent article, Gur'ev et al.[68] obtained rate coefficients for rotational relaxation of HF(v = 0, J = 8) by several chaperone gases by measuring the relaxation losses that occur when light is made to pass through a resonantly absorbing medium. Their rate coefficients k_R for rotational relaxation of HF(v = 0, J = 8) by M, where M is an atom or molecule, correspond to collision-induced relaxation probabilities of 0.1 for M = HF, 3×10^{-3} for M = H_2 or D_2, and $\leq 5 \times 10^{-4}$ for M = He, Ar, Kr, or Xe. Gur'ev et al.[68] point out that such low probabilities call for a more thorough analysis of vibrational-rotational relaxation of HF molecules in comparison with the usual assumption that R → R, T relaxation is instantaneous. Vasil'ev et al.[69] showed that resonance transfer of rotational energy from HF molecules to H_2 or D_2 plays an important role in rotational deactivation of rotationally excited HF molecules with $J \geq 7$. They found that the rate of rotational deactivation of HF(v',J') by either He or Xe decreases with increasing J' and that more than 100 collisions are required for complete deactivation of rotationally excited HF molecules formed in the F + H_2, reaction. Vasil'ev et al.[69] also found that R → R, i.e., resonance transfer in HF + H_2, and HF + D_2 systems enhance the rotational deactivation rates by an order of magnitude, compared with the deactivation by He or Xe atoms.

The rate coefficients for this study for the rotational relaxation of $HF(v_1 = 0, J_1 = 5, 10, 15)$ by $HF(v_2 = 0, J_2)$ molecules are shown in Figs. 10 through 12. These rate coefficients contain contributions from both R → R and R → T energy-transfer processes. The R → T mechanism with $\Delta J = -1$ is the main mechanism for de-excitation of rotationally excited HF species. The contribution from the R → R mechanism for $\Delta J = -1$ is approximately one-third of the total contribution to the (R → R + R → T) rate coefficients. At low J, de-excitation of rotationally excited HF molecules by multiquantum rotational transitions is much more probable than at high J (Fig. 12), where de-excitation with $\Delta J = -2$ is more than one order of magnitude smaller than de-excitation with $\Delta J = -1$. The total rate coefficients for de-excitation of rotationally excited $HF(v_1 = 0$ and $1, J_1 = 5, 10, 15)$ by $HF(v_2 = 0, J_2)$ molecules are shown in Figs. 13 and 14. It can be seen from these curves that the rate coefficients for de-excitation from the higher rotational levels are much smaller than rate coefficients for de-excitation from the lower J levels. These results concur with those reported by Polanyi and Woodall[18] and Ding and Polanyi,[19] who showed that for hydrogen halides the probability of rotational deactivation decreases with increasing rotational quantum number J. The tendency for the high J levels to relax less rapidly than the lower J levels is a consequent of the large spacings between adjacent rotational states of high J. Most of the rotational transitions observed by Deutsch[20] had J values greater than 15, which indicates that the high rotational states had not Boltzmannized. The nonequilibrium rotational distribution occurs because the rotational level spacings become so large

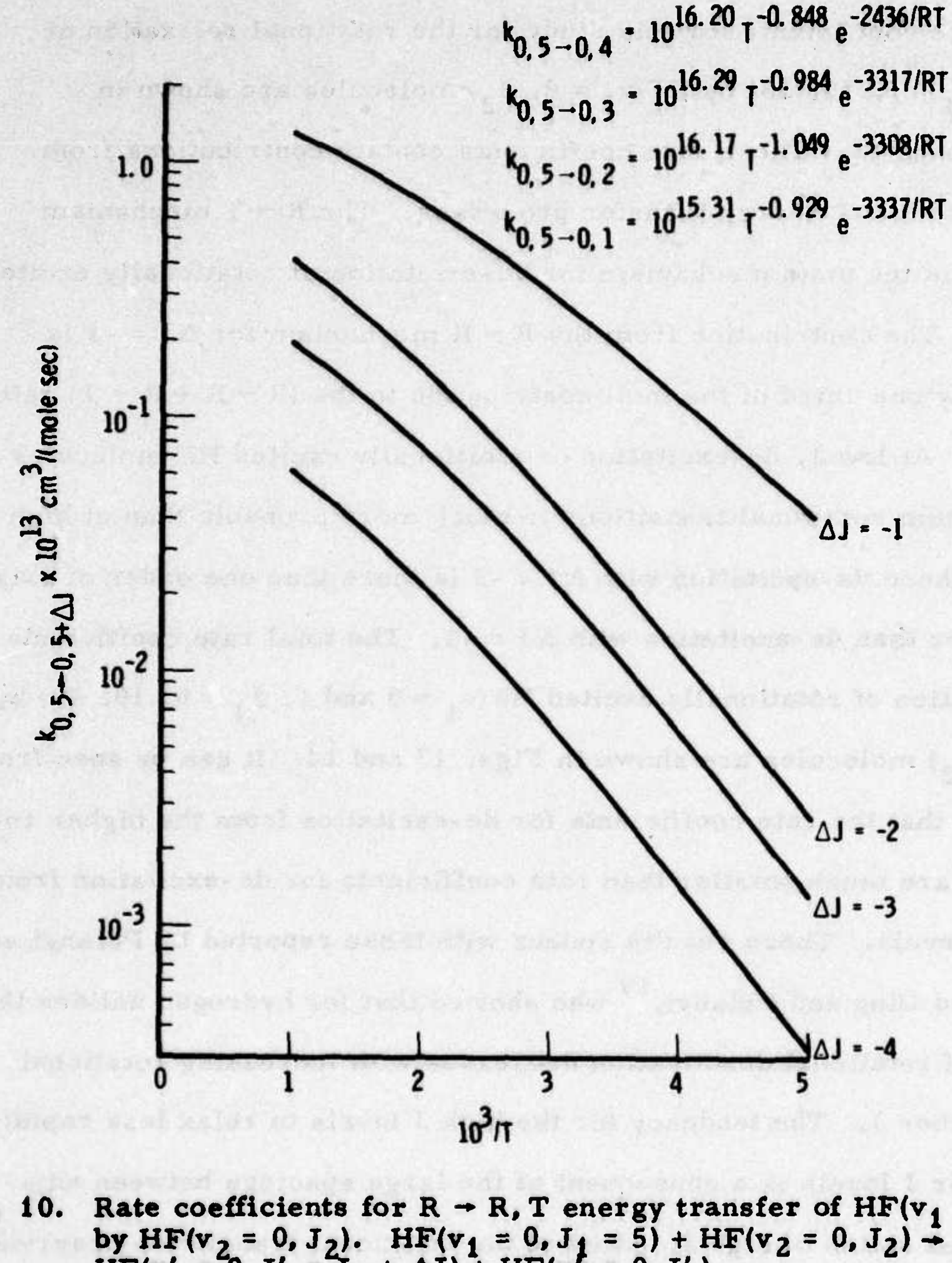

Fig. 10. Rate coefficients for R → R, T energy transfer of HF($v_1 = 0, J_1 = 5$) by HF($v_2 = 0, J_2$). HF($v_1 = 0, J_1 = 5$) + HF($v_2 = 0, J_2$) → HF($v_1' = 0, J_2' = J_1 + \Delta J$) + HF($v_2' = 0, J_2'$).

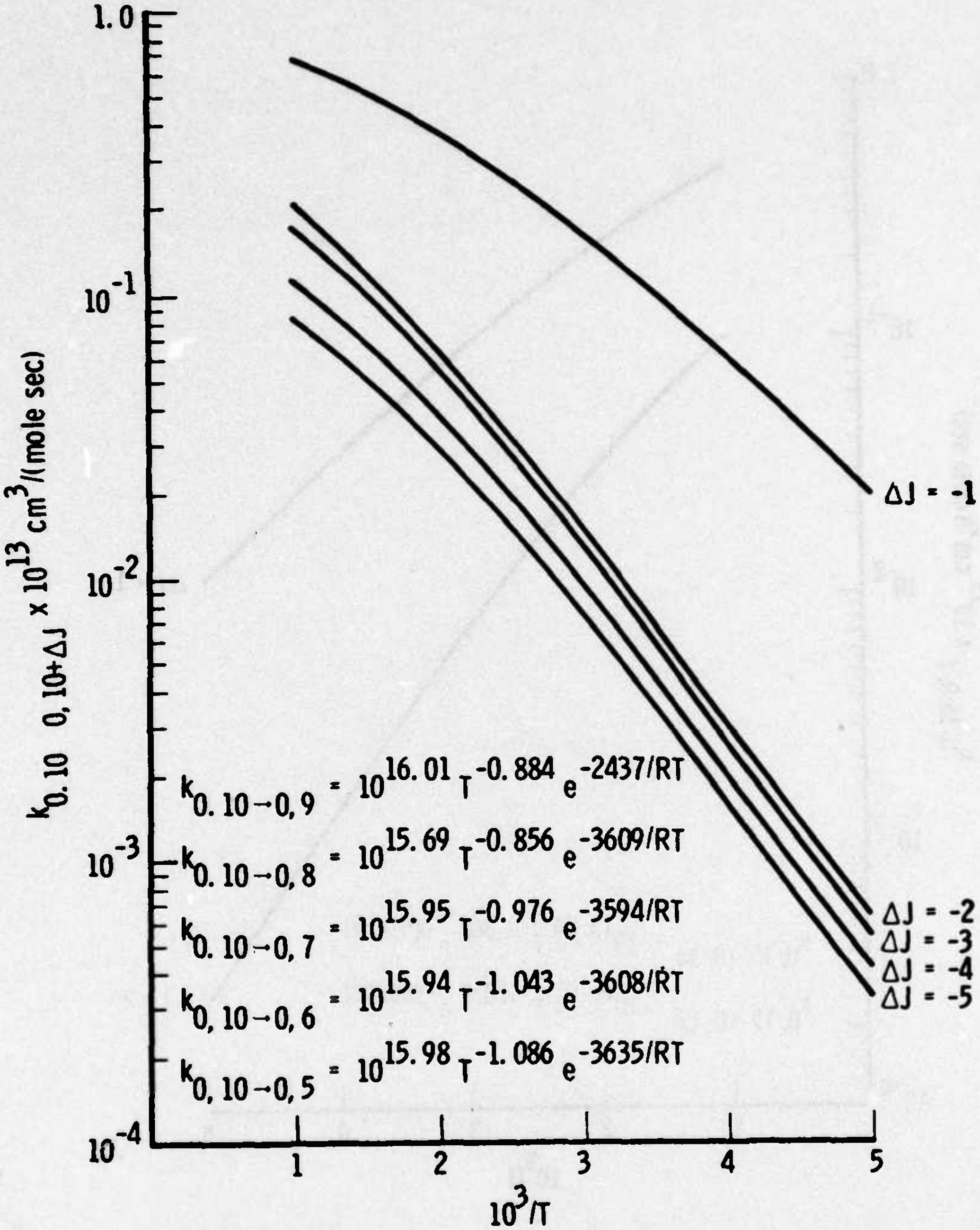

Fig. 11. Rate coefficients for R → R, T energy transfer of HF($v_1 = 0, J_1 = 10$) by HF($v_2 = 0, J_2$). HF($v_1 = 0, J_1 = 10$) + HF($v_2 = 0, J_2$) → HF($v_1' = 0, J_1' = J_1 + \Delta J$) + HF($v_2' = 0, J_2'$).

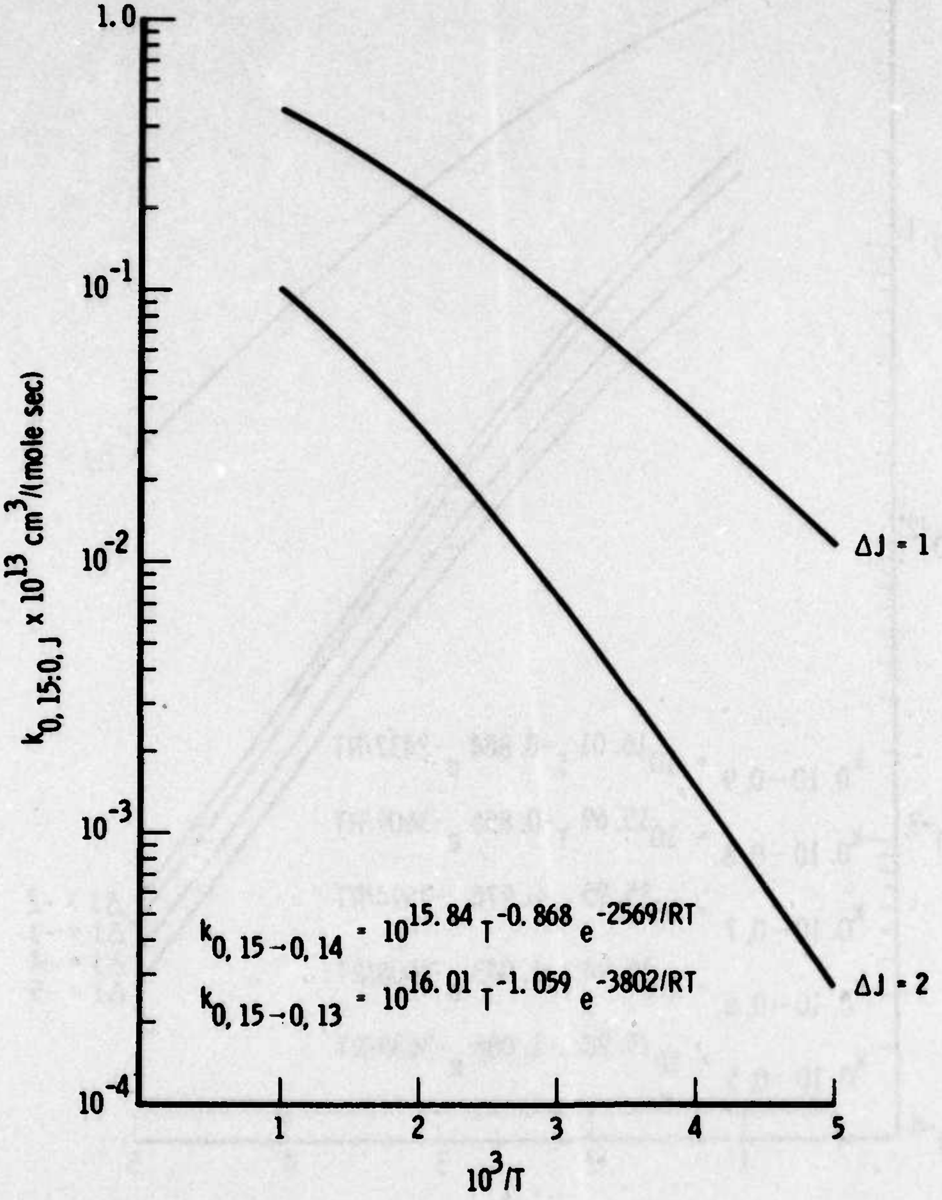

Fig. 12. Rate coefficients for R → R, T energy transfer of HF($v_1 = 0, J_1 = 15$) by HF($v_2 = 0, J_2$). HF($v_1 = 0, J_1 = 15$) + HF($v_2 = 0, J_2$) → HF($v_1' = 0, J_1 + \Delta J$) + HF($v_2' = 0, J_2'$).

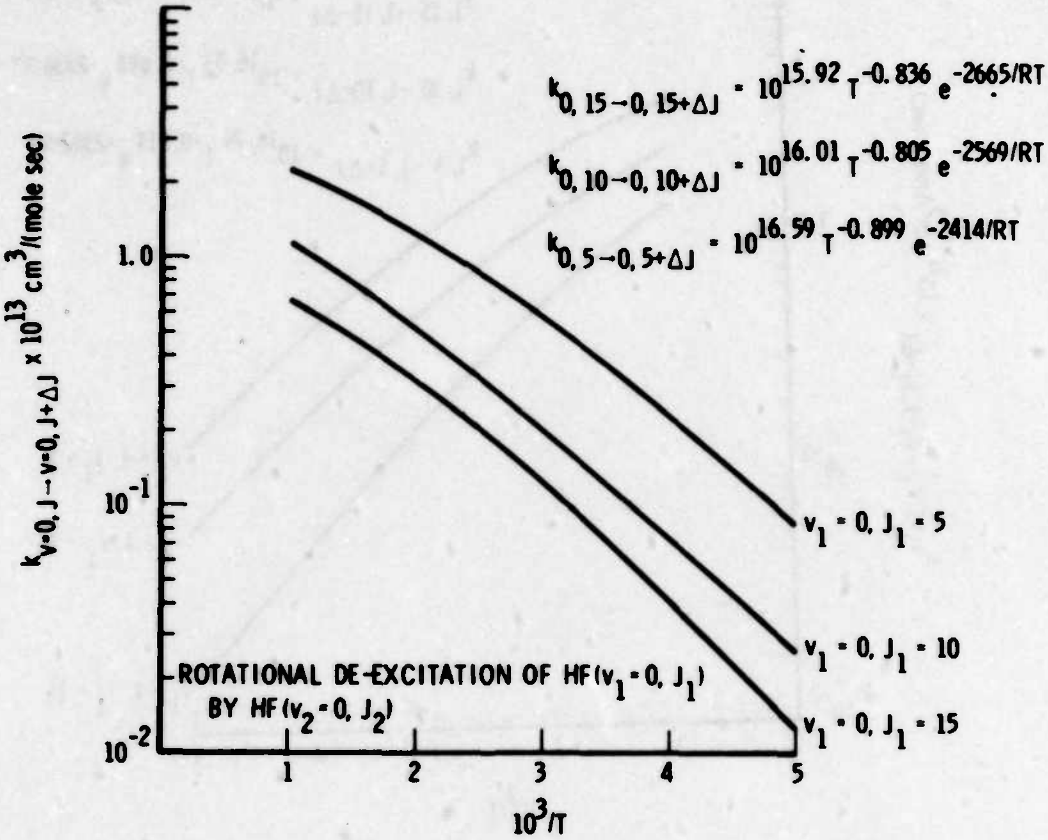

Fig. 13. Total rate coefficients for rotational de-excitation of HF($v_1 = 0, J_1 = 5$, 10, and 15) by HF($v_2 = 0, J_2$). HF($v_1 = 0; J_1$) + HF($v_2 = 0, J_2$) → HF($v_1' = 0, J_1 + \Delta J$) + HF($v_2' = 0, J_2'$).

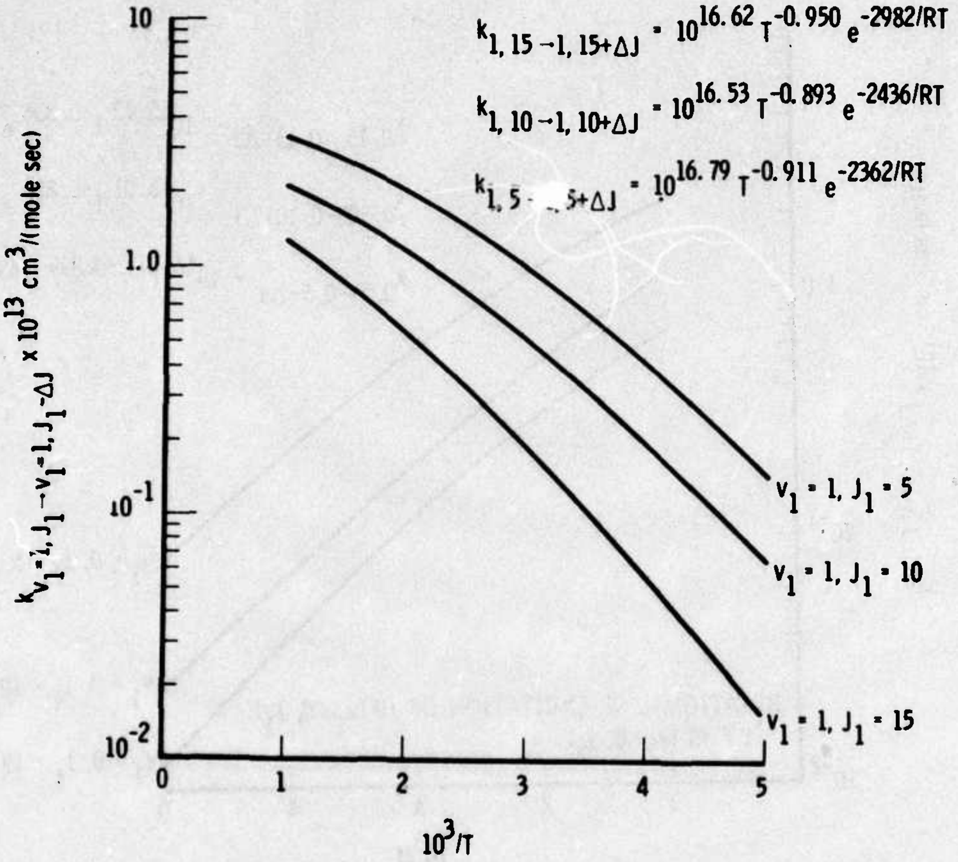

Fig. 14. Total rate coefficients for rotational de-excitation of HF($v_1 = 1$, $J_1 = 5$, 10, and 15) by HF($v_2 = 0$, J_2). HF($v_1 = 1$, J_1) + HF($v_2 = 0$, J_2) → HF($v_1' = 1$, $J_1 + \Delta J$) + HF($v_2' = 0$, J_2').

that a few collisions no longer induce rotational relaxation by $\Delta J = -1$ transitions. The transition probabilities for rotational de-excitation of HF($v_1 = 0$, J_1) by HF($v_2 = 0$, J_2) molecules at T = 300 K are given in Table XII. Rotational relaxation out of the high J levels into the low J levels by multiquantum transitions is a very inefficient process. A transition from J = 15 to J = 12 occurs about one in a thousand collisions. A transition from J = 3 to J = 2 occurs about one in three collisions, whereas a transition from J = 3 to J = 0 occurs about one in fifty collisions. Multiquantum J transitions are much more probable at the low J levels than at the high J levels. Even at low J levels, the probability of multiquantum transitions are at least an order of magnitude smaller than the probability of a single-quantum ΔJ transition. Hinchen and Hobbs[70] measured rotational relaxation effects in HF + M collisions by means of a double resonance infrared experiment. Their R → R, T rates at low J values are at least one order of magnitude larger than the values predicted in this study. The rate model used by Hinchen and Hobbs[70] to calculate the specific rate coefficients did not include v → R and R → v processes found to be very important in HF-HF collisions in this study.

Table XII. Rotational Transition Probabilities for HF-HF Collisions at T = 300 K

J	ΔJ = -1	ΔJ = -2	ΔJ = -3
1	0.45		
2	0.40	0.065	
3	0.37	0.055	0.022
4	0.35	0.047	0.020
5	0.32	0.040	0.019
6	0.30	0.030	0.017
7	0.28	0.025	0.015
8	0.25	0.017	0.014
9	0.22	0.015	0.012
10	0.20	0.010	0.010
11	0.18	0.009	0.008
12	0.15	0.008	0.007
13	0.14	0.007	0.005
14	0.12	0.006	0.003
15	0.10	0.005	0.001

V. SUMMARY

The v → v processes occur by intermolecular energy exchange mechanisms in which the most probable paths involve single vibrational quantum transitions. The v → v rate coefficients decrease with increasing v, and most v → v processes are near resonant with an energy defect of less than 100 cm^{-1}. Both the vibrational and the rotational states of the reagents and product species must be used in calculating energy defects. When proper energy defects are used, both endothermic and exothermic HF-HF v → v rate coefficients decrease with increasing v, and the values of the rate coefficients in the endothermic or the exothermic direction will not exceed the gaskinetic value.

The v → R processes occur by intramolecular energy-transfer mechanisms. The vibrationally excited HF molecule converts one or more quanta of its vibrational energy into rotational energy. In an HF system, it is predicted that v → v up-pumping coupled with v → R de-excitation with large ΔJ changes provide the mechanisms necessary to explain the high J states observed by Deutsch in his HF rotational laser. The v → R rate coefficients increase with increasing v. The vibrationally excited HF rotor takes the initial energy mismatch ΔE, corresponding to rotationaless HF molecules, away through v → R nonresonant energy-transfer processes. This initial energy defect goes into rotational motion of the colliding molecules. For many of the important v → R energy-transfer processes, the final energy defect for the process is less than 200 cm^{-1}. The multiquantum v → R transitions provide more ways to distribute the vibrational energy of the vibrationally excited HF molecules into rotational energy, i.e., into very high rotational quantum states.

Many of the R → v processes are fast because of the small energy defect (about 200 cm^{-1}) found for the corresponding v → R processes.

Both R → R and R → T processes occur in the rotational de-excitation of rotationally excited HF molecules. The probability of rotational de-excitation decreases with increasing rotational quantum numbers J. The single rotational quantum transitions are more probable than the multiple rotational quantum transitions.

HF dimers do not have to be formed at room temperature to explain the fast v → R self-relaxation rates measured by various experimental techniques. In a subsequent report, the temperature-dependent rate coefficients for HF(v = 1) self-deactivation, when the v → R, R → v, and R → R,T rate coefficients presented here are used in a rotational nonequilibrium computer program to model the laser-induced infrared experimental technique used to measure this rate, will be explained.

The v → v and v → R rate coefficients were found to have a $T^{0.5}$ temperature dependence since the cross sections for these processes were practically independent of the collision energy. The R → R rate coefficients have a complex temperature dependence since the cross section for these processes were found to be dependent on collision energy.

REFERENCES

1. N. Cohen and J. F. Bott, in Handbook of Chemical Lasers, edited by R. W. F. Gross and J. F. Bott (Wiley-Interscience, New York, 1976).
2. M. A. Kwok and R. L. Wilkins, J. Chem. Phys. 63, 2453 (1975).
3. J. R. Airey and S. F. Fried, Chem. Phys. Lett. 8, 23 (1971).
4. D. L. Thompson, J. Chem. Phys. 57, 2589 (1972).
5. H. K. Shin, Chem. Phys. Lett. 10, 81 (1971), 11, 628 (1971), J. Chem. Phys. 59, 879 (1973).
6. J. R. Airey and I. W. M. Smith, J. Chem. Phys. 57, 1669 (1972).
7. R. M. Osgood, Jr., P. B. Sackett, and A. Javan, J. Chem. Phys. 60, 1464 (1974).
8. M. A. Kwok and R. L. Wilkins, J. Chem. Phys. 63, 2453 (1975).
9. N. Cohen and J. F. Bott, Applied Optics, 15, 28 (1976).
10. H. K. Shin, J. Chem. Phys. 63, 2901 (1975).
11. H. K. Shin and Y. H. Kim, J. Chem. Phys. 64, 3634 (1976).
12. W. H. Green and J. K. Hancock, IEEE J. of Quantum Electron. QE 9, 50 (1973).
13. J. K. Hancock and W. H. Green, J. Chem. Phys. 57, 4515 (1972).
14. J. K. Hancock and A. W. Saunders, Jr., J. Chem. Phys. 65, 1275 (1976).
15. J. L. Ahl and T. A. Cool, J. Chem. Phys. 58, 5540 (1973).
16. R. R. Stephens and T. A. Cool, J. Chem. Phys. 56, 5863 (1972).
17. H. Chen and C. B. Moore, J. Chem. Phys. 54, 4072, 4080 (1973).

18. J. C. Polanyi and K. B. Woodall, J. Chem. Phys. 56, 1563 (1972).

19. A. M. G. Ding and J. C. Polanyi, Chem. Phys. Lett., 10, 39 (1975).

20. T. F. Deutsch, Appl. Phys. Lett., 11, 18 (1967).

21. J. C. Polanyi, Disc. Faraday Soc. 33, 279 (1972).

22. R. L. Wilkins, J. Chem. Phys. 51, 912 (1972).

23. J. C. Polanyi and D. C. Tardy, J. Chem. Phys. 51, 5717 (1969).

24. M. A. Kwok and R. L. Wilkins, "The Role of Rotational Energy in Hydrogen Fluoride Kinetic Systems," to be submitted for publication.

25. R. L. Wilkins, J. Chem. Phys. 57, 912 (1972).

26. R. L. Wilkins, J. Chem. Phys. 58, 2326 (1973).

27. G. C. Berend and R. L. Thommarson, J. Chem. Phys. 58, 3203 (1973).

28. T. A. Dillon and J. C. Stephenson, J. Chem. Phys. 60, 4286 (1974).

29. H. K. Shin, Chem. Phys. Lett., 26, 450 (1974).

30. R. L. Wilkins, J. Chem. Phys. 59, 698 (1973).

31. R. L. Wilkins, J. Chem. Phys. 58, 3038 (1973).

32. J. M. White and D. L. Thompson, J. Chem. Phys. 61, 719 (1974).

33. G. C. Berend and R. L. Thommarson, J. Chem. Phys. 58, 3203 (1973).

34. C. A. Coulson, Valence (Oxford University Press, New York and Oxford, 1961) p. 305.

35. C. J. E. Del Bene and J. A. Pople, J. Chem. Phys. 55, 2296 (1971).

36. D. R. Yarkony, S. V. O'Neil, H. F. Schaefer, III, G. P. Baskin, and C. F. Bender, J. Chem. Phys. 60, 855 (1974).

37. P. A. Kollman and L. C. Allen, J. Chem. Phys. 52, 5085 (1970).

38. G. H. F. Dierchsen and W. P. Kraemer, Chem. Phys. Lett. 6, 419 (1970).

39. L. A. Curtiss and J. A. Pople, J. Mol. Spectroscopy, 61, 1 (1976).

40. D. F. Smith, J. Mol. Spectroscopy 3, 473 (1959).

41. E. U. Frank and F. Meyer, Z. Electrochem. 63, 577 (1959).

42. T. R. Dyke, B. J. Howard, and W. Klemperer, J. Chem. Phys. 56, 2442 (1972).

43. G. A. Parker, R. L. Snow, and R. T. Pack, Chem. Phys. Lett., 33, 399 (1975).

44. V. I. Gaydaenko and V. K. Nikulin, Chem. Phys. Lett. 1, 360 (1970). V. K. Nikulin, Zh. Tekh. Fiz. 41, 41 (1970) [English translation of Soviet Phys. Tech. Phys. 16, 28 (1971).]

45. R. G. Gordon and Y. S. Kim, J. Chem. Phys. 56, 3122 (1972); Y. S. Kim and R. G. Gordon, J. Chem. Phys. 60, 1842 (1974); 4323 (1974), 4332 (1974), 61, 1 (1974).

46. A. I. M. Rae, Chem. Phys. Lett., 18, 574 (1973).

47. J. C. Cohen and R. T. Pack, J. Chem. Phys. 61, 2372 (1974).

48. A. D. Buckingham, Advances in Chemical Phys. 12, 107 (1967).

49. L. M. Raff, D. L. Thompson, L. B. Sims, R. N. Porter, J. Chem. Phys. 56, 5998 (1972).

50. R. N. Porter, L. M. Raff, and W. H. Miller, J. Chem. Phys. 63, 2214 (1975).

51. G. Emanuel, personal communication.

52. S. Gill, Proc. Cambridge Phil. Soc. 47, 96 (1951).

53. J. T. Muckerman, J. Chem. Phys. 54, 1155 (1971).

54. R. L. Wilkins, J. Chem. Phys. 59, 698 (1973).

55. M. Karplus, R. N. Porter, and R. D. Sharma, J. Chem. Phys. 43, 3239 (1965).

56. J. D. Kelley, J. Chem. Phys. 53, 3864 (1970).

57. T. A. Dillon and J. C. Stephenson, Phys. Rev. A6, 1460 (1972); J. Chem. Phys. 58, 2056 (1973).

58. P. McGuire and J. P. Toennies, J. Chem. Phys. 62, 4623 (1975).

59. M. M. Audibent, C. Joffrin, and J. Ducuing, Chem. Phys. Lett., 19, 26 (1973); J. Chem. Phys. 61, 4357 (1974).

60. J. E. Dove, D. J. Jones, and H. Teitelbaum, Proceedings of the Fourteenth International Symposium on Combustion (The Combustion Institute, Pittsburgh, 1973).

61. J. E. Dove and H. Teitelbaum, Chem. Phys. 6, 431 (1974).

62. P. F. Bird and W. D. Breshears, Chem. Phys. Lett. 13, 529 (1972).

63. B. M. Hopkins and H. L. Chen, J. Chem. Phys. 58, 1277 (1973).

64. M. A. Nazar, J. C. Polanyi, W. J. Skrlac, and J. J. Sloan, Chem. Phys. Lett. 16, 411 (1976).

65. G. E. Streit and H. S. Johnston, J. Chem. Phys. 64, 95 (1976).

66. R. R. Stephens and T. A. Cool, J. Chem. Phys. 56, 5863 (1972).

67. G. D. Downey, D. W. Robinson, and J. H. Smith, J. Chem. Phys. 66, 1685 (1977).

68. V. I. Gur'ev, G. K. Vasil'ev, and O. M. Batovskii, JETP Lett., 23, 230 (1976).

69. G. K. Vasil'ev, E. F. Makarov, A. G. Ryabenko, and V. L. Tal'roze, Sov. Phys. JETP, 41, 617 (1976).

70. J. J. Hinchen and R. H. Hobbs, J. Chem. Phys. 65, 2732 (1976).

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