

# Cross-correlation trajectory study of vibrational relaxation of DF( $v = 1$ to 7) by DF( $v = 0$ ) and of HF by HF<sup>a)</sup>

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Three-dimensional quasiclassical trajectories and a cross-correlation method of analysis are used to study the vibrational relaxation of DF( $v_1 = 1$  to 7) by DF( $v_2 = 0$ ). Rate constants are calculated for  $V-V$  and  $V-R, T$  energy transfer. As was seen in earlier studies on HF-HF, the  $V-R, T$  mechanism becomes increasingly important at higher initial  $v_1$ , as the  $V-V$  transfer moves further off resonance and also becomes increasingly endothermic. Both factors contribute to the decrease of  $V-V$  transfer rates with increasing  $v_1$  for the higher values of  $v_1$ . Comparisons are made with results of a classical path study of vibrational relaxation in DF-DF and with experiment where possible. New results on the HF-HF  $V-V$  transfer rates are presented.

## I. INTRODUCTION

There have recently been many experimental and theoretical studies of vibrational energy transfer in the hydrogen fluoride and deuterium fluoride systems. Vibrational relaxation rate constants are of interest not only in their own right, but also in the numerical modeling of the performance of high-power HF and DF chemical lasers. The main source of power loss in these lasers is the collisional deactivation of upper vibrational levels.

In earlier work,<sup>1,2</sup> we have presented results of fully three-dimensional quasiclassical calculations of vibrational energy transfer in hydrogen (deuterium) fluoride systems. A cross-correlation method of analysis was introduced<sup>1</sup> to relate certain average quantities calculated from quasiclassical trajectories to rate constants for vibration-to-vibration ( $V-V$ ) and vibration-to-rotation, translation ( $V-R, T$ ) energy transfer. The cross-correlation method<sup>1</sup> is similar in spirit to the moment method,<sup>3</sup> although the emphasis is placed on the correlation in changes of internal and/or translational states of the two molecules due to collisions. Results of a cross-correlation trajectory study of vibrational deactivation of HF( $v_1 = 1$  to 7) by HF( $v_2 = 0$ ) were also given.<sup>2</sup>

In the present paper, the cross-correlation trajectory approach<sup>1</sup> is applied to the system in which a DF( $v_1 = 1$  to 7) molecule is collisionally deactivated by a DF( $v_2 = 0$ ) molecule at 300 K. As in previous work,<sup>1,2</sup> this calculation is completely three-dimensional, with each molecule having three translational, two rotational, and one vibrational degrees of freedom. New results on the  $V-V$  transfer rate constants are also given for the HF-HF system.

In contrast to the case<sup>2</sup> where HF( $v_1 = 1$  to 7) is deactivated by HF( $v_2 = 0$ ), a system for which a number of experimental measurements of rate constants have been made,<sup>5-11</sup> corresponding measurements for deactivation of only the  $v_1 = 1$  and 2 have been reported.<sup>12-16</sup> There

have, however, been two previous extensive theoretical studies of this system. One of these also uses the quasiclassical trajectory approach.<sup>17</sup> The other is a classical path calculation.<sup>18</sup> We comment in detail on the relation between the present results and the previous theoretical work.<sup>17,18</sup>

In Sec. II, only a few details of the present calculation are given, since the method was described previously.<sup>1,2</sup> The resulting theoretical rate constants are given in Sec. III, together with comparisons to existing experimental rate constants, and with previous theoretical results.<sup>17,18</sup> In Sec. III, we also examine the behavior of the  $V-V$  rate constants with increasing initial state  $v_1$ , and give calculations to distinguish the separate effects of increasing frequency mismatch and of increasing endothermicity. A summary of the present work is given in Sec. IV.

## II. DETAILS OF CALCULATION

Three-dimensional classical trajectories were calculated as before,<sup>1,2</sup> using a potential energy surface given in Ref. 19, which is a least squares fit (plus an added dispersion term) to *ab initio* SCF data of Yarkony *et al.*<sup>20</sup> The vibrational potential of each molecule was taken to be a Morse oscillator potential, with parameters derived from spectroscopic data.<sup>21</sup>

The trajectory initial conditions were selected via the Monte Carlo technique,<sup>22</sup> as outlined in Sec. III of Ref. 1. The initial and final vibrational action variables (corresponding to the vibrational quantum numbers) were evaluated numerically via an integral over one vibrational cycle, as in Ref. 1. The initial and final separation of the center-of-mass of each molecule were each 10 Å. This rather large initial separation is desirable due to the very large, long-range dipole-dipole interaction in DF-DF. The trajectories were integrated in Cartesian coordinates, using the numerical integration routine DEROOT.<sup>23</sup> The calculations were performed on a CDC 7600 computer, requiring on the average 15 s per trajectory. From 1300 to 2400 trajectories were

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used for each of the seven systems reported here (the number depending on the numerical uncertainties in each case). No chemically reacting trajectories were observed in the present study.

The cross-correlation method of analysis<sup>1,2</sup> was used in order to relate the trajectory results to rate constants. The deactivation of vibrationally excited DF can occur by either the  $V-V$  or  $V-R, T$  routes, i. e.,

$$DF(v_1 = v) + DF(v_2 = 0) \rightarrow DF(v_1 = v - m) + DF(v_2 = m) \quad (V-V), \quad (2.1)$$

$$DF(v_1 = v) + DF(v_2 = 0) \rightarrow DF(v_1 = v - n) + DF(v_2 = 0) \quad (V-R, T), \quad (2.2)$$

with  $m$  and  $n$  integers (usually equaling 1). The probability of  $V-V$  energy transfer at a given impact parameter  $b$  and relative velocity  $V_R$  is formally given by<sup>1,2</sup>

$$P_{V-V}(b, V_R) = -\langle \Delta v_1 \cdot \Delta v_2 \rangle (b, V_R), \quad (2.3)$$

when quantum  $\Delta v$ 's greater than unity can be neglected. In Eq. (2.3),  $\Delta v_i$  is the change in vibrational state of molecule  $i$ . The brackets in Eq. (2.3) represent a Monte Carlo average over trajectory initial conditions (of vibrational, rotational, and orbital phases) at a given  $b$  and  $V_R$ . The quantum mechanical  $V-V$  process [Eq. (2.1)] becomes increasingly endothermic as  $v_1$  increases. As a result, many trajectories selected from the Maxwell-Boltzmann distribution of initial conditions lack enough total energy to allow the quantum mechanical  $V-V$  to occur. The contribution to  $P_{V-V}$  in the cross-correlation of Eq. (2.3) from these trajectories was set equal to zero, as suggested by Truhlar.<sup>24</sup> Similar energetic arguments for chemically reactive trajectories are discussed in Ref. 25. Our earlier work<sup>2</sup> did not consider this effect. The amended  $V-V$  rate constants for the HF-HF system are given later in Table III. The total deactivation rates and  $V-R, T$  rates are essentially unaffected, and are also reported there.

The probability for  $V-R, T$  is related to the cross-correlation<sup>1,2</sup>

$$P_{V-R,T}(b, V_R) = \langle \Delta v_1 \cdot (\Delta v_1 + \Delta v_2) \rangle (b, V_R), \quad (2.4)$$

again, where quantum  $\Delta v$ 's greater than unity can be neglected. Rate constants for  $V-V$  and  $V-R, T$  are obtained by Monte Carlo integration of the above cross-correlations over impact parameter and relative velocity [see Eqs. (2.6) and (2.7) of Ref. 2]. The rate constant  $k_{\text{Total}}$  is the sum  $k_{V-V}$  and  $k_{V-R,T}$  (except for the case  $v_1 = 1$  and  $v_2 = 0$ ). As mentioned in Ref. 2, when  $v_1 = 1$  and  $v_2 = 0$ , and  $V-V$  process of

$$DF(v_1 = 1) + DF(v_2 = 0) \rightarrow DF(v_1 = 0) + DF(v_2 = 1) \quad (2.5)$$

is physically unobservable by straightforward deactivation studies, because the product vibrational states are identical to those of the reactants. In this case, the deactivation of  $v_1 = 1$  arises solely from the  $V-R, T$  process, and one finds,<sup>1,2</sup> for the  $v_1 = 1$  case only, that  $k_{\text{Total}}$  equals  $k_{V-R,T}$ .

TABLE I. Rate constants<sup>a</sup> using quasiclassical cross-correlation method  $DF(v_1 = 1 \text{ to } 7) + DF(v_2 = 0)$  at 300 K.

System	$k_{\text{Total}}$	$k_{V-V}$	$k_{V-R,T}$
1-0	0.18 (0.16) <sup>b</sup>	...	0.18 (0.16)
2-0	26 (4)	26 (4)	0.7 (0.3)
3-0	17 (2)	16 (3)	1.3 (0.3)
4-0	40 (7)	36 (7)	5 (1)
5-0	79 (17)	63 (16)	16 (5)
6-0	57 (7)	27 (5)	30 (4)
7-0	77 (9)	9 (2)	68 (9)

<sup>a</sup>All rate constants in units of  $10^{-12}$  cc molecule<sup>-1</sup> s<sup>-1</sup>.

<sup>b</sup>Value in parenthesis is one standard error. The actual error may be larger due to limited sample size and a non-Gaussian distribution.

### III. RESULTS AND DISCUSSION

Results of our cross-correlation trajectory study of vibrational relaxation of  $DF(v_1 = 1 \text{ to } 7)$  by  $DF(v_2 = 0)$  at 300 K are presented in Table I. Reported there are the total rate constant, the rate constant for  $V-V$  energy transfer, and for  $V-R, T$  energy transfer.

The  $V-V$  rate constants increase from initial states  $v_1 = 2$  to  $v_1 = 5$ , apart from the drop between  $v_1 = 2$  to  $v_1 = 3$ . They then decrease from  $v_1 = 5$  to  $v_1 = 7$ . The decrease from  $v_1 = 2$  to 3 may not be statistically significant, due to a limited sample size of trajectories. However, we believe that the overall rise in  $k_{V-V}$  to  $v_1 = 5$  and the ultimate fall off are real features, both in this system and in the corresponding HF system.

As mentioned earlier, the  $V-V$  process becomes increasingly endothermic as  $v_1$  increases. We have performed a calculation for the HF-HF system to distinguish the two effects of vibrational frequency mismatch and of endothermicity on the  $V-V$  rate constants.

We first repeated our previous calculations<sup>2</sup> for  $HF(v_1 = 2, 4, \text{ and } 6) + HF(v_2 = 0)$ , but substituted harmonic oscillator vibrational potentials for the previously used Morse potentials. The  $V-V$  process for this harmonic oscillator system should now be very nearly resonant (distorted only by the vibrational-rotational coupling), and so have essentially no mismatch, and also not be endothermic. We wished in this calculation to assure ourselves that under these conditions there would be a monotonic increase in  $V-V$  transfer rate with increasing  $v_1$ . Such a monotonic increase would be predicted by the simple Sharma-Brau theory.<sup>26,27</sup>

As discussed in Sec. II the cross-correlation  $-\langle \Delta v_1 \cdot \Delta v_2 \rangle$  gives a measure of the likelihood of a  $V-V$  event [recall, however, that Eq. (2.3) is only valid in the absence of multiquantum transitions]. In Table II, we give the average value of  $-\langle \Delta v_1 \cdot \Delta v_2 \rangle$  for impact parameters up to 7 Å for the  $HF(v_1 = 2, 4, 6) + HF(v_2 = 0)$  system with harmonic oscillator (column two) vs Morse (column three) potentials for the HF-HF system. Because the energy levels with the two potentials are not equal, a precise quantitative comparison is difficult. However, qualitatively they behave very differently.

In the harmonic oscillator case, the cross-correla-

TABLE II. Effect of vibrational frequency mismatch and endothermicity on  $V-V$  energy transfer: average value of  $-\langle \Delta v_1 \cdot \Delta v_2 \rangle$  for HF( $v_1=2, 4, 6$ )+HF( $v_2=0$ ).<sup>a</sup>

$v_1$	Harmonic oscillator potentials	Morse oscillator potentials	Morse potentials including quantum threshold effects <sup>b</sup>
2	0.4	0.013	0.013
4	1.4	0.034	0.016
6	2.4	0.010	0.002

<sup>a</sup>This cross-correlation function is proportional to  $P_{V-V}$ .

<sup>b</sup>See Sec. III.

tion increases monotonically with  $v_1$ . In this case, there is neither vibrational frequency mismatch nor endothermicity. There is now a steady increase of  $V-V$  transfer with  $v_1$ , due to the increased vibrational amplitude at higher  $v_1$ , and thus the stronger dipole-dipole coupling. The value of  $-\langle \Delta v_1 \cdot \Delta v_2 \rangle$  can be orders of magnitude larger in the harmonic case than in the Morse (Table II), indicating much more rapid  $V-V$  exchange in the near resonant case. Indeed, the fact that  $-\langle \Delta v_1 \cdot \Delta v_2 \rangle$  in column one exceeds unity indicates that multi-quantum  $V-V$  is very important for the harmonic system.

For the Morse oscillator system, the cross-correlation has a maximum at  $v_1=4$ , and drops at  $v_1=6$ . This drop at higher  $v_1$  is due to a mismatch in the mechanical vibration frequencies of the two molecules. It is separate from endothermicity effects, discussed below, since those are absent in the purely classical calculation of  $\langle \Delta v_1 \cdot \Delta v_2 \rangle$ . Quantum mechanically, the  $V-V$  transfer in Eq. (2.1) can occur in only discrete amounts and becomes very endothermic at high  $v_1$ , due to vibrational anharmonicity. However, classically, this endothermic "barrier" to  $V-V$  simply does not exist. Thus, trajectories that lack enough total energy to overcome the quantum mechanical  $V-V$  endothermicity would still contribute to the classical  $V-V$  cross correlation in Eq. (2.3), unless specifically excluded. By excluding them, we obtain some measure (cf. the last column in Table II with the preceding column) of this quantum endothermicity effect. The contribution to the quantum  $V-V$  probability, from trajectories in that portion of the Maxwell-Boltzmann distribution with total energy below the quantum mechanical energy threshold, should be zero. The decrease from  $v_1=4$  to  $v_1=6$  in Table II, already present even for purely classical calculations due to frequency mismatch (column three), is seen to be further enhanced by the increasing quantum endothermicity (column four). We conclude from Tables I and II that the initial increase in  $V-V$  transfer from  $v_1=2$  to  $v_1=5$  (Table I) is due to the enhanced dipole-dipole coupling, and the decrease from  $v_1=5$  to  $v_1=7$  is due partly to the increasing off-resonance character of Eq. (2.1) and partly to the increasing endothermicity.

Our results presented in Table I for the DF-DF system are consistent with the findings in the discussion of Table II, above. The classical path-quantum vibration calculations of Poulsen and Billing<sup>18</sup> for the DF-DF system exhibit the same qualitative trends in  $k_{V-V}$ , seen here.

The rate constants for  $V-R, T$  energy transfer are reported in the last column of Table I. The  $V-R, T$  rate constants of Table I monotonically increase as  $v_1$  increases. The percent contribution of  $V-R, T$  energy transfer ( $100\% \times k_{V-R, T}/k_{\text{Total}}$ ), for the present work and for Ref. 18, monotonically increase from  $v_1=2$  through  $v_1=7$ . By  $v_1=7$ , the  $V-R, T$  mechanism is quite dominant. The same behavior was seen in the relative proportion of  $V-R, T$  vs  $V-V$  in Refs. 2 and 28 for HF-HF relaxation.

The rate constant  $k_{\text{Total}}$  in column one of Table I is the sum of  $k_{V-V}$  and  $k_{V-R, T}$ . In the analogous HF-HF system, a number of experimental measurements of  $k_{\text{Total}}$  for HF( $v_1=1$  to 7) have been made.<sup>5-11</sup> However, only the rate constants for deactivation of DF( $v_1=1$  and 2) by DF( $v_2=0$ ) have been measured.<sup>12-16</sup> The experimental dependence of the deactivation constants for the higher values of  $v_1$  is thus unknown. The experimental rate constants reported for DF( $v_1=1$ )+DF( $v_2=0$ ) are 0.71, 0.64, 0.49, and 0.60 in units of  $10^{-12}$  cc molecule<sup>-1</sup> s<sup>-1</sup> in Refs. 12-15, respectively. The present theoretical rate constant is 0.18 in these units, and, for Ref. 18, it is 0.16. Agreement between the present work and experiment is fair, being a factor of 3 to 4 too low. The experimental rate constants for DF( $v_1=2$ )+DF( $v_2=0$ ) deactivation, reported in Refs. 14 and 16, are  $18 \times 10^{12}$  and  $20 \times 10^{12}$  cc molecule<sup>-1</sup> s<sup>-1</sup>, respectively. Our theoretical rate constant is  $26 \times 10^{12}$ . Here, agreement with experiment is much better. Reference 18 reports a value of  $8.3 \times 10^{12}$  for this rate constant. The nonmonotonic behavior of  $k_{\text{Total}}$  from  $v_1=5$  to 7 is because  $k_{\text{Total}}$  is the sum of  $k_{V-V}$  and  $k_{V-R, T}$ , which have different dependence on  $v_1$ .

In Table III, we present updated values of the HF-HF rate constants of Ref. 2. The  $V-V$  rate constants have been reanalyzed to include the energetic threshold effects discussed in Sec. II. The results here also reflect a somewhat larger sample size of trajectories than used before.<sup>2</sup> Aside from the  $V-V$  rate constants, the present results are similar to those given in Ref. 2, and conclusions regarding comparisons with previous theoretical and experiment results are unchanged.<sup>2,11</sup>

The present method and that of Ref. 18 differ in several ways, in use of different vibrational potentials and use, in the case of Ref. 18, of rigid-rotor trajectories to serve as a basis for a classical path method, for example. We have studied<sup>2</sup> differences in the calculated rate constants, using the Morse potential vs the

TABLE III. Rate constants<sup>a</sup> using quasiclassical cross-correlation method HF( $v_1 = 1$  to 7) + HF( $v_2 = 0$ ) at 300 K.

System	$k_{\text{Total}}$	$k_{V-V}$	$k_{V-R,T}$
1-0	-0.8 (0.8) <sup>b</sup>	...	-0.8 (0.8)
2-0	16 (3)	15 (3)	1.0 (0.3)
3-0	28 (3)	23 (3)	5 (1)
4-0	38 (5)	20 (4)	18 (3)
5-0	63 (6)	7 (1)	57 (5)
6-0	136 (14)	2.7 (0.9)	133 (14)
7-0	542 (65)	0.4 (0.4)	542 (65)

<sup>a</sup>All rate constants in units of  $10^{-12}$  cc molecule<sup>-1</sup> s<sup>-1</sup>.

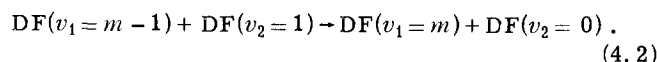
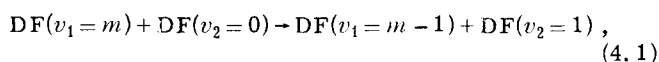
<sup>b</sup>Value in parentheses is one standard error. The actual error may be larger due to limited sample size and a non-Gaussian distribution.

“equivalent harmonic oscillator” (EHO) potential employed in Ref. 18. We also investigated<sup>29</sup> the effect on calculated energy transfer rate constants of neglecting vibrational-rotational coupling as in the rigid-rotor forced-oscillator model, that is, of using rigid-rotor trajectories to serve as a basis for a classical path calculation. Both effects were substantial.<sup>2,29</sup>

In Ref. 1, we compared the present method with that used in Ref. 17. The differences included the potential energy surfaces employed, the selection of trajectory initial conditions, method of determining vibrational action (corresponding to the vibrational quantum number), and the method of determining transition probabilities from trajectory data. For these reasons, a quantitative comparison of the current results with those in Ref. 17 is difficult. There are a number of qualitative differences between the present results and those of Ref. 17. (These same qualitative differences were noted by Poulsen and Billing<sup>18</sup> in comparing their classical-path results with those in Ref. 17.)

Our trajectory results indicate that multiple-collisions (i. e., collisions in which  $R \cdot dR/dt$  changes sign more than once, where  $R$  is a vector connecting the center-of-mass of each molecule) make a very large contribution to the energy transfer rate constants for the present potential energy surface. The potential energy surface<sup>19</sup> employed here has a deep attractive well 6.9 kcal. This lead to occurrence of multiple collisions in about 35% of our trajectories. Moreover, these 35% of the trajectories accounted for approximately 90% of the value of the energy transfer rate constants. The potential energy surface used in Ref. 17 had a much shallower well 2.6 kcal, and collision complexes were not observed there. Multivibrational quantum  $V-R, T$  transitions were found to be very important in Ref. 17. In the present work, less than 1% of the trajectories exhibited multivibrational quantum  $V-R, T$  or  $V-V$  transitions. Multivibrational quantum transitions were unimportant in the classical-path calculation.<sup>18</sup>

As a final comment, we address the question of detailed balance in a classical trajectory calculation such as the one presented here. That is, the relationship between the rate constants for the reactions



In calculating the rate constant for Reaction (4.1), we have sampled from a Boltzmann distribution of rotational levels at 300 K. The final distribution of  $j$  states is not necessarily Boltzmann. If one were to calculate the rate constant for Reaction (4.2), for comparison in detailed balance with that for Reaction (4.1), the initial distribution of  $j$  states would need to be the same as the final  $j$  distribution from Reaction (4.1). Such a calculation has not been performed here. It was shown earlier<sup>30</sup> that unless such effects are included, tests of “detailed balance” can yield large apparent deviations from this principle (a factor of four in the case investigated<sup>30</sup>).

#### IV. SUMMARY

In this paper, we have used the cross-correlation trajectory approach<sup>1,2</sup> to calculate rate constants for vibration-to-vibration ( $V-V$ ) and vibration-to-rotation, translation ( $V-R, T$ ) energy transfer for the system DF( $v = 1$  to 7) colliding with DF( $v_2 = 0$ ) at 300 K, and for the corresponding HF-HF system.

Rate constants for deactivation of DF( $v_1 > 2$ ) have not been measured experimentally. In the cases where comparisons with experiment were possible, the agreement was fair.

The  $V-V$  rate constants increase (apart from one possibly statistically insignificant decrease) from  $v_1 = 2$  to a maximum at  $v_1 = 5$ , and then fall off at higher  $v_1$ . The decrease from  $v_1 = 5$  to  $v_1 = 7$  appears to be due both to the increasing vibrational frequency mismatch and the increasing endothermicity in Eq. (2.1).

The  $V-R, T$  rate constants increased monotonically and quite rapidly as  $v_1$  increased. As the  $V-V$  process moved further from resonance (towards larger  $v_1$ ), the percent  $V-R, T$  steadily increased. This trend in  $V-R, T$  relaxation was also seen by Poulsen and Billing.<sup>18</sup>

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