Cross-correlation trajectory study of vibrational relaxation of HF ($v=1$–7) by HF ($v=0$)[a]

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Results are presented for a three-dimensional quasiclassical trajectory study of the vibrational deactivation of vibrationally excited HF ($v = 1$–7) by ground vibrational HF. A cross-correlation method of analysis is used to calculate probabilities and rate constants for V–V and V–RT transitions using trajectory results. Comparisons are made of calculated total deactivation rate constants (V–V plus V–RT) with experimental values. The V–RT dominates the relaxation for higher v states, and increases particularly rapidly with increasing v. Comparisons are made with recent classical-path calculations for this system, and in the use of Morse versus equivalent harmonic oscillator potentials.

I. INTRODUCTION

In an earlier paper[1] (hereafter denoted as Paper I) the results of a quasiclassical trajectory study of vibration to vibration (V–V) energy transfer were presented for the collision

$$\mathrm{HF}(v=1)+\mathrm{HF}(v=1)\rightarrow\mathrm{HF}(v=0)+\mathrm{HF}(v=2) \qquad (1.1)$$

and its deuterium analogue. This calculation was fully three dimensional; that is, each molecule had three translational, two rotational, and one vibrational degrees of freedom.

In Paper I a cross-correlation method was introduced to relate changes in vibrational state of each molecule to probabilities. This method is similar in spirit to the often used moment method.[2,3] A relation between the latter and semiclassical arguments has been discussed.[4] A realistic potential energy surface, an analytic fit[5] based on *ab initio* SCF points[6] plus an added dispersion term was employed. Calculated rate constants for Reaction (1.1) agreed well with experimental values, both for the HF and DF systems.

The current paper treats the vibrational relaxation of vibrationally excited HF ($v=1$ through $v=7$) by ground vibrational HF. The cross-correlation method of analysis is again used, together with quasiclassical trajectories to calculate energy transfer cross sections and rate constants for V–V (vibration to vibration) and V–RT (vibration to rotation and translation). Comparisons of calculated rate constants for the total relaxation of the excited HF (the sum of the V–V and V–RT rate constants) are made with experimental values. Comparisons are also made with recent classical path calculations of Billing and Poulsen[7] (BP). The "equivalent harmonic oscillator" approximation for the vibrational potential, used in Ref. 7, is tested separately below by comparing with calculations using Morse oscillators.

The cross-correlation method of Paper I used here is summarized in Sec. II. Details of the quasiclassical trajectory computation are given in Sec. III. Section IV summarizes recent experimental measurements for this system and comparisons are made with our theoretical results. In Sec. V a brief review of the classical path calculation of BP[7] is given. In that section a comparison is made of the results of the classical path calculation of Ref. 7 and our cross-correlation trajectory approach. Section V also contains a test of the equivalent harmonic oscillator approximation by comparing with results using a Morse oscillator potential. A summary of our findings is given in Sec. VI.

II. CROSS-CORRELATION METHOD OF ANALYSIS

In our quasiclassical trajectory calculation we have used a cross-correlation method[1] of analysis in which correlations in the changes in vibrational state of each molecule are calculated. An approximate semiclassical justification for relating quasiclassical averages and quantum mechanical expectation values has been given in Ref. 4.

Here, the cross-correlation method is applied to deactivation of HF($v_1=v$) by HF($v_2=0$), where $v=1$–7, due to both the V–RT and the V–V processes, as follows,

$$\mathrm{HF}(v_1=v)+\mathrm{HF}(v_2=0)\rightarrow\mathrm{HF}(v_1=v-m)+\mathrm{HF}(v_2=0) \qquad (V\text{–}RT), \quad (2.1)$$

$$\mathrm{HF}(v_1=v)+\mathrm{HF}(v_2=0)\rightarrow\mathrm{HF}(v_1=v-n)+\mathrm{HF}(v_2=n) \qquad (V\text{–}V), \quad (2.2)$$

where m and n are integers (most often both equaling 1).

The V–V energy transfer mechanism occurs when there is a simultaneous downward change in quantum number of molecule 1 and upward change for molecule 2. The cross correlation which describes this criterion was seen in Paper I to be

$$P_{V\text{–}V}(b, V_R) = -\langle \Delta v_1 \Delta v_2 \rangle (b, V_R), \qquad (2.3)$$

where Δv_i is the change in vibrational state of molecule i, and the brackets denote an ensemble average over trajectories as in Paper I. Equation (2.3) neglects mul-

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tiquantum changes in vibrational state. The probability P_{V-V} depends on the given impact parameter b and relative velocity V_R. The function $\Delta v_1 \Delta v_2$ is nonzero only when both molecules undergo a change in vibrational state (i.e., a $V-V$ process). In a $V-RT$ event, as in Eq. (2.1), $\Delta v_1 = -m$ and $\Delta v_2 = 0$. The product $\Delta v_1 \Delta v_2$ in this case would be zero and would not contribute to the $V-V$ cross section. The $V-RT$ probability is related in Paper I to the cross correlation (2.4) for the case that the Δv's are only 0 or 1:

$$P_{V-RT}(b, V_R) = \langle \Delta v_1 (\Delta v_1 + \Delta v_2) \rangle (b, V_R) \ . \tag{2.4}$$

The probability for the total deactivation of molecule 1 ($V-V$ plus $V-RT$) is found from Eqs. (2.3) and (2.4) to be

$$P_{\mathrm{Tot}}(b, V_R) = \langle (\Delta v_1)^2 \rangle (b, V_R) \ . \tag{2.5}$$

When $v_1 = 1$ the $V-V$ process in Eq. (2.2) cannot be observed, so one should use Eq. (2.4) for P_{Tot} instead of Eq. (2.5).

The cross sections related to the three correlations in Eqs. (2.3)–(2.5) are found by integrating each over impact parameters,

$$\sigma(V_R) = 2\pi \int_0^\infty P(b, V_R)\, b\, db \ . \tag{2.6}$$

This integral was evaluated via a Monte Carlo stratified sampling technique discussed in Paper I. The corresponding rate constant is given by Eq. (2.7):

$$k(T) = \langle V_R \sigma(V_R) \rangle (T) \ , \tag{2.7}$$

where the average in Eq. (2.7) is over a Maxwell–Boltzmann distribution of relative velocities at a given temperature T.

III. CALCULATION OF QUASICLASSICAL TRAJECTORIES

Details of selecting trajectory initial conditions were the same as presented in Sec. III of Paper I. The initial and final separation distance R of the molecular centers of mass was 10 Å for each trajectory. The trajectories were integrated in Cartesian coordinates. A numerical procedure described in Paper I was used to determine the vibrational action-angle variables. The trajectory calculations were performed on a CDC-175 computer. On the average, each trajectory required 45 sec computation time.

IV. COMPARISON OF THEORY AND EXPERIMENT

The collision-induced vibrational relaxation of vibrationally excited HF by HF in its ground vibrational state has been the subject of much experimental[8–13] and theoretical[7,14] interest. The vibrational relaxation is classified as $V-V$ or $V-RT$.

Energy transfer processes, in general, occur more readily as the amount of internal energy transferred into translational energy decreases. Thus, it is usually found that the rate constant for $V-V$ transfer is much larger than that for $V-RT$. For a harmonic vibrational potential, the $V-V$ process of Eq. (2.2) is nearly resonant. That is, there is little conversion of vibration into translational or rotational energy. However, the HF molecule is very anharmonic.[15] Because the vibrational energy levels become more closely spaced as v increases, the $V-V$ process in Eq. (2.2) becomes increasingly endothermic as v increases.

TABLE I. Experimental and theoretical rate constants for deactivation of HF(v) by HF(0).

	k^{tot} (10^{-12} cc molecule^{-1} sec^{-1})						
$v=1$	2	3	4	5	6	7	Reference
1.8							Bott[8]
	16	17	44	65			Airey[9]
	25	49	43				Osgood[10]
1.6	16	26	27	58[b]	101[b]		Kwok[11]
	13	19	32	46	52	43	Poole[12]
		28	72				Douglas[13]
0.2	19	28	53	69	156	455	This work[a]

[a] Intermolecular potential from Ref. 5, Morse oscillator vibrational potentials, 300 K.
[b] M. A. Kwok and N. Cohen, personal communication reported in Ref. 14.

Because of this large vibrational anharmonicity, the $V-RT$ process of Eq. (2.1) makes a very important contribution to the total rate constant for vibrational deactivation in HF. In fact, the present work and that of Billing and Poulsen[7] indicate that the $V-RT$ process becomes the dominant relaxation mechanism for higher v states. The experimental work on this system has yielded thus far only measurements of the total rate constant for deactivation of the vibrationally excited HF molecule, rather than giving the relative contributions of the $V-V$ and $V-RT$ pathways.[8–13] Because of the disagreement between the various measurements of the total rate constant, we briefly comment on them. For ease of comparison, the experimental results of Refs. 8–13 are given in Table I.

In the experiment of Osgood, Sackett, and Javan[10] a hydrogen fluoride chemical laser is used to optically excite ground state HF molecules into vibrational levels 1 through $v-1$, where level v is the one to be measured. Level v is then populated through collisional $V-V$ energy transfer. The method of analysis of the experiment of Osgood *et al.*[10] involves many competing rate constants due to the simultaneous populations in levels 1 through v. Their analysis (for levels 1–4) also used the assumption of the harmonic oscillator (HO) model,[16] namely, that for the $V-RT$ process the rate constant increases linearly with increasing v state. Based on more recent experimental work involving deactivation of HF with a variety of other collision partners,[17,18] it is now believed that the $V-RT$ rate constants scale faster than linearly with v. An experimental dependence of v^n with $n = 2.7 \pm 0.2$ is currently suggested[19] for $V-RT$.

The experiment of Kwok and Wilkins[11] is similar to that of Osgood *et al.* in that the upper vibrational levels are populated by $V-V$ energy transfer. The kinetic analysis becomes increasingly complex as v increases. For the lower vibrational states, the results of Kwok and Wilkins[11] agree reasonably well with the other ex-

TABLE II. Rate constants[a] using quasiclassical cross-correlation method with Morse oscillator vibrational potentials.

System	k^{tot}	k^{V-V}	k^{V-RT}
1–0	0.2(0.1)[b,c]	···	0.2(0.1)
2–0	19(3)	17(3)	1.7(0.5)
3–0	28(4)	24(4)	4(1)
4–0	53(10)	31(7)	22(5)
5–0	69(10)	9(3)	60(10)
6–0	156(18)	14(3)	142(15)
7–0	455(49)	17(3)	438(48)

[a]Rate constants in units of 10^{-12} cc molecule^{-1} sec^{-1}.
[b]The $v=1$ case only, the deactivation is completely V–RT.
[c]Value in parentheses is one standard error.

perimental results,[9,11,13] apart from those of Osgood *et al.*,[10] which are about a factor of 2 higher.

The experimental techniques of Airey and Smith[9] and of Poole and Smith[12] are basically the same as each other, with improvements in detection sensitivity in the latter case. In this experiment, vibrationally excited HF is formed by the exothermic chemical reactions

$$H + F_2 \rightarrow F + HF^* \tag{4.1}$$

and

$$F + H_2 \rightarrow H + HF^* \ . \tag{4.2}$$

The quenching of the infrared chemiluminescence upon addition of HF(0) is studied. As in the previously discussed experiments, there is an initial population in several excited vibrational states, and therefore the expressions relating the observed chemiluminescence intensities to rate constants are complicated.

The results of Poole and Smith[12] are seen to be in reasonable agreement with the earlier work of Airey and Smith[9] and of Kwok and Wilkins.[11] There is some disagreement with the results of Ref. 10, which are 1.9, 2.6, and 1.3 times larger for $v=2$, 3, and 4 respectively.

The most direct measurement of these relaxation rates was recently presented by Douglas and Moore.[13] In this experiment, ground vibrational HF was excited by a hydrogen fluoride laser directly to $v=4$. The population of $v=3$ and $v=4$ was monitored by measuring their fluorescence. The kinetic analysis in this case was much simpler than in the experiments discussed previously. An important experimental observation was that HF($v=4$) relaxes by losing a single quantum yielding HF($v=3$). This single quantum mechanism had often been assumed,[9–12] but Douglas and Moore have provided the most direct evidence of its validity. The relaxation data of Douglas and Moore[13] are limited to $v=3$ and $v=4$.

We have used the cross-correlation method of Sec. II and quasiclassical trajectories using the potential energy surface in Ref. 5 and Morse oscillator vibrational potentials[15] to calculate the rate constants for deactivation of HF(v) by HF(0), for $v=1$–7. Our results for the total deactivation are given in Table I along with the experimental values. The rate constants for V–V and V–RT are given in Table II.

The theoretical results for k^{tot} are seen to be in fair agreement with the two rate constants reported by Douglas and Moore.[13] The rate of increase in going from states $v=3$ to $v=4$ is steeper in Ref. 13 than in our theoretical study or in the measurements of Poole and Smith.[12] The apparent decrease in rate constant from $v=6$ to $v=7$ seen in Ref. 12 may be an artifact of the complex kinetic analysis required.

The present results for k^{tot} for this system are roughly 1.5–3 times larger than the experimental values of Poole and Smith[12] for $v=2$ through $v=6$. The experimental results of Ref. 12 may themselves be somewhat too low in light of the more direct measurements of Douglas and Moore.[13] Thus, theoretical rate constants for k^{tot} appear to be quite reasonable in predicting the total deactivation rates for the $v=2$–5 systems.

Probably the most serious disagreement with experiment is for the deactivation of HF(1) by HF(0). Our calculated rate constant is substantially smaller than the experimental rate constants reported in Refs. 8 and 11 [see these references for discussion of other measurements on the HF(1)–HF(0) system]. For the $v=1$ case only, the total deactivation is completely due to V–RT, and so Eq. (2.4) is used. For the other six cases the total deactivation is V–RT plus V–V, and so Eq. (2.5) is used.

In Table II the calculated V–V and V–RT rate constants for this system are listed, as well as the total rate constant, but as mentioned before, only the total rate constants have been measured experimentally. In Table II one sees a dramatic increase in importance of the V–RT pathway as the initial v_1 increases. At low values of v_1 the deactivation is primarily due to V–V. As v_1 increases, the importance of V–RT steadily grows.

One predicts, from Table II, a more dramatic rate of increase of the V–RT rate constants with v than is predicted by the HO model in Ref. 16 (which stated that $k_{v,0\rightarrow v-1,0} = vk_{1,0\rightarrow 0,0}$). Attempts to model the performance of a hydrogen fluoride chemical laser[20] have indicated the need to use a V–RT rate constant that increases more rapidly with v than in the HO model, in order to accurately model the power output of the laser. The increase indicated in Table II for Morse oscillators is more rapid than any assumed to date for the HF–HF system.

As a further comment on the calculation for the Morse systems, it is noted that for $v=6$ and 7 a loss of more than one vibrational quantum was observed in 6% and 12% of the trajectories, respectively. The loss of 1.5 quanta or more was found in 3% and 6% of the trajectories for $v=6$ and 7, respectively.[21] The present analysis of Sec. II neglects the probabilities due to multiple quantum transitions. As noted previously, Douglas and Moore[13] experimentally observed HF($v=4$) to relax by a single quantum mechanism. Whether this mechanism holds for $v=6$ and $v=7$ has not been directly tested experimentally.

The correlations in the changes of the dynamical variables of the HF–HF system and how the correlations

TABLE III. Correlation coefficients for changes in dynamical variables for $HF(v_1=v)+HF(v_2=0)$ system.[a]

		Correlation coefficients[b]						
x	y	$v=1$	$v=2$	$v=3$	$v=4$	$v=5$	$v=6$	$v=7$
Δv_1	Δv_2	−0.99	−0.96	−0.93	−0.83	−0.45	−0.45	−0.24
Δv_1	ΔJ_1^2	−0.20	−0.03	−0.07	−0.32	−0.57	−0.76	−0.80
Δv_1	ΔJ_2^2	0.01	−0.06	−0.10	−0.30	−0.55	−0.69	−0.64
Δv_1	ΔE_{trans}	−0.03	0.05	0.03	−0.17	−0.31	−0.41	−0.48
Δv_2	ΔJ_2^2	−0.01	−0.03	−0.04	0.01	−0.09	0.12	0.00
Δv_2	ΔJ_1^2	0.20	0.01	−0.08	−0.03	−0.08	0.18	0.03
ΔJ_1^2	ΔJ_2^2	−0.44	−0.37	−0.32	0.09	0.06	0.24	0.21
ΔE_{trans}	$(\Delta J_1^2+\Delta J_2^2)$	−0.84	−0.51	−0.35	−0.16	0.07	0.19	0.21

[a]Potential energy surface from Ref. 5, Morse oscillator vibrational potentials, 300 K.
[b]See Eq. (4.3).

change with increasing v are of interest. The correlation coefficient between two variables x and y is given by

$$r=\left(\sum_i (x_i-\bar{x})(y_i-\bar{y})\right)\left[\left(\sum_i (x_i-\bar{x})^2\right)\left(\sum_i (y_i-\bar{y})^2\right)\right]^{-1}. \tag{4.3}$$

If $r=1$, a perfect, positive linear correlation exists between x and y. If $r=-1$, x and y have a perfect, negative linear correlation. And if $r=0$, there is no linear correlation. In Table III the correlation coefficients of Eq. (4.3) for the seven systems studied are given.

The correlations seen for the case $v=1$ are very similar to the ones that appeared in Table II of Paper I for the HF(1)+HF(1) system. The change in vibrational quantum number of one molecule in the HF(1)+HF(0) collision shows a very strong, negative linear correlation with the change in vibrational quantum number of the other. This correlation would be observed for a predominantly $V-V$ mechanism. Of course, the $V-V$ exchange for HF(1)+HF(0) is not observable experimentally because the product molecules are identical to the reactants.

As the initial v of the deactivated molecule increases, the amount of negative correlation between Δv_1 and Δv_2 becomes steadily smaller from $v_1=1$ through $v_1=7$. This decrease in correlation is expected, due to the increased off-resonance character of the $V-V$ process at larger v, making it less probable relative to the $V-RT$. The weakening in the $\Delta v_1-\Delta v_2$ correlation coefficient as v_1 increases seen in Table III does not require that the $V-V$ rate constants monotonically decrease. What the weakening in the $\Delta v_1-\Delta v_2$ linear correlation does imply is that the $V-RT$ mechanism becomes more important relative to the $V-V$. This result is seen in Table II.

As v_1 increases there is an increasingly strong negative correlation between Δv_1 and the change in approximate rotational energy of molecule 1, as well as a somewhat weaker negative correlation with the change in rotational energy of molecule 2 and with the change in translational energy, reflecting a tendency to convert the vibrational energy to energy of these other internal coordinates.

The trend in Table III of the weakening of the correlation between the translational energy change and the net change in rotational energy, i.e., between ΔE_{trans} and $\Delta(J_1^2+J_2^2)$, as v increases is a reflection of the weakening of that between Δv_1 and Δv_2. At small v the dominant relaxation mechanism of the excited HF is $V-V$ and so the change in translational energy is chiefly due to $\Delta(J_1^2+J_2^2)$. If $V-V$ were the only mechanism of vibrational deactivation of molecule 1, then any change in E_{trans} would have to come exclusively from a change in total rotational energy, i.e., the ΔE_{trans} vs $(\Delta J_1^2+\Delta J_2^2)$ correlation coefficient would be −1. As the $V-RT$ mechanism becomes more important relative to the $V-V$, the ΔE_{trans} vs $(\Delta J_1^2+\Delta J_2^2)$ correlation would weaken. This result is seen in Tables II and III.

Some of the present findings can be compared with those of Wilkins,[14] who has also made an extensive trajectory study of vibrational relaxation in the HF–HF system. As discussed in Paper I, there are several differences in technique between the present calculation and that in Ref. 14. These include the potential energy surfaces used, selection of initial conditions, and the method of analyzing results, discussed in Paper I.

Wilkins[14] predicts a high probability for vibrational to rotational energy conversion within the same molecule. Multiquantum $V-RT$ processes are also calculated to be very important.[14] Some evidence of an internal vibrational to rotational energy transfer, is reflected as a large, negative correlation of Δv_1 with ΔJ_1^2 in the present Table III for the larger initial values of v_1. As noted before, some multiquantum transitions for $v_1=6$ and 7, were seen, although not as extensively as in Ref. 14. The lack of quantitative agreement with Ref. 14 is primarily due to the nature of the potential energy surfaces and to the methods of analysis in the two calculations outlined in Paper I.

We close this section with a comment on the number of trajectories used for each system. For each initial v state at least 500 trajectories were used. However, for the $v_1=6$ and $v_1=7$ cases where some trajectories exhibited a very large Δv_1, 850 and 1000 trajectories were used, respectively.[21] Even with this number of trajectories the standard errors reported may be unrealistically small. One should perhaps sample 2 or 3 times as many trajectories as reported here to be assured of converged values, because of the presence of a few cases with large Δv_1's. (The erratic behavior in k^{V-V} for $v_1=5$ through $v_1=7$ is caused by these large Δv_1 fluctuations.) The distribution of Δv_1's may not be even nearly Gaussian, particularly in the tails. However, to make as many comparisons with other results as possible, these lesser numbers were used.

V. COMPARISON OF QUASICLASSICAL AND CLASSICAL PATH CALCULATIONS

Billing and Poulsen[7] have used a classical path assumption[5,22-28] to calculate the rate constants of V–RT and V–V energy transfer in Eqs. (2.1) and (2.2), i.e., the translational and rotational degrees of freedom were treated classically by calculating rigid-rotor trajectories. These trajectories were then used to calculate a time-dependent interaction potential that acts as a forcing function on the vibrational motion of the molecules. The vibrational motion was then treated quantum mechanically using this time-dependent force.

Billing and Poulsen[7] used harmonic oscillator wave functions for calculating the quantum mechanical vibrational dynamics. To account for the fact that the HF molecule is actually quite anharmonic, for each molecule they used a frequency ω_1 or ω_2 appropriate to the energy difference in the transition being considered.[7] For example, for the reaction

$$\mathrm{HF}(v_1)+\mathrm{HF}(v_2)\rightarrow \mathrm{HF}(v_1+n)+\mathrm{HF}(v_2+m)\,, \tag{5.1}$$

they use ω_1 and ω_2 given by

$$n\hbar\omega_1 = E_{v_1+n}-E_{v_1}\,, \tag{5.2}$$

$$m\hbar\omega_2 = E_{v_2+m}-E_{v_2}\,. \tag{5.3}$$

TABLE IV. Rate constants[a] of Billing and Poulsen.[7]

System	k^{tot}	k^{V-V}	k^{V-RT}
1–0	0.81	···	0.81[d]
2–0	6.4(2.1)[b]	3.7[c]	2.7
3–0	10(3)	3.7	6.3
4–0	19(6)	4.3	15
5–0	27(6)	2.2	25
6–0	43(14)	0.9	42
7–0	82(28)	0.2	82

[a]All rate constants in units of 10^{-12} cc molecule^{-1} sec^{-1}.
[b]Value in parentheses is one standard error, estimated from Fig. 1 of Ref. 7.
[c]V–V rate constants estimated from Fig. 3 of Ref. 7.
[d]From Tables V and VII of Ref. 7.

TABLE V. Rate constants[a] using quasiclassical cross-correlation method with equivalent harmonic oscillator vibrational potentials.[b]

System	k^{tot}	k^{V-V}	k^{V-RT}
1–0	0.3(0.2)[c,d]	···	0.3(0.2)
2–0	9(1)	8(1)	0.6(0.2)
3–0	12(2)	10(2)	1.4(0.6)
4–0	32(7)	27(6)	5(2)
5–0	29(5)	18(3)	11(2)
6–0	42(9)	7(2)	35(9)
7–0	95(19)	6(2)	89(19)

[a]All rate constants in units of 10^{-12} cc molecule^{-1} sec^{-1}.
[b]See Eqs. (5.2) and (5.3).
[c]For the $v=1$ case only, the deactivation is completely V–RT.
[d]Value in parentheses is one standard error.

The energy levels E_n are derived from spectroscopic measurements.[27] Using these equivalent harmonic ocsillator frequencies of Eqs. (5.2) and (5.3), each molecule is given an initial vibrational energy appropriate to vibrational states v_1 and v_2, respectively. Because this equivalent harmonic oscillator (EHO) method was used to match spectroscopic *spacings* in energies of the quantum states the energies of the quantum states for the EHO potential are substantially lower than those of the true molecule.

In order to compare our quasiclassical moment method with the classical path approach of Billing and Poulsen,[7] we have performed a trajectory study on the series of systems HF(v)+HF(0), $v=1$–7, and have used the cross-correlation method of analysis presented in Sec. II, Eqs. (2.3)–(2.7). Although a Morse oscillator vibrational potential is more appropriate to describe the HF vibrations, we have necessarily used, for purposes of this comparison only, the modified harmonic oscillator (EHO) potentials of Billing and Poulsen[7] with frequencies given in Eqs. (5.2) and (5.3) in order to make a direct comparison with Ref. 7. The selection of initial conditions and use of action-angle variables in this calculation were the same as described before.

Table IV contains the total deactivation, V–V, and V–RT rate constants calculated by Billing and Poulsen.[7] In Table V are the present rate constants calculated via the quasiclassical cross-correlation method using the intermolecular potential of Ref. 5 and EHO vibrational potentials described above. The agreement between our work and that of Billing and Poulsen[7] for the total rate of deactivation is seen to be quite good for the seven systems studied. The methods agree to within 20% for initial $v=3$, 5, 6, and 7. Our results are roughly 50% larger for initial $v=2$ and 4. The largest disagreement is for initial state $v=1$. Within the framework of the numerical uncertainty of both calculations, the calculated total deactivation rates of the two studies are in excellent agreement, the quite different approaches of the methods not withstanding.

In Table V are the V–V rate constants calculated here, again using EHO potentials. The corresponding results

of Billing and Poulsen[7] are given in Table IV. While the two methods for calculating the total rate of deactivation agreed well, it is seen from Tables IV and V that the quasiclassical cross-correlation method gives results for $V-V$ transfer that are much higher than in Ref. 7. There is some qualitative agreement in that the maximum $V-V$ rate constant in each case is for $v=4$, with the rate constants monotonically decreasing from $v=4$ through $v=7$. This decrease is expected: The $V-V$ process becomes increasingly endothermic with increasing v, in the quantum case, if one quantum transitions are involved. In both the quantum and classical calculations the transitions become increasingly off resonant with increasing v_1.

The differences between the two methods of calculating the $V-V$ rate constants are not due to numerical uncertainties. The separate rate constants for $V-V$ and $V-RT$ have not been measured experimentally, so one cannot compare the different $V-V$ predictions with experiment. Further study of off-resonant $V-V$ transfer using a more exact quantum mechanical method would be useful.[28]

Two major approximations in the dynamics used in Ref. 7 are the "classical path" and the EHO approximations. Elsewhere,[29] we have investigated the accuracy of the first approximation by comparing their classical analogue with exact classical results. (k^{V-RT} for the classical path EHO in Ref. 29 is less than that for the exact EHO reported here by a factor of about 4 for $v_1=7$.) The EHO approximation is investigated below.

The theoretical rate constants for $V-RT$ energy transfer using the EHO approximation (for comparison with Ref. 7) are presented in Table V, and the corresponding results of Billing and Poulsen[7] in Table IV. Since the two methods agreed well for the total rate constants but not for the $V-V$ rate constants, the $V-RT$ (the difference of the two rate constants) show substantial discrepancies. In this case, the classical path plus EHO approach,[7] predicts a larger $V-RT$ rate constant than does the present quasiclassical plus EHO method for $v=1-6$.

The sensitivity of the dynamics to using the EHO potential rather than the more realistic Morse potential can be judged by comparing the results in Tables II and V. The $V-V$ results for the EHO and Morse studies show qualitative similarity. The $V-RT$ rate constants for the Morse oscillator at large initial v_1 are much larger than the EHO results (a factor of 4.5 at $v_1=7$), perhaps because for a given v_1, the Morse oscillator has a greater energy and hence larger amplitude than the EHO.

VI. SUMMARY

We have used the quasiclassical trajectory approach with a cross-correlation method of analysis[1] to calculate rate constants for $V-V$ and $V-RT$ energy transfer for the system $HF(v_1)$–$HF(0)$, $v_1=1-7$, at 300 K.

For this series of reactions, two sets of calculations were presented, each using the intermolecular potential of Ref. 5. In the first set, Morse oscillator vibrational potentials were used to compare with experiment. For the rate constants of total deactivation the present results were in fair agreement with the direct measurement of Douglas and Moore,[13] and were generally 1.5–3 times larger than the experimental values of Poole and Smith.[12]

The present $V-RT$ rate constants increased faster with increasing v state than predicted by the HO model.[16] This rapid increase had been suspected by workers modeling the HF chemical laser system,[20] and more direct data would be desirable to test the result.

In the second set, equivalent harmonic oscillator vibrational potentials were used with frequencies chosen matching vibrational energy level differences from spectroscopic measurement and to compare with the classical path results (with EHO) of Ref. 7. The two sets of results were found to agree quite closely in calculating the total rate of deactivation, but the quasiclassical trajectory results showed a much larger portion of the total rate constant being due to $V-V$ transfer than did those of Billing and Poulsen.[7]

Two quasiclassical calculations reported here, which differed only in the vibrational potentials employed, EHO versus Morse, were compared, to evaluate the EHO assumption used in Ref. 7. It was found that the Morse oscillator potential gave $V-RT$ rate constants much larger than did the EHO when v_1 was large (cf. Tables II and V).

The results of the present quasiclassical trajectory study on hydrogen fluoride have been encouraging for k^{tot} in those cases where comparisons with experiment are possible. Potential energy surfaces for other systems of molecules would be useful. When more exact dynamical quantum mechanical results on $V-V$ and $V-RT$ collisions become available for systems, to avoid a classical path approximation,[7] a further test of the present methods will be possible. We have investigated the seriousness of neglecting the vibration–rotation coupling in the classical path approximation elsewhere.[29] It was found that neglect of the vibration–rotation coupling leads to discrepancies in calculated $V-RT$ rate constants when compared with results in which the coupling was included.

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