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Converged close coupling calculations for V–V energy transfer: $2HF(v=1)\rightarrow HF(v=2)+HF(v=0)$

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Abstract. We report accurate dynamical calculations for V-V energy transfer in the collision of two $HF(v=1)$ molecules for a realistic potential energy surface.

Key words: Scattering — Close Coupling — Vibration-to-vibration collisional energy transfer — Pipeline vector computer

Close coupling (CC) calculations [1-6] provide the most systematic available method for performing converged quantum mechanical calculations of state-to-state collisional transition probabilities. So far converged transition probabilities have been calculated for vibrational-rotational transitions in atom–diatom collisions but only for rotational transitions in systems with four or more atoms [3-11]. Here we report the first converged transition probabilities for vibration-to-vibration (V–V) energy transfer in three-dimensional collisions. The system considered is

$$HF(v_1=1, j_1=0)+HF(v_2=1, j_2=0)\rightarrow HF(v_1'=2, j_1')+HF(v_2'=0, j_2') \qquad (1)$$

with zero total angular momentum, where v_i and j_i denote vibrational and rotational quantum numbers and primes denote final values.

The interaction potental V_{int} assumed for the present calculation is a modification of the rigid rotor interaction potential of Alexander and DePristo [12]. We introduce vibrational dependence into this potential by generalizing the approximation of Gianturco et al. [13] for the short-range vibrational force and by incorporating the correct r_i-dependence of the permanent multipole moments, where r_i is the bond length of molecule i. Thus we multiplied the r-dependent coefficients [12] $A_{\lambda_1\lambda_2\lambda}(r)$, where r is the distance between the centers of mass of the two molecules, by the function [13] $\exp[\alpha_{\lambda_1\lambda_2\lambda}(r_1+r_2-2r_e)]$, where $\alpha_{\lambda_1\lambda_2\lambda} = d \ln A_{\lambda_1\lambda_2\lambda}/dr|_{r=r_{tp}}$, where r_{tp} is a high-energy translational turning point ($4.1a_0$) and r_e is the equilibrium intermolecular distance ($1.733a_0$), and we replaced the dipole and quadruple moments by $\mu_e+\beta_{\lambda_1\lambda_2\lambda}(r_i-r_e)$ and $\Theta_e+\gamma_{\lambda_1\lambda_2\lambda}(r_i-r_e)$, respectively. The parameters needed to specify our modifications are given in Table 1. The diatom vibrational potential is taken from Murrell and Sorbie [14] and the vibrational-rotational energy levels are calculated from the parameters given by Webb and Rao [15]. Vibrational matrix elements were evaluated using a new quadrature scheme [16], and we did not neglect the rotational-quantum number dependence of the vibrational wave-functions.

In the CC calculations, the system wave function is expanded in products of radial functions times symmetrized vibrational-rotational-orbital basis functions [17]. The use of N basis functions leads to N coupled differential equations, which are solved by R matrix propagation [18, 19] using a code vectorized for the Control Data Corporation Cyber 205 pipelined vector computer [20, 21]. Relative to estimated times for unvectorized calculations on a Digital Equipment Corporation VAX 11/780 with scalar floating point accelerator, we achieved enhancements in computation speed increasing from a factor of 1200 for $N=400$, which was used in early convergence studies, to a factor of 1700 for $N=948$, which is the largest N considered here.

The CC calculations yield state-to-state transition probabilities $P^{VV}_{j_1'j_2'}$ for process (1) for a set of initial relative translational energies E_{rel}. Because the two molecules are indistinguishable, these probabilities are final states which are combinations of $v_1'=2$, j_1'; $v_2'=0$, j_2' and $v_1'=0$, j_2'; $v_2'=2$, j_1' [17]. The sum of the rotational quantum numbers is denoted j_{sum} and the sum of $P^{VV}_{j_1'j_2'}$ over all processes involving $j_1'+j_2'$ quanta of rotational excitation is called $P^{VV}_{j'_{\text{sum}}}$. The total V-V probability, obtained by summing the previous probability over $P^{VV}_{j'_{\text{sum}}}$, is called P^{VV}. The present calculations of these probabilities are very well converged with respect to integration ranges and step sizes, with the largest source of error being due to the finite number of terms in the wavefunction channel expansion. The final converged calculations are based on 948 channels, with the R matrix for these

Table 1. Parameters for the interaction in (a.u.)

λ_1	λ_2	λ	$\alpha_{\lambda_1\lambda_2\lambda}$	$\beta_{\lambda_1\lambda_2\lambda}$	$\gamma_{\lambda_1\lambda_2\lambda}$
0	0	0	2.38		
0	1	1	2.42		
1	0	1	2.42		
1	1	2	0.738	0.838	
1	2	3	0.850	0.918	3.00
2	1	3	0.850	0.918	3.00
μ_e, Θ_e			0.7066[a]	1.64[b]	

[a] Ref. [12] used $\mu = 0.716$ a.u.

[b] Rev. [12] used $\Theta = 1.93$ a.u.

Table 2. Partially summed transition probabilities

E_{rel} (meV)	P_0^{VV}	P_1^{VV}	P_2^{VV}	P^{VV}
2.455	0.88	0.035	0.003	0.92
29	0.92	0.037	0.014	0.98

channels propagated from $2a_0$ to $150a_0$. The channel-selection criterion that yields these channels is $j_{\text{sum}} \leq 10$ for $v_1 + v_2 \leq 2$, $j_{\text{sum}} \leq 8$ for $v_1 + v_2 = 3$ or 4, and $j_{\text{sum}} \leq 1$ $v_1 + v_2 = 5$. The best converged values of P^{VV} and $P^{VV}_{j'_{\text{sum}}}$ for two values of E_{rel} are shown in Table 2. The convergence checks, based on calculations with $N = 694$, 824, 880, and 948, indicate that P^{VV} is converged to about 0.01 and the $P^{VV}_{j'_{\text{sum}}}$ are converged to about ±2 in the last significant figure.

The largest $P^{VV}_{j'_1 j'_2}$ for the final basis are given in Table 3. The most striking aspect of these rotational energy distributions is the peaking of the V-V energy transfer cross sections at a final state that is nonresonant by 172 $\text{cm}^{-1}$and the fact that transition probabilities to other channels with smaller translational energy defects are smaller by factors of $\geq 3 \times 10^1$. It would be interesting to learn the sensitivity of this result to the nature of the potential [22].

Although the present calculations, being restricted to zero total angular momentum, cannot be compared to experiment, they provide benchmarks for testing approximate dynamical theories that can more easily be applied to all total angular momenta.

Further details of these calculations, as well as converged calculations of transition probabilities for rotation-to-rotation energy transfer in *HF-HF* collisions in which the molecules are assumed rigid, will be published elsewhere [23].

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Table 3. State-to-state transition probabilities

j_1'	j_2'	ΔE (cm^{-1})[a]	2.455[b]	29[b]
0	0	172	0.88	0.92
1	0	134	0.03	0.03
0	1	131	0.006	0.01
1	1	93	0.0006	0.012
2	0	58	0.002	0.0009

[a] Translational energy defect (172 $\text{cm}^{-1} = 21$ meV)

[b] E_{rel} in meV (29 meV $= 234$ cm^{-1})

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