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Monte Carlo Trajectory Study of Ar + H_2 Collisions

Translation to Vibration Energy Transfer from Different Initial States

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We present here rate constants for vibrational state changes induced by collisions of Ar atoms with H_2 molecules with initial vibrational quantum numbers v = 0, 4, 6, 10, and 13. All of the other initial collision conditions were selected from equilibrium distributions at 4500°K. The rates were calculated using quasiclassical trajectory methods and the final vibrational quantum number v' was obtained by the histogram method for $|\Delta v| = 1$ and smooth sampling for $|\Delta v| > 1$ (1). The potential energy surface on which the trajectories were calculated is the full potential as reported elsewhere (1). The rate constants we report here are the most accurate and complete set obtainable from a study of this kind. They were obtained from a total of 2663, 4594, 3351, 2650, and 1976 trajectories for v = 0, 4, 6, 10, and 13 respectively.

The cross sections $\sigma_{b\to n}(v,T\to v')$ presented here are computed by averaging over both the initial relative velocity V_R and the initial bound (b) rotational states and by summing over all nondissociative (n: bound and quasibound) final rotational states. The rate constants are $k_{b\to n}(v,T\to v') = \langle V_R\rangle \sigma_{b\to n}(v,T\to v')$ where $\langle V_R\rangle = (8kT/\pi\mu)^{\frac{1}{2}}$.

Figure 1 shows the cross sections. Statistical errors (associated with Monte Carlo averaging) are smallest (7-10%) for $\Delta v = -1$, but increase for large $|\Delta v|$ to about 100% at the end points where only one trajectory may be contributing to the cross section. The cross sections are 1-5 Å^2 for $\Delta v = \pm 1$ for all $v \geq 4$. Larger Δv occur with smaller cross sections, but the smallest for which we can give a value is only 10^{-4} times that for $\Delta v = \pm 1$. By plotting the same data so as to display the negative of the surprisal (2,3), as we do in Figure 2, better symmetry about $\Delta v = 0$ appears. The disparity between positive and negative Δv insofar as the range over which the cross section varies is reduced, and on either side of $\Delta v = 0$ the size of the average slope is nearly the same, in contrast to Figure 1. There is also a definite trend toward monotonicity (less crossing of lines connecting points of different initial states). However, curvature between line segments connecting individual points is not much improved from Fig. 1.

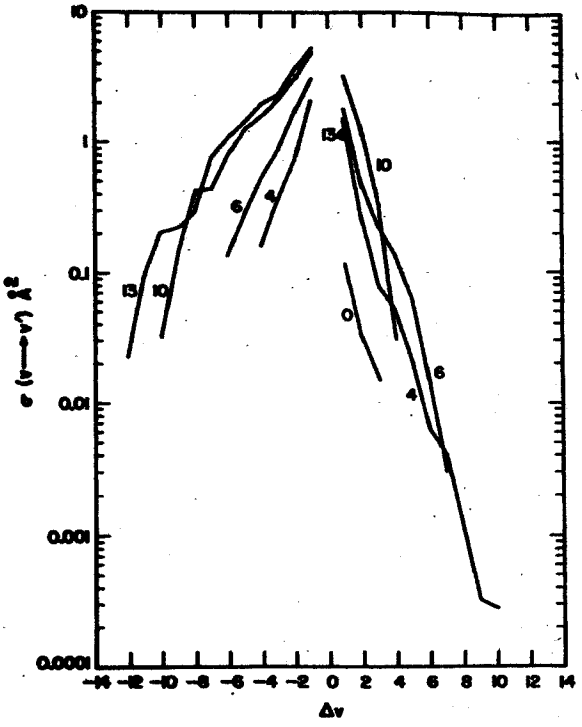

Figure 1. A plot showing how the cross section $\sigma_{v \to v'}$ $(v,T \to v')$ depends on change of vibrational quantum number $\Delta v = v' - v$ for initial $v = 0, 4, 6, 10,$ and 13

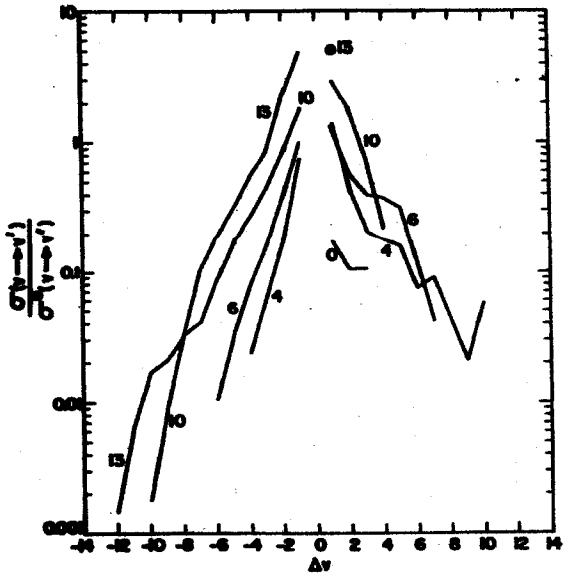

Figure 2. A surprisal plot for $Ar + H_2$ vibrational energy transfer collisions for the initial states $v = 0, 4, 6, 10,$ and 13 of H_2. The prior expectations $\sigma^o_{v \to v'}(v,T \to v')$ were calculated using the prescription suggested by Ben-Shaul et al. (2) and expressed analytically by Procaccia and Levine (3). The accurate energy states of H_2 were used in the calculations and all nondissociative (bound and quasibound) final states were included. As for the trajectory results, however, averaging over initial states included only bound states.

Table I compares ratios of $\Delta v = \pm 1$ transition rates from our trajectories with those from the Landau-Teller harmonic oscillator (LTHO) model: $k(v \to v+1) = (v+1)k(0 \to 1)$ and $k(v \to v-1) = vk(1 \to 0)$. The agreement is good for $v \to v-1$ but not so good for $v \to v+1$, in which case our rates increase with increasing v more rapidly than does LTHO. This trend changes at v=13 which can be explained by the ease of dissociation from v=13 and the small number of rotational states for $v' = 14$. We also compare our $\Delta v = \pm 1$ transitions with $k(4 \to 5)$ and $k(4 \to 3)$. This is because $k(0 \to 1)$ is the most uncertain of the rates reported here.

Table I. Comparison of $k_{b \to n}(v, T \to v+1)$ with LTHO model.

v	$k(v \to v+1)/k(0 \to 1)$		$k(v \to v-1)/k(1 \to 0)$	
	present	LTHO	present	LTHO
0	1.00	1.00	--	--
4	13.	5.00	4.9	4.00
6	15.	7.00	7.2	6.00
10	27.	11.00	12.	10.00
13	10.	14.00	13.	13.00

v	$k(v \to v+1)/k(4 \to 5)$		$k(v \to v-1)/k(4 \to 3)$	
	present	LTHO	present	LTHO
0	0.08	0.20	--	--
4	1.00	1.00	1.00	1.00
6	1.19	1.40	1.48	1.50
10	2.09	2.20	2.34	2.50
13	0.77	2.80	2.59	3.25

One of the most important aspects of our results is the ease with which multiquantum transitions occur. Collisions with v = 6 lead to almost all values of v' including dissociation. We present transition probabilities defined as $k_{b \to n}(v, T \to v')$ divided by the collision frequency $Z = \langle V_R \rangle \pi D^2$ where D is the zero-energy turning point of the spherically averaged interaction potential. Table II shows in tabular form what is also evident in Figure 1, that $\Delta v = 7$ is observed with a probability of 0.2% as large as $\Delta v = 1$. For comparison we give results calculated from equations used by McElwain and Pritchard and by Johnston and Birks. McElwain and Pritchard (4) obtained an analytic fit to transition probabilities calculated using the Jackson Mott distorted-wave treatment of collinear collisions. For the results in Table II we substituted accurate energy levels into their equation. Johnston and Birks (5) used an equation based on the vibrational matrix elements alone but renormalized to an experimental relaxation time (6) as extrapolated by the method of Landau and Teller. According to either of these models multiquantum transitions greater than $\Delta v = \pm 2$ would be less important than our trajectories indicate for $\Delta v = 7$. For $\Delta v = \pm 6$ our results differ from these models by 5-15 orders of magnitude. Previous models (4,5,7) of dissociation of H_2 in shock tubes assumed multiquantum transitions are unimpor-

tant. Our results indicate that they should be considered. McElwain and Pritchard and Johnston and Birks used special assumptions for the probability of dissociation. Our dissociation probabilities are smaller than those of Johnston and Birks but much larger than those of McElwain and Pritchard.

Table II. $k_{b\to n}(v = 6, T = 4500°K \to v')/Z$

v	present	McElwain-Pritchard	Johnston-Birks
0	4.29(-3)	5.92(-18)	2.13(-10)
1	9.02(-3)	8.67(-15)	1.07(-8)
2	1.65(-2)	2.45(-11)	2.90(-7)
3	2.67(-2)	1.12(-7)	5.99(-6)
4	5.08(-2)	7.03(-4)	1.17(-4)
5	9.43(-2)	2.71(-2)	3.27(-3)
6	--	--	--
7	5.56(-2)	1.44(-2)	1.57(-3)
8	1.52(-2)	4.68(-4)	3.99(-5)
9	6.89(-3)	1.80(-6)	2.20(-6)
10	4.16(-3)	6.23(-9)	1.86(-7)
11	1.93(-3)	6.03(-11)	2.16(-8)
12	4.28(-4)	1.60(-12)	3.29(-9)
13	9.51(-5)	1.19(-13)	6.45(-10)
14	0.	2.64(-14)	1.63(-10)
diss.	1.82(-3)	1.88(-14)	4.83(-3)

As a test for how well the trajectory results satisfy detailed balance, we examined the ratio of our calculated forward and reverse rates for the six cases for which we had data. We found agreement with the ratios predicted by the prior expectations to within the statistical errors.

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