

## Quantum Theory of D + H<sub>2</sub> Rearrangement Collision: Effects of Vibrational Excitation

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A quantum mechanical approach is used to calculate the cross sections and rate constants of  $D + H_2(v_\alpha = 1, 0) \rightarrow DH(v_\beta = 0, 1) + H$ . With  $v_\alpha = 0$ , present results are in agreement with classical calculation. With  $v_\alpha = 1$ , cross sections for the vibrational adiabatic transition ( $v_\alpha = 1$  to  $v_\beta = 1$ ) is an order of magnitude larger than that for the vibrational non-adiabatic transition ( $v_\alpha = 1$  to  $v_\beta = 0$ ). This result is in agreement with recent experiments but in disagreement with classical-trajectory calculations.

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The rearrangement scattering of hydrogen atoms by hydrogen molecules is the simplest kind of gas-phase exchange reaction. Many theoretical and experimental investigations of this system have been carried out in recent years.

Theory has advanced from earlier one-dimensional models to three-dimensional calculations. Although there are some such quantum studies,<sup>1-6</sup> most theoretical calculations are based on classical mechanics.

It is generally accepted that classical-trajectory calculations will give correct results except at very low energies where quantum-mechanical tunneling may be important. This assumption is based on comparisons between quantal and classical cross sections with the initial molecule in the vibrational ground state.

Recently infrared lasers are used to selectively prepare and detect vibrationally excited molecules. Thus the important question of vibrational enhancement can now be directly studied with experiments. The rate constants of  $H + H_2(v_\alpha = 1) \rightarrow H_2(v_\beta = 0, 1) + H$  were measured by Gordon *et al.*<sup>7</sup> and the rate constants of  $D + H_2(v_\alpha = 1) \rightarrow DH + H$  were measured by Kneba, Wellhausen, and Wolfrum.<sup>8</sup> Both groups came to the same conclusion that the vibrational adiabatic channel ( $v_\alpha = 1$  to  $v_\beta = 1$ ) is strongly preferred to the nonadiabatic channel ( $v_\alpha = 1$  to  $v_\beta = 0$ ). This is in sharp disagreement with the prediction of classical mechanics. All classical-trajectory calculations give about equal probability of transition for both channels.

In this Letter, we report the results of a quantum calculation for the rearrangement collision of  $D + H_2(v_\alpha = 1, 0) \rightarrow DH(v_\beta = 0, 1) + H$ . Our results with  $v_\alpha = 0$  are in agreement with classical results. Our results with  $v_\alpha = 1$  are quite different. We found that the cross section for the vibrational adiabatic channel is about one order of mag-

nitude larger than that of the nonadiabatic channel, in agreement with experiment. This suggests there may be large unexpected quantum effects in rearrangement scattering with excited molecules.

From the formal theory of scattering,<sup>9</sup> one obtains the cross section for the rearrangement from the entrance channel ( $\alpha$ ) to the exit channel ( $\beta$ ),

$$\sigma_{\beta\alpha}(\hat{k}_\beta) = \frac{\mu_\alpha \mu_\beta}{(2\pi\hbar^2)^2} \frac{k_\beta}{k_\alpha} |T_{\beta\alpha}|^2,$$

where  $k_\alpha, \mu_\alpha$  and  $k_\beta, \mu_\beta$  are relative momentum and reduced mass of the respective channels,  $\alpha$  and  $\beta$ .

The  $T$  matrix  $T_{\beta\alpha}$  can be transformed into<sup>1</sup>

$$T_{\beta\alpha} = \langle \chi_\beta^{(-)} | V_\beta' | \Psi_\alpha^{(+)} \rangle,$$

where  $\chi_\beta^{(-)}$  is the exit-channel wave function,  $V_\beta'$  is the difference between the total potential and the potential that generated  $\chi_\beta^{(-)}$ , and  $\Psi_\alpha^{(+)}$  is the entrance-channel eigenfunction of the total Hamiltonian.

If  $\Psi_\alpha^{(+)}$  is substituted in  $T_{\beta\alpha}$  with the elastic-scattered wave function  $\chi_\alpha^{(+)}$  in the entrance channel, the distorted-wave Born approximation (DWBA) is obtained. However, the ordinary DWBA does not allow the distortion of the target. In contrast to electron-atom collision, the mass of the target in the present case is comparable to the mass of the projectile. Therefore, the target molecule should be allowed to distort also.

In the present calculation, we have used an adiabatic model to approximate the total wave function.<sup>1,2,4</sup> This model assumes that the molecule adiabatically follows the incoming atom. Both the rotational and vibrational wave functions of the molecule are instantaneously adjusted to the potential which includes the effect caused by the presence of the incoming atom. This allows

the molecule to stretch somewhat and align itself toward the incoming atom. As a result, the molecular wave function is expressed as a linear combination of the eigenfunctions of the isolated molecule. This wave function asymptotically goes to the eigenfunction of the initial state of the incoming molecule. The energy released by this adjustment has the effect of lowering the potential seen by the incoming atom. In a sense, this model is equivalent to the perturbed-stationary-state approach in electron-atom scattering.<sup>10</sup>

If  $R$  is the distance between the molecule and the incoming atom, the adiabatic molecular wave function and the corresponding eigenvalue will both contain  $R$  as a parameter. Therefore the eigenvalue is a function of  $R$  and is essentially the potential governing the relative motion between the molecule and the atom. This relative motion is then simply an elastic scattering. The total wave function  $\Psi_{\alpha}^{(+)}$  is thus approximated by this scattered wave function times the adiabatic molecular wave function. The details of this method were published elsewhere.<sup>1,2,4</sup> When it was applied to the  $H + H_2$  system with the initial molecule in the vibrational ground state, the results were in good agreement with other quantal and classical calculations.<sup>11</sup> When it was applied to the  $D + H_2$  scattering,<sup>12-14</sup> the results were again in reasonable agreement with those of a molecular-beam experiment.<sup>15</sup> In the present work, we further developed this method and calculated the  $T$ -matrix elements for vibrationally excited molecules.

We present our results on the potential surface proposed by Truhlar and Horowitz,<sup>16</sup> who fitted the *ab initio* points of Liu<sup>17</sup> and of Siegbahn and Liu,<sup>18</sup> into an analytic form [Liu-Siegbahn-Truhlar-Horowitz (LSTH) surface]. In Fig. 1, we show the rearrangement cross sections for both the vibrationally adiabatic and nonadiabatic channels. The initial  $H_2$  molecule is in the  $v_{\alpha}=1$ ,  $j_{\alpha}=0$  state. Within each manifold of the final vibrational state ( $v_{\beta}$ ), cross sections to all possible rotational states ( $j_{\beta}$ ) are summed together. The energy  $E$  is the relative translational energy in the entrance channel. It is seen that the cross section for  $v_{\alpha}=1$  to  $v_{\beta}=1$  are much larger than that of  $v_{\alpha}=1$  to  $v_{\beta}=0$ .

Since experimental results involving  $v_{\alpha}=1$  are reported in terms of rate constants, we averaged our present quantum cross sections according to the Boltzmann distribution over the translational energy to obtain the corresponding rate constants. The comparison of these constants

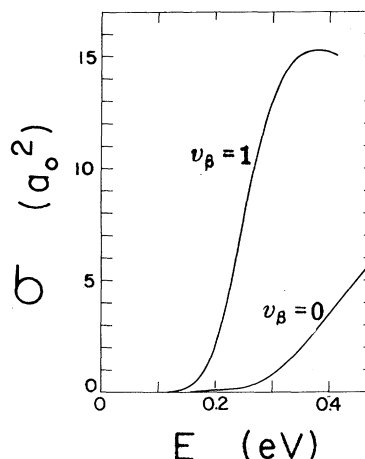


FIG. 1. Rearrangement scattering cross sections of the reaction  $D + H_2(v_{\alpha}=1) \rightarrow DH(v_{\beta}) + H$ , with use of the Liu-Siegbahn-Truhlar-Horowitz potential.

are shown in Table I. Other theoretical values are also presented in the table.

The experimental value for the rate constant of  $H + H_2$  reaction with  $v_{\alpha}=0$  ( $K_{0 \rightarrow \text{all}}$ ) at 300 °K is  $1.18 \times 10^8$  cm<sup>3</sup>/mole-sec according to Heidner and Kasper,<sup>19</sup> but is  $3.31 \times 10^8$  cm<sup>3</sup>/mole-sec according to Gordon *et al.*<sup>7</sup> There is a factor-of-3 difference. Within this uncertainty, experimental results, as seen in Table I, show very little isotopic effect. Rate constants for  $H + H_2$  and  $D + H_2$  are about the same order of magnitude.

Until recently, most theoretical results were obtained on the semiempirical Porter-Karplus (PK) potential surface.<sup>27</sup> On this surface the classical results agree reasonably well with quantum results for the  $v_{\alpha}=0$  case. These results are also in general agreement with experiment. However, on the supposedly more accurate *ab initio* LSTH potential, theoretical results become smaller by about a factor of 3. On the LSTH surface, our present quantum results for  $K_{0 \rightarrow \text{all}}$  and  $K_{1 \rightarrow 0}$  are also in good agreement with the classical results on the same surface, as seen in Table I, but our result for  $K_{1 \rightarrow \text{all}}$  is much larger than the corresponding classical result.

To compare the calculated rate constants with experimental ones involves both the potential surface and the dynamics. Since we wish to discuss mainly the dynamics, we compare the ratio  $K_{1 \rightarrow 1} / K_{1 \rightarrow 0}$  ( $K_{1 \rightarrow 1} \approx K_{1 \rightarrow \text{all}} - K_{1 \rightarrow 0}$ ), which seems to be fairly independent on the surface. Experimentally, the order of magnitude of this ratio is certain, although the exact number has to be estimated at present, since the necessary data are not from the same source. For  $H + H_2$ ,  $K_{1 \rightarrow \text{all}}$

TABLE I. Rate constants obtained from present adiabatic distorted-wave theory, experimental measurements and other theories in units of cubic centimeters per mole-second. The present theory is for  $D+H_2 \rightarrow DH+H$  rearrangement scattering and other theories are all for that of  $H+H_2 \rightarrow H_2+H$ . The potential surfaces used in the calculations are indicated in the table. The superscripts are the sources of data and  $a(n)$  should read as  $a \times 10^n$ .

Rate constants	Present theory LSTH	Experiment	Other theory		
			Classical LSTH	PK	Rotational sudden approximation PK
$K_{0 \rightarrow a11}$	0.562(8)	0.118(9) <sup>a</sup> H+H <sub>2</sub> 0.331(9) <sup>b</sup> H+H <sub>2</sub> 0.184(9) <sup>c</sup> D+H <sub>2</sub>	0.70(8) <sup>g</sup>	0.25(9) <sup>i</sup>	
$K_{1 \rightarrow 0}$	0.328(11)	0.18(12) <sup>a</sup> H+H <sub>2</sub>	0.33(11) <sup>h</sup>	0.80(11) <sup>h</sup>	0.97(11) <sup>l</sup>
$K_{1 \rightarrow a11}$	0.299(12)	0.311(13) <sup>b</sup> H+H <sub>2</sub> 0.72(13) <sup>d</sup> D+H <sub>2</sub>	0.76(11) <sup>h</sup>	0.50(12) <sup>j</sup> 0.24(12) <sup>h</sup>	0.34(12) <sup>l</sup>
$\frac{K_{1 \rightarrow 1}}{K_{1 \rightarrow 0}}$	8.11	[ $\approx 5.0 - 16$ ] <sup>e</sup> H+H <sub>2</sub> [ $\approx 10$ ] <sup>f</sup> D+H <sub>2</sub>	1.03 <sup>h</sup>	2.0 <sup>h</sup>	2.5 <sup>l</sup>
				1.0 <sup>k</sup>	

<sup>a</sup>Ref. 19.      <sup>e</sup>Refs. 7 and 19, see text.      <sup>i</sup>Ref. 23.  
<sup>b</sup>Ref. 7.      <sup>f</sup>Ref. 8, see text.      <sup>j</sup>Ref. 24.  
<sup>c</sup>Ref. 20.      <sup>g</sup>Ref. 21.      <sup>k</sup>Ref. 25.  
<sup>d</sup>Ref. 8.      <sup>h</sup>Ref. 22.      <sup>l</sup>Ref. 26.

from Gordon *et al.*, and  $K_{1 \rightarrow 0}$  from Heidner and Kasper will give  $K_{1 \rightarrow 1}/K_{1 \rightarrow 0} = 16$ . On the other hand, as mentioned earlier, the value of Gordon *et al.* is larger than that of Heidner and Kasper by a factor of 3 in  $K_{0 \rightarrow a11}$ , which both groups measured. Scaling the value of  $K_{1 \rightarrow a11}$  of Gordon *et al.* down by a factor 3 (or  $K_{1 \rightarrow 0}$  of Heidner and Kasper up by a factor of 3), we obtain the lower limit of  $K_{1 \rightarrow 1}/K_{1 \rightarrow 0} \approx 5$ . For  $D+H_2$ , Kneba *et al.* only reported  $K_{1 \rightarrow a11}$ , but their statement "the exchange reaction must take place predominantly by conservation of the vibrational excitation"<sup>8</sup> implies that  $K_{1 \rightarrow 1}$  is also an order of magnitude larger than  $K_{1 \rightarrow 0}$ . These are the values which we present in the table. The classical-trajectory calculations predicted that the value of this ratio should be 1 on the LSTH potential<sup>22</sup> and 1.0-2.0 on the PK potential<sup>22,25</sup>.

Our quantum result for  $K_{1 \rightarrow 1}/K_{1 \rightarrow 0}$  is 8.11 which is certainly in general agreement with experiment. Our result is to be compared with the classical result of 1.03 on the same potential surface. Since our value of  $K_{1 \rightarrow 0}$  is practically the same as the classical one, the large difference comes entirely from the  $v_\alpha = 1$  to  $v_\beta = 1$  transition.

The quantum mechanical results from the sudden approximation of Bowman and Lee<sup>26</sup> indicated that the value of this ratio should be 2.5, which is between the classical and our quantum result.

That  $K_{1 \rightarrow 1}$  should be larger than  $K_{1 \rightarrow 0}$  can be partly understood from the Franck-Condon factor.<sup>28</sup> With both the initial and product molecules in the vibrationally excited state, the wave functions are stretched to overlap in a larger region, the overlap integral becomes larger, and the probability of transition is increased.

In addition, we carried out an identical calculation on the Porter-Karplus potential surface.<sup>27</sup> The absolute values of the rate constants are about four times larger, but the ratio of  $K_{1 \rightarrow 1}/K_{1 \rightarrow 0}$  is about the same as obtained on the LSTH potential surface.

It is interesting to note that our present quantum results agree with classical ones for both  $K_{0 \rightarrow a11}$  and  $K_{1 \rightarrow 0}$ . This again confirms that for  $v_{\alpha,\beta} = 0$ , the classical theory is adequate. However, our present results indicate that the classical theory and quantum-mechanical sudden approximation give too small a value for  $K_{1 \rightarrow 1}$  in relation to  $K_{1 \rightarrow 0}$ . Our results, in agreement with experiment, show that  $K_{1 \rightarrow 1}$  is about one order of magnitude larger than  $K_{1 \rightarrow 0}$ . Thus, the dynamic effect of the vibrational enhancements is mainly exhibited in  $K_{1 \rightarrow 1}$ . This is not only important in those enhancements but also may have far-reaching consequences in the practical question of population inversion.

In conclusion, we note that (1) the quantum theory lends further support to the vibrational en-

hancement in that with one vibrational quanta, the reactive cross section increases by 3 to 4 orders of magnitude; (2) the quantum cross section is much larger than the classical one when the target molecule is in a vibrationally excited state, although in the vibrational ground state, the quantum effect is small; (3) the quantum theory predicts that the vibrational adiabatic reaction channel ( $\nu_\alpha = 1$  to  $\nu_\beta = 1$ ) is strongly preferred to the nonadiabatic channel, and we believe this is a general feature of a wide class of reactions; (4) only by taking quantum effect into proper consideration in vibrational enhancement and population inversion can one bring theory and experiment into agreement.

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