New Reduced Dimensionality Rate Constants for D + H₂(v=0,1) and H + D₂(v=0,1) and a Test of CEQB/G Theory

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A new expression for the reduced dimensionality (CEQB) cumulative reaction probability is given after taking careful account of total angular momentum constraints. New CEQB rate constants are calculated from 200 to 2000 K for the reactions D + H₂ and H + D₂ by using the ab initio LSTH potential, and for the reactions with $H_2(v=1)$ and $D_2(v=1)$ from 200 to 600 K. A comparison with rate constants calculated by using the more approximate CEQB/G theory is made. Very good agreement is found between the CEQB and CEQB/G thermal rate constants. However, for the vibrationally excited reactions, some differences are found, especially at and below room temperature due to subtle vibrationally nonadiabatic effects in the tunneling region. These are analyzed by using a simple vibrationally adiabatic model.

I. Introduction

There are several realistic methods currently in use to calculate thermal rate constants for A + BC reactions. These have recently been reviewed by Schatz.[1] Among them is one which we developed based on solving the Schroedinger equation in the reduced dimensionality space of the distance from A to the center of mass of BC, and the BC internuclear distance, and treating the internal angular (bending) motion adiabatically. We have termed this general approach the reduced dimensionality theory of reactions.[2,3] Within this theory is a hierarchy of approximations, and one, termed CEQB/G, has been applied most often and most recently to the $O(^3P)$ + H₂, D₂, and HD reactions.[4-6]

In the CEQB/G theory the cumulative reaction probability is calculated for the ground bend state. Then the probability for a given excited bend state at total energy E is obtained from the ground bend probability evaluated at the energy E minus $E^*_{n_b}$, the nth bending energy evaluated at the transition state, and referenced to the ground bend energy.

The method in which the reaction probability is explictly calculated for each bend state is termed CEQB, and it was recently applied to the Cl + HCl reaction.[7] There has not, however, been a comparison of the CEQB/G and CEQB methods. That is the main subject of this paper. Specifically we will compare CEQB/G and CEQB thermal rate constants between 200 and 2000 K for the D + H₂ and H + D₂ reactions, and rate constants for the diatomics initially in the first excited vibrational states between 200 and 600 K.

In the next section a brief review of the CEQB and CEQB/G methods will be given, followed in section III by a description of the calculational details. Results and discussion are given in section IV.

II. Theory

The rate constant for an A + BC atom-diatom reaction can be expressed as the thermal trace of the cumulative reaction probability, $P(E)$, as follows[3]

$$k(T) = \frac{1}{hZ(T)} \int_0^\infty dE \; P(E) \exp(-E/k_BT) \qquad (1)$$

where E is the total energy, h is Planck's constant, k_B is the Boltzmann constant, $Z(T)$ is the total atom-diatom electronic translational-rotational-vibrational partition function. $P(E)$ is given by

$$P(E) = \sum_{J=0}^\infty (2J + 1)P^J(E) \qquad (2)$$

where the distinguishable particle partial wave cumulative probability $P^J(E)$ is given by

$$P^J(E) = \sum_{vj\Omega} \sum_{v'j'\Omega'} P^J_{vj\Omega \to v'j'\Omega'}(E) \qquad (3)$$

and where $P^J_{vj\Omega \to v'j'\Omega'}(E)$ is the detailed state-to-state reaction probability between the initial and final vibrational/rotational states (vj,Ω) and $(v'j',\Omega')$, respectively. Ω is the projection of J, the total angular momentum quantum number, on a body-fixed z axis, defined to be the position vector of A to the center of mass of BC; its range is −min (j,J) to min (j,J).[8]

For vibrationally resolved initial states the corresponding rate constant $k_v(T)$ is given by

$$k_v(T) = \frac{e^{E_v/k_BT}}{hZ_{trans}(T) \; Z_{rot}(T)} \int_0^\infty dE \; P_v(E)e^{-E/k_BT} \qquad (4)$$

where $P_v(E)$ is cumulative reaction probability for the vth vibrational state (given by (2) and (3) without the summation over v) and E_v the corresponding vibrational energy. Clearly, a thermal trace of (4) over vibrational states yields (1).

Reduced Dimensionality Theory and J-Shifting. In the reduced dimensionality theory[2,3] the centrifugal sudden (CS) approximation[1] is made; i.e., Ω is assumed to be a conserved quantum number, and additionally the bending quantum number n_b is assumed to be an adiabatically conserved quantum number. In this theory the reduced dimensionality (rd) approximation to $P^J(E)$, denoted $P^J_{rd}(E)$, is given by

$$P^J_{rd}(E) = \sum_{n_b} \sum_\Omega P^J(E;\Omega,n_b) \qquad (5)$$

where $P^J(E;\Omega,n_b)$ is the reduced dimensionality reaction probability, summed over initial and final vibrational states, for a given adiabatic bend state, specified, in general, by the two quantum numbers Ω and n_b. In the reduced dimensionality approximation Ω is also the vibrational angular momentum quantum number (which is conventionally denoted as l or K), and in the harmonic approximation the adiabatic bend energy does not depend on Ω, and so we drop that quantum number in labeling the reduced dimensionality reaction probability.

The J-dependence of $P^J(E;n_b)$ is approximated by an energy shift[2,3,7] of the partial wave cumulative probability for J = 0. This approximation has also been used recently by Nakamura and co-workers,[9,10] who point out the similarity of it, in spirit, to the

(1) Schatz, G. C. *Annu. Rev. Phys. Chem.* **1988**, *39*, 317.
(2) Bowman, J. M. *Adv. Chem. Phys.* **1985**, *61*, 115.
(3) Bowman, J. M.; Wagner, A. F. In *The Theory of Chemical Reaction Dynamics*; Clary, D. C., Ed.; Reidel: Boston, 1986; pp 47-76.
(4) Bowman, J. M.; Wagner, A. F. *J. Chem. Phys.* **1987**, *86*, 1967.
(5) Wagner, A. F.; Bowman, J. M. *J. Chem. Phys.* **1987**, *86*, 1976.
(6) Bowman, J. M. *Chem. Phys. Lett.* **1987**, *141*, 545.
(7) Sun, Q.; Bowman, J. M.; Schatz, G. C.; Sharp, J.; Connor, J. N. L. Reduced-dimensionality quantum calculations of the thermal rate constants for the Cl + HCl reaction: Comparison with CSDW, CCH, and experimental results *J. Chem. Phys.*, to be submitted for publication.

(8) See, for example: Schatz, G. C.; Kuppermann, A. *J. Chem. Phys.* **1976**, *65*, 4668.
(9) Ohsaki, A.; Nakamura, H. *Chem. Phys. Lett.* **1987**, *142*, 37.
(10) Ohsaki, A.; Nakamura, H.; Park, S. C. *Comput. Phys. Commun.* **1989**, *52*, 291.

modified wave number approximation.[11] The $J = 0$ probability is the sum over initial and final vibrational state-to-state probabilities, $P^{J=0}_{v \to v'}(E;n_b)$. These are termed CEQB probabilities because they are obtained from a two-mathematical dimensional Schroedinger equation, which resembles the one for the collinear reaction but with an effective potential given by the electronic potential for the collinear configuration plus the adiabatic bend energy. The approximation to obtain the J-dependence of $P^J(E;n_b)$ is termed J-shifting.[7] In this approximation

$$P^J_{rd}(E) = P^J_m(E) - \Delta P^J(E) \tag{6}$$

where

$$P^J_m(E) = \sum_{n_b=0}^{\infty} (\alpha + 1) P^{J=0}(E - E^*_J; n_b) \tag{7}$$

$$\Delta P^J(E) = \sum_{n_b=\Omega_{max}+1, \Omega_{max}+3, \dots}^{\infty} P^{J=0}(E - E^*_J; n_b) \tag{8}$$

where

$$\alpha = \min (n_b, \Omega_{max}), \quad \Omega_{max} = \min (j_{max}, J)$$

where j_{max} is the lesser of the maximum open rotational quantum number of the reactant and product at the total energy E. Finally

$$P^{J=0}(E;n_b) = P^{CEQB}(E;n_b) \equiv \sum_v \sum_{v'} P^{CEQB}_{v \to v'}(E;n_b) \tag{9}$$

where $P^{CEQB}_{v \to v'}(E;n_b)$ is the CEQB vibrational state-to-state reaction probability for the state with the n_b quanta of vibrational excitation, $P^{CEQB}(E;n_b)$ is the CEQB cumulative reaction probability, and $E^*_J = B^J J(J+1)$ is the (linear) triatomic rotational energy at the transition state. Thus, the CEQB approximation for $P(E)$ is obtained from eq 2 and (5)–(9). The corresponding CEQB approximation for $P_v(E)$ is obtained from these equations without the summation over v in eq 9.

The derivation of eq 6 is quite short and proceeds as follows (with more details given in ref 7). First, recall that in the harmonic approximation Ω varies from $-n_b$ to n_b in steps of two, and also $|\Omega| \leq \min (J, j)$. Let j_{max} be the lesser of the maximum of j and j' at the total energy E. Then, as a result of the CS approximation, Ω cannot be larger than j_{max}. Thus, letting Ω_{max} be min (J, j_{max}), the inequalities for Ω can be written as $|\Omega| \leq \Omega_{max}$, and also $|\Omega| \leq n_b$, in steps of two. For example, for $J = 0$, $\Omega = 0$, and only even bend states contribute to the $J = 0$ cumulative probability, i.e.,

$$P^{J=0}_{rd}(E) = \sum_{n_b=0,2,\dots}^{\infty} P^{J=0}(E;n_b) \tag{10}$$

Now consider $J = 1$ in which case $\Omega = 0$ and ± 1. Only even bend states contribute to the $\Omega = 0$ component of the cumulative probability, and only odd bend states contribute to the $\Omega = \pm 1$ components. Thus,

$$P^{J=1}_{rd}(E) = \sum_{n_b=0,2,\dots}^{\infty} P^{J=0}(E - E^*_{J=1}; n_b) + \\ 2 \sum_{n_b=1,3,\dots}^{\infty} P^{J=0}(E - E^*_{J=1}; n_b) \tag{11}$$

This can be rearranged to give

$$P^{J=1}_{rd}(E) = \sum_{n_b=0}^{\infty} P^{J=0}(E - E^*_{J=1}; n_b) + \sum_{n_b=1}^{\infty} P^{J=0}(E - E^*_{J=1}; n_b) - \\ \sum_{n_b=2,4,\dots}^{\infty} P^{J=0}(E - E^*_{J=1}; n_b) \tag{12}$$

Similar expressions for $J > 1$ hold, and the general expression for the partial wave cumulative probability is

$$P^J_{rd}(E) = \sum_{n_b=0}^{\infty} P^{J=0}(E - E^*_J; n_b) + \sum_{n_b=1}^{\infty} P^{J=0}(E - E^*_J; n_b) \dots + \\ \sum_{n_b=\Omega_{max}}^{\infty} P^{J=0}(E - E^*_J; n_b) - \sum_{n_b=\Omega_{max}+1, \Omega_{max}+3,\dots}^{\infty} P^{J=0}(E - E^*_J; n_b) \tag{13}$$

(11) For a review, see: Takayanagi, T. *Adv. Atom. Mol. Phys.* **1965**, *1*, 149.

The last summation in (13) is the term $\Delta P^J(E)$ given by eq 8. The sum of the other terms in (13) is P^J_m. To see that, note that each of those terms can be split into two sums running from the indicated lower limit to Ω_{max}, and then from $\Omega_{max} + 1$ to ∞. Thus,

$$P^J_m(E) = \sum_{n_b=0}^{\Omega_{max}} P^{J=0}(E - E^*_J; n_b) + \sum_{n_b=1}^{\Omega_{max}} P^{J=0}(E - E^*_J; n_b) + \\ \dots P^{J=0}(E - E^*_J; n_b = \Omega_{max}) + \sum_{n_b=\Omega_{max}+1}^{\infty} P^{J=0}(E - E^*_J; n_b) + \\ \sum_{n_b=\Omega_{max}+1}^{\infty} P^{J=0}(E - E^*_J; n_b) + \dots \sum_{n_b=\Omega_{max}+1}^{\infty} P^{J=0}(E - E^*_J; n_b) \tag{14}$$

There are $\Omega_{max} + 1$ sums terminating at Ω_{max}, which can be summed together to give $\sum_{n_b=0}^{\Omega_{max}} (n_b + 1) P^{J=0}(E - E^*_J, n_b)$ and $\Omega_{max} + 1$ of the remaining sums which go to ∞. Thus,

$$P^J_m(E) = \sum_{n_b=0}^{\Omega_{max}} (n_b + 1) P^{J=0}(E - E^*_J; n_b) + \\ \sum_{n_b=\Omega_{max}+1}^{\infty} (\Omega_{max} + 1) P^{J=0}(E - E^*_J; n_b) \tag{15}$$

This expression can be rewritten as eq 7 with the use of the parameter α.

Equation 6 differs from the previous approximate expression for $P^J_{rd}(E)$,[2,3]

$$P^J_{rd}(E) \approx \sum_{n_b=0}^{\infty} (n_b + 1) P^{J=0}(E - E^*_J; n_b) \tag{16}$$

For (16) to be a good approximation it is necessary that $\Delta P^J(E)$ be negligible and that $P^J_m(E)$ be well approximated by (16) itself. This will be the case if only a few bending states contribute to $P^J_m(E)$, and if Ω_{max} is larger than that number of states. This situation applies when the bending energies are much larger than the rotational energies for comparable values of the corresponding quantum numbers. For many reactions, and certainly all of the ones we have considered, this condition is very well satisfied.

The CEQB/G approximation[2,3] consists of making approximation (16) and also approximating $P^{J=0}(E - E^*_J; n_b)$ for excited bends by

$$P^{J=0}(E - E^*_J; n_b) \approx P^{J=0}(E - E^*_J - E^*_{n_b}; n_b=0) \tag{17}$$

where $E^*_{n_b}$ is the transition-state bending energy measured relative to the ground bend energy. This approximation clearly simplifies the calculation of rate constants since the reaction probability for the ground bend state is the only one which is explicitly used in the rate constant calculation. It allows for a very compact form for the rate constant, namely

$$k^{CEQB/G}(T) = \\ \frac{Z^*_{rot} Z^{*'}_{bend}}{hZ(T)} \int_0^{\infty} dE \, P^{CEQB}(E; n_b=0) \exp(-E/k_B T) \tag{18}$$

where $P^{CEQB}(E; n_b=0)$ is the cumulative reaction probability for the ground bend

$$Z^*_{rot} = \sum_J (2J + 1) e^{-E^*_J/k_B T} \tag{19a}$$

and, in the harmonic approximation

$$Z^{*'}_{bend} = [1 - \exp(-\hbar \omega^*_b / k_B T)]^{-2} \tag{19b}$$

where ω^*_b is the transition-state bending frequency. The CEQB/G rate constant for the initial vibrational state v is given by

$$k^{CEQB/G}_v(T) = \\ \frac{e^{E_e/k_B T} Z^*_{rot} Z^{*'}_{bend}}{hZ_{trans}(T) Z_{rot}(T)} \int_0^{\infty} dE \, P^{CEQB}_v(E; n_b=0) \exp(-E/k_B T) \tag{20}$$

Although we have argued previously[2] that the CEQB/G approximation should be generally valid, we never explicitly tested it. We do so in the next section by comparing CEQB and CEQB/G rate constants for the D + H$_2$ and H + D$_2$ reactions,

TABLE I: CEQB and CEQB/G Thermal Rate Constants[a] **(cm³/(molecule s)) for D + H₂**

T, K	CEQB	CEQB/G
200	0.202(-17)	0.208(-17)
300	0.338(-15)	0.337(-15)
400	0.615(-14)	0.596(-14)
500	0.388(-13)	0.370(-13)
600	0.140(-12)	0.131(-12)
700	0.362(-12)	0.335(-12)
800	0.759(-12)	0.696(-12)
900	0.138(-11)	0.125(-11)
1000	0.226(-11)	0.204(-11)
1200	0.495(-11)	0.439(-11)
1400	0.900(-11)	0.786(-11)
1600	0.145(-10)	0.125(-10)
1800	0.212(-10)	0.181(-10)
2000	0.290(-10)	0.248(-10)

[a] Numbers in parentheses are powers of 10; 0.202(-17) = 0.202 × 10⁻¹⁷.

TABLE II: CEQB and CEQB/G Thermal Rate Constants[a] **(cm³/(molecule s)) for H + D₂**

T, K	CEQB	CEQB/G
200	0.222(-19)	0.228(-19)
300	0.173(-16)	0.172(-16)
400	0.657(-15)	0.641(-15)
500	0.646(-14)	0.622(-14)
600	0.314(-13)	0.300(-13)
700	0.101(-12)	0.958(-13)
800	0.251(-12)	0.235(-12)
900	0.520(-12)	0.485(-12)
1000	0.950(-12)	0.879(-12)
1200	0.244(-11)	0.223(-11)
1400	0.499(-11)	0.450(-11)
1600	0.871(-11)	0.781(-11)
1800	0.136(-10)	0.122(-10)
2000	0.196(-10)	0.177(-10)

[a] Numbers in parentheses are powers of 10; e.g., 0.222(-19) = 0.222 × 10⁻¹⁹.

and for the reactions with $H_2(v=1)$ and $D_2(v=1)$. Note we use the distinguishable atom approach to obtain the rate constants for these homonuclear systems. This approach has been shown by Schatz and Kuppermann[8] to be quite accurate for H + H₂ to temperatures as low as 200 K.

III. Calculations

The potential surface used in these calculations is the LSTH potential.[12] Bending energies were calculated as a function of the AB and BC bond distances for the collinear geometry in the harmonic approximation. Reaction probabilities for seven bending states were calculated for D + H₂ and H + D₂ by using the collinear hyperspherical code of Schatz and co-workers.[13] For D + H₂ calculations were done at 86 energies for each bending state, and 171 energies for H + D₂ for each bending state, in the total energy range 0.3–2.0 eV. Thermal rate constants were obtained by numerical integration of eq 1.

IV. Results and Discussion

A comparison of the CEQB and CEQB/G thermal rate constants for D + H₂ and H + D₂ is given in Tables I and II over the temperature range 200–2000 K. In general the agreement is very good; however, as T increases the CEQB/G rate constants deviate increasingly from the CEQB ones, falling below them by 10% at 1000 K and 15% at 2000 K for D + H₂, and 7% at 1000 K and 10% at 2000 K for H + D₂. Note that at 200 K the CEQB/G result is slightly larger than the CEQB one. The reason is that at this low temperature the term $\Delta P^J(E)$ is not completely

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(13) Badenhoop, J. K.; Koizumi, H.; Schatz, G. C. *J. Chem. Phys.* **1989**, *91*, 142.

TABLE III: CEQB and CEQB/G Rate Constants[a] **(cm³/(molecule s)) for D + H₂($v=1$)**

T, K	CEQB	CEQB/G
200	0.533(-13)	0.214(-13)
300	0.335(-12)	0.202(-12)
400	0.109(-11)	0.787(-12)
500	0.250(-11)	0.200(-11)
600	0.467(-11)	0.399(-11)

[a] Numbers in parentheses are powers of 10; e.g., 0.533(-13) = 0.533 × 10⁻¹³.

negligible, and a small error is introduced in using eq 16 instead of (6) in the CEQB/G theory.

Although these differences are small in these systems, they do grow with increasing temperature, and it is important to understand the cause. First, it is important to note that if only the ground bending state contributed to the rate constant the CEQB and CEQB/G results would be identical. Thus, the differences are due to contributions of the excited bending states, and the approximate way they are treated in the CEQB/G theory. These contributions are significant even at moderate temperatures. For example, at 600 K excited bend state account for 29% of the total rate constant for D + H₂, and 37% for H + D₂.

The energy shift approximation for excited bends used in the CEQB/G theory would be exact if the effective adiabatic potential for a given bend state was simply given by the one for the ground bend plus $E^*_{n_b}$. That cannot be rigorously true because the adiabatic bend energy goes to zero asymptotically. Thus, the effect of adding a constant energy to the ground bend surface is to produce a barrier which is thicker than the one on the effective excited bend surface. For energies below the barrier, this implies smaller tunneling probabilities for the shifted potential than for the actual one. This would result in somewhat smaller rate constant for the shifted potential relative to the actual one and thus is a possible explanation for why the CEQB/G rate constant is slightly less than the CEQB one.

Of course, other differences could also exist between the shifted ground bend potential and the true one. For example, the maximum on the actual effective potential could be larger than on the energy-shifted surface. That would have the effect of lowering the CEQB rate constant relative to the CEQB/G one. In the present case it appears that either the maximum in the true excited bend potentials is slightly less than the one in the shifted potentials, and/or the true barriers are thinner than the shifted ones. In any case it is clearly desirable to do a full CEQB calculation instead of the CEQB/G one.

Consider now the comparisons between CEQB and CEQB/G rate constants for D + H₂($v=1$) and H + D₂($v=1$). Before we present these, some details of the CEQB/G calculation are in order. As described in the previous section, the CEQB/G calculation is based on an energy shift of the bend energy relative to the ground bend state, evaluated at the transition state. For the vibrationally excited reactions, the transition state is not at the saddle point. In order to determine the energy shift to be used, we proceeded operationally as follows for both reactions. We examined the CEQB cumulative probabilities $P_1^{CEQB}(E;n_b)$ for the ground and first two excited bend states, plotted in Figure 1 for D + H₂($v=1$), and determined the lowest energy where the probabilities first equal 0.1. Defining that energy as the reaction threshold energy, we determined the bend energy shift as the difference in the threshold energies for $n_b = 1$ and 0, and also $n_b = 2$ and 1. That energy is 0.06 eV for D + H₂($v=1$) and 0.07 eV for H + D₂($v=1$).

The CEQB and CEQB/G rate constants are shown in Tables III and IV, where some differences are seen, especially at low temperatures. Not only are the differences larger than for the thermal rate constant, they are prominent at low T instead of at high T. The reason for this is that the energy shift approximation breaks down in the tunneling region, and actually works much better at higher energies, as seen already in Figure 1. To understand this, we have plotted in Figure 2 the vibrational state-to-state reaction probabilities $P_{1\rightarrow 0}^{CEQB}(E;n_b)$ and $P_{1\rightarrow 1}^{CEQB}(E;n_b)$ for
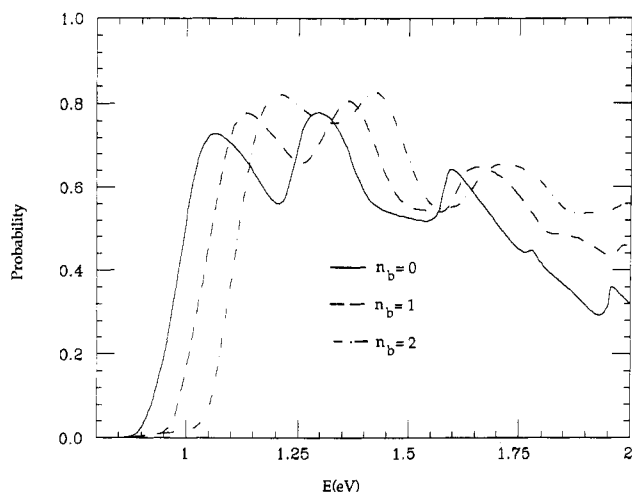
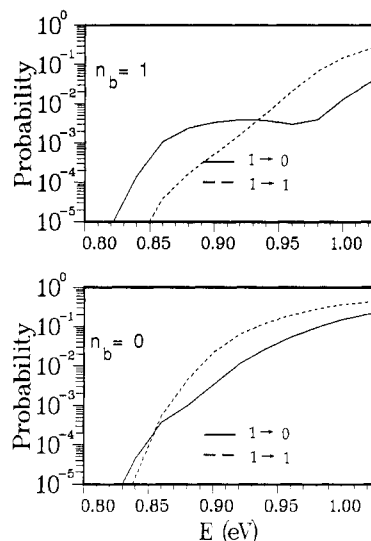**Figure 1.** $P_1^{CEQB}(E;n_b)$ versus the total energy for D + H₂(v=1).

Figure 2. Semilog plots of $P_{1\to0}^{CEQB}(E;n_b)$ and $P_{1\to1}^{CEQB}(E;n_b)$ versus the total energy for D + H₂(v=1) → DH(v=0,1) + H.

TABLE IV: CEQB and CEQB/G Rate Constants^a (cm³/(molecule s)) for H + D₂(v=1)

T, K	CEQB	CEQB/G
200	0.2265(-14)	0.1295(-14)
300	0.1421(-13)	0.7917(-14)
400	0.5239(-13)	0.3439(-13)
500	0.1528(-12)	0.1179(-12)
600	0.3707(-12)	0.3163(-12)

^{a} Numbers in parentheses are powers of 10; e.g., 0.2265(-14) = 0.2265 × 10⁻¹⁴.

the ground and first excited bend states. As seen, the vibrationally nonadiabatic probability $P_{1\to0}^{CEQB}(E;n_b)$ is greater than the vibrationally adiabatic one in the deep tunneling region. This behavior had been seen before in the H + H₂(v=1) → H₂(v') + H in both reduced dimensionality CEQB[14] and accurate quantum[15] calculations. For D + H₂(v=1), there is evidence for this behavior in the recent accurate quantum calculations of Zhang and Miller.[16] A significant result is that while $P_{1\to1}^{CEQB}(E;n_b=1)$ does shift to higher energies relative to the ground bend one, the vibrationally adiabatic probability shifts to slightly *lower* energies in the deep tunneling region. This curious effect is enough to cause the
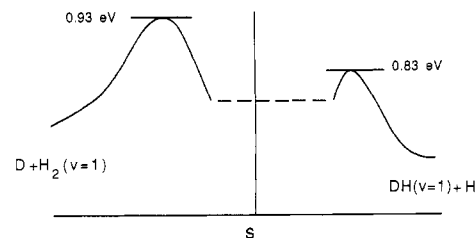

Figure 3. Schematic plot showing vibrationally adiabatic barriers for D + H₂(v=1) → DH(v=1) + H.

cumulative reaction probability $P_1^{CEQB}(E;n_b=1)$ to exceed $P_1^{CEQB}(E;n_b=0)$ in the deep tunneling region, and hence $P_1^{CEQB}(E;n_b=1)$ contributes significantly to the rate constant $k_1^{CEQB}(T)$ at low temperatures.

Some clues to understanding this curious effect are provided by the following "poor man's" vibrationally adiabatic analysis, which is suited for vibrationally excited states.[17] Vibrational eigenvalues were calculated in mass-weighted Jacobi coordinates for the DH₂ effective potential surface for the ground bend as functions of the separation of D to the center of mass of H₂, and the separation of H to the center of mass of DH. The results of this calculation are sketched in Figure 3. Adiabatic barriers were found in both arrangement channels for the first excited vibrational state, with the total energies indicated. (These energies appear to be in very good agreement with those calculated by Garrett et al.[18,19] who used a different calculational method.) Thus, the vibrationally adiabatic reaction D + H₂(v=1) → DH(v'=1) + H must tunnel through two adiabatic barriers for E less than 0.83 eV, one in the entrance channel, and the other in the exit channel. For the first excited bend the two adiabatic barriers are even larger, 0.97 and 0.87 eV, respectively. As expected, $P_{1\to1}^{CEQB}(E;n_b=1)$ does exhibit a shift to higher energies relative to $P_{1\to1}^{CEQB}(E;n_b=0)$. However, the nonadiabatic reaction probability $P_{1\to0}^{CEQB}(E;n_b=1)$ does not shift to higher energies in going from the ground to the first excited bend, and in the deep tunneling region it is greater than $P_{1\to1}^{CEQB}(E;n_b=1)$. Evidently, the vibrationally adiabatic barriers are not particularly relevant to the vibrationally nonadiabatic reaction probability. It even appears that increasing the bend excitation enhances the vibrational nonadiabatic reaction in the deep tunneling region. This is a subtle, though significant, effect at low temperatures. Thus, the energy shift approximation does not work, even qualitatively, for the vibrationally nonadiabatic reaction in the tunneling region, and it is this breakdown which is responsible for the substantial difference between the CEQB and CEQB/G rate constants at low temperatures. The same observation apply qualitatively to the H + D₂(v=1) reaction.

The major point of the paper has been to compare CEQB/G and CEQB thermal rate constants for D + H₂ and H + D₂,and also for the vibrationally excited reactions. It was found that some differences exist between the two sets of rate constants, especially for the vibrational excited reactants. These findings are of relevance to other theories[20,21] which have been restricted to explicit consideration of the ground bending state. Comparisons of the present rate constants with other calculations and experiment (including new ones up to 2000 K[22]) will be done in a separate paper.

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