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# FEATURE ARTICLE

## Reduced Dimensionality Theory of Quantum Reactive Scattering

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We review reduced dimensionality theories of quantum reactive scattering for systems with activation barriers in which a subset of the full number of degrees of freedom are coupled together. The emphasis in this article is on a particular theory in which the internal bending/angular motion of a reaction system is treated adiabatically. Additional approximations in the spirit of transition-state theory are reviewed and shown to be quite accurate and useful. Example systems include the $O(^3P)$ + $H_2$ reaction and the paradigm H + $H_2$ reaction, for which new comparisons are made with recent accurate three-dimensional calculations. Not only do these atom–diatom examples illustrate the quantitative accuracy of the reduced dimensionality/adiabatic bend theory, but also they clearly demonstrate the existence of quantized transition states. These are quantum states of the three-atom transition states that are responsible for the steplike energy dependence of the cumulative reaction probability. A brief review of recent applications of the reduced dimensionality theory to photodetachment spectroscopy of the transition state is also given. Finally, we review the recent extension of the reduced dimensionality theory to diatom–diatom reactions and illustrate the method to the $H_2$ + CN reaction.

## Introduction

There has been a recent surge in progress in exact quantum reactive scattering calculations for atom–diatom systems containing hydrogen atoms or molecules.[1-11] Much of the effort has been directed at the paradigm H + $H_2$ reaction (and its isotopomer variations). This reaction continues to be of fundamental importance because it is one of a handful of systems that can be tackled theoretically in essentially an exact fashion, from the potential energy surface to the quantum dynamics of the nuclear motion. Exact results for this reaction (and others) play the role of benchmarks against which simpler and more general approximate methods can be tested. These exact calculations tax the capabilities of current supercomputers, and for non-hydrogenic systems, they will likely tax the capabilities of future supercomputers. For such systems and certainly for more complex ones such as diatom–diatom systems or electronically nonadiabatic atom–diatom systems, approximation methods are needed. Approximation methods may also offer the advantage of providing insight more readily into the dynamics than exact ones.

Over the past decade or so several approximate theories of reactive scattering have been developed in which more than one, but less than all, the degrees of freedom are fully coupled. We refer to these theories as *reduced dimensionality* theories to emphasize the reduction in treating all degrees of freedom exactly. The approximate treatment of some degree(s) of freedom is the distinguishing feature of such theories. Two theories that have

been used extensively treat the internal angular motion of a the triatomic system in atom–diatom reactions in the sudden[12,13,17] and adiabatic[14-17] approximations. These theories make diametrically opposite assumptions about the internal angular motion. The sudden theory assumes that motion is "frozen" throughout the collision, whereas the adiabatic theory assumes it changes but with preservation of the bending quantum number(s). The sudden approximation is valid when the interaction time is short compared to the (perturbed) angular motion of the diatomic molecule. The adiabatic approximation applies in the opposite situation, i.e., when the interaction time is comparable or short compared to the perturbed angular motion. In general the angular motion of most molecules is slow compared to the interaction times for hyperthermal or even thermal collisions. However, if there is a large amount of induced angular hindering of the diatom by the atom, then simple, sudden dynamics does not apply, except at high collision energies. For those reactions that are angularly highly constrained, the adiabatic approximation is the appropriate choice, even as we shall see at hyperthermal collision energies. This article will focus exclusively on the adiabatic-bend approximation, and henceforth the reduced dimensionality theory will refer to that approximation. In addition, this article is not intended to be a comprehensive or historical review of the reduced dimensionality theory; the reader interested in such a review should read ref 14.

In the next section we present the relevant physical ideas and equations of the reduced dimensionality theory. Additional approximations to this theory in the spirit of transition-state theory will be made. These approximations not only make the theory easier to apply; they are conceptually useful because they are a bridge from a fully dynamical theory to the much simpler transition-state theory.

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An important aspect of the reduced dimensionality theory is that it makes very specific predictions about the influence of the quantized energies of the transition state on the energy dependence of the total reactivity, the so-called *cumulative reaction probability* (CRP), of a reaction. These predictions are demonstrated for the $O(^3P) + H_2$ reaction and further analyzed for the $H + H_2$ reaction. Comparisons with exact quantum calculations for both systems are also made in that section. A brief review of recent applications of the adiabatic-bend theory to photodetachment spectroscopy studies of the transition state of heavy–light–heavy systems is also given in that section. Finally, a review of the recent extension of the reduced dimensionality theory to diatom–diatom reactions is given, followed by a review of the highlights of the first application of the method to the $H_2 + CN \rightarrow H + HCN$ reaction. A prognosis for the future is given in the final section.

## Theory for Atom–Diatom Reactions

**Introduction and Definitions.** In most applications of the reduced dimensionality theory, the central quantity of interest is the so-called *cumulative reaction probability* (CRP).[14,15] As we shall see, there are several CRPs of interest; however, all have the property that they involve summations of the detailed state-to-state reaction probabilities over at least a subset of the quantum states of the reactants and products (see below for examples). The *exact* CRP obtained from a complete summation over the reactant and product quantum states will be denoted $P(E)$, and it has a simple relationship to the familiar thermal rate coefficient:[14,15,18]

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

where $E$ is the total energy, $h$ is Planck's constant, $k_B$ is the Boltzmann constant, and $Z(T)$ is the total atom–diatom partition function (translational, rotational, and vibrational) at the temperature $T$. In general $P(E)$ is expressed in terms of a partial wave expansion over the total angular momentum of the system, which for concreteness we shall consider to be an atom–diatom system, i.e.

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

where $J$ is the total angular momentum quantum number. The partial wave CRP, $P^J(E)$ is defined as

$$P^J(E) \equiv \sum_{vj\Omega} \sum_{v'j'\Omega'} P^J_{vj\Omega \to v'j'\Omega'}(E) \quad J = 0, 1, \ldots \qquad (3)$$

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 $(v,j,\Omega)$ and $(v',j',\Omega')$, respectively. Upper limits of summation are not given; however, it should be understood that only energetically open channels are included in these and other sums. The quantum number $\Omega$ (or $\Omega'$) is the projection of $J$ on the body-fixed $z$ axis for the reactant (or product), and its range is $-\min(j_<, J)$ to $\min(j_<, J)$[19,20] where $j_<$ is the lesser of $j$ and $j'$.

Another partial wave CRP that is of interest is the initial vibrational state-selected one, defined by

$$P^J_v(E) \equiv \sum_{j\Omega} \sum_{v'j'\Omega'} P^J_{vj\Omega \to v'j'\Omega'}(E) \qquad (4)$$

Note that this CRP and the one given by eq 3 involve many terms in the summations over $j$, $\Omega$, $j'$, and $\Omega'$. This is due to the fact that there are typically many more rotational states open in the reactants and products than vibrational states. An order of magnitude value for the number of states is $10^2$–$10^3$, at thermal energies, depending on the molecular vibrational/rotational energies, reaction exo(endo)ergicity, etc. Of course that number increases substantially with $E$ and with $J$, so that if a rate constant

is desired at hyperthermal temperatures, the number of states can easily exceed $10^3$.

In an exact scattering calculation, all the energetically open rotational/vibrational states are coupled, and clearly it is the dense manifold of rotational states that is responsible for the huge computational effort in such a calculation. It is, therefore, also clear that an approximation that uncouples the rotational motion would greatly reduce the computational effort. The reduced dimensionality theory does exactly that. It does so by treating the rotational motion in a body-fixed frame as an adiabatically evolving hindered rotation/bending motion. This approximation has the effect of replacing the quantum numbers $j$, $\Omega$ and $j',\Omega'$ by triatomic molecule bending quantum numbers (see below). For reactions with "tight" transition states, the energies of the adiabatic bend states are substantially greater than the rotational energies of the reactant and product diatom. Thus, as we shall see below, the large sum over the rotational states is replaced by a much smaller sum over bending states in the approximate theory for the CRPs.

**Adiabatic-Bend Approximation.** In the reduced dimensionality (RD) theory of reactions with a linear transition state, the bending quantum numbers $n_b = 0, 1, 2, \ldots$ and $\Omega$ of the triatomic complex are assumed to be conserved. Note that $\Omega$ is the same quantum number defined above, but in addition it is the vibrational angular momentum quantum number for linear molecules and, more importantly for the present discussion, linear transition states. Also, note that the assumption that $\Omega$ alone is conserved is made in the *centrifugal sudden* theory of reactive scattering.[21]

The reduced dimensionality approximation to the partial wave CRP is given by

$$P^{J/RD}(E) = \sum_{n_b} \sum_{\Omega} P^J(E;\Omega,n_b) \qquad J = 0, 1, \ldots \qquad (5)$$

where $P^J(E;\Omega,n_b)$ is the RD reaction probability, summed over initial and final vibrational states for the adiabatic bending state specified, in general, by the two quantum numbers $\Omega$ and $n_b$. In terms of the initial and final vibrational state-to-state reaction probabilities, which are the quantities actually calculated (see below), we have

$$P^J(E;\Omega,n_b) = \sum_v \sum_{v'} P^J_{v \to v'}(E;\Omega,n_b) \qquad J = 0, 1, \ldots \qquad (6)$$

The initial vibrational state-selected CRP is given by

$$P^{J/RD}_v(E) = \sum_{n_b} \sum_{\Omega} P^J_v(E;\Omega,n_b) \qquad (7)$$

where

$$P^J_v(E;\Omega,n_b) = \sum_{v'} P^J_{v \to v'}(E;\Omega,n_b) \qquad (8)$$

An important property to note here is that $P^J_v(E;\Omega,n_b)$ cannot exceed unity. This follows from the unitarity of the scattering matrix in the reduced dimensionality theory for each bending state. Unitarity guarantees that for each initial vibrational state the sum of all the reactive *and* nonreactive transition probabilities must be unity. Thus, the sum of the reactive ones alone, i.e., $P^J_v(E;\Omega,n_b)$, cannot exceed unity.

In the harmonic description of the bending motion, which we adopt henceforth, $\Omega$ is restricted to the range $-n_b$ to $n_b$ in steps of 2[22] while also being restricted to lie between $-\min(j_<,J)$ and $\min(j_<,J)$. With these restrictions on $\Omega$, it can be shown that[23]

$$P^{J/RD}(E) = \sum_{n_b=|\Omega|,|\Omega|+2,\ldots}^\infty \sum_{\Omega=0,\pm1,\ldots}^{\pm\Omega_{max}} P^J(E;\Omega,n_b) \qquad (9)$$

$$J = 0, 1, \ldots \qquad \Omega_{max} = \min(J,j_<)$$

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(22) See, for example: Rapp, D. *Quantum Mechanics*; Holt, Rinehart and Winston: New York, 1971; p 235.
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[An analogous expression holds for $P_v^{J/RD}(E)$ with $P^J(E;\Omega,n_b)$ replaced by $P_v^J(E;\Omega,n_b)$.] To be explicit, note that for fixed $J$ the quantum number $\Omega$ has the values $\Omega = 0, \pm 1, ..., \pm\Omega_{max}$, and for fixed $\Omega$, the quantum number $n_b$ takes the values $n_b = |\Omega|, |\Omega| + 2, ...$. Another consequence of the harmonic approximation is that the bending energy is independent of $\Omega$. Thus, $P^J(E;\Omega,n_b)$ is independent of $\Omega$, and henceforth the $\Omega$ dependence will be dropped.

**Energy-Shift Approximations.** The complete adiabatic-bend theory requires the solution of a two-mathematical-dimensional Schrödinger equation for each bending state and each value of the total angular momentum.[14,15] Another approach we have taken is to introduce *energy-shift approximations* to relate the CRPs for nonzero $J$ and $n_b$ to those for $J$ and $n_b$ equal to zero, by simple energy shifts.[14,15] We have been guided by transition-state theory in choosing these energy shifts. Recall that the location of the transition state is the bottleneck region for the reaction. Therefore, evaluating the rotational and bending energy shifts there makes good physical sense. It also turns out that by additional, simple approximations to the CRPs, transition-state theory can be recovered from the reduced dimensionality theory.[15]

*J*-Shifting Approximation. A very useful approximation for the $J$ dependence of $P^J(E;n_b)$ and $P_v^J(E;n_b)$ is an energy-shift relative to the probability for $J = 0$, i.e.

$$P^J(E;n_b) \approx P^{J=0}(E - E_J^*;n_b) \qquad (10a)$$

$$P_v^J(E;n_b) \approx P_v^J(E - E_J^*;n_b) \qquad J = 0, 1, ... \qquad (10b)$$

where $E_J^* = B^*J(J + 1)$ is the (linear) triatomic rotational energy at the transition state. Note that $E_{J=0}^* = 0$. It can be shown after careful consideration of inequalities between $n_b$, $\Omega$, and $J$ that $P^{J/RD}(E)$ and $P_v^{J/RD}(E)$ are given by[23]

$$P^{J/RD}(E) \approx \sum_{n_b=0,1,...}^{\infty} (a + 1)P^{J=0}(E - E_J^*;n_b) -$$

$$\sum_{n_b=\Omega_{max}+1,\Omega_{max}+3,...}^{\infty} P^{J=0}(E - E_J^*;n_b) \qquad (11a)$$

$$P_v^{J/RD}(E) \approx \sum_{n_b=0,1,...}^{\infty} (a + 1)P_v^{J=0}(E - E_J^*;n_b) -$$

$$\sum_{n_b=\Omega_{max}+1,\Omega_{max}+3,...}^{\infty} P_v^{J=0}(E - E_J^*;n_b) \qquad J = 0, 1, ... \qquad (11b)$$

where

$$a = \min (n_b,\Omega_{max})$$

For a given $J$, the smallest value of $n_b$ in the second sum in eqs 11a and 11b is $\Omega_{max} + 1$ (recall that $\Omega_{max} = \min (j_<,J)$), whereas in the first sum $n_b$ starts at 0. In most cases the sum over $J$ for $P(E)$ maximizes at $J \neq 0$, and so the contribution from the second sum is expected to be small, because the reaction probability for highly excited bending states is usually very small compared to those for the ground and first few excited bending states. Similarly, $n_b$ is typically smaller than $\Omega_{max}$ for those values of $J$ where the summand is large, and so $a$ is generally equal to $n_b$. Thus, the above expressions are frequently well approximated by

$$P^{J/RD}(E) \approx \sum_{n_b=0,1,...}^{\infty} (n_b + 1)P^{J=0}(E - E_J^*;n_b) \qquad (12a)$$

$$P_v^{J/RD}(E) \approx \sum_{n_b=0,1,...}^{\infty} (n_b + 1)P_v^{J=0}(E - E_J^*;n_b) \qquad (12b)$$

which contains the familiar degeneracy factor $(n_b + 1)$ for the bending energy of a linear molecule.

Before proceeding, we note that the probabilities for $J = 0$ are simply the collinear exact quantum bend (CEQB) probabilities. This terminology is appropriate because they are obtained from a two-mathematical dimensional Schrödinger equation, which resembles that for the collinear reaction, but with an effective potential given by the bare potential plus the adiabatic bending
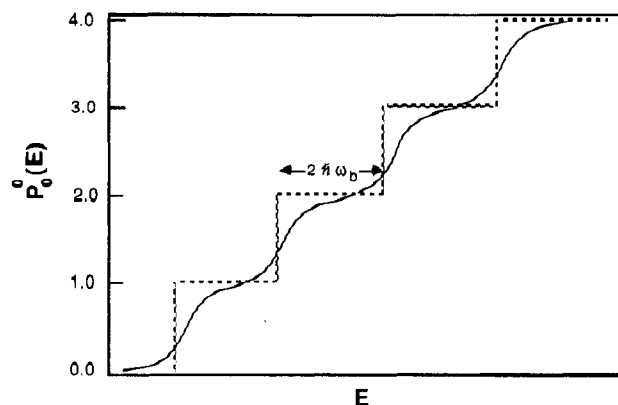


**Figure 1.** Schematic plot of an idealized classical (dashed curve) and quantum (solid curve) cumulative reaction probability for the ground bend and zero total angular momentum for a reaction with a linear transition state.

energy. We have used the label "CEQB" in the literature to emphasize this point.

Finally it is interesting to note that the $J$-shifting approximation is similar in spirit to the *modified wave number theory* of rotationally inelastic scattering.[24]

**Bend Energy-Shift Approximation.** Another energy-shift approximation that can be made to $P_v^{J=0}(E;n_b)$ is

$$P_v^{J=0}(E;n_b) \approx P_v^{J=0}(E - n\hbar\omega_b^*;n_b=0) \qquad (13)$$

where $n\hbar\omega_b^*$ is the harmonic bending energy of the transition state relative to the ground bend state. This approximation has been denoted CEQB/G in the literature, where G stands for the ground bend.

It is instructive at this point to consider an "idealized" CRP for $J = 0$ and for the initial vibrational state, $v = 0$. For $J = 0$, $\Omega = 0$, and thus only even bending states contribute to the CRP. Thus, from (11b)

$$P_0^{J/RD}(E) = \sum_{n_b=0,2,4,...}^{\infty} P_0^{CEQB}(E;n_b) \qquad (14)$$

As already noted $P_0^{CEQB}(E;n_b)$ cannot exceed unity for a given bend state $n_b$. Physically the behavior of $P_0^{CEQB}(E;n_6)$ is well-known; it is very small for energies below a reaction threshold energy and it may rise rapidly to a value near unity. In the most simple-minded, classical model $P_0^{CEQB}(E;n_b)$ is given by a step function:

$$P_0^{CEQB}(E;n_b) \approx \theta(E - E_{n_b}^{th})$$

which is zero for $E < E_{n_b}^{th}$ and unity for $E \geq E_{n_b}^{th}$ where $E_{n_b}^{th}$ is a reaction threshold energy for the $n_b$th bend state. Thus, in the simple, idealized, classical model $P_0^{J/RD}$ is the sum of step functions separated in energy by $2\hbar\omega_b^*$ in the harmonic approximation. The resulting staircase function is shown in Figure 1. Also shown in the figure is a more realistic, quantum representation of $P_0^{J/RD}(E)$, emphasizing the role of tunneling below the threshold energies $E_{n_b}^{th}$.

Next, we briefly review the expressions for the thermal rate coefficients obtained from the various versions of the reduced dimensionality theory.

**Summary of Reduced Dimensionality Rate Coefficients.** The expression for the RD partial wave CRP, eq 9, can be directly inserted into eq 2 and then into eq 1 to obtain the reduced dimensionality rate coefficient. Using the more approximate CEQB expression for the RD CRP, based on $J$-shifting and the approximate treatment of the limits on $\Omega$, leads to a simplified expression for the rate coefficient that brings out the connections to transition-state theory. In terms of that approximate CRP the corresponding expressions for the rate coefficient and the vibrational state-selected ones are[15]

(24) For a review, see: Takayangi, T. *Adv. At. Mol. Phys.* **1965**, *1*, 149.

$$k^{RD}(T) = \frac{Z_{rot}{}^*(T)}{hZ(T)} \int_0^\infty dE \sum_{n_b=0,1,...}^\infty (n_b + 1)P^{CEQB}(E;n_b)e^{-E/k_BT}$$

(15a)

$$k_v^{RD}(T) = \frac{e^{E_v/k_BT}Z_{rot}{}^*(T)}{hZ_{trans}(T) Z_{rot}(T)} \int_0^\infty dE \sum_{n_b=0,1,...}^\infty (n_b + 1)P_v^{CEQB}(E;n_b)e^{-E/k_BT}$$

(15b)

where $E_v$ is the vibrational energy of the diatom, and $Z_{rot}$ and $Z_{trans}$ are the partition functions for the diatom rotation, and the atom–diatom relative translational energy, respectively, and

$$Z_{rot}{}^*(T) = \sum_{J=0,1,...}^\infty (2J + 1) \exp(-E_J{}^*/k_BT)$$

If the bend energy-shift approximation is also used, then

$$k^{RD}(T) \approx \frac{Z_{rot}{}^*Z_{bend}{}^*}{hZ(T)} \int_0^\infty dE \, P^{CEQB}(E;n_b=0)e^{-E/k_BT}$$

(16a)

$$k_v^{RD}(T) \approx \frac{e^{E_v/k_BT}Z_{rot}{}^*Z_{bend}{}^*}{hZ(T)} \int_0^\infty dE \, P_v^{CEQB}(E;n_b=0)e^{-E/k_BT}$$

(16b)

where

$$Z_{bend}{}^* = (1 - \exp(-\hbar\omega_b{}^*/k_BT))^{-2}$$

Note the presence of the familiar partition functions for the various degrees of freedom of the transition state.

**Energy-Shifting Approximations Applied to Exact $J = 0$ Cumulative Reaction Probability.** The energy-shift approximations described above can also be applied to the *exact* partial wave CRP for $J = 0$ to obtain approximate CRPs for $J > 0$.[23] To do this, we invoke the centrifugal sudden (CS) approximation for $J > 0$, which is that $\Omega$ is a good quantum number. Thus in the CS approximation the partial wave CRP can be written as

$$P^{J/CS}(E) = \sum_{\Omega=-\Omega_{max}}^{\Omega_{max}} P_\Omega^J(E) \qquad J = 0, 1, ... \quad (17)$$

where

$$P_\Omega^J(E) = \sum_v \sum_j \sum_{v'} \sum_{j'} P_{vj\Omega \to v'j'\Omega}^J(E) \qquad J = 0, 1, ... \quad (18)$$

Now note that for $J = 0$ we have $\Omega = 0$, and so strictly speaking, the $J$-shifting approximation can be applied only to $P_{\Omega=0}^J(E)$, which is a single component of $P^{J/CS}(E)$. To treat components $P_\Omega^J(E)$ with $\Omega \neq 0$, the bending energy-shift approximation is also used. As already noted, in the harmonic bend approximation $\Omega$ ranges from $-min$ $(j_<,n_b)$ to min $(j_<,n_b)$ in steps of 2 for a given bend quantum number $n_b$. Thus, for example, the $\Omega = 0$ component of $P_\Omega^J(E)$ implicitly has contributions from all even bending states, and the $\Omega = 1$ component implicitly has contributions from all odd bending states. In the bending energy-shift approximation, $P_{\Omega=\pm1}^J(E)$ is obtained from $P_{\Omega=0}^J(E)$ by simply energy shifting by the first excited bend energy at the transition state (measured relative to the ground bend energy). In general we have

$$P_\Omega^J(E) \approx P_{\Omega=0}^J\left(E - E_{n_b=|\Omega|}^*\right) \qquad J = 0, 1, ... \quad (19)$$

where $E_{n_b}^*$ is the bending energy at the transition state measured relative to the ground bend (i.e. $E_{n_b=0}^* = 0$). $P_{\Omega=0}^J(E)$ in turn is related to $P_{\Omega=0}^{J=0}(E)$ by the rotational energy $J$ shift. Combining these two shifts, we have

$$P_{\Omega=0}^J(E) \approx P_{\Omega=0}^{J=0}(E - E_J{}^*) \qquad J = 0, 1, ... \quad (20a)$$

$$P_{\Omega=\pm1}^J(E) \approx P_{\Omega=0}^{J=0}(E - E_J{}^* - E_{n_b=1}^*) \qquad J = 1, 2, ... \quad (20b)$$

$$P_{\Omega=\pm2}^J(E) \approx P_{\Omega=0}^{J=0}(E - E_J{}^* - E_{n_b=2}^*) \qquad J = 2, 3, ... \quad (20c)$$

$$\vdots$$

$$P_{\Omega=\pm\Omega_{max}}^J(E) \approx P_{\Omega=0}^{J=0}(E - E_J{}^* - E_{n_b=J}^*) \qquad J = \Omega_{max}, \Omega_{max} + 1, ... \quad (20d)$$

Then, using eqs 20 in eq 17, we obtain the following approximate expressions for $P^{J/CS}(E)$ and $P(E)$:

$$P^{J/CS}(E) \approx P_{\Omega=0}^{J=0}(E - E_J{}^*) +$$
$$2(1 - \delta_{J0}) \sum_{n_b=1,2,...}^{\Omega_{max}} P_{\Omega=0}^{J=0}(E - E_J{}^* - E_{n_b}^*) \qquad J = 0, 1, ... \quad (21)$$

where $\delta_{J0}$ is the Kronecker delta.

**Rate Coefficients.** The rate coefficient based on the $J$-shifting and bend-energy shifting approximations applied to the exact cumulative reaction probability for $J = 0$ can be obtained by inserting (21) into (2) and then (2) into (1). Rather than give the resulting expression, which has already been given,[23] we give a simplified expression for $k(T)$ derived after making a number of very reasonable approximations. That expression is

$$k(T) \approx \frac{C^*(T) Z_{rot}{}^*(T)}{hZ(T)} \int_0^\infty dE \, P_{\Omega=0}^{J=0}(E) \exp(-E/k_BT) \quad (22)$$

where

$$C^*(T) \equiv \left(1 + \frac{2 \exp(-\hbar\omega_b{}^*/k_BT)}{1 - \exp(-\hbar\omega_b{}^*/k_BT)}\right) \equiv \coth\left(\frac{1}{2}\hbar\omega_b{}^*/k_BT\right)$$

(23)

This equation allows the full 3D $k(T)$ to be estimated from a calculation that computes only the $J = 0$ ($\Omega = 0$) CRP.

Equations 22 and 23 were conjectured previously by Colton and Schatz.[25] Their result was given in the context of CS H + H₂ reactive scattering using a converged set of $J = 0, 1, 2, ...,$ partial waves but with $\Omega$ restricted to $\Omega = 0$ and $\Omega = \pm1$. Note that when a set of $\{P_{\Omega=0}^J(E)\}$ has been calculated, it is necessary to invoke only the bending energy shift approximation (9); the $J$-shift approximation is not needed, and $k(T)$ can be calculated without the $J$-shift approximation.

Next, we consider two atom–diatom systems that have received a great deal of attention, both theoretically and experimentally. Our focus will be on validating the reduced dimensionality theory by comparing RD cumulative probabilities with very recent exact quantum ones and also interpreting the structure in the energy dependence of the CRP.

## Applications to Atom–Diatom Reactions

$O(^3P) + H_2$. The $O(^3P) + H_2$ reaction is one of the most extensively studied reactions. Theoretically it was the first system for which an ab initio potential surface was developed[26,27] specifically to be used in reduced dimensionality (adiabatic bend) calculations of cumulative reaction probabilities and rate coefficients.[28,29] The comparison of RD rate coefficients with experiment[30,31] (including one with H₂ vibrationally excited) as well as comparison of variational transition-state theory (with semiclassical tunneling corrections) with experiment[31,32] showed very good agreement, indicating that the potential surface is probably quite realistic.

Recently, accurate three-dimensional quantum calculations of CRPs for $J = 0$ were reported[33] for a semiempirical potential

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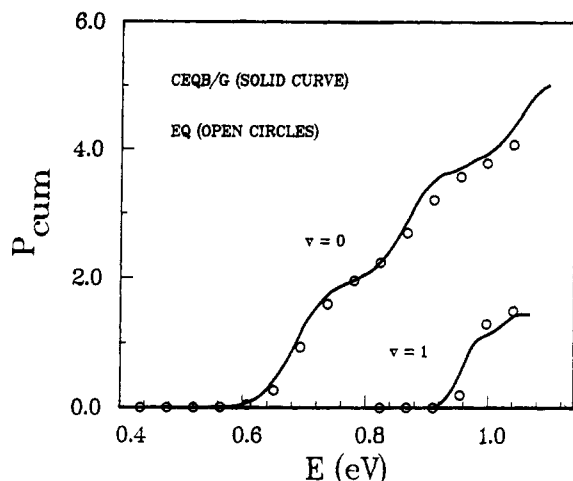(32) Garrett, B. C.; Truhlar, D. G. *Int. J. Quantum Chem.* **1986**, *29*, 1463; **1987**, *31*, 17.

**Figure 2.** Comparison of reduced dimensionality (CEQB/G) and accurate quantum[33] initial vibrational state-selected cumulative reaction probabilities for zero total angular momentum for the $O(^3P) + H_2(v)$ reaction. $E$ is the total energy, and the probabilities are a sum over the two identical final arrangement channels.
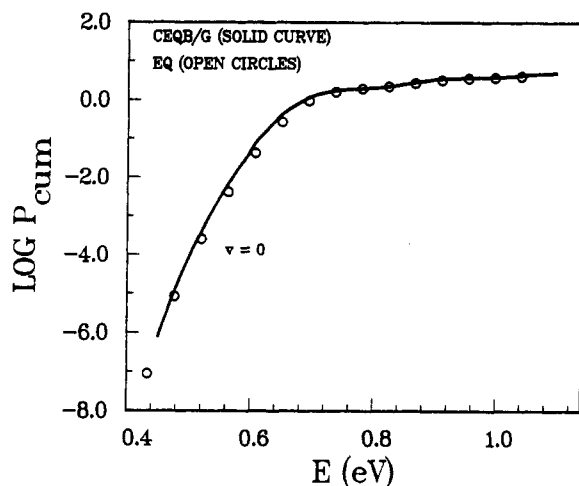


**Figure 3.** Same as Figure 2 but in an semilog plot.

surface[34] which is similar to the ab initio surface. These were used in the first direct comparisons of reduced dimensionality, CEQB/G, and exact CRPs for $H_2(v=0)$ and $H_2(v=1)$.[35] The results are shown in Figures 2 and 3. Note in particular in Figure 2 the steplike structure of the CRP for $H_2(v=0)$. The origins of this structure was discussed in the previous section, where an idealized CRP was shown in Figure 1. As discussed previously each initial-vibrational-state CRP, $P_v^{CEQB}(E;n_b)$, cannot exceed unity for a given rearrangement channel. For $O + H_2$ there are two equivalent arrangement channels, and thus the CRPs shown in Figures 2 and 3 have been multiplied by 2 to reflect this.[35] Also, recall that for $J = 0$ only even bending states contribute to the CRP, and thus the step-risers should be separated by roughly $2\hbar\omega_b^*$. For this reaction that separation equals 0.18 eV, which is in good agreement with the results in Figure 2. This comparison between reduced dimensionality and exact CRPs was the first to show the remarkable steplike features of an accurate CRP. As seen in the semilog plot in Figure 3 there is very good agreement even in the deep tunneling region, which is important for the thermal rate constant at room temperature and below. (An exact rate coefficient, which requires a sum over partial wave CRPs, each of which entails considerably more computational effort than
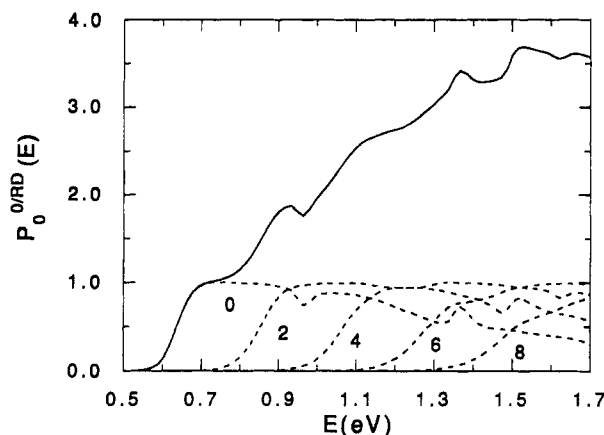


**Figure 4.** Initial vibrational state-selected, reduced dimensionality cumulative reaction probability for the $H + H_2(v=0)$ reaction for zero total angular momentum versus the total energy $E$. The dashed curves are reaction probabilities for individual bending states indicated. (Only even bending states contribute to the cumulative reaction probability.)

to calculate than the $J = 0$ CRP, has not been reported.)

$H + H_2$. Several tests of reduced dimensionality theories have been reported for the $H + H_2$ reaction. In the earliest, CEQ and CEQB/G rotationally averaged integral cross sections were compared with the accurate three-dimensional ones up to a total energy of 0.6 eV.[36] The CEQ theory is the simplest energy-shift approximation, in which the CRP for a given bending state is approximated by the collinear exact quantum reaction probability shifted down in energy by the transition-state bending energy.[14,15,36] This effectively replaces the adiabatic bending energy by the electronic potential plus the bending energy at the transition state (relative to the transition-state energy). The CEQB/G cross section was in very good agreement throughout the energy range including the tunneling region; however, the CEQ cross section was smaller than the accurate and CEQB ones in the tunneling region. The origin of that inaccuracy is the approximate treatment of the bending energy just described, which results in a barrier that is thicker than the true adiabatic one and hence leads to an underestimate of the tunneling.

Another more recent comparison[37] was made between CEQB/G and centrifugal sudden rotationally averaged cross sections for the vibrationally excited reaction $H + H_2(v=1) \rightarrow H_2(v'=0)$, $H_2(v'=1) + H$. The agreement with the CS results was very good for the vibrational state-to-state cross sections over the energy range of the CS calculations, 0.8–1.0 eV, total energy.

Very recently, exact three-dimensional partial wave CRPs for $H + H_2$ for $J = 0$ and 4, up to 1.65 eV, were reported.[38] This presents an opportunity to test the reduced dimensionality method up to higher energies than was done previously.

We calculated CEQB reaction probabilities for 10 bending states in the harmonic approximation up to 2.0-eV total energy. In Figure 4 we present $P_0^{0/RD}(E)$ and the individual components $P_0^{0/RD}(E;n_b)$ for $J = 0$. Each component $P_0^{0/RD}(E;n_b)$ is bounded by unity, and so $P_0^{0/RD}(E)$ cannot exceed the number of bending states included in the summation over $n_b$. In a classical picture of the dynamics, only those bending states with barriers $E_{n_b}^*$ below $E$ would contribute to the summation, and the threshold behavior for the classical $P_0^{0/RD}(E)$ would show very sharp onsets at the classical threshold energies for each bending state. Quantum mechanically, tunneling smooths out the threshold behavior, as seen. Nevertheless, the appearance of bending thresholds is seen clearly just above the threshold for each bending state especially for $E$ up to about 1.0 eV. Another important point is that each $P_0^{0/RD}(E;n_b)$ is seen to rise to near unity and then with increasing energy begin to decline. This is the quantum mechanical signature of "recrossing", which is the reflection of flux back across the

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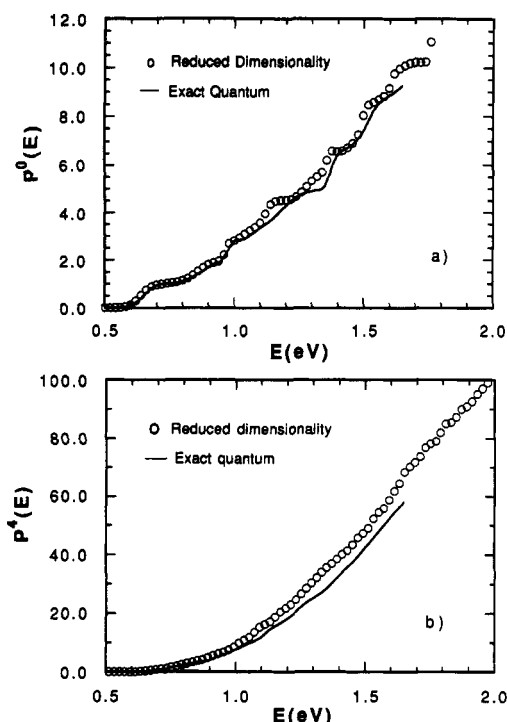
**Figure 5.** Comparison of reduced dimensionality and exact quantum[38] cumulative reaction probabilities for total angular momentum equal to 0 (a) and 4 (b) for the H + $H_2$ reaction. $E$ is the total energy.

**TABLE I: Comparison of Reduced Dimensionality $L^2$ (RD $L^2$), Three-Dimensional $L^2$ (3D $L^2$), and Coupled Channel (CCH) Resonance Energies (eV) and the One "Vibrationally Bonded" State for Nonrotating IHI ($n_s$, $n_b$, and $n_a$ Are the Symmetric Stretch, Bend, and Antisymmetric Stretch Quantum Numbers)**

| $n_s$ | $n_b$ | $n_a$ | RD $L^{2a}$ | 3D $L^{2b}$ | CCH$^c$ |
|---|---|---|---|---|---|
| 0 | 0 | 0 (bound state) | 0.134 | 0.137 | |
| | | | | 0.137$^d$ | |
| 1 | 0 | 0 | 0.146 | 0.151 | 0.149 |
| 2 | 0 | 0 | 0.157 | 0.162 | 0.159 |
| 0 | 0 | 2 | 0.325 | 0.335 | 0.339 |
| 1 | 0 | 2 | 0.341 | 0.353 | 0.353 |
| 2 | 0 | 2 | 0.357 | 0.369 | 0.368 |
| 3 | 0 | 2 | 0.372 | 0.380 | 0.381 |
| 0 | 0 | 4 | 0.551 | 0.574 | |

$^a$ Reference 44. $^b$ Reference 51. $^c$ Reference 56. $^d$ Reference 62.

transition state in the direction of reactants.

At energies above 1.0 eV the simple steplike structure of $P_0^{0/RD}(E)$ is less pronounced. This is due to two factors. One is the change in the threshold behavior for highly excited bend states, which is less abrupt than the lower bending states. This is understandable from the fact that the barrier on the effective potential widens as well as increases as $n_b$ increases, and the wider the barrier the more gradual is the increase in the reaction probability in the tunneling region. The second factor is the gradual decrease of reaction probabilities $P_0^{0/RD}(E;n_b)$ from unity. The combination of the two factors is to give a result that is fairly smooth. There is additional structure in $P_0^{0/RD}(E)$ that has nothing to do with thresholds but is due to dips and blips in $P_0^{0/RD}(E;n_b)$, which are in fact resonances. These features are of much current interest in the H + $H_2$ reaction; however, they are beyond the scope of this article and we refer the interested reader to the literature for details.[1,39-43]

In Figure 5 we compare the CRPs $P^{0/RD}(E)$ and $P^{4/RD}(E)$ with the accurate quantum CRP (the accurate results were read off a plot). For $J = 0$ there is excellent agreement up to 1.0 eV, where three bending states, 0, 2, and 4, are open. Above that, the reduced dimensionality CRP appears to be out of phase a bit with the accurate result. A thorough analysis of the differences between the RD and accurate CRPs at higher energies remains to be done; however, it is possible that the harmonic treatment of the higher bending states is increasingly inaccurate. Another possibility is that at higher energies nonadiabatic coupling between the $\Omega = 0$ bending states is becoming significant. Overall though the agreement is quite good throughout the energy range of the accurate calculations.

We calculated $P^{4/RD}(E)$ using the $J$-shifting approximation and using the rotational constant, assuming the transition state is located at the saddle point. Note that even and odd bending states contribute to this CRP and thus that the magnitude of this CRP

is considerably greater than the $J = 0$ CRP. Note first the much smoother energy dependence of this (and the exact) CRP compared to that for $J = 0$. Overall there is good agreement with the accurate CRP; however, as for $J = 0$, the agreement deteriorates somewhat at the higher energies, presumably due to same factors discussed for the $J = 0$ case. Another factor, however, that could play a role is the breakdown of the CS assumption, i.e., that $\Omega$ is a good quantum number. This would be another mechanism for nonadiabatic coupling, which cannot be operative for $J = 0$, where $\Omega$ is rigorously zero. This needs further study.

## Photodetachment Spectroscopy

The reduced dimensionality theory has recently been applied by us[44,45] and by Neumark and co-workers[46-50] to model their recent photodetachment experiments of heavy–light–heavy anions, e.g., IHI⁻, ClHCl⁻, and IHBr⁻. In this application the wave functions of the adiabatic-bend Hamiltonians were used to calculate Franck–Condon transition intensities governing the photodetachment of the anion to form the unstable, neutral reactive system. Many, though not all, of the peaks they observed are due to overlap of the ground vibrational state of the anion with resonance states of the neutral system. The positions of these peaks correspond to the quasibound states of the unstable triatomic system which are centered at or near the transition state. Thus, these positions, their heights, and their widths yield a "spectroscopy of the transition state". They have also been calculated by using three-dimensional $L^2$[51] and scattering methods[52-56] for $J = 0$.

The IHI⁻ → IHI + e⁻ experiment is especially interesting given the extensive previous theoretical interest in IHI.[57-62] This

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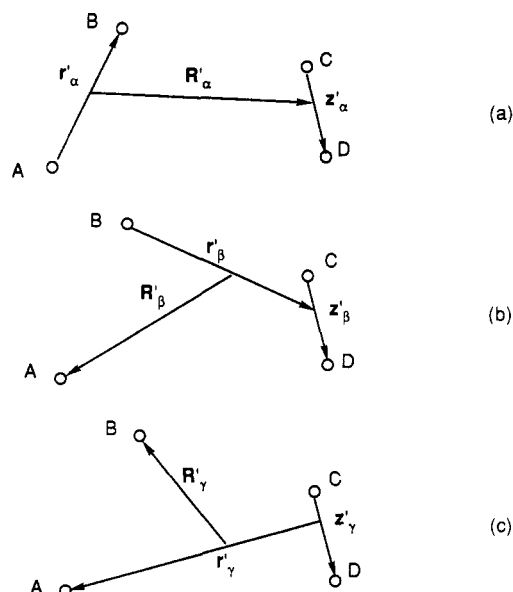(43) Schatz, G. C.; Kuppermann, A. *Phys. Rev. Lett.* **1975**, *35*, 1266.

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**Figure 6.** Jacobi coordinates for three arrangements of an AB + CD reaction, appropriate for the $H_2$ + CN → H + HCN reaction.

seminal, early work discovered very sharp resonances in collinear quantum calculations,[57,58] as well as the existence of "vibrationally bonded" bound state(s) in collinear[59] and approximate[60,61] and variational three-dimensional calculations.[62] More recently, in response to the photodetachment experiments, reduced dimensionality,[44] three-dimensional L[2],[51] and coupled channel scattering calculations[56] were reported on IHI. A comparison of the resonance energies for the ground bending state from these calculations is given in Table I, along with a comparison of the one vibrationally bonded state. As seen, the reduced dimensionality results are quite accurate overall, and it is especially noteworthy that there are no "spurious" predictions of either bound or resonance states. In strictly collinear calculations there are four vibrationally bonded states;[44,62] however, in the reduced dimensionality calculations there is only one such state, in agreement with accurate three-dimensional calculations.[51,62]

Next, we move to the area of diatom–diatom reactions, for which the first collinear quantum calculations[63–65] and the first reduced dimensionality calculations of the $H_2$ + CN → H + HCN reaction have been reported.[66,67]

### Theory for Diatom–Diatom Reactions

Diatom–diatom reactions present an enormous increase in complexity relative to atom–diatom reactions because the number of internal degrees of freedom increases from three to six. Clearly, it will be extremely difficult to fully couple six degrees of freedom, and a reduced dimensionality approach will be needed to study such reactions for the foreseeable future.

There are myriad ways to formulate a reduced dimensionality approach to diatom–diatom reactions. A general theory of diatom–diatom reactions would in principle have to account for the possibility of three diatom–diatom arrangements, i.e., AB + CD, AC + BD, AD + BC, and 12 atom–triatom arrangements, i.e., A + BCD, A + BDC, A + DBC, etc., for a total of 15 possible arrangement channels. Of course many conceivable channels would be energetically closed or simply not stable molecular arrangements. In light of this, we have formulated a first theory at the opposite end of this totally general approach in which only the reaction AB + CD → A + BCD is energetically open. That



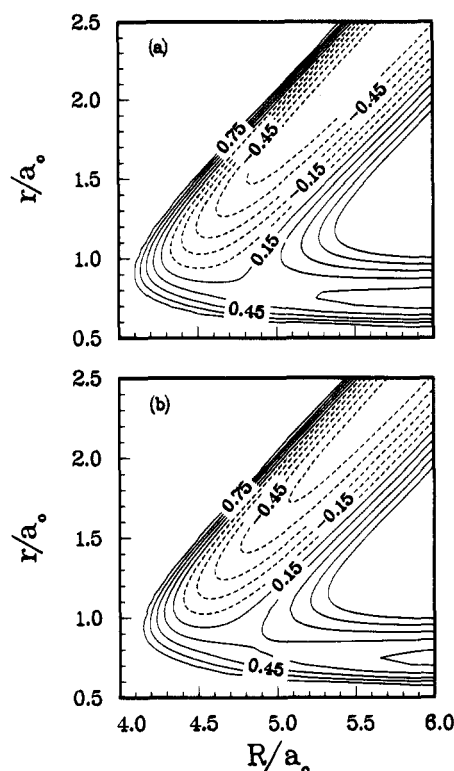**Figure 7.** Reference (a) and effective ground bend (b) potentials for $H_2$ + CN reaction. Contour values are in electronvolts, $R$ is the mass scaled distance between the centers of mass of $H_2$ and CN, $r$ is the mass scaled $H_2$ internuclear distance, and the CN internuclear distance is fixed at its saddle-point value.

is, a reaction in which the CD bond is nonreactive. For this case there are three possible arrangement channels, shown in Figure 6, in terms of the appropriate Jacobi vectors for each arrangement. The approach we have implemented is to fully couple the three radial stretching degrees of freedom and to treat the three bending degrees of freedom approximately. This approach is then the natural extension of the atom–diatom reduced dimensionality theory we just reviewed.

$H_2$ + CN. The $H_2$ + CN → H + HCN reaction is exemplary of this class of reaction, and we shall focus on it hereafter. Ab initio calculations of the reactants, products, and linear saddle point energies and normal modes have been reported.[68,69] We have developed a semiglobal potential surface[66] describing the above reaction based on those calculations and other known properties of the reactants and products. This surface is semiglobal because it does not describe the HNC isomer nor does it contain the high-energy, nonlinear insertion channels.[68]

We have used this six-mode, semi-ab initio potential to obtain an effective reduced dimensionality, three-degree-of-freedom potential. The reduction in dimensionality is achieved by treating the three internal bending degrees of freedom adiabatically. In general this surface is given by the sum of the potential for a reference geometry plus the bend energies. In the present case, the reference potential is for a linear configuration of the four atoms, H'–H–C–N and therefore is an explicit function of three internuclear distances $R_{H'H}$, $R_{HC}$, and $R_{CN}$. (The three other distances are determined from these three in the linear geometry.) The nonlinear bending motions are treated adiabatically, and the energy for each bending state is added to the reference potential. For a linear tetraatomic molecule there are two doubly degenerate bends, and in the harmonic approximation the bending frequencies can be found by the standard FG matrix method. One important result of this normal-mode analysis is that at the saddle point the higher frequency bending normal mode correlates with the HCN

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bend, and the lower frequency mode (which is mainly the bending of the distal H′ atom) goes to zero in both the reactant and product arrangement channels.

The effective potential is given by

$$V_{\text{eff}}(R_{\text{H'H}}, R_{\text{HC}}, R_{\text{CN}}; v_{b_1}, v_{b_2}) =$$
$$V_{\text{ref}} + \hbar\omega_1(v_{b_1} + 1) + \hbar\omega_2(v_{b_1} + 1)$$

where $v_{b_1}$ and $v_{b_2}$ are the bending quantum numbers, and $\omega_1$ and $\omega_2$ are the bending frequencies, which are functions of $R_{\text{HH'}}$, $R_{\text{HC}}$, and $R_{\text{CN}}$. Equipotential contour plots of $V_{\text{ref}}$ and $V_{\text{eff}}$ for $v_{b_1} = v_{b_2} = 0$ are given in Figure 7 for the linear configuration and in mass-scaled coordinates. The barrier height and exoergicity of the reference potential are 4.1 and −20.5 kcal/mol, respectively. These characteristics together with the early location of the barrier are similar to those of the potential energy surface for the F + $H_2$ reaction.[70-72]

The reduced dimensionality Hamiltonians for the nonrotating system, in mass-scaled Jacobi coordinates for the reactant a and product b arrangement channels (shown in Figure 6) are[73]

$$H_a = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial z_a^2} + \frac{\partial^2}{\partial r_a^2} + \frac{\partial^2}{\partial R_a^2}\right) + V_{\text{eff,a}}(z_a, r_a, R_a; v_{b_1}, v_{b_2})$$

$$H_b = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial z_b^2} + \frac{\partial^2}{\partial r_b^2} + \frac{\partial^2}{\partial R_b^2}\right) + V_{\text{eff,b}}(z_b, r_b, R_b; v_{b_1}, v_{b_2})$$

where $R_a$ is the mass-scaled distance between the centers of mass of $H_2$ and CN, $R_b$ is the mass-scaled distance between H′ and the center of mass of HCN, $r_a$ is the $H_2$ mass-scaled internuclear distance, $r_b$ is the distance of H to the center of mass of CN, and $z_{a(b)}$ is the mass-scaled CN internuclear distance, which is the same in both arrangement channels.

The solution of the Schrödinger equation is described in detail elsewhere;[73,66] however, we give a brief overview of the steps involved. First, a new set of coordinates is used to reexpress the Schrödinger equation. These are based on hyperspherical coordinates which have been of great use in atom–diatom reactive scattering.[4,5,7,8,57,58] The hyperradius $\rho$ plays the role of a reaction progress variable, and a two-dimensional basis set in terms of an angular variable and $z$ is constructed. The total wave function is expanded in terms of this basis set, and then coupled channel equations in $\rho$ are propagated into the near-asymptotic region. There, the solution matrix is transformed into mass-scaled Jacobi coordinates in the two arrangement channels, and the propagation is continued into the asymptotic region, where the scattering boundary conditions are applied. State-to-state reaction probabilities are then obtained as a function of the total energy. These can be used to obtain corresponding thermal rate coefficients using generalizations[67] of the expressions given above for atom–diatom reactions.

Next, we review selected reaction probabilities and thermal rate coefficients, including comparisons with experiment for $H_2$ + CN.

## Reaction Probabilities

We calculated reaction probabilities, $P_{v_{H_2}, v_{CN} \rightarrow v_{CN}, v_b, v_{CH}}(E)$ for total energies $E$ between 0.45 and 1.0 eV, at 0.01-eV increments, for the ground bend state of HCN and up to 1.06 eV for the first excited bend. These probabilities are for the ground state of the lower frequency bend of the four-atom system. The quantum numbers labeling $HCN_{v_{CN}, v_{CH}}$ refer to the two stretching modes of vibration, which are not harmonic and which are mainly



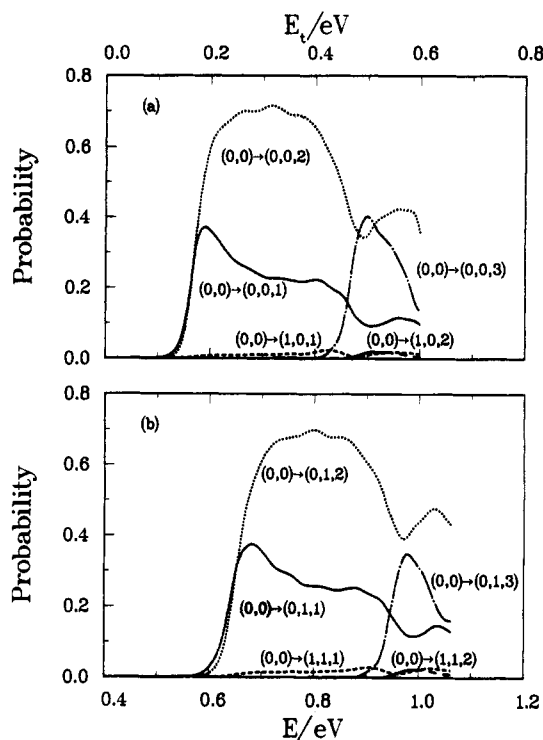**Figure 8.** Reduced dimensionality reaction probabilities for $H_2(0)$ + $CN(0) \rightarrow HCN(v_{CN}, v_b, v_{CH})$ + H as a function of the total energy $E$ and the initial translational energy $E_t$, for $v_b = 0$ and 1.

(though, of course, not completely) CN and CH stretches, respectively.

Consider first the reaction probabilities for $H_2$ and CN in their ground vibrational states to form HCN in the ground and first excited bend states. Probabilities greater than 0.01 are shown in Figure 8. As seen, the most significant are those with the CH stretch excited but the CN stretch unexcited. There is in fact a population inversion in the CH stretch. The reaction threshold energy, defined as the lowest energy where the total reaction probability (for the ground bend state of HCN) is 0.01, is 0.52 eV. The reaction probabilities for the first excited bend are essentially the same as those for the ground bend but shifted to higher energies by a nearly constant amount equal to the excited bend energy at the transition state. From these plots it is clear that the reaction exoergicity is channeled effectively into vibrational excitation of the new CH bond and predominantly by exciting it to a level 2 quanta greater than the vibrational state of the reactant $H_2$.

Reaction probabilities for $CN(1)$ + $H_2(0)$ and $H_2(1)$ + $CN(0)$ were also calculated. For the reaction with CN vibrationally excited the translational energy threshold energy is 0.068 eV *higher* than the threshold energy for the reaction with $H_2$ vibrationally excited. This indicates that vibrationally exciting $H_2$ is far more effective in promoting reaction than vibrationally exciting CN. This is not an energetic effect; rather it is due to the passive role played by the CN in the reaction and the active role played by the $H_2$.

**Thermal Rate Coefficients and Comparison with Experiment.** Thermal rate coefficients were calculated for $H_2(0)$ + $CN(0)$, $H_2(0)$ + $CN(1)$, and $H_2(1)$ + $CN(0)$ by using generalizations of the methods described earlier for atom–diatom reactions. Experimental rate coefficients have been measured for the first[67,74,75] and second[75] reactions. The comparison between theory

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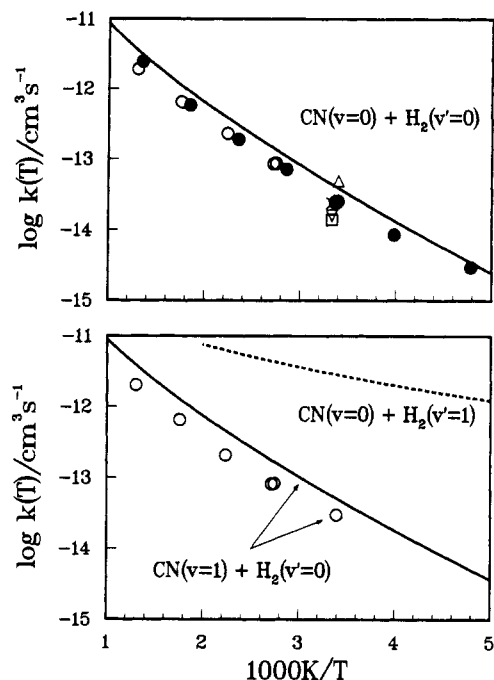(75) Sims, I. R.; Smith, I. W. M. *Chem. Phys. Lett.* **1988**, *149*, 565.

**Figure 9.** Calculated and experimental rate coefficients for $CN(v)$ + $H_2(v')$ → $HCN$ + $H$.

and experiment is given in Figure 9, where it is seen that the theoretical results are somewhat larger than experiment; however, the overall agreement is good.

For the $H_2(0)$ + $CN(1)$ reaction, the theoretical predictions are in fairly good agreement with these experimental results, although as in the thermal rate constant, theory is somewhat larger than experiment. Both theory and experiment find very little enhancement of the reaction by vibrationally exciting CN. By contrast the theoretical predictions indicate that vibrationally exciting $H_2$ leads to a very large increase in the rate coefficient. Unfortunately, there are no experimental measurements of the rate with $H_2$ vibrationally excited.

**The Future**

As the details of more chemical reactions are discovered ex-

perimentally, the need for theory will surely grow. Inevitably, as experiment probes deeper, so will theory, and this means that quantum methods will become computational workhorses, joining with the very useful classical and semiclassical methods. Clearly though as theory and experiment begin considering larger systems, it will be necessary to apply reduced dimensionality methods. These may resemble the one reviewed in this article, or they may develop along a different directions. This depends on the physical insight that is accumulated as more reactive systems are studied.

The field of reactive scattering is expanding in new areas, and among them are experiments that probe the transition state and those that prepare or probe polyatomic reactants or products in specific vibrational states.[76] These types of experiment are particularly amenable to analysis using the methods reviewed here. This is because these experiments do not demand the full output of an exact solution to the Schrödinger equation (although that would always be welcomed).

Another area where reduced dimensionality theories can make contributions is to electronically nonadiabatic reactions. The reactive sudden approximation has already been applied to a number of atom–diatom systems, and very recently an new version of the method based on optical potentials has been applied to the $H_2$ + $H_2^+$ reaction.[77] We anticipate much more activity using reduced dimensionality in this area in the future.

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