Quantum mechanical calculations of the rate constant for the 
H₂+OH→H+H₂O reaction: Full-dimensional results and comparison 
to reduced dimensionality models

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The cumulative reaction probability is calculated for the H₂+OH→H+H₂O reaction in its full (six) 
dimensionality for total angular momentum J=0. The calculation, which should give the 
(numerically) exact result for the assumed potential energy surface, yields the cumulative reaction 
probability directly, without having to solve the complete state-to-state reactive scattering problem. 
Higher angular momenta (J>0) were taken into account approximately to obtain the thermal rate 
constant k(T) over the range 300°<T<700°. The result deviates significantly from the experimental 
rate constant, suggesting that the potential energy surface needs to be improved. A systematic series 
of reduced dimensionality calculations is carried out in order to characterize the behavior and 
reliability of these more approximate treatments; a comparison of the full dimensional results with 
previous reduced dimensionality calculations is also made.

I. INTRODUCTION

The most detailed theoretical description of a chemical 
reaction, i.e., the state-to-state differential scattering cross 
section at a well defined collision energy, requires that one 
solves the Schrödinger equation to obtain the S matrix 
S_{n_p \rightarrow n_r} (J,E), the state-to-state transition amplitudes as a 
function of total energy E and total angular momentum J. 
(n_r and n_p denote reactant and product quantum states, re- 
spectively.) All attributes of the reaction can be expressed in 
terms of the S matrix, from the most detailed cross sections 
noted above to the least detailed quantity, namely, the 
thermal rate constant k(T) which resolves neither reactant nor 
product quantum states. All of the averaging over initial and 
final quantum states inherent in the definition of the rate 
constant are conveniently contained in the cumulative reac-


dation probability (CRP),

\[ N(E) = \sum_{J=0}^{\infty} (2J+1) \sum_{n_r,n_p} |S_{n_r \rightarrow n_p}(J,E)|^2, \]  \(1) \]
in terms of which the thermally averaged rate constant is given by

\[ k(T) = \left[ 2\pi \hbar Q_r(T) \right]^{-1} \int_{-\infty}^{\infty} e^{-E/kT} N(E) dE, \]  \(2) \]

where Q_r is the reactant partition function per unit volume. 
[The microcanonical rate constant, which is usually of most 
interest for unimolecular reactions, is also given in terms of 
the CRP,

\[ k(E) = \left[ 2\pi \hbar \rho_r(E) \right]^{-1} N(E), \]  \(3) \]

where \( \rho_r \) is the reactant density of states.] Therefore, if one is 
interested only in the rate constant itself, it would clearly be 
desirable to be able to calculate the CRP directly, without 
having to determine the complete S matrix. The purpose of 
this paper is to describe such a theoretical approach to the 
reaction H₂+OH→H+H₂O. (Some of the results of this 
work have been reported in an earlier Communication.\(^1\))

Though accurate reactive scattering calculations have 
been carried out in recent years for several atom-diatom 
systems, e.g., H₂+H, F+H₂, Cl+HCl, there are just be-


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investigate initial state-selected reaction probabilities for the 
H₂+OH→H+H₂O reaction. The reactant asymptotic region 
was included exactly, so that reaction probabilities for a 
given initial (vibrational and rotational) state could be calcu-
lated. Five degrees of freedom were included in their calcu-
lation, neglecting only the OH vibration. Within this approxi-
mation they reported reaction probabilities for a set of 
vibrationally and rotationally excited H₂ and rotationally ex-
cited OH initial states.

As noted above, our interest is the direct (but correct, 
i.e., without approximations) calculation of the CRP of Eq. 
(11). Seideman and Miller 16-18 developed a practical schema

FIG. 1. Atomic displacements for motion along the six normal mode coordinates of the H₂+OH saddle point. (a)-(f) correspond to O₁→O₆, arranged as in 
Table I. The Cartesian x and z coordinates define the plane of the transition state. The arrows are drawn to scale.
TABLE I. Frequencies and grid parameters.

<table>
<thead>
<tr>
<th>Coordinate</th>
<th>Frequency (a.u.)</th>
<th>$E&lt;0.2$ eV</th>
<th>$0.2$ eV $\leq E&lt;0.4$ eV</th>
<th>$E&gt;0.4$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_1$</td>
<td>0.016 153</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$Q_2$</td>
<td>0.003 907</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>$Q_3$</td>
<td>0.003 781</td>
<td>5</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>$Q_4$</td>
<td>0.002 607</td>
<td>4</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Composite grid</td>
<td>71 389</td>
<td>89 017</td>
<td>216 363</td>
<td></td>
</tr>
</tbody>
</table>

To perform such calculations, one should note other related approaches that deal with the flux-flux time correlation function. Their approach requires the use of some basis set (or grid) to represent the Hamiltonian in the transition state region of the potential energy surface. The CRP is expressed in terms of a modified Green's function $[E-(H-i\epsilon)]^{-1}$, where $\epsilon$ is an absorbing potential at the edge of the grid that imposes outgoing wave boundary conditions for the Green's function. The numerical grid for such calculations is considerably smaller than for a full scattering calculation, resulting in considerably less computational effort for the rate calculation than for a complete state to state calculation.

The original formulation of the direct CRP calculation involved the solution of a system of equations with a large number of right-hand side vectors: the action of the Green's function on each grid point in the reactant absorbing strip had to be computed. More recent work has circumvented this difficulty: a Hermitian reaction probability operator was introduced which was shown to have only a small number of nonvanishing eigenvalues. These eigenvalues, which have shown to lie between 0 and 1, can be viewed as the rigorous generalization of the transmission probabilities of the transition state theory. The cumulative reaction probability is simply the sum of the eigenvalues of the reaction probability operator. A efficient iterative scheme for calculating the eigenvalues of the reaction probability operator was also presented. Again a set of a linear equations has to be solved, but compared to the original formulation, the number of right-hand side vectors, and therefore the computational effort, is drastically reduced. Now not the number of grid points in the reactant absorbing strip but the number of nonvanishing eigenvalues of the reaction probability operator determines the number of right-hand sides in the system of equations to be solved.

This article is organized as follows. In Sec. II the general methodology is reviewed and the numerical details are presented. Section III shows results for the cumulative reaction probability for vanishing total angular momentum ($J=0$). These results are used to calculate to thermal reaction rate as described in Sec. IV. Comparison to experimental data and to theoretical results of reduced dimensionality calculations is given. In Sec. V aspects of reduced dimensionality treatment are discussed extensively. Series of five-dimensional, four-dimensional, three-dimensional, and two-dimensional calculations are presented and compared to the full-dimensional result. Errors induced by the different reduced dimensionality models are analyzed.

II. CALCULATION OF $N(E)$

Following the approach developed by Seideman and Miller and Manthe and Miller, the cumulative reaction probability is computed as

$$N(E) = \text{tr}[\hat{P}(E)] = \sum_k p_k(E),$$

(4)

where $\hat{P}(E)$ is the reaction probability operator, defined by

$$\hat{P}(E) = 4 \sqrt{\epsilon} \hat{G}(E)^{\dagger} \hat{G}(E) \sqrt{\epsilon},$$

(5)

and $p_k(E)$ are its eigenvalues, the eigen reaction probabilities. The Green's function

$$\hat{G}(E) = [E - (\hat{H} - i\epsilon)]^{-1}$$

(6)

involves the Hamiltonian operator of the molecular system, and $\epsilon$ is an absorbing potential, $\epsilon(a, b)$ being the part in the reactant (product) region.

Normal coordinates of the transition state are employed which results in a Watson form of the Hamiltonian. In the present work we limit attention to zero total angular momentum and neglect vibrational angular momentum terms, since they were seen in earlier work to have negligible effect, which is expected be also the case here. The resulting Hamiltonian reads

$$\hat{H} = \sum_{n=1}^{6} \frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_n^2} + V(Q),$$

(7)

where $Q_n$ are the mass-weighted normal coordinates of the six vibrational modes at the transition state. These normal coordinates are depicted in Fig. 1. $Q_1$ is best characterized as an O--H stretching mode. $Q_5$ describes mainly an in-plane H$_2$ rotation with approximately unchanged OH position, while $Q_3$ is the analogous out-of-plane motion. H$_2$--OH bending, or a simultaneous H$_2$ and OH rotation, is given by $Q_4$. The coordinates $Q_3$ and $Q_4$ are most strongly influenced by the reactive rearrangement. $Q_5$ is the H$_2$ stretch mode and coordinate $Q_6$ represents the motion of the H$_2$ hydrogen atom towards OH. Harmonic analysis at the transition state geometry results in real frequencies for the coordinates $Q_1$ to $Q_5$, while an imaginary value is found for the reaction coordinate $Q_6$. The frequencies are displayed in Table I. The potential $V(Q)$ is taken from the Schatz–Elgersma fit to ab-initio results of Walch and Dunning which was employed also in previous calculations of the H$_2$+OH→H+H$_2$O reaction.

Discrete variable representations (DVR) are used for the representation of the Hamiltonian and the absorbing potentials. A Gaussian–Hermite DVR is employed in the coordinates $Q_1$ to $Q_4$. Depending on the specific coordinate and energy four to seven grid points per coordinate are required to reach convergence. For the reaction coordinate $Q_5$ and the $Q_6$ coordinate which is strongly coupled a sinc-function DVR is employed. The grid spacing is chosen to allow for a maximum kinetic energy of 2.2 eV. The composite 6D grid
TABLE II. Parameters for absorbing potentials.

<table>
<thead>
<tr>
<th>c₁</th>
<th>c₂</th>
<th>λ</th>
<th>q₀</th>
<th>q_max</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.375</td>
<td>0.625</td>
<td>1.5 eV</td>
<td>10 a.u.</td>
<td>37 a.u.</td>
</tr>
</tbody>
</table>

is truncated at a potential cutoff of 2.2 eV. The final grid consist of about 100 000 points for lower energies up to about 200 000 points for higher energies. More details are given in Table I.

The absorbing potentials are taken as functions of the two strongly coupled degrees of freedom, Q₅ and Q₆, and defined as follows:

\[ ε_p(q) = \begin{cases} 
0, & \text{for } q < q_0 \\
λ \frac{(q - q_0)^4}{(q_{max} - q_0)^4}, & \text{for } q > q_0
\end{cases} \]

\[ ε_f(q) - ε_p(-q), \tag{8} \]

where

\[ q = c₁ Q₅ + c₂ Q₆. \tag{9} \]

Only the part of the surface for \(-q_{max} < q < q_{max}\) is included in the description. The parameters are given in Table II. The results obtained with these parameters are stable, and should be accurate, to at least 10% for all but the lowest energies (E < 0.05 eV) reported.

As can be seen from the above description, a number of parameters must be adjusted in the calculation. Elaborate adjustment of each parameter in a full six-dimensional calculation of \(N(E)\) would clearly be prohibitive because of the extreme computational effort of such calculations. Therefore the following scheme was employed. First two-dimensional calculations including only the coordinates \(Q₅\) and \(Q₆\) were performed for a set of total energies \(E\). The parameters \(λ, q_0,\) and \(q_{max}\) were adjusted by systematic parameter variation in these calculations. Since the numerical effort of two-dimensional calculations is comparatively small, a large numbers of calculations can be performed easily. Next the kinetic and potential energy cutoffs employed in the definition of the DVR grid were likewise obtained from two-dimensional calculations. The number of DVR-grid points required in the other four coordinates \(Q₁\) to \(Q₄\) was determined by three-dimensional calculations. For each of these coordinates calculations including the coordinates \(Q₅, Q₆,\) and the coordinate in question were performed and the number of DVR-grid points in the coordinate in question is increased until convergence was achieved. It should be noted that the number of DVR-grid points required depends on the total energy \(E\). Therefore this procedure was repeated for different energy regions. Finally a few full six-dimensional calculations were performed for different sets of parameters to ensure that the parameter values were sufficient also for the full calculation.

The eigenvalues \(p_k\) of the reaction probability operator \(\hat{P}\) were calculated by the Lanczos scheme described in Ref. 20. Starting from a random initial vector \(\tilde{\psi}_0\) a Lanczos-iteration sequence including reorthogonalization

\[ ψ_n = \hat{P} ψ_{n-1} - \sum_{k=0}^{n-1} ψ_k \langle ψ_k|\hat{P}|ψ_{n-1}\rangle \tag{10} \]

is used to generate a orthonormal basis spanning the Krylov space \(\{\tilde{\psi}_0, \tilde{\psi}_1^0, \tilde{\psi}_2^0, ..., \tilde{\psi}_n^0\}\). The representation of \(\hat{P}\) within the basis \(\{\tilde{\psi}_0, \tilde{\psi}_1, ..., \tilde{\psi}_n\}\) is then used to calculate the \(p_k\)'s by direct numerical diagonalization. \(N(E)\) is calculated directly by summing the diagonal elements

\[ N(E) = \sum_{k=0}^{n} \langle ψ_k|\hat{P}|ψ_k\rangle. \tag{11} \]

The order \(n\) of the scheme is taken sufficiently large to yield converged results. At low energies 3 to 4 iterations are sufficient for this purpose while for the highest energies the required iterations increases up to 44.

The symmetry of the \(H₂\) reactant in the \(H₂+OH\rightarrow H+H₂O\) reaction causes a degeneracy of the eigen reaction probabilities \(p_k\). The reaction can proceed equivalently in two ways: The OH can attack either the one side of the \(H₂\) or the other. At the energies under consideration these two pathways do not interfere with each other. The normal coordinates employed here are constructed so that only one of the two pathways is explicitly included in the calculation. Therefore only one of each two degenerate \(p_k\)'s is obtained.

To account for the second set of \(p_k\)'s the resulting \(N(E)\) of Eq. (8) is multiplied by two.

Every action of the reaction probability operator \(\hat{P}\) on a vector employed in the Lanczos iteration sequence requires two operations of the Greens function \(\hat{G}\) (or its Hermitian conjugate) on a vector, or equivalently, the solution of two complex systems of linear equations of the form

\[ \hat{A} x = f, \tag{12} \]

where in the present case

\[ \hat{A} = E - (\hat{H} - iε) = \hat{G}(E)^{-1}, \tag{13} \]

and

\[ f = ψ, \quad x = \hat{G}(E)ψ. \tag{14} \]

Given the size of basis involved in a six-dimensional problem, a direct solution, which requires storage of the Hamiltonian matrix in the core memory of the computer, is not feasible. Moreover, direct methods scale in time roughly as the cube of the order of the linear system and hence become prohibitively expensive as the dimensionality increases. Iterative methods do not require storage of the matrix and are particularly efficient for the case of sparse matrices which arise from discrete variable representations.

A variety of iterative methods for solving linear systems exists, a number of which are, at least in principle, applicable also to complex problems. In the present work we extended the generalized minimal residual (GMRES) algorithm, proposed by Saad and Schultz,²⁴ to the case of a general complex matrix. GMRES can be considered as a generalization of the minimal residual (MINRES) method²³ to nonsymmetric systems. It is based on application of the Arnoldi process²¹ to compute an \(l_2\)-orthornormal basis of the Krylov subspace \(K_k = v_1, Av_1, ..., A^{k-1}v_1\), where the initial vector...
is a normalized residue, $v_1 = (f - A x_0)/\|f - A x_0\|$. $x_0$ is an initial guess for the solution vector $x$, and $k$ numbers the iterations. In this representation the system is upper Hessenberg and hence inexpensive to solve. Saad and Schultz proposed a solution which minimizes the residual norm over $K_k$, by analogy to the MINRES method. In the present work we extended the algorithm of Ref. 24 to the case of a complex matrix and implemented it with a preconditioning matrix, as suggested in Refs. 27. Equation (12) is thus replaced by

$$\hat{B}^{-1} \hat{A} x = \hat{B}^{-1} f,$$

(15)

where the preconditioner $\hat{B}$ is chosen to be as similar as possible to $A$ (so as to minimize the number of iterations by operating with a matrix $\hat{B}^{-1} A$ that is similar to unity) but such that $\hat{B}^{-1}$ is easy to compute. Several preconditioners were tested and found to improve the performance of the method to various degrees. These include a separable and an adiabatic two- and three-dimensional approximations to the Hamiltonian and a diagonal preconditioner $B = \text{diag}(\hat{A})$. Extensive comparisons found the optimal preconditioner to be the simple diagonal matrix, consisting of the diagonal elements of $\hat{A}$. The other more sophisticated (but more expensive to apply) preconditioners were found to reduce the number of iterations but result in an overall increase in the computational time as compared to the diagonal preconditioner. We stress, however, that this result is problem dependent, namely, it depends on the structure of the Hamiltonian matrix and hence on the choice of coordinate system. Particular care was taken to fully exploit the sparsity of the Hamiltonian as fully as possible by rearranging the matrix repeatedly so as to perform only nonzero multiplications. In the course of this work we tested several alternative iterative methods that are adaptable to complex systems, including a variation of Davidson's method and the generalized conjugate Gradient algorithm. We found GMRES to outperform these methods. This finding is to a certain extent also problem dependent, namely, it depends on the desired accuracy and on the availability of an initial guess. We expect it to hold more generally in calculations of the Green's matrix, however, regardless of the precise structure and dimensionality of the Hamiltonian. Most of the comparisons of different algorithms were performed for the $H+H_2$ reaction, using normal mode coordinates as discussed in Ref. 18, and for reduced dimensionality versions of the $H_2+OH$ problem.

### III. RESULTS FOR $H_2+OH\rightarrow H+H_2O$

Figure 2 displays the cumulative reaction probability for zero total angular momentum ($J=0$) as a function of the total energy. The zero of energy is chosen to be the energy of the reactants $H_2$ and $OH$ in their respective ground state, i.e., including zero point vibrational energy. One interesting observation, in contrast to the findings for simple three-atom reactions, is that there is no remnant of the staircase structure predicted by classical transition state theory. This difference in behavior results from the increased number of degrees of freedom in the four-atom reaction $H_2+OH\rightarrow H+H_2O$ and can be understood by examining the different eigen reaction probabilities $p_k$, displayed in Fig. 3. As pointed out in earlier work the $p_k$'s can be interpreted as the contributions of the different states of the activated complex to the cumulative reaction probability. Figure 3 shows that all $p_k$'s increase from 0 to 1 with increasing energy, but before an individual $p_k$ has even nearly reached its final value the next $p_k$ has already gained a considerable value. The different $p_k$ contributions to $N(E)$ are thus overlapping, resulting in a smoothly increasing structure for $N(E)$.

The dotted line in Fig. 2 displays approximate results for $N(E)$ calculated by Wang and Bowman. In this treatment all radial coordinate are included exactly, while all angular coordinates are treated by an adiabatic approximation. The description of the angle-type coordinates employs a harmonic approximation for the angular motion. The agreement with the full 6D results is quite good. At higher energies the approximate values tend to be too small. This deviation is explained easily. The approximate results assume harmonic potentials for the angular motion, while the real potentials are anharmonic. Therefore the energy of states which show excitation in an angular coordinate is too high in
the approximate description. Consequently, the total density of states, and also \( N(E) \), is too small at a given energy \( E \). Since the harmonic approximation becomes less accurate for higher excited states, the deviations can be expected to increase with increasing energy as observed in Fig. 2.

**IV. THERMAL RATE CONSTANT**

The thermal rate constant is the quantity which is observed in experiment, and it is given by the Boltzmann average of the cumulative reaction probability

\[
k(T) = \frac{1}{2 \pi h Q_\infty(T)} \int_0^\infty e^{-E/kT} N_{\text{tot}}(E) dE.
\]

Here \( N_{\text{tot}}(E) \) is the total cumulative reaction probability,

\[
N_{\text{tot}}(E) = \sum_j (2J+1) N_j(E), \tag{17}
\]

where \( N_j(E) \) is the cumulative reaction probability for a total angular momentum \( J \) and \( Q_j \) is the partition function of the reactants. Assuming separability of vibrational and rotational motion at the transition state (the "J shifting"\(^{31}\) or modified wave number\(^{32}\) approximation) each \( N_j(E) \) can be calculated by shifting the \( J=0 \) value by the appropriate rotational energy

\[
E_{\text{rot}}^k = J(J+1) \frac{\hbar^2}{I_k}, \tag{18}
\]

where \( I_k \) is the rotational energy of the activated complex with the \( J,K \)-rotational quantum numbers. Inserting Eqs. (17) and (18) in Eq. (16) yields

\[
k(T) = \frac{Q_{\text{rot}}^*}{2 \pi h Q_\infty(T)} \int_0^\infty e^{-E/kT} N_{J=0}(E) dE, \tag{19}
\]

where \( Q_{\text{rot}}^* \) is the rotational partition function of the activated complex. Within the parameter range under consideration it can be well approximated by its classical limit

\[
Q_{\text{rot}}^*(T) = \hbar^3 \sqrt{\frac{\pi(kT)^3}{8 I_A I_B I_C}}, \tag{20}
\]

where \( I_A, I_B, \) and \( I_C \) are the three principle moments of inertia of the activated complex.

The reactant partition function \( Q_r(T) \) consists of contributions from the vibrational and rotational motion of the \( H_2 \) and \( OH \) reactant molecules and from their relative translational motion. For \( OH \) an electronic contribution

\[
Q_{\text{elec}}^*(T) = 1 + e^{-\Delta E_{\text{elec}}/kT}
\]

\((\Delta E_{\text{elec}}=140 \text{ cm}^{-1})\) is included. It results from the spin-orbit splitting of the \( ^3\Pi \) ground state of \( OH \). Since only one of these electronic states correlates to the activated complex, no multiplying factors due to electronic degeneracy (or near degeneracy) are included.

Before presenting calculated rate constants for the \( H_2+OH\rightarrow H+H_2O \) reaction a problem of the potential energy surface employed has to be mentioned. The potential energy surface was constructed by Schatz and Elgersma\(^{14}\) as a fit to the ab initio results of Walch and Dunning.\(^{15} \)

However, the geometry of the transition state given by the Schatz–Elgersma-fit differs significantly from the original Walch and Dunning transition state geometry. Therefore, two sets of moments of inertia of the activated complex can be used alternatively in Eq. (20): the Schatz–Elgersma-surface results in \( I_A=4079 \) a.u., \( I_B=37 \) 570 a.u., \( I_C=41 \) 509 a.u. while the Walch and Dunning data gives \( I_A=983 \) a.u., \( I_B=42 \) 288 a.u., \( I_C=43 \) 270 a.u. \( Q_{\text{rot}}^* \) values derived from these moments of inertia are smaller by a factor of about 0.5 for the Walch and Dunning data compared to the Schatz and Elgersma fit. To be consistent in the treatment of internal and rotational motion, rotational constants corresponding to the Schatz Elgersma fit are used throughout the present work. This should enable comparison to other theoretical work, where the overall rotational motion was not approximated as separable. Analogous results employing the Walch–Dunning geometry can be obtained by multiplying the rates presented below by a factor of 0.53.

The rate constant calculated using Eq. (16) is shown as the solid curve in Fig. 4. The energy range considered allows calculation of the rate constant for temperatures between 300 and 700 K. For lower temperatures energies below 0.05 eV contribute and for higher temperatures energies above 0.5 eV would have to be included. The experimental reaction rates\(^{12}\) are indicated by crosses in Fig. 4. One sees that the calculated reaction rate is larger than the experimental one, and that it decreases more slowly with increasing \( 1/T \) than the experimental one. We do not believe that the \( J \)-shifting approximation can be this much in error at these relatively low energies, so the conclusion is that this lack of agreement is due to inaccuracies in the potential energy surface.

Independent of agreement with the experimental data, the results of the full-dimensional calculation are interesting for comparison with approximate calculations. There have been a number of reduced dimensionality quantum calculations of the \( H_2+OH\rightarrow H+H_2O \) reaction based on the Schatz–Elgersma surface. The Wang and Bowman\(^{5,30} \) calcu-
Citations are defined in terms of normal coordinates, assum-
ding coordinates as described in Sec. II for the full-dimensional prob-
rable. These separable coordinates are described in a
lem. For example, if motion in the OH stretch-type normal
transition state geometry. The reduced dimensionality reac-
tion is displayed in Fig. 4 as a dashed line. Clary’s rate decreases less
strongly with increasing $1/T$ than the full-dimensional result.
It is in better agreement with experiment than the exact full-
dimensional calculation, but we believe that this agreement
is fortuitous (see below).

To get more insight into the effects of reduced dimen-
sionality approximation, reduced dimensionality calculations based on the normal coordinates employed in this work were
performed. Details are described in Sec. V. For comparison
with Clary’s results $k(T)$ was calculated including only the
normal coordinates $Q_4$, $Q_5$, and $Q_6$. This set of normal co-
dinates resembles most closely the set of Jacobi-type coordi-
nates employed in Clary’s work. The resulting reaction rate
is displayed in Fig. 4 as dash-dotted line. The difference
from Clary’s result is rather small, especially the temperature
dependence is very similar. This suggests that the deviation
between Clary’s calculation and the present full-dimensional one results from the neglect of three internal degrees of free-
dom in Clary’s calculation and not from a failure of the
J-shifting approximation invoked in the full-dimensional calcu-
lations. We conclude that Clary’s calculation is less accu-
rate than the present one for the given potential energy sur-
face but cancellation of errors produces better agreement of
his results with experiment.

V. EFFECTS OF DIMENSIONALITY

The previous section has demonstrated that theoretical results for the $H_2+OH\rightarrow H+H_2O$ reaction rate depend sensi-
tively upon how the different degrees of freedom are taken
into account. Many theoretical studies of reaction dynamics, es-
specially in larger systems, are based on models where mo-
tion in several degrees of freedom is neglected or treated adiabatically. Since such approximations will remain essen-
tial, it is important to investigate their effect. To this end we
have tested several reduced dimensionality models.

Though one expects such “reduced dimensionality” ap-
proximations to work best if local mode (or bond) coordi-
nates are used, it may often be the case for complex systems
that one will have only a normal mode description of the
transition state region. Thus our reduced dimensionality calcu-
lations are defined in terms of normal coordinates, assum-
ing motion in different sets of these coordinates to be separ-
able. These separable coordinates are described in a
harmonic approximation employing the frequency at the
transition state geometry. The reduced dimensionality reac-
tion probability is calculated employing the remaining coordi-
nates as described in Sec. II for the full-dimensional prob-
lem. For example, if motion in the OH stretch-type normal
coordinate $Q_1$ is assumed to be separable, a reduced dimension-
sionality cumulative reaction probability $N_{SP}(E)$ is calcu-
lated employing a Hamiltonian where the $Q_1$ coordinate is
frozen at its equilibrium value $Q_1=0$. The $Q_1$ mode is then
convoluted in the usual microcanonical fashion to produce the approximate cumulative reaction probability for the full
system,

$$N_{app}(E) = \sum_{n_1} N_{SP}[E - \hbar \omega_1 (n_1 + \frac{1}{2})].$$

(22)

Analogous procedures are employed when separability of
other degrees of freedom is assumed. The ratio of such ap-
proximate cumulative reaction probability to the exact full-
dimensional one, $[N_{app}(E)/N(E)]$, is used to measure the
accuracy of the approximate treatment.

In the calculations presented below separability of dif-
ferent sets of the coordinates $Q_1$ to $Q_4$ will be investigated.
Since the coordinate $Q_5$ is strongly coupled to the reaction
coordinate $Q_6$, nonsensical results are obtained if it is as-
sumed to be uncoupled. Thus all calculations below include
at least two degrees of freedom fully coupled, with the re-
mainings uncoupled ones convoluted microcanonical to ob-
tain the approximate $N(E)$ (all for $J=0$).

Figure 5 displays $N_{app}/N$ as a function of energy for various 5D calculations, i.e., where only one of the coordi-
nates is assumed to be separable and harmonic. It is imme-
diately seen that this approximation yields significant errors independent of the actual coordinate which is treated as be-
ing separable. Deviations are especially strong in the tunnel-
ing regime. There the approximate cumulative reaction prob-
ability is lower by a factor of up to 20 compared to the exact
6D result. Due to the exponential dependence of $N(E)$ on the
energy in this regime, even minor errors in the potential in-
duced by the separability approximation result in crucial er-
ors in the cumulative reaction probability. Since the assump-
tion of separability and harmonicity tends to overestimate the
potential energies, the approximate cumulative reaction probabilities are too small. For higher energies $N(E)$, where

![Figure 5. $N_{app}/N$ ratio as a function of energy for different five-dimensional approximations. Modes being separated are $Q_1$ (full line), $Q_2$ (long dashed line), $Q_3$ (dashed line), and $Q_4$ (dotted line).](image-url)
more states of the activated complex contribute to \(N(E)\), the precise energies of individual states are no longer of such crucial importance, and the deviation of \(N_{\text{app}}(E)\) from \(N(E)\) decreases with increasing energy. But even for the highest energies under consideration errors can be significant. In Fig. 5 the \(N_{\text{app}}\) are to low by 20\% to 50\% for three of the four cases studied.

So far general trends have been discussed. We now consider the effect of assuming separability of individual vibrational modes and the immediate findings are rather surprising. Separating (i.e., assuming separability for) the vibrational mode \(Q_1\), which describes O–H stretching motion, shows a larger effect on the results than separating any other mode; even at the highest energies under consideration \(N_{\text{app}}\) barely reaches above 50\% of the exact \(N(E)\). These findings are in apparent contradiction to the assumptions utilized in previous work on the \(\text{H}_2+\text{OH} \rightarrow \text{H}+\text{H}_2\text{O} \) reaction\(^7\), where the O–H stretching motion is assumed to be the least important degree of freedom. However, care has to be taken in such comparisons, since the present study normal coordinates as displayed in Fig. 1 gives the key to the explanation. Results are rather independent of which coordinates are separated. Only when all coordinates except \(Q_4\) are separated, \(N_{\text{app}}/N\) becomes considerably smaller than for any other combination. This finding is in agreement with results of Fig. 5 and Fig. 6; if \(Q_1\) is treated as separable larger errors are caused unless \(Q_4\) is also approximated as separable.

FIG. 6. \(N_{\text{app}}/N\) ratio as a function of energy for different four-dimensional approximations. Modes being separated are \(Q_1\) and \(Q_2\) (full line), \(Q_1\) and \(Q_3\) (long dashed line), \(Q_1\) and \(Q_4\) (dashed line), \(Q_2\) and \(Q_3\) (dotted line), \(Q_2\) and \(Q_4\) (dash–dot line), and \(Q_3\) and \(Q_4\) (thick full line).

Finally, Fig. 7 shows the result of various 3D calculations, i.e., \(N_{\text{app}}/N\) ratios obtained when three modes are approximated as separable. Differences compared to Fig. 6 are rather small, especially for higher energies. For lower energies the reaction rates are further decreased which is easily explained by the above arguments. Results are rather independent of which coordinates are separated. Only when all coordinates except \(Q_4\) are separated, \(N_{\text{app}}/N\) becomes considerably smaller than for any other combination. This finding is in agreement with results of Fig. 5 and Fig. 6; if \(Q_1\) is treated as separable larger errors are caused unless \(Q_4\) is also approximated as separable.
Therefore care has to be taken in judging the importance of the potential energy surface employed. Therefore comparison rates derived from the Schatz-Elgersma surface for the to experimental rates provides an unambiguous test of the quality of the surface. In the example presented here reaction probabilities and reaction rates for larger systems. Calculating these quantities for a four-atom reaction including all six internal degrees of freedom is demonstration of the power of this approach. To the best of our knowledge there have been no other exact quantum calculation of the cumulative reaction probability on a such a system up to now.

When reaction rates are calculated by an exact full quantum method the only remaining source of errors is generally the potential energy surface employed. Therefore comparison to experimental rates provides an unambiguous test of the quality of the surface. In the example presented here reaction rates derived from the Schatz-Elgersma surface for the reaction showed significant deviations from the experimental rates. Improvement of this surface thus appears to be necessary in order to obtain a quantitative description of this reaction.

Clearly the range of systems for which exact full-dimensional calculations are feasible is limited. Even for the reaction, which is a rather simple example of a four-atom reaction, the numerical effort of the full-dimensional calculation presented here is considerable: On an up to date workstation a few weeks of CPU time are required to compute the results presented. Therefore the development of approximate treatments is an important issue. But availability of exact reaction rates for a given potential energy surface is important, at least to serve as a reference when judging the quality of approximate results. As an example of the investigation of approximate treatments, reduced dimensionality treatments have been investigated in this work. Comparison to reduced dimensionality calculation of other authors as well as a systematic study of normal coordinate based reduced dimensionality have been presented. The findings indicates that correlation between motion in different normal coordinates can be important. In the present case, this results in a strong effect of the OH stretching type normal coordinate. Out-of-plane motion of the activated complex is found to be the least important degree of freedom.

VI. CONCLUSIONS

An exact quantum, full-dimensional calculation of the \((J=0)\) cumulative reaction probability for the reaction has been presented. From this data the reaction rate is calculated for temperatures between 300 and 700 K.

This calculation is of interest for several reasons. First, it demonstrates that the technique developed in Refs. 17 and 18 and Ref. 20 allows for efficient calculations of cumulative reaction probabilities and reaction rates for larger systems. Calculating these quantities for a four-atom reaction including all six internal degrees of freedom is demonstration of the power of this approach. To the best of our knowledge there have been no other exact quantum calculation of the cumulative reaction probability on a such a system up to now.

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30 J. M. Bowman and D. Wang (private communication).