Coupled-channel statistical theory of the $N(^{2}\text{D}) + \text{H}_2$ and $O(^{1}\text{D}) + \text{H}_2$ insertion reactions

Edward J. Rackham, Fermin Huarte-Larranaga¹, David E. Manolopoulos *

Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, UK

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Abstract

A detailed statistical theory of atom–dihalom insertion reactions is derived by combining the early statistical ideas of Pechukas and Light with the coupled-channel capture theory of Clary and Henshaw. The theory is applied to the $N(^{2}\text{D}) + \text{H}_2$ and $O(^{1}\text{D}) + \text{H}_2$ reactions and found to give results in good agreement with the exact quantum mechanical integral cross sections reported recently by Honvault and Launay. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Honvault and Launay have recently made significant progress in the quantum theory of chemical reactions by using their hyperspherical coordinate method to perform the first exact state-to-state calculations on the insertion reactions $N(^{2}\text{D}) + \text{H}_2$ [1,2] and $O(^{1}\text{D}) + \text{H}_2$ [3,4]. The potential energy surfaces of these reactions have deep wells (with depths of 5.5 and 7.3 eV, respectively), and they are consequently considerably more difficult to treat quantum mechanically than abstraction reactions like $\text{F}(^{2}\text{P}) + \text{H}_2$ [5]. The fact that benchmark results are now available for two different insertion reactions is therefore very impressive, and it is also very useful since these results can be used to test a variety of approximate theories.

One of the oldest approximate theories of insertion reactions is the statistical theory of Pechukas and Light [6]. The basic assumption of this theory is one of ergodicity: once the collision complex (NH$_2$ or H$_2$O) has formed it is equally likely to fall apart into any accessible reactant or product channel subject to the conservation of the total energy and angular momentum. In the case of the $N(^{2}\text{D}) + \text{H}_2$ reaction, there is clearly some justification for this assumption, since the exact reaction probabilities for this reaction have been shown to follow the Poisson distribution law that signifies quantum chaos in the collision complex [2]. Furthermore, the small departures from the Poisson Law observed by Honvault and Launay, which they attributed to product channels with large orbital angular momentum barriers and small kinetic energies [2], are quite consistent with a statistical theory (such as the one proposed by Pechukas and Light [6]) in which the effect of orbital angular momentum barriers is included. The only remaining question is therefore whether or
not sufficiently accurate results for reactions like N(\(^{2}\)D) + H\(_{2}\) and O(\(^{1}\)D) + H\(_{2}\) can actually be predicted using such a theory. 

In order to answer this question, it is desirable to drop some of the simplifying assumptions made by Pechukas and Light [6], such as the assumption that the interaction between the atom and the diatomic in each arrangement is spherically symmetric. This assumption is no longer necessary for either N(\(^{2}\)D) + H\(_{2}\) or O(\(^{1}\)D) + H\(_{2}\) because globally accurate potential energy surfaces are now available for both reactions [7–9]. Furthermore, the methods that are needed to treat anisotropic long-range interactions between atoms and diatomic molecules are now very well established in terms of the coupled-channel (CC) and coupled-states (CS) capture theories developed by Clary and Henshaw [10]. The obvious thing to do is therefore to combine these more modern capture theories with the earlier statistical ideas of Pechukas and Light, and this is what we do in Section 2. The resulting theory is then applied to the two reactions in Section 3, where the results are compared with those of Honvault and Launay’s exact calculations [1–4]. Our conclusions are presented in Section 4.

2. Theory

2.1. Detailed-balancing statistical theory

The exact quantum mechanical expression for a state-to-state integral cross section between an initial state \(vj\) of the reactants and a final state \(v'j'\) of the products in an atom–diatom chemical reaction is

\[
\sigma_{v'f \rightarrow vj}(E) = \frac{\pi \hbar^2}{2\mu(E - E_{vj})(2j + 1)} \times \sum_{j'f} (2j' + 1)p_{v'f', vj}^j(E),
\]

where \(\mu\) is the collision reduced mass, \(E\) is the total available energy, \(E_{vj}\) is the internal energy of the reactant state, and \(l\) and \(l'\) are the reactant and product orbital angular momentum quantum numbers. In the exact theory, the probability \(P_{v'f', vj}^j(E)\) in Eq. (1) is the square modulus of a scattering matrix element between channels \(vj\) and \(v'j'\) at the specified value of the total angular momentum quantum number:

\[
P_{v'f', vj}^j(E) = |S_{v'f', vj}^j(E)|^2.
\]

Since the scattering matrix is symmetric, this is the same as the probability \(P_{v'f', vj}^j(E)\) of a transition from channel \(v'j'l'\) to channel \(vjl\), and any approximate theory which maintains this symmetry is guaranteed to satisfy the principle of detailed balance [6].

With this in mind, it is natural to approximate \(P_{v'f', vj}^j(E)\) for an insertion reaction by

\[
P_{v'f', vj}^j(E) \approx \frac{P_{v'f', vj}^j(E)p_{v'j}^j(E)}{\sum_{v'f'} p_{v'f'}^j(E)},
\]

where \(p_{v'j}^j(E)\) is the capture probability (i.e., the probability of forming the collision complex) from the reactant channel \(vjl\), \(p_{v'f'}^j(E)\) is the capture probability from the product channel \(v'jl'\), and the sum over \(v'f'l'\) in the denominator runs over all energetically accessible reactant and product channels. Eq. (3) evidently satisfies the detailed balance requirement, and it is clear that within this approximation the ratio

\[
f_{v'f'}^j(E) = \frac{p_{v'f'}^j(E)}{\sum_{v'f'} p_{v'f'}^j(E)}
\]

can be interpreted as the fraction of collision complexes with angular momentum \(J\) and energy \(E\) that dissociate into the product channel \(v'jl'\).

The theory of Pechukas and Light [6] can be recovered from Eqs. (1) and (3) by making the further approximation that the interaction between the atom and the diatomic in each arrangement is spherically symmetric, \(V = V(R)\), and then computing the capture probabilities \(p_{v'j}^j(E)\) using classical capture theory:

\[
p_{v'j}^j(E) \approx \begin{cases} 1 & \text{if } E - E_{vj} > \max_r [V(R) + \hbar^2 l(l+1)/2\mu R^2], \\ 0 & \text{otherwise}. \end{cases}
\]

(If one retains only the leading term in the London expansion of \(V(R)\), so that \(V(R) = -C_6/R^6\) for neutral systems, then this expression for \(p_{v'j}^j(E)\) can
of course be simplified further [6].) However, as discussed in Section 1, the assumption that \( V = V(R) \) is no longer necessary for either of the reactions we are considering in this Letter.

### 2.2. Coupled-channel capture theory

A more rigorous way to compute the capture probabilities \( p_{ij}^j(E) \) in Eq. (3) is provided by the CC capture theory of Clary and Henshaw [10]. This theory involves solving a set of close-coupled equations within each arrangement with the standard inelastic scattering form [11,12]

\[
\Psi''(R) = W(R) \Psi(R),
\]

where

\[
W'_{ij,\gamma ij}(R) = \left[ \frac{2\mu}{\hbar^2} (E_{ij} - E) + \frac{l(l + 1)}{R^2} \right] \delta_{ij} \delta_{\gamma \gamma} \delta_{ff} + \frac{2\mu}{\hbar^2} V'_{ij,\gamma ij}(R),
\]

and

\[
V'_{ij,\gamma ij}(R) = \frac{[(2l'+ 1)(2l + 1)]^{1/2}}{(2J + 1)}
\]

\[
\times \sum_{k} \langle j'k'\gamma'k'0|jkl0\rangle \langle jk\gamma0|j'k'\gamma'k'0 \rangle V_{ij,\gamma ij}(R),
\]

with

\[
V_{ij,\gamma ij}(R) = 2\pi \int_{0}^{\pi} \sin \gamma \, d\gamma \int_{0}^{\infty} \, dr \, \phi_{ij}(r) Y_{jk}(\gamma, 0)
\]

\[
\times V(R, r, \gamma) \phi_{ij}(r) Y_{jk}(\gamma, 0).
\]

Here \( \langle jk0|j\lambda k0 \rangle \) is a vector-coupling coefficient, \( \phi_{ij}(r) \) is a diatomic vibrational wavefunction, \( Y_{jk}(\gamma, 0) \) is a spherical harmonic, and \( V(R, r, \gamma) \) is the interaction potential between the atom and the diatomic molecule. (Note that this interaction potential is not assumed to be spherically symmetric: \( V(R, r, \gamma) \) depends on the diatomic bond length \( R \) and the Jacobi angle \( \gamma \) in addition to the atom–diatom distance \( R \).)

In order to solve Eq. (6) subject to capture boundary conditions, we use the log derivative method [13,14], which involves integrating the matrix Riccati equation

\[
Y'(R) = W(R) - Y(R)^2
\]

for the log derivative matrix

\[
Y(R) = \Psi'(R)\Psi(R)^{-1}.
\]

Since Eq. (10) is a first-order differential equation, the value of \( Y(R) \) is uniquely determined once an appropriate initial value has been specified. It is not possible to define an exact quantum mechanical capture initial value, but it is possible to do so within the WKB approximation. Specifically, if we let \( C \) be the orthogonal matrix that diagonalises the coupling matrix at the capture radius \( R = R_c \),

\[
\tilde{C} W(R_c) C = -k_c^2,
\]

then the appropriate initial value is given by [10]

\[
\tilde{C} Y(R_c) C = \begin{cases} 
   -ik_c & \text{if } k_c^2 > 0, \\
   +|k_c| & \text{if } k_c^2 < 0.
\end{cases}
\]

The WKB capture approximation to \( Y(R_c) \) is thus a complex and symmetric matrix, and it follows from Eq. (10) and the symmetry of \( W(R) \) that \( Y(R) \) will remain complex and symmetric for all \( R \geq R_c \). (The origin of the complex arithmetic is the \(-ik_c\) in Eq. (13), which plays the role of an absorbing boundary condition at \( R = R_c \).

The basic idea is therefore to use Eq. (13) to initialise \( Y(R) \) at the capture radius \( R = R_c \), and then to integrate Eq. (10) from \( R_c \) to \( R_a \), where \( R_a \) lies at the entrance to the collision complex and \( R_a \) lies beyond the range of the interaction potential. Once \( Y(R_a) \) has been computed, it can be used to calculate a scattering matrix \( S'(E) \) using the standard formula

\[
S'(E) = \left[ Y(R_a) O(R_a) - O'(R_a) \right]^{-1}
\]

\[
\times \left[ Y(R_a) I(R_a) - I'(R_a) \right],
\]

where \( O(R) \) and \( I(R) \) are diagonal matrices with open-channel elements

\[
O_{ij}(R) = k_{ij}^{1/2} R h_{ij}(k_{ij} R),
\]

and closed-channel elements

\[
O_{ij}(R) = |k_{ij}|^{1/2} R k_{ij}(|k_{ij}| R),
\]

\[
I_{ij}(R) = k_{ij}^{1/2} R h_{ij}^2(k_{ij} R),
\]

\[
I_{ij}(R) = |k_{ij}|^{1/2} R l_{ij}(|k_{ij}| R),
\]

\[
I_{ij}(R) = k_{ij}^{1/2} R h_{ij}^2(k_{ij} R),
\]

\[
I_{ij}(R) = |k_{ij}|^{1/2} R l_{ij}(|k_{ij}| R),
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I_{ij}(R) = k_{ij}^{1/2} R h_{ij}^2(k_{ij} R),
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I_{ij}(R) = |k_{ij}|^{1/2} R l_{ij}(|k_{ij}| R),
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I_{ij}(R) = k_{ij}^{1/2} R h_{ij}^2(k_{ij} R),
\]

\[
I_{ij}(R) = |k_{ij}|^{1/2} R l_{ij}(|k_{ij}| R),
\]

\[
I_{ij}(R) = k_{ij}^{1/2} R h_{ij}^2(k_{ij} R),
\]

\[
I_{ij}(R) = |k_{ij}|^{1/2} R l_{ij}(|k_{ij}| R),
\]
and $k_i^2 = 2\mu(E - E_v)/\hbar^2$. (The functions $h_1^{(1)}(x)$ and $h_1^{(2)}(x)$ in Eqs. (15) and (16) are spherical Hankel functions, and $k_l(x)$ and $i_l(x)$ in Eqs. (17) and (18) are modified spherical Bessel functions [15].)

All of this is clearly very similar to a standard inelastic scattering CC calculation [11,12]. However, the key difference is that, since the log derivative matrix $Y(R)$ is complex-symmetric rather than real-symmetric, the open-channel submatrix of $S'(E)$ in Eq. (14) is not unitary. Physically, this lack of unitarity arises from capture by the collision complex, and allows us to compute the CC capture probability $p'_{vjl}(E)$ from channel $vjl$ as

$$ p'_{vjl}(E) = 1 - \sum_{v'j'l'} |S'_{v'j'l',vjl}(E)|^2, \quad (19) $$

where the sum runs over all the open channels.

2.3. Coupled-states capture theory

A considerably cheaper alternative to the CC capture theory described above is to make the CS (centrifugal-sudden [12] or coupled-states [16]) approximation within each arrangement [10]. This results in a smaller set of close-coupled equations for each value of the approximately conserved projection of the angular momentum on the atom–diatom axis. The elements of the CS coupling matrix $W(R)$ thus depend parametrically on the projection quantum number $l$ and are given by [12,16]

$$ W^R_{v'j'l'}(R) = \left[ \frac{2\mu}{\hbar^2} (E_{v'j'} - E) + \frac{l(l + 1)}{R^2} \right] \delta_{v'v} \delta_{j'j} $$

$$ + \frac{2\mu}{\hbar^2} v^k_{v'j'l'}(R), \quad (20) $$

where

$$ l = [J(J + 1) + j(j + 1) - 2k^2 + 1/4]^{1/2} - 1/2. \quad (21) $$

Since the CS close-coupled equations have the same form as in Eq. (6), the above capture theory carries over essentially unaltered. The only new twist comes from Eq. (21): the CS approximation requires the spherical Bessel functions in Eqs. (15)–(18) to be evaluated for non-integral values of $l$. Appropriate algorithms for doing this were devised by Temme [17,18] the year after the CS approximation was first introduced [12,16], and they are now readily available in the second edition of Numerical Recipes [19].

2.4. Symmetry considerations

In addition to the total angular momentum quantum number $J$ and the energy $E$, two further quantities are conserved in an exact calculation on an $A + B_2$ reaction: the $B_2$ diatomic permutation parity $p$ and the triatomic inversion parity $P$. It is therefore important to know how to treat these additional symmetries within the present theory.

The treatment of the diatomic parity $p$ is straightforward. In the $A + B_2$ reactant arrangement, one simply retains even or odd values of $j$ according to whether $p = (-1)^j$ is plus or minus one. The $A B_2$ collision complex so formed will then dissociate into either a symmetric or an antisymmetric linear combination of the two $A B + B$ product arrangements. However, since these arrangements are treated separately within the present theory, and since they are degenerate, the net effect of this is that only one of the two product arrangements need be retained.

The treatment of the triatomic parity $P = (-1)^{J+l}$ is also straightforward within the CC method, where one simply retains channels with even or odd values of $j + l$ according to whether $P = \pm 1$. However, it is less obvious how to deal with this parity within the CS approximation, where $l$ is no longer an integer and $P$ is therefore not well-defined. The right way to proceed seems to be to note that if one were to first construct the correct parity-adapted linear combinations of $+k$ and $-k$ states, and then apply the CS approximation (i.e. neglect the off-diagonal Coriolis coupling), one would obtain identical CS equations to those given above, but with $k$ ranging from 0 to $\min(J,j)$ in one parity block and from 1 to $\min(J,j)$ in the other. This is the way we have treated the triatomic parity in the CS calculations described below, where only the larger of the two parity blocks (with $k = 0$) contributes to the calculated cross sections from the $(v = 0, j = 0)$ initial state of the $H_2$ molecule.
3. Results and discussion

3.1. N(2D) + H₂

The N(2D) + H₂(X¹Σ⁺) → NH(X¹Σ⁻) + H(3S) reaction was the first insertion reaction to be considered by Honvault and Launay [1,2], who performed their exact hyperspherical coordinate calculations on the ground adiabatic (1^2A′′) potential energy surface of Pederson et al. [7]. This surface has a deep potential well corresponding to the NH₂ collision complex, with a well depth of 5.5 eV at a C₄ᵥ symmetry equilibrium geometry. In addition, there is a small insertion barrier in the reactant valley with a height of 84 meV and a saddle point with C₄ᵥ symmetry. As a result of the tunnelling through this insertion barrier, the exact quantum mechanical cross sections of Honvault and Launay [1] were found to be significantly larger at low collision energies than the quasi-

![Graph 1](image1.png)

Fig. 1. Computed N(2D) + H₂(v = 0, j = 0) → NH(v') + H integral cross sections at three different collision energies. Solid lines with circles: present statistical results. Dashed lines with diamonds: exact quantum mechanical results of Honvault and Launay [1].

![Graph 2](image2.png)

Fig. 2. Computed N(2D) + H₂(v = 0, j = 0) → NH(v', j') + H integral cross sections at Eₘₐₜ = 165 meV. Solid lines: CC statistical theory. Dotted lines: CS statistical theory. Dashed lines: exact quantum mechanical results of Honvault and Launay [1].

classical trajectory (QCT) cross sections reported by Pederson et al. [7].

The results of our statistical calculations on the N(2D) + H₂(v = 0, j = 0) reaction are compared with Honvault and Launay’s results in Figs. 1 and 2. In these calculations, we included all channels with internal energies E₂ ≤ 0.8 eV (relative to the bottom of the asymptotic reactant valley), and integrated Eq. (10) from a mass-scaled capture radius of Rₐ = 4 bohr to an asymptotic radius of Rₐ = 7 bohr in each arrangement. The fact that the integration range could be taken to be so small made even the full CC capture calculations relatively easy. Decreasing Rₐ to 3 bohr and increasing Rₐ to 8 bohr was found to have a negligible effect on the computed reaction probabilities.
Fig. 1 shows the resulting NH($v'$) product vibrational distributions at the three collision energies considered by Honvault and Launay [1]. The CC and CS statistical methods were found to give identical results for these vibrational distributions to graphical accuracy. One sees that, instead of underestimating the exact reactive cross sections at the lowest collision energy (70 meV), the present statistical theory slightly overestimates them. Since the underlying capture theory calculations were well converged with respect to the choice of the capture radius $R_c$, the WKB approximation in Eq. (13) cannot be blamed for this discrepancy. The small disagreement between the absolute values of the statistical and exact cross sections in the uppermost panel of Fig. 1 must therefore be attributed to a breakdown of the statistical assumption in Eq. (3), this being the only other approximation in the CC statistical theory. The agreement with Honvault and Launay’s exact results becomes noticeably better by the time the collision energy reaches 165 meV, where there are more open channels in the reactant and product arrangements and the statistical assumption has increased validity.

Fig. 2 shows that the good agreement between the statistical and exact results at this higher collision energy extends to the more detailed level of the NH($v'$,$j'$) product rotational distributions. At this level, a slight difference between the CC and CS statistical results becomes apparent at high rotational quantum numbers. It is interesting that this difference almost exactly cancels when one sums over the $j'$ quantum number to obtain the product vibrational distributions in Fig. 1. The only apparent effect of making the CS approximation is thus to sharpen the high-$j'$ tails of the product rotational distributions as seen in Fig. 2.

3.2. O(1D) + H$_2$

The O(1D) + H$_2$(X$^1\Sigma^+_g$) → OH(X$^2\Pi$) + H($^2$S) reaction is very similar in many respects to the N(2D) + H$_2$ reaction considered above, but there is one significant difference. The best available ground adiabatic (X$^1\Lambda'$) potential energy surface for this reaction again has a very deep well, with a depth of 7.3 eV at the C$_{2v}$ symmetry equilibrium geometry of the water molecule [8,9]. However, it does not have an insertion barrier in the entrance channel. As a result, both the exact quantum mechanical [3] and QCT [4] cross sections for this reaction decrease with increasing collision energy, and since there is no tunnelling in the reactant arrangement the QCT approximation is comparatively reliable [4,20].

The results of our statistical calculations on the O(1D) + H$_2$ reaction are compared with Honvault and Launay’s results in Figs. 3–5. In these calculations, we retained all channels with internal energies $E_{ij} \leq$ 0.5 eV, and integrated Eq. (10) from a mass-scaled capture radius of $R_c = 4$ bohr to an asymptotic radius of $R_c = 8$ bohr in each arrangement. These parameters were again determined to give well-converged reaction probabilities at all three of the collision energies studied by Honvault and Launay [3].

![Computed O(1D) + H$_2$(v = 0, j = 0) → OH(v') + H integral cross sections at three different collision energies. Solid lines with circles: present statistical results. Dashed lines with diamonds: exact quantum mechanical results of Honvault and Launay [3].](image)
Fig. 4. Computed O($^1$D) + H$_2$(v = 0, j = 0) → OH(v’,j’) + H integral cross sections at $E_{coll}$ = 25 meV. Solid lines: CC statistical theory, Dotted lines: CS statistical theory. Dashed lines: exact quantum mechanical results of Honvault and Launay [3].

Fig. 3 shows that the product OH(v’) vibrational distributions for this reaction are almost perfectly statistical: the difference between the present (CC and CS) statistical results and Honvault and Launay’s exact results is probably too small to be detectable experimentally. It is not clear whether the better agreement between the statistical results and the exact results for this reaction is due to its deeper potential energy well (7.3 versus 5.5 eV), or to its greater exothermicity (1.9 versus 1.3 eV), both of which might be expected to improve the validity of the statistical assumption in Eq. (3).

Figs. 4 and 5 show that the agreement seen in Fig. 3 extends to the more detailed level of the product OH(v’,j’) rotational distributions at the lowest (25 meV) and highest (100 meV) collision energies considered by Honvault and Launay. Once again, one sees a small difference between the CC and CS results at this more detailed level, in very much the same way as for the N($^2$D) + H$_2$ reaction in Fig. 2.

Finally, it is worth mentioning that O($^1$D) + H$_2$ → OH(v’,j’) + H product state distributions very similar to those shown in Figs. 3–5 have recently been measured by Yang and co-workers [20] using the Rydberg tagging time-of-flight technique. The present calculations suggest that the distributions observed in this study were essentially statistical in the sense of Eq. (3).
4. Concluding remarks

In this Letter, we have derived two modern statistical theories of atom–diatom insertion reactions by combining the early statistical ideas of Pechukas and Light [6] with the CC and CS capture theories of Clary and Henshaw [10]. The accuracy of these theories has been calibrated by comparing their predictions with Honvault and Launay’s exact results for N(2D) + H₂ and O(1D) + H₂ [1–4]. It is particularly encouraging that even the simple CS statistical theory was found to give absolute state-to-state integral cross sections in satisfactory agreement with the exact results for both reactions (see Figs. 1–5). This theory is computationally trivial by modern standards, and indeed the present CS calculations took only a few minutes of computer time on a Pentium III PC.

Perhaps the most interesting conclusion that can be drawn from the present results is that state-to-state reaction cross sections for reactions with strongly bound intermediate complexes are comparatively insensitive to either the potential energy surface or the dynamics in the collision complex region. This follows because the capture probabilities \( p_{ij}^T(E) \) that enter the statistical formula in Eq. (3) can be computed without any reference to the potential in the region of the strongly bound well. The basic assumption that leads to Eq. (3) and allows us to eliminate the well region from the calculation is that the dynamics of the collision complex is ergodic; this assumption seems to be well justified for the N(2D) + H₂ and O(1D) + H₂ reactions on the basis of the results in Figs. 1–5. It may be interesting in future work to see whether or not the assumption is equally well justified for less strongly exothermic insertion reactions such as C(1D) + H₂.

Given the success of the present calculations, we are now also considering various extensions of the theory, including: (a) the inclusion of electronically non-adiabatic effects, (b) an extension to polyatomic insertion reactions, and (c) the statistical calculation of differential reaction cross sections. As far as the first of these extensions is concerned, there are a number of interesting issues that could be addressed, such as whether or not the present approach is sophisticated enough to predict the correct \( ^1 \Lambda \)-doublet populations in the OH(2Π) product of O(1D) + H₂ [21]. The extension to polyatomic insertion reactions should be facilitated by the fact that the present theory only requires the long-range intermolecular forces in each arrangement, which are considerably simpler to calculate than the full potential energy surface of a polyatomic chemical reaction [22,23]. Finally, the calculation of differential cross sections should also in principle be quite straightforward [24], although this requires a second statistical assumption (the random phase approximation) in addition to the assumption we have made in Eq. (3).

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References