

APPLICATIONS OF QUANTUM STATISTICAL METHODS TO THE TREATMENT OF COLLISIONS

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I. INTRODUCTION

In chemical kinetics, statistical theories were first developed to understand unimolecular reactions and predict their rates (see, for example, [1, 2]). In the field of molecular reaction dynamics, we would expect statistical models to be well suited to reactions proceeding through formation and decay of a strongly bound collision complex. Examples would be the reaction

of electronically excited atoms with H_2 [$C(^1D)$, $N(^2D)$, $O(^1D)$, and $S(^1D)$, for instance]. Here, atom M inserts into the $H-H$ bond with the subsequent formation of a transient HMH complex, which then decays to form $MH + H$ products.

Statistical models for reactions involving the formation and decay of a complex were first proposed in the 1950s to describe nuclear collisions [3]. These models were then applied to molecular collisions [4]. Molecular statistical theories were put on a firm theoretical footing by Miller [5], who used as justification the formal theory of resonant collisions [6–8].

Pechukas and Light [9, 10] pioneered a statistical theory to predict the rate and product internal state distribution of the reaction of an atom with a diatomic molecule. This theory was based on Light's work on the phase space theory of chemical kinetics [11, 12] but, in addition, imposed detailed balance. This work has formed the basis of modern quantum mechanical treatments of complex-forming chemical reactions [13–17]. Here, once the complex is formed, it can fall apart to yield any accessible reactant or product subject to conservation of the total energy and angular momentum.

Pechukas and Light [9, 10] made some additional simplifications: First, they assumed that the capture probability was zero or one, depending on whether the reactants had sufficient energy to surmount the centrifugal barrier for each partial wave (related to the total angular momentum J of the collision complex). Second, they assumed that the long-range potential could be described by an inverse power law, $-C R^{-n}$. These assumptions, particularly the latter, were reasonable in an era where calculation of a potential energy surface (PES) was a major undertaking.

Subsequently, Clary and Henshaw [13] showed how to apply time-independent (TID) coupled-states and close-coupling methods to the determination of capture probabilities for systems with anisotropic long-range interactions. More recently, Manolopoulos and coworkers [14, 15] combined the statistical considerations of Pechukas and Light with the Clary–Henshaw TID quantum capture probabilities, using, in addition, accurate *ab initio* potential energy surfaces. This so-called “quantum statistical” method has been applied to a number of atom–diatom reactions that proceed through the formation and decay of a deeply bound complex. Guo has demonstrated how a time-dependent (wavepacket, WP) determination of the scattering wave function can be used in an equivalent quantum-statistical investigation of reactions proceeding through deep wells [18].

In related work, Quack and Troe [19] developed an adiabatic channel model to describe the unimolecular decay of activated complexes.

This theory has been applied to a variety of processes, including the OH + O reaction [20].

González-Lezana [21] has written a comprehensive review of the use and applicability of quantum statistical models to treat atom–diatom insertion reactions. A good agreement with full quantum reactive scattering calculations has been found for properties such as the differential cross sections for the reactions of C(^1D) and S(^1D) with H_2 , while less satisfactory agreement was found for the O(^1D) and N(^2D) + H_2 reactions [15]. This comparison illustrates a limitation of the statistical theory: how to assess the accuracy of the approach without recourse to more onerous calculations. The differential cross-section of the product of a statistical reaction should have forward–backward symmetry. This is often not quite the case because the quenching of interferences between partial waves is not complete, particularly in the forward and backward directions [22].

Typically, fully quantum scattering calculations involve expansion of the scattering wavefunction in terms of all the triatomic states that are energetically accessible during the collision. The computational difficulty scales poorly with the number of these internal states. Both the large number of accessible vibrational states of a triatomic as well as the rotational degeneracy of the states corresponding to the A + BC orbital motion contribute to this bottleneck. Deep wells in any transient $\text{ABC}^\ddagger$ complexes are particularly problematic. An example is the O(^1D) + $\text{H}_2 \rightarrow \text{OH} + \text{H}$ reaction, for which the PESs are illustrated schematically in Fig. 1. Even without taking anharmonicity into account, there are >1900 H_2O vibrational levels

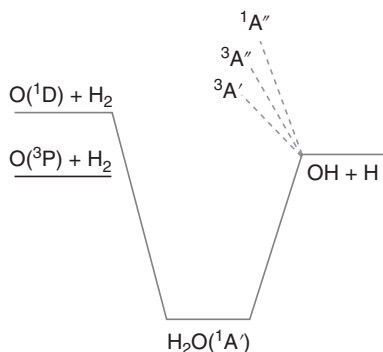


Figure 1. Schematic diagram of the potential energy surfaces of the OHH system. Only the lowest ($^1\text{A}'$) PES was taken into account in the initial quantum statistical calculations on the O(^1D) + H_2 reaction [14, 15]. Note that H_2O ($^1\text{A}'$) well lies $\approx 59,000\text{ cm}^{-1}$ below the O(^1D) + H_2 asymptote. Adapted from Rackham *et al.* 2001 [14] and Rackham *et al.* 2003 [15].

with energy below the $\text{O}(^1\text{D})+\text{H}_2$ asymptote. And this does not include rotational levels. Thus, full quantum reactive scattering calculations for complex-mediated reactions are a heroic task [23].

In the quantum statistical method, the close-coupled scattering equations are solved outside of a minimum approach distance, the “capture radius” R_{C} , at which point the number of energetically accessible states (open channels) is much less than at the minimum of the $\text{ABC}^\ddagger$ complex. Also, because the point of capture occurs well out in the reactant and/or product arrangement, one does not need to consider the mathematical and coding complexities associated with the transformation from the reactant to product states [24]. It is these simplifications that make the quantum statistical method so attractive.

Formation of a transient complex does not always lead to chemical reaction. The complex may decay to the reactant arrangement, resulting in an inelastic collision. The present review outlines the application of quantum statistical theory to nominally nonreactive collisions that access PESs having one or more deep wells. Consider, the generic $\text{A} + \text{BC} \rightarrow \text{ABC}^\ddagger \rightarrow \text{AB} + \text{C}$ collision. The inelastic event $\text{A} + \text{BC}(v, j) \rightarrow \text{A} + \text{BC}(v', j')$ can occur in a direct (non-complex-forming) collision, either through an encounter in which the partners approach in a repulsive geometry or at a larger impact parameter, where the centrifugal barrier prevents access to the complex. In addition, complex formation ($\text{ABC}^\ddagger$) and subsequent decay into the reactant arrangement will also contribute to inelasticity.

In general, weak, glancing collisions contribute substantially to rotational inelasticity. Thus, one might naively expect that both direct and complex-forming processes will contribute to rotational inelasticity. By contrast, vibrational inelasticity in collisions on basically repulsive PESs is very inefficient [25, 26], because the variation of repulsive PESs with the vibrational modes of the molecular moiety is weak. Thus, one might anticipate that the formation of a transient complex, in which substantial change in the bond distances might occur, could make a major contribution to vibrational relaxation.

Also, for $\text{A} + \text{BC}$ collision systems where one of the reactants is an open-shell species, typically (as shown schematically in Fig. 1), there are a number of electronic states that correlate with the $\text{A} + \text{BC}$ (or $\text{AB} + \text{C}$) asymptote. Of these states, one (or, only a few) leads to strongly bound $\text{ABC}^\ddagger$ intermediates, while the others are repulsive. The branching between the energetically accessible fine-structure levels of the products (in the case of OH, the spin-orbit and Λ -doublet levels) will be controlled by the coupling between the various electronic states as they coalesce in

the product arrangement, as the complex decays. We might predict that this branching, which can often be measured experimentally [27, 28], would be insensitive to any couplings within the $ABC^\dagger$ complex, where the excited electronic states lie high in energy, and hence be an ideal candidate for prediction by a quantum-statistical calculation.

Reactions involving isotopologs of the same atom,



where $\tilde{B}$ designates an isotopolog of B, are an additional example where the quantum statistical method can provide predictions and useful insight into potential experiments.

The next section contains a formal review of the quantum-statistical method, followed, in the remainder of this review, by a discussion of applications of this method to the problems introduced earlier in this section. In addition, and related to our discussion of inelastic collisions in the presence of a collision complex, we will use the quantum statistical method to calculate transport cross sections, which are weighted averages of differential cross sections. Here, the goal will be the determination of transport cross sections for the $A + BC$ collision pair, in the presence of a deep $ABC^\dagger$ well.

II. QUANTUM STATISTICAL THEORY

Here, we describe the extension of the quantum statistical method to inelastic scattering, in the TID formulation due originally to Manolopoulos and coworkers [14, 15, 21]. Guo and coworkers have described an equivalent time-dependent formulation [29, 30], which they have applied to a number of reactive collisions. In principle, this time-dependent methodology could also be applied to inelastic scattering.

Consider the collision of two particles with internal structure, for example an open-shell molecule or atom, with total angular momenta j_1 and j_2 , respectively. We suppress any other labels, for example the fine-structure manifold F_i for an open-shell molecule, required to designate fully the levels. The integral cross section for a transition between the initial level pair $i = (j_1, j_2)$ and a final level pair $f = (j'_1, j'_2)$ at total energy E is given by the expression

$$\sigma_{i \rightarrow f} = \frac{\pi \hbar^2}{2\mu(E - E_i)[j_1][j_2]} \sum_{Jj'_{12}L'j_{12}L} (2J+1) P_{\tilde{f}j'_{12}L', ij_{12}L}^J(E) \quad (2)$$

In Eq. (2), E_i is the internal energy of the initial level pair, μ is the collision reduced mass, J is the total angular momentum, L and L' are the initial and

final orbital angular momenta, and $[x] \equiv 2x + 1$. The angular momenta $\mathbf{j}_{12}$ and $\mathbf{j}'_{12}$ are vector sums of $\mathbf{j}_1 + \mathbf{j}_2$, and $\mathbf{j}'_1 + \mathbf{j}'_2$, respectively. Note that the cross section for transition from pair j_1, j_2 to pair j'_1, j'_2 involves, implicitly, a multiple summation over the projection quantum numbers of both angular momenta, as well as that of the orbital angular momentum of the collision partners. For the collision of a molecule with a structureless atom, we have $j_2 = j'_2 = 0$, $j_{12} = j_1$, and $j'_{12} = j'_1$.

The thermal rate constant as a function of temperature is given by [31]:

$$k_{i \rightarrow f}(T) = \left(\frac{8}{\pi \mu} \right)^{1/2} \frac{1}{(k_B T)^{3/2}} \int_0^\infty \sigma_{i \rightarrow f}(E_c) E_c e^{-E_c/k_B T} dE_c \quad (3)$$

In Eq. (3), k_B is the Boltzmann constant and E_c is the collision energy ($E_c = E - E_i$).

In a quantum description, the probability $P_{ff'_{12}L', ij_{12}L}^J(E)$ of a transition between the initial and final scattering states (channels) for total angular momentum J is given by the square modulus of the T (or S) matrix element between these states:

$$P_{ff'_{12}L', ij_{12}L}^J(E) = \left| T_{ff'_{12}L', ij_{12}L}^J \right|^2 = \left| \delta_{ff'_{12}L', ij_{12}L} - S_{ff'_{12}L', ij_{12}L}^J \right|^2 \quad (4)$$

The S matrix can be obtained by the imposition of scattering boundary conditions with a TID close-coupling determination of the scattering wave function. Several extensive reviews of the general equations for inelastic scattering (with application to rotationally inelastic scattering) are available [32–34].

In the quantum statistical theory [14, 15], the probability $P_{ff'_{12}L', ij_{12}L}^J(E)$ in Eq. (2) is computed as

$$P_{ff'_{12}L', ij_{12}L}^J(E) = p_{ij_{12}L}^J(E) f_{ff'_{12}L'}^J(E) \quad (5)$$

where $p_{ij_{12}L}^J(E)$ is the capture probability, namely the probability of forming the collision complex from the initial level pair i in the scattering channel j_{12}, L for total angular momentum J . In Eq. (5), $f_{ff'_{12}L'}^J(E)$ is the fraction of collision complexes with total angular momentum J , which dissociates into the final level pair in the scattering channel j'_{12}, L' and equals

$$f_{ff'_{12}L'}^J(E) = \frac{p_{ff'_{12}L'}^J(E)}{\sum_{f''j''_{12}L''} p_{f''j''_{12}L''}^J(E)} \quad (6)$$

As discussed by Rackham *et al.* [14], the quantum statistical cross sections obey detailed balance.

Since the scattering event can lead to the formation of a collision complex, the S matrix element is not unitary. Unlike the theory of Pechukas and Light [9, 10], the quantum statistical capture probability can lie between zero and one. The capture probability for initial level pair i in the scattering channel j_{12}, L can be computed as

$$p_{ij_{12}L}^J(E) = 1 - \sum_{f'j'_{12}L'} |S_{f'j'_{12}L', ij_{12}L}|^2 \quad (7)$$

where the sum is over all open channels.

The scattering equations for the quantum statistical theory are identical to those in conventional inelastic scattering. The difference lies in the boundary conditions. In the quantum statistical theory, the close-coupling equations are integrated out from the capture radius, which defines the outer extent of the complex. As in the treatment of inelastic and reactive collisions, it is convenient to use the log-derivative method [35, 36]. In our work, we have implemented Airy boundary conditions, corresponding to a linear reference potential at R_C [37]. In this way, for systems involving multiple attractive and repulsive PESs at R_C , fluxes on all the surfaces are treated on an equal footing. Unlike conventional scattering, for which the log-derivative matrix is real, here the log-derivative matrix is complex. The radial scattering differential equations are integrated using a linear reference potential in each sector [38].

An alternative to solution of the full, close-coupling equations is the use of the coupled-state approximation (CS) [39]. Rackham *et al.* [14] provided details on the implementation of the CS approximation within the quantum statistical method.

In applications of the quantum statistical theory, the scattering wave function, and hence its logarithmic derivative, is usually expanded in a body-fixed basis since the interaction is expressed more simply than in a space-fixed basis. In the asymptotic region, the log derivative is transformed to the space-fixed frame [40], and the standard scattering boundary conditions are applied.

In reactive collisions, the product can be formed only by formation and decay of the collision complex, that is, in an indirect collision. By contrast, collision-induced inelastic transitions can proceed both directly, without the intervention of a collision complex, and indirectly. The probability $P_{ff'_{12}L', ij_{12}L}^J(E)$ in the expression in Eq. (2) for the state-to-state cross section is given by the exact expression (Eq. (4)) for a direct collision added to the cross section predicted by the statistical approximation (Eq. (5)) for an indirect collision.

III. FINE-STRUCTURE BRANCHING IN REACTIVE $\text{O}(^1\text{D}) + \text{H}_2$ DYNAMICS

In the original application of the quantum statistical method to the $\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$ reaction [14, 15], a single PES, of $^1\text{A}'$ symmetry and including the $\text{H}_2\text{O}(\tilde{\text{X}}^1\text{A}')$ well, was employed. As discussed above, these calculations were compared with full, quantum reactive scattering calculations [23] to check the validity of the statistical approximation.

This single-PES treatment of this reaction does not capture several important features of the dynamics. As Fig. 1 shows, there are four PESs that emanate from the product $\text{OH} + \text{H}$ asymptote. The two states of triplet spin multiplicity correlate with the $\text{O}(^3\text{P}) + \text{H}_2$ asymptote [41]. The highest-energy state, $^1\text{A}''$, correlates with the first excited singlet H_2O state [42]. The energy spacing between these PESs decreases as the products separate, and we may expect nonadiabatic effects in the dynamics.

In addition, the OH molecule is an open-shell radical possessing nonzero orbital and spin angular momenta. As shown in Fig. 2, the levels of OH are split into two fine-structure manifolds separated by the spin-orbit splitting. The lower/upper fine-structure manifolds are designated F_1 and F_2 , respectively. The lower rotational levels lie close to the Hund's case (a) limit, with projection quantum numbers $\omega = \frac{1}{2}$ and $\frac{3}{2}$, respectively, for the two manifolds, but rapidly go to intermediate-case coupling as j increases. Each rotational/fine-structure level $j F_i$, where $i = 1$ or 2 , is further split into two nearly degenerate levels, called Λ -doublets, of

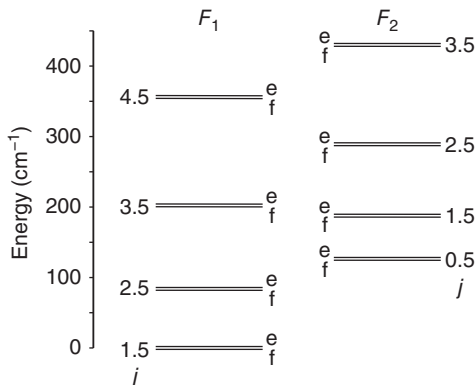


Figure 2. Energies of the lower rotational/fine-structure levels of the $\text{OH}(\text{X}^2\Pi, v = 0)$ manifold. The Λ -doublet splitting has been exaggerated for clarity.

opposite parity, with symmetry index ϵ equal to $+1$ and -1 for the e and f levels, respectively [43, 44].

In their experimental investigations of the dynamics of the $\text{O}(^1\text{D}) + \text{H}_2$ reaction, Butler, Wiesenfeld, and their coworkers [27, 28] employed laser fluorescence detection to probe the OH products over a wide range of rotational levels. The most striking feature of the product state distribution was the propensity for the OH product to appear preferentially in the $\Pi(\text{A}')$ Λ -doublet levels [45]. This aspect of the product state distribution is not captured in the single-PES calculations.

By including all four OHH PESs (Fig. 1) and the open-shell nature of the OH product, Alexander *et al.* [37] were able to compute multiplet-resolved cross sections for the formation of the OH rotational/fine-structure product levels. They carried out internally contracted multireference configuration interaction (icMRCI) calculations [46] of the four PESs emanating from the OH + H asymptote as a function of the OH bond length r and the Jacobi coordinates R and θ . Figure 3 presents plots of these PESs for the OH bond

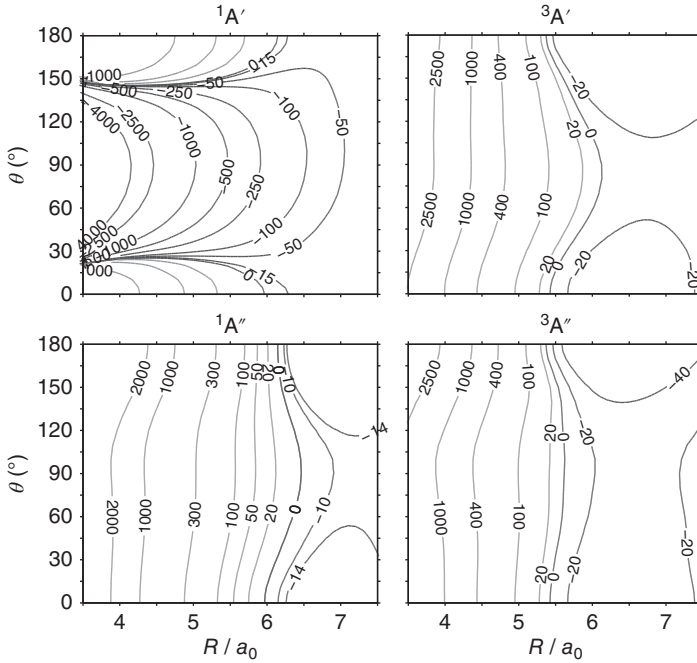


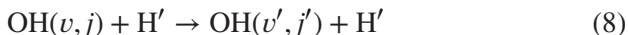
Figure 3. Contour plots (in cm^{-1}) of the $\text{OH}(r_0)\text{-H}$ PESs for the (top row) $^1\text{A}'$, $^3\text{A}'$, and (bottom row) $^1\text{A}''$, $^3\text{A}''$ states determined at the $v = 0$ vibrationally averaged OH bond length $r_0 = 1.8116a_0$. The angle $\theta = 0^\circ$ corresponds to linear OHH geometry.

length fixed at the equilibrium value $r_0 = 1.8116a_0$. We see that the $^1A'$ PES is quite anisotropic, being significantly repulsive near linear geometry, but is strongly attractive in bent geometries, leading to the deep $H_2O(\tilde{X}^1A')$ minimum. The other three PESs are considerably less anisotropic and primarily repulsive (except for a weak van der Waals attractive region in a long range). We see that the A' and A'' states of a given spin multiplicity are degenerate in linear geometry; the linear approach of $OH(X^2\Pi)$ to $H(^2S)$ yields $^1\Pi$ and $^3\Pi$ states, both doubly degenerate.

As will be seen in the next sections, the availability of these PESs allows calculation of cross sections and rate constants for $OH + H$ inelastic collisions, as well as treatment of the $O(^1D) + H_2$ reaction. The treatment of the scattering with inclusion of all four PESs and the open-shell nature of the OH and H collision partners is considerably more complex than in the single-PES calculations.

IV. INELASTIC $OH + H$ COLLISIONS

Atahan and Alexander [47] reported a theoretical study of rovibrational relaxation in $OH + H$ collisions. For these processes, relaxation can occur through direct (noncapture) scattering, without exchange of H , namely



by decay of the complex back to the original arrangement



or by decay of the complex accompanied by H exchange



Schematically, the PESs can be adapted from Fig. 1, as shown in Fig. 4.

Here, we outline the treatment of the inelastic scattering dynamics, including the electronic degrees of freedom. The total Hamiltonian for the $OH + H$ system can be written as

$$H(\mathbf{R}, \mathbf{r}, \mathbf{q}) = T_{\text{nuc}}(\mathbf{R}) + H_{\text{el}}(\mathbf{q}; \mathbf{R}, \mathbf{r}) + H_{\text{mol}}(\mathbf{q}; \mathbf{r}) \quad (11)$$

In Eq. (11), the electronic coordinates are denoted collectively as $\mathbf{q}$. The total Hamiltonian includes the nuclear kinetic energy T_{nuc} , the electronic interaction H_{el} between OH and H , and the Hamiltonian H_{mol} describing the isolated OH molecule. The latter includes vibrational and rotational motion of OH , as well as the spin-orbit interaction and the Λ doubling [48].

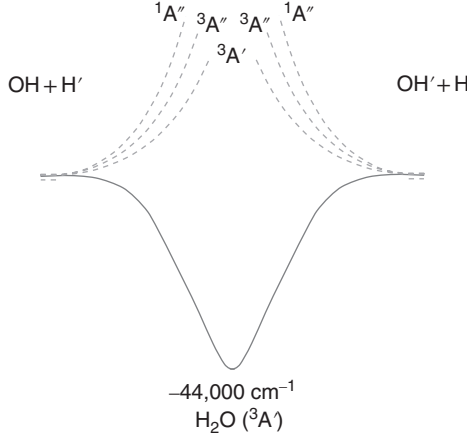


Figure 4. Schematic diagram of the potential energy surfaces relevant to $\text{OH}(v, j) + \text{H} \rightarrow \text{OH}(v', j') + \text{H}$ inelastic scattering. Relaxation can occur through both noncapture (direct) inelastic scattering (Eq. (8)) as well as direct (no hydrogen exchange; Eq. (9)) and exchange processes (Eq. (10)), both of which can sample the deep H_2O (^3A) well.

The overall wave function of the OH–H system was expanded in an uncoupled, Hund’s case (a) basis

$$|JMKvj\lambda\sigma\sigma_{\text{H}}\rangle = ([J]/8\pi)^{1/2} D_{MK}^{J*}(\Omega) \times ([j]/2)^{1/2} d_{k\omega}^j(\theta) \chi_{vj}(r) |\lambda\sigma\rangle |\sigma_{\text{H}}\rangle \quad (12)$$

Here, the D and d designate full and reduced rotation matrix elements [49], Ω denotes the Euler angles relating the space and body frames, and J is the total angular momentum, with projections M and K along the space-frame Z and body-frame z (i.e., along $\vec{r}$ axis), respectively. The function χ describes the OH vibrational wave function. The rotational angular momentum of the OH radical is j , which has projections k and ω along $\vec{R}$ and $\vec{r}$, respectively. The ket $|\lambda\sigma\rangle$ represents the OH electronic wave function, where λ and σ are the projections of the OH electronic orbital and spin angular momenta along $\vec{r}$ and $\omega = k + \sigma$. The ket $|\sigma_{\text{H}}\rangle$ denotes the electronic wave function of the H atom, with projection σ_{H} of the H atom spin along $\vec{R}$.

The matrix elements of the electronic Hamiltonian H_{el} in the basis defined in Eq. (12) are linear combinations of the interaction potentials of the four OHH electronic states. The calculation of these matrix elements is described in detail in Ref. [37]. It should be noted that the matrix

elements were determined by numerical quadrature in r and θ . The rovibrational/fine-structure energies and wave functions of the OH radical are obtained by diagonalizing H_{mol} in a definite-parity, Hund's case (a) basis defined by

$$|\omega\epsilon\rangle = 2^{-1/2}[|\lambda\sigma\rangle + \epsilon|\lambda, -\sigma\rangle] \quad (13)$$

where ω can take on the positive-definite values $\frac{1}{2}$ and $\frac{3}{2}$, and $\epsilon = \pm 1$. The e and f λ -doublets have $\epsilon = +1$ and -1 , respectively. In this basis, the matrix of H_{mol} is diagonal in ϵ , and its matrix elements have been given previously [48, 49].

The OHH wave function is expanded in the basis of Eq. (12). Premultiplication by each of the basis functions, integration over all electronic and nuclear coordinates except R , and evaluation of the resulting matrix elements lead to the corresponding set of close-coupled equations. These equations are solved subject to the capture boundary conditions, as discussed in Section II.

For direct scattering, the inelastic transition probabilities and resulting cross sections are proportional to the square of the corresponding T -matrix elements [Eq. (4)]. For the contribution to the inelastic cross sections arising from collisions that enter the attractive well, the cross sections are given by the quantum statistical expression [Eq. (5)] regardless of whether the identity of the proton is retained or not. Further, since the initial and final H atom spin projection is not specified, cross sections between specific OH initial and final rotational/fine-structure levels are computed by averaging and summing over the initial and final H atom spin projections:

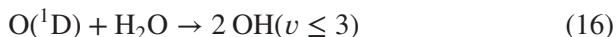
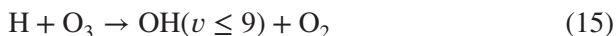
$$\sigma_{jF_i\epsilon \rightarrow j'F'_i\epsilon'} = \frac{1}{2} \sum_{\sigma_H\sigma'_H} \sigma_{jF_i\epsilon\sigma_H \rightarrow j'F'_i\epsilon'\sigma'_H} \quad (14)$$

The following sections describe the application of the quantum statistical method for the calculation of cross sections and rate constants for various processes involving collisions of the OH radical with hydrogen atoms. These calculations have employed the above formalism with the PESs presented in Section III.

A. OH + H Vibrational Relaxation

The OH radical is an important species in combustion, the earth's atmosphere, and in the interstellar medium. In the earth's atmosphere, vibrationally excited OH is generated in the mesopause and the stratosphere

and troposphere, by reactions 15 and 16, respectively:



Knowledge of the rates of OH vibrational relaxation is needed to model the atmospheric chemistry of the OH radical, which is an important oxidant in the atmosphere. The collisional vibrational relaxation of OH($X^2\Pi$) by inert gasses and diatomic and polyatomic molecules has been the subject of a number of experimental studies (see [50] and references cited therein).

Smith and Williams [51] have argued that the rate of vibrational relaxation for interaction of potentially reactive collision partners should be greater than for nonreactive encounters. In particular, in a radical–radical collision, a deep well can usually be accessed without a barrier. In this case, as discussed in Section I, the bond length of the molecular collision partner(s) should be strongly coupled with the other degrees of freedom. Consequently, a statistical model will be appropriate to compute the rate of vibrational relaxation. A further consequence is that the relaxation rate should not depend significantly on the vibrational level since the rate of relaxation will depend primarily on the rate of formation of the collision complex [51].

We have seen in Figs. 3 and 4 that a deep well exists in the PES of one of the states emanating from OH + H. Thus, the quantum statistical method [14, 15] should be appropriate to compute the rate of OH vibrational relaxation in collision with H atoms. Atahan and Alexander [47] employed the coupled-states [14, 39] version of the quantum statistical method to compute the rate of vibrational relaxation of OH($v = 1, 2$) in collision with H atoms. As discussed earlier (Eqs. 8–10), there will be both direct and indirect contributions to the cross section, and hence the rate constant (Eq. (3)). Recall (Fig. 1) that the O(^1D) + H₂ channel is endoergic, so that the OHH complex can only decay to OH + H.

Figure 5 displays the dependence on the collision energy of the cross section for vibrational relaxation of the lowest OH($X^2\Pi$) rotational/fine-structure level ($j = \frac{3}{2} F_1$, see Fig. 2) to the $v = 0$ ground vibrational level, summed over all final rotational/fine-structure levels. We see that the vibrational relaxation cross section is dominated by the contribution from formation and decay of the OHH collision complex. The indirect contribution decreases with increasing collision energy. The inset in Fig. 5 shows that the direct contribution increases with increasing collision energy, but is insignificant compared to the indirect contribution for all

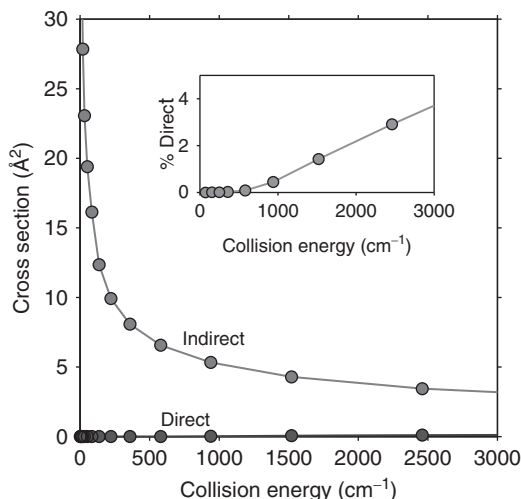


Figure 5. Direct and complex-mediated initial state-selected total cross section for $\text{OH}(v=1, F_1, j=3/2) + \text{H} \rightarrow \text{OH}(v=0) + \text{H}$ vibrational relaxation. The cross section is averaged and summed over the initial and final Λ -doublet levels, respectively. The inset panel reveals the relative size of the direct (noncomplex mediated) contribution.

collision energies. We observe, as argued by Smith and Williams [51], that vibrational relaxation is rendered feasible only by entrance into the OHH complex.

It is interesting to investigate the dependence of the vibrational relaxation cross section on the initial $\text{OH}(v=1)$ rotational/fine-structure level. Figure 6 presents the initial-state-selected cross sections for vibrational relaxation of rotational levels j in the F_1 fine-structure manifold (see Fig. 2). A similar dependence of the vibrational relaxation cross section with increasing rotational excitation was also found for rotational levels within the F_2 fine-structure manifold [47]. The cross sections are seen to decrease with increasing rotational excitation. A decrease in the rate constant for $\text{OH}(\text{A}^2\Sigma^+)$ electronic quenching in collision with various partners with increasing rotational excitation has also been seen (see [52] and references therein).

This dependence on the initial rotational excitation can be ascribed to the angular dependence of the interaction. As discussed in Section III, the PES for the $^1\text{A}'$ state of OHH is very anisotropic and is strongly attractive only for bent geometries, but very repulsive in linear geometries. With increasing rotational excitation, it is harder for the collision partners to align to the attractive geometries and gain access to the deep well.

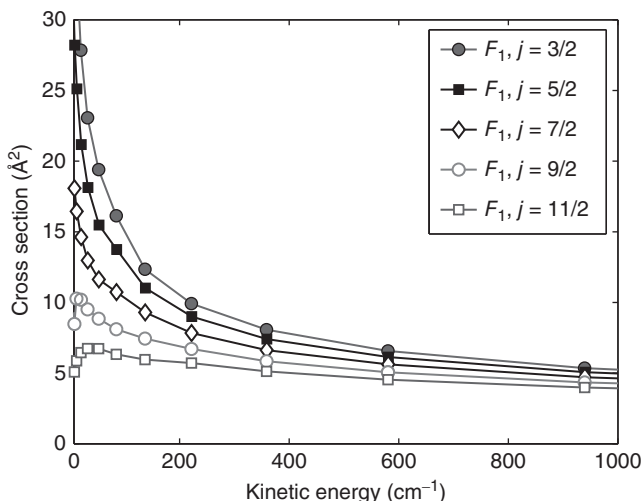


Figure 6. Cross sections for the vibrational relaxation of $\text{OH}(v=1)$ initial rotational levels j in the lower, F_1 fine-structure manifold to $\text{OH}(v=0)$ in collision with H atoms. The cross section is averaged and summed over the initial and final Λ -doublet levels, respectively. Reprinted with permission from Atahan and Alexander 2006 [47]. Copyright 2006 American Chemical Society.

Figure 7 displays the temperature dependence for the vibrational relaxation of $\text{OH}(v=1)$. Also plotted are the corresponding experimentally measured room-temperature rate constants [53]. In the experiments, vibrationally excited OH was prepared by photolysis of vibrationally excited water in known, steady-state concentrations of H atoms. The rotational relaxation of nascent, vibrationally excited OH should be rapid compared to vibrational relaxation. The agreement of the measured and computed room-temperature vibrational relaxation rate constant is excellent.

We compare in Fig. 7 the temperature-dependent rate constants for vibrational relaxation of OH $v=1$ and 2. The latter vibrational level can relax to both the $v=0$ and 1 levels. We see that the relaxation rate constants for the two vibrational levels are very similar in magnitude. This conforms with the supposition mentioned above that relaxation through the formation and decay of a strongly bound collision complex should not depend strongly on the vibrational level.

The $\text{OH}(v=1 \text{ and } 2)$ vibrational relaxation rate constants are much larger in magnitude than rate constants measured for the relaxation of $\text{OH}(v)$ by closed-shell collision partners, especially inert gasses [50]. In collision with the open-shell H atom, formation and decay of a collision complex provide a mechanism for much more rapid vibrational relaxation.

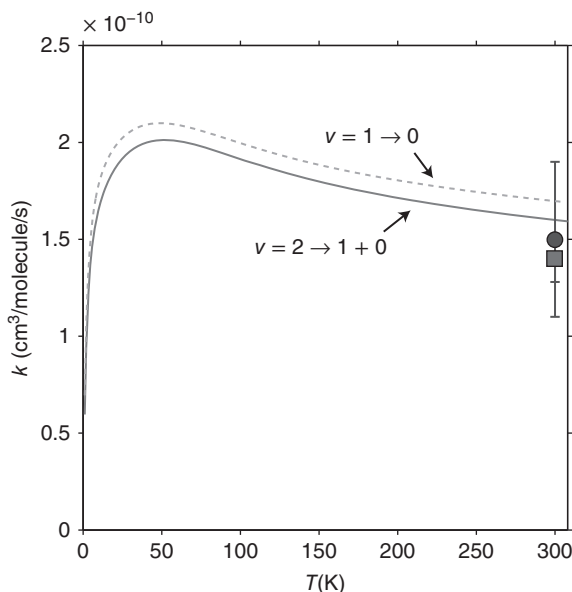


Figure 7. Comparison of thermally averaged vibrational removal rate constants for $\text{OH}(v = 1, 2)$ in collision with H atoms. The experimental $v = 1$ room-temperature value is from [53]. The filled circle and filled square designate rate constants derived from experiments in which H_2O was excited, respectively, to the $|13\rangle$ or $|12\rangle$ stretch levels before photolysis. Reprinted with permission from Atahan and Alexander 2006 [47]. Copyright 2006 American Chemical Society.

B. OH + D Isotope Exchange

A major source of OD in interstellar clouds is the isotope exchange reaction between OH and D atoms [54]. The relative abundance of OH and OD depends on isotope fractionation processes and can be interpreted to put constraints on interstellar chemistry [55]. Isotope exchange in OH + D collisions can occur at low temperatures such as those in the interstellar medium since this reaction can proceed without an activation barrier, on the strongly attractive $^1\text{A}'$ PES (see Fig. 3). Atahan *et al.* [56] have carried out coupled-states calculations employing the quantum statistical method [14, 15] to compute the rate constants for the $\text{OH}(\text{X}^2\Pi) + \text{D}(^2\text{S}) \rightarrow \text{OD}(\text{X}^2\Pi) + \text{H}(^2\text{S})$ reaction.

As can be seen in Fig. 4, hydrogen atom exchange can occur only through the formation and decay of the OHD collision complex. To compute cross sections for the $\text{OH} + \text{D} \rightarrow \text{OD} + \text{H}$ reaction, one needs capture probabilities for both the OH + D and OD + H arrangements.

In the case of OH + D, the Jacobi coordinates are identical to those for OH + H, so the PESs shown in Fig. 3 can be used directly. Since the locations of the center of masses of OH and OD differ, the Jacobi coordinates (R, r, θ) for the OD + H arrangement are shifted slightly.

Figure 8 compares the predicted OH($j = \frac{3}{2}, F_1$) + D $\rightarrow$ OD(j', F') + H cross sections as a function of the OD rotational quantum number j' . Exactly as in the case of the O(1D) + H₂ reaction discussed in Section III, the OD products are predicted to be formed preferentially in the A' Λ -doublet level. This is not surprising. The Λ -doublet propensity is an outcome of the decay of the OHH($^1A'$) complex and the concomitant coupling, as the products separate, with the three repulsive states ($^1A'', ^3A', ^3A''$; see Fig. 1) [37]. One would then predict comparable A'/A'' propensity rules for the O(1D) + H₂ reaction and the OH + D $\rightarrow$ OD + H isotope exchange reaction, at least in a statistical model where the dynamics of the decay of the complex are assumed to be uncoupled with how the complex is formed.

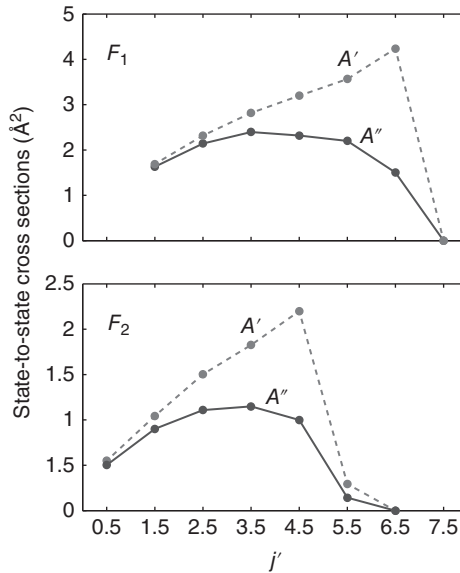


Figure 8. Cross sections for the production of the energetically accessible OD rotational-fine-structure levels in the reaction D + OH($j = 3/2, F_1$) $\rightarrow$ OD(j', F_i, ϵ) + H at a collision energy of 6.7 K. The dashed and solid curves designate, respectively, final levels of nominal A' and A'' symmetry, respectively. In the F_1 spin-orbit manifold, the A' and A'' reflection symmetry labels correspond, respectively, to $\epsilon = +1$ and $\epsilon = -1$ [45]. This assignment is reversed for levels in the F_2 manifold. Reprinted from Atahan *et al.* 2005 [56] with the permission of AIP Publishing.

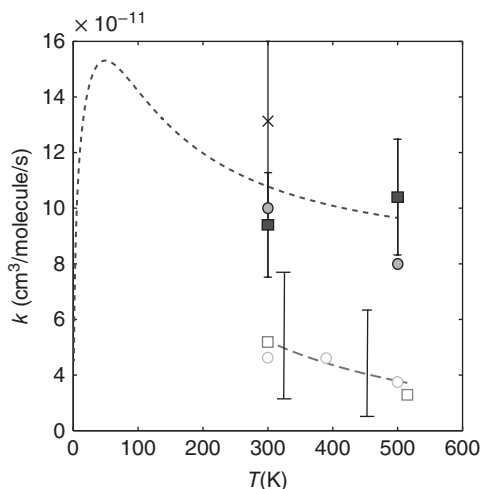


Figure 9. Computed rate constant (solid curve) for the isotope exchange reaction $\text{OH} + \text{D} \rightarrow \text{OD} + \text{H}$. The open circles and open squares represent experimental data from Howard and Smith [57] obtained using H_2O or HNO_3 , respectively, as the OH precursor. The dashed curve is the fit proposed by these authors. The “X” denotes the experimental rate constant of Kaufman and coworkers [58]. The filled data points represent earlier theoretical predictions: circles from [57] and squares from [59]. Reprinted from Atahan *et al.* 2005 [56] with the permission of AIP Publishing.

The temperature dependence of the rate constant for the $\text{OH} + \text{D} \rightarrow \text{OD} + \text{H}$ isotope exchange reaction, as predicted by the quantum statistical calculations of Atahan *et al.* [56], is shown in Fig. 9.

We see that these predictions are comparable to earlier theoretical predictions at a few temperatures [57, 59]. We observe an increase in the rate constant with decreasing temperature (a negative temperature dependence), which is expected for barrierless reactions [57, 60].

Because the zero-point energy of OD is substantially less than that of OH, the $\text{OH} + \text{D} \rightarrow \text{OD} + \text{H}$ isotope exchange reaction is very exoergic [54]. In 2012, the OD molecule was first observed in the interstellar medium [61]. We are hopeful that calculations, of the type described here, will be useful in understanding the observed rotational populations of OD, and, more fundamentally, how it is formed and what is its abundance relative to OH.

C. OH + H Rotationally Inelastic Collisions

The hydroxyl (OH) radical is one of the most abundant hydrides in diffuse interstellar clouds and has been widely observed through its rotational,

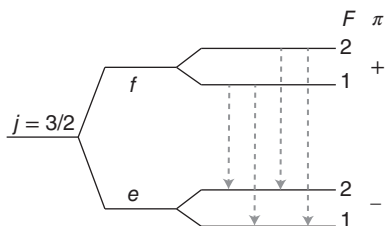


Figure 10. Hyperfine doubling of the lowest Λ -doublet of OH (see Fig. 2). The quantum number F is the total (molecular plus nuclear spin I ; $F = j + I$) angular momentum, while π designates the parity. The arrows indicate the OH maser transitions. Adapted with permission from Atahan and Alexander 2006 [47]. Copyright 2006 American Chemical Society.

Λ -doublet, and hyperfine transitions [62]. Maser emission on various OH hyperfine transitions, as illustrated in Fig. 10, has been observed [63], a consequence of the deviation of the interstellar environment from thermodynamic equilibrium.

Knowledge of both radiative and collisional transition rates is required for the interpretation of the spectroscopic observations. The dominant atomic and molecular collision partners in the interstellar medium are hydrogen molecules and, in some environments, hydrogen atoms.

There has been considerable interest in rotationally inelastic collisions of OH with H_2 . The most recent investigations include the theoretical studies of Offer *et al.* [64] and Schewe *et al.* [65]. Offer and van Hemert [66] carried out quantum scattering calculations and published for the astrophysical community a table of OH– H_2 rate constants, based on calculations employing PESs computed by Offer *et al.* [64]. Schewe *et al.* compared energy-dependent state-to-state cross sections computed with the PESs computed by Ma *et al.* [67] with those measured in an experiment where Stark deceleration was used to vary the collision energy.

By contrast, there has been little work on the calculation of rate constants for rotationally inelastic collisions of OH with hydrogen atoms. The first rigorous treatment of this process was carried out by Shapiro and Kaplan [68]. At that time *ab initio*, PESs were available only for the OH $^1A'$ and $^3A''$ states (see Figs. 1 and 3). Shapiro and Kaplan used these to construct approximate PESs for the two other states. Their scattering calculation employed the exponential Born approximation, which is roughly comparable to a first-order solution of the close-coupled equations.

As part of their study of OH collisional relaxation, Atahan and Alexander [47] reported coupled-states calculations of rate constants for rotational/fine-structure transitions in OH–H collisions. Despite the

approximations made by Shapiro and Kaplan, their rate constants agreed reasonably with those of Atahan and Alexander.

Currently, we are investigating cross sections and rate constants for collision-induced transitions over a wider range of rotational/fine-structure levels than treated by Atahan and Alexander [47], with the goal of a more complete astrophysical modeling of the excitation of OH.

V. OH + O REACTION AND VIBRATIONAL RELAXATION

The $\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$ reaction is a prototype radical–radical reaction. The reverse reaction is an extremely important chain branching step in combustion. Figure 11 presents a schematic diagram of the PESs of the OOH system. In addition to chemical reaction, in collision with O atoms, vibrationally excited OH can undergo nonreactive vibrational relaxation. Because of its importance, a number of theoretical methods have been used to study the dynamics of the $\text{OH} + \text{O}$ reaction (see [69] and references contained therein). Recently, full TID reactive scattering calculations have been carried out on an accurate PES [70] for the lowest ($^2A''$) state of the HOO system [69]. Reactive cross sections for $\text{OH}(v=0, j) + \text{O} \rightarrow \text{H} + \text{O}_2$ as a function of energy are shown in Fig. 12.

The quantum reactive scattering calculations in Fig. 12 do increase with decreasing energy, indicative of a barrierless reaction. Nevertheless, there is some indication [70, 71, 73, 74] that an important fraction of the reactive trajectories does not proceed through the $\text{HOO}(^2A'')$ complex. A consequence of this “dynamical bottleneck” would be an overestimation, by the quantum statistical method, of cross sections for the $\text{OH}(v=0, j) + \text{H} \rightarrow \text{O}_2 + \text{H}$ reaction. This overprediction is seen clearly in Fig. 12, particularly

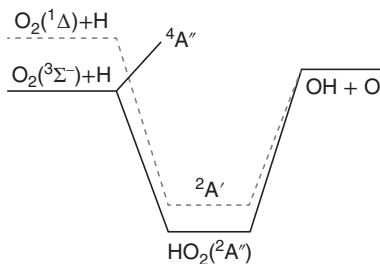


Figure 11. Schematic diagram of the potential energy surfaces of the OOH system. Note that the $\text{O}_2(^1\Delta) + \text{H}$ asymptote is endoergic for collision of O with OH in $v=0$, but becomes energetically allowed when OH is vibrationally excited. The wells in the $^2A''$ and $^2A'$ states lie, respectively, 22,500 and 15,600 cm^{-1} below the $\text{OH} + \text{O}$ asymptote.

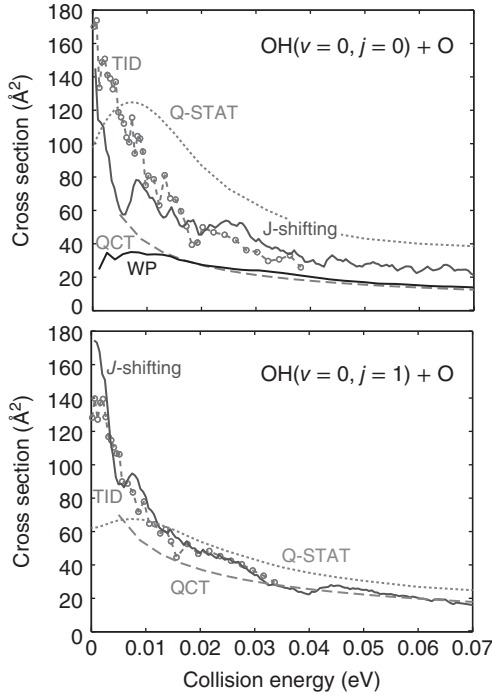


Figure 12. Cross sections for the $\text{OH}(v=0, j) + \text{H} \rightarrow \text{O}_2 + \text{H}$ reaction (top panel $j=0$, bottom panel $j=1$), as predicted by the quantum-statistical method [71], compared with predictions [69] of TID and time-dependent (wavepacket, WP) fully quantum calculations, as well as from application of the J -shifting approximation [72], and quasi-classical trajectory calculations.

for $j=0$. The inaccuracies of the WP method compared to the presumably correct TID calculations are due to the difficulties in damping outgoing waves with long de Broglie wavelengths [71].

The thermal rate constant is given (Eq. (3)) by a weighted average of the cross section. The maximum in the weighting function occurs at $E_c = k_B T$. We see from Fig. 12 that the degree of overestimation discussed in the preceding paragraph is small for $E_c \gtrsim 200 \text{ cm}^{-1}$ or, in K units, $\gtrsim 290 \text{ K}$.

Motivated by experiments by Khachatrian and Dagdigian [75], we have used the quantum statistical method to calculate cross sections for vibrational relaxation of $\text{OH}(X^2\Pi, v=1)$ by collisions with $\text{O}(^3P)$ over a wide range of temperatures. These predictions are summarized in Fig. 13. The experiments of Khachatrian and Dagdigian measure the total rate of removal of $\text{OH}(v=1)$. This can occur by inelastic quenching [$\text{OH}(v=1) + \text{O} \rightarrow \text{OH}(v=0) + \text{O}$] or reaction, each process occurring

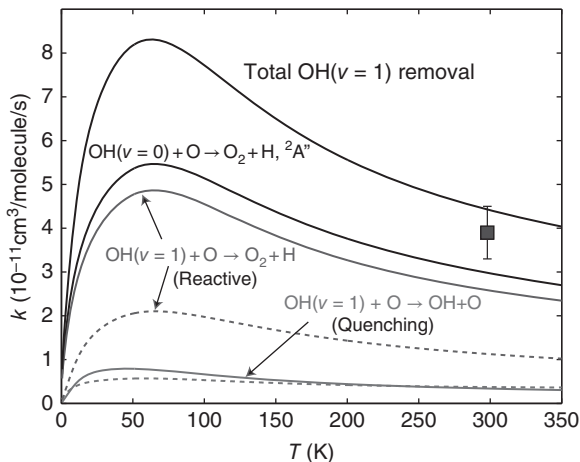


Figure 13. Comparison of the coupled-states, statistical rate constants for reactive and inelastic quenching of the $\text{OH}(\text{X}^2\Pi, v = 1)$ state by collision with $\text{O}(^3\text{P})$ atoms as a function of temperature. The solid and dashed curves designate, respectively, collisions occurring on the lowest $^2\text{A}''$ and $^2\text{A}'$ PESs. The uppermost curve designates the rate constant for the total (inelastic plus reactive) removal. The room-temperature value of this $\text{OH}(v = 1)$ total removal from the experiments of Khachatrian and Dagdigian [75] is also shown. For comparison, the heavy black curve (the second highest curve) designates the calculated CS-ST rate constant for *reactive* removal of the $\text{OH}(\text{X}^2\Pi, v = 0)$ state. At 298 K, the recommended value (Ref. 4) for this rate constant is $3.3 \pm 0.7 \times 10^{-11} \text{ cm}^3/\text{molecule/s}$. Reprinted from Kłos *et al.* 2008 [71] with the permission of AIP Publishing.

on either the lowest ($^2\text{A}''$) or the first-excited ($^2\text{A}'$) PES (see Fig. 11). We observe that reaction on the lowest ($^2\text{A}''$) PES is the primary pathway for the removal of $\text{OH}(v = 1)$. The probability of reaction on the excited ($^2\text{A}'$) PES is significantly reduced, likely because the reactive asymptote is significantly less exoergic: $\Delta E_0 = -3100 \text{ cm}^{-1}$ for $\text{OH}(v = 1) \rightarrow \text{O}_2(^3\Sigma_g^-)$ compared to -880 cm^{-1} for $\text{OH}(v = 1) \rightarrow \text{O}_2(^1\Delta)$; see Fig. 11. We also observe (solid vs dashed curves) that vibrationally inelastic collisions are equally probable on both the $^2\text{A}''$ and $^2\text{A}'$ PESs, indicative, within the statistical model, that access to the two $\text{OOH}^\dagger$ wells (of very similar depth, see Fig. 11) is equally probable for both electronic states.

VI. INELASTIC COLLISIONS OF THE CH RADICAL

The CH radical is the simplest carbon-containing radical and plays a role in combustion at high temperature. This species has also been observed

in the interstellar medium [76–78] in the atmospheres of the sun, stars, and planets [79, 80], and in comets [81]. The CH radical was one of the first molecules to be detected in the interstellar medium and is abundant in interstellar clouds [62].

As discussed in Section IV.C, knowledge of radiative and collisional rates with the dominant species (e.g., H_2 , H atoms) is required for the determination of molecular concentrations from the observed spectroscopic intensities. The radiative transition rates are well known for CH. However, until the work described in Sections VI.A and VI.B, rate constants for transitions between CH rotational/fine-structure levels induced by the most abundant interstellar species, namely H_2 and H atoms, were not known. Rate constants for CH–He collisions [82, 83] were employed as surrogates, either unscaled or scaled. Section VI.A describes our calculation of CH– H_2 rate constants, while Section VI.B describes calculations for CH–H collisions.

Figure 14 shows the energies of the lower levels of the $\text{CH}(\text{X}^2\Pi) v = 0$ vibrational level. These rotational levels of this electronic state lie close to the Hund's case (b) limit. The angular momentum exclusive of electron spin s is denoted as n , which can have the values 1, 2, etc. The CH total angular momentum j is the vector sum of n and s , with magnitude $n + \frac{1}{2}$ (F_1 fine-structure manifold) or $n - \frac{1}{2}$ (F_2 fine-structure manifold). As with $\text{OH}(\text{X}^2\Pi)$, each rotational/fine-structure level consists of two nearly degenerate Λ -doublet levels, designated e and f .

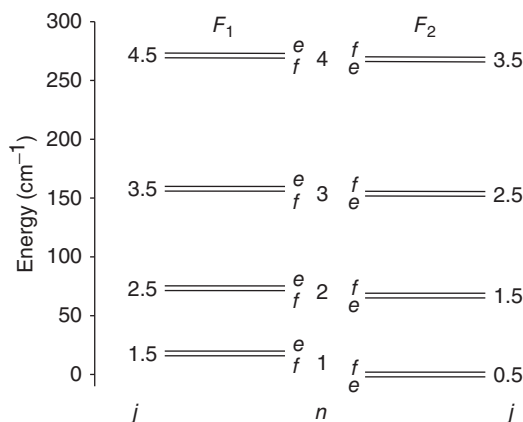


Figure 14. Energies of the lower rotational/fine-structure levels of the $\text{CH}(\text{X}^2\Pi, v = 0)$ manifold. The Λ -doublet splitting has been exaggerated for clarity.

A. CH + H₂

The interaction of CH(X²Π) with H₂ can be reactive or nonreactive. Two reactive pathways are possible, namely abstraction (Eq. (17)) and recombination (Eq. (18)).



The abstraction reaction is slightly endoergic (−1200 cm^{−1}), while the CH₃ well lies 37,000 cm^{−1} below the CH + H₂ asymptote.

There have been several previous theoretical studies of the CH + H₂ reaction. The energetics and critical points for the formation of the CH₃ complex and its decay to CH₂ products have been characterized [84, 85]. Medvedev *et al.* [86] carried out a MRCI calculation of the global ground-state PES. The deep CH₃ well was found to be accessible from the CH + H₂ reactants without an energy barrier. This PES has been used to compute $J = 0$ reaction probabilities, and the reaction rate constant has been computed through quasi-classical trajectory calculations [87].

Dagdigan [88] has carried out icMRCI calculations [46] to determine the nonreactive interaction of CH(X²Π) with H₂. Here, the CH and H₂ bond lengths were fixed, and the interaction was determined as a function of four coordinates, namely the intermolecular separation R , the angle θ_C between $\mathbf{R}$ and the CH internuclear axis, the angle θ_H between $\mathbf{R}$ and the H₂ internuclear axis, and the dihedral angle ϕ_H between the CH and H₂ axes.

Because of the CH orbital degeneracy, two states emanate from the CH + H₂ asymptote. It is convenient to employ quasi-diabatic basis functions appropriate to describe the isolated CH molecule, namely in terms of the two components, with projections $\Lambda = \pm 1$ along the CH internuclear axis, of the CH electronic orbital angular momentum [64, 67, 89]. These states are linear combinations of Cartesian wave functions $|\Pi_x\rangle$ and $|\Pi_y\rangle$, with orbital occupancy $\cdots \pi_x$ and $\cdots \pi_y$, respectively. For planar geometry, these states have definite A' and A'' symmetry, respectively, with the CH–H₂ complex lying in the xz plane.

In nonplanar geometry ($\phi_H \neq 0^\circ$), the adiabatic states can be expressed as rotations of the Cartesian wave functions through a “mixing angle.” This mixing angle was computed [90] by rotating CASSCF orbitals to achieve the maximum overlap with CASSCF orbitals computed in planar geometry ($\phi_H = 0^\circ$). The diagonal ($\Delta\Lambda = 0$) and off-diagonal ($\Delta\Lambda = \pm 2$) terms of the interaction were fit at a given value of R with appropriate [67, 89] angular expansions in order to make the evaluation of matrix elements of

the potential between scattering basis functions efficient. Groenenboom *et al.* [91] have given the expression for the matrix element of the potential for a ${}^2\Pi^{-1}\Sigma^+$ molecule–molecule interaction in the primitive diabatic body-frame basis.

The potentials for both states are repulsive for $R \leq 1.5a_0$. In principle, then, conventional inelastic scattering calculations could be carried out. However, there were two complications that made this approach to computing inelastic cross sections difficult. Despite the fact that the CH and H_2 bond lengths were kept fixed, the lowest adiabatic state had a well depth of 6210 cm^{-1} . Thus, a very small radial sector width and large CH rotational basis would be required in the scattering calculations. In addition, the upper adiabatic state had a local maximum near $R = 3a_0$, indicative of an avoided crossing with a higher state (correlating with $CH(A^2\Delta) + H$). Consequently, the quasi-diabatization procedure will not be valid for small R .

To get around these problems, the quantum statistical method [14, 15] was employed to compute CH– H_2 inelastic cross sections [92]. In this case, the radial integration of the scattering equations was begun at $R = 4.0a_0$. Inelastic transitions can occur by both direct collisions and indirectly through the formation and decay of the CH_3 collision complex. In principle, the collision complex could also decay with the formation of $CH_2 + H$ products, provided that the total energy is above that of these separated products. Decay of the complex to $CH_2 + H$ was neglected since this pathway is endoergic and the indirect cross sections decrease rapidly with increasing energy. Scattering calculations were performed for total energies $E_{\text{tot}} \leq 1200\text{ cm}^{-1}$.

Figure 15 presents the contributions to the integral cross sections for two transitions out of the $n = 1\ F_1e$ initial level in collision with $H_2(j = 1)$. We see that both the direct and indirect contributions to these cross sections increase rapidly for energies just above the energetic threshold and begin to decline in magnitude beyond $E_{\text{tot}} = 200\text{ cm}^{-1}$. We see that at these low energies, the indirect contributions have magnitude comparable to the direct contributions. This confirms the discussion in Section I: because weak, glancing collisions contribute significantly to rotationally inelastic collisions, especially those with small Δj (Δn), we can expect direct (not complex-mediated) processes to dominate. The contribution of indirect collisions to the integral cross section drops off rapidly with increasing energy and is very small at the higher energy ($E_{\text{tot}} = 1200\text{ cm}^{-1}$). The small computed magnitude of the indirect contribution at high energy justifies our neglect of decay of the complex to $CH_2 + H$, since this channel does not open until $E_{\text{tot}} = 1190\text{ cm}^{-1}$.

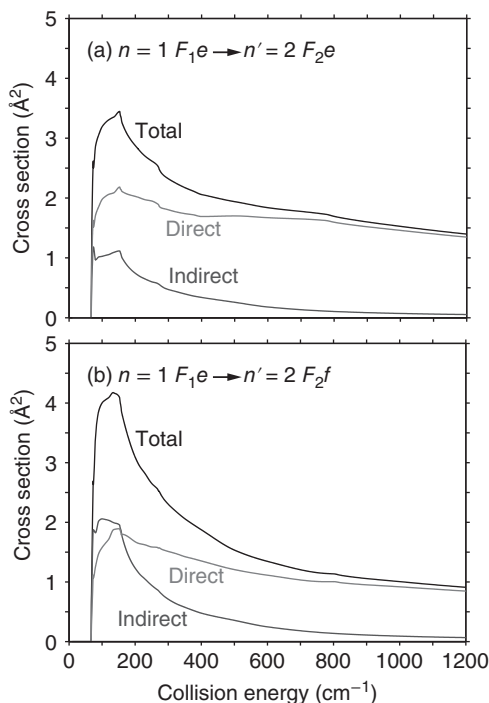


Figure 15. Cross sections for direct and indirect collisions and total (the sum of the direct and indirect) integral cross sections for the (a) $n = 1 F_1e \rightarrow n' = 2 F_2e$ and (b) $n = 1 F_1e \rightarrow n' = 2 F_2f$ transitions in collision with H_2 .

The cross sections for indirect scattering depend on the product of the capture probability (Eq. (7)) of the initial level and the probability (Eq. (6)) that the complex decay to a specific final level. The latter decreases in magnitude as the total energy decreases because of the larger number of decay channels accessible, and this is the main reason why the indirect cross sections decrease significantly with increasing energy. In addition, the capture probabilities for the initial level do display a slight decrease in magnitude with increasing energy [92].

The state-to-state cross sections for collisions of $CH(X^2\Pi)$ with He [82, 83], and other inert gasses, display very strong propensities for transitions between certain pairs of rotational/ Λ -doublet levels. Here, we examine the extent of collisional propensities in $CH(X^2\Pi) + H_2$ collisions. Figure 16 presents integral cross sections, including the direct and indirect contributions, for transitions out of the $n = 1 F_1e/f$ levels to the $n' = 2 F_1e/f$ and F_2e/f levels in collision with *ortho*- $H_2(j = 1)$ and *para*- $H_2(j = 0)$.

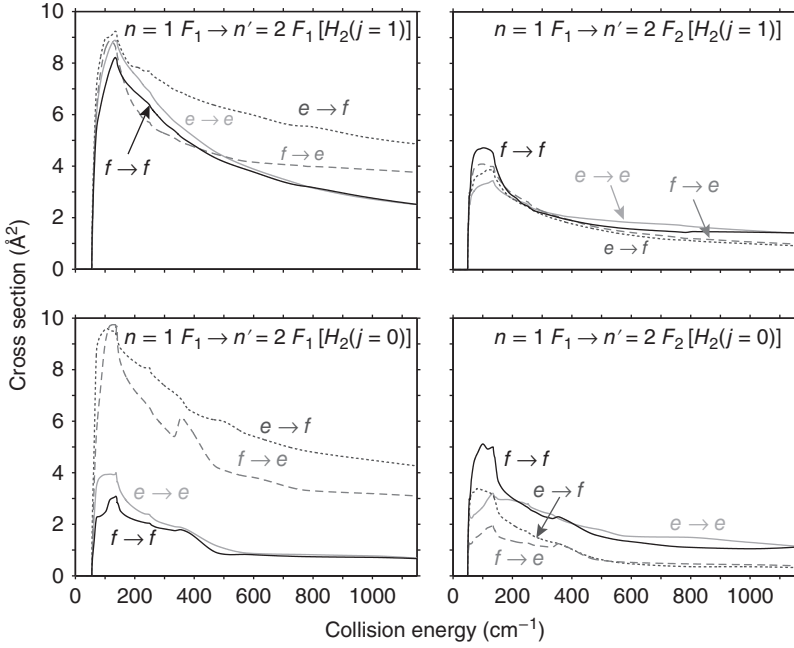


Figure 16. Integral cross sections (sum of direct and indirect contributions) as a function of the collision energy for collisions between the CH $n = 1 F_1 e/f$ Λ -doublet levels and *ortho*-H₂($j = 1$) and *para*-H₂($j = 0$) for transitions to the $n' = 2 F_1 e/f$ and $F_2 e/f$ levels.

The cross sections are seen to rise rapidly above the energetic threshold and decrease slowly in magnitude at higher collision energies. Unlike the situation for OH–H₂ [65] for which the cross sections for collisions with H₂($j = 1$) are much larger than for H₂($j = 0$), the cross sections for CH–H₂ collisions are comparable in magnitude for the two nuclear spin modifications. This suggests that, in contrast to OH–H₂ collisions, the long-range part of the potential does not play a significant role in the inelastic scattering dynamics.

We see in Fig. 16 that the cross sections for fine-structure conserving transitions (i.e., $F_1 \rightarrow F_1$) are larger than for fine-structure changing transitions (i.e., $F_1 \rightarrow F_2$). This was also found [92] to be the case for transitions out of the $n = 1 F_2$ levels. The cross sections show some dependence on the initial and final Λ -doublet levels. We see for the $F_1 \rightarrow F_1$ transitions in collision with H₂($j = 0$) that the cross sections for the $e \rightarrow f$ and $f \rightarrow e$ transitions are significantly larger than for the $e \rightarrow e$ and $f \rightarrow f$ transitions. However, strong Λ -doublet propensities are not observed for other transitions. The relatively weak Λ -doublet propensities found here

for CH–H₂ collisions contrast greatly with the dramatic propensities observed in both CH–He and OH–H₂ collisions [67, 82]. This reflects the presence of the deep CH₃ well and the considerable anisotropy of the CH–H₂ potential.

We have frozen the CH bond length in our calculations. The calculated indirect cross sections could be affected by relaxation of this bond length as the CH₃ complex is formed, an effect not included in our calculations.

Macdonald and Liu [93, 94] carried out a molecular beam study of state-resolved collisions of CH with hydrogen molecules, in particular the D₂ isotopolog. They found experimental evidence for the role of the methyl complex in collisions of CH with D₂ through observation of CD products from the decay of the transiently formed CHD₂ complex. They determined relative cross sections for the formation of rotationally excited CH and CD as a function of collision energy. As discussed in detail elsewhere [92], reasonable agreement of the measured relative cross sections with calculated values was found for the inelastically scattering CH radicals.

Because of the astrophysical importance of CH collisions with H₂, rate constants for collision-induced transitions between the 16 lowest rotational/fine-structure levels (involving $n = 1 - 4$, see Fig. 14) of CH in collision with H₂ ($j = 0, 1$) over the temperature range of 10–300 K have been computed. These are reported in the supplementary material in Ref. [92]. These rate constants are being used in collisional-radiative modeling of interstellar CH [95].

B. CH + H

Similar to OH + H, four PESs emanate from the CH($X^2\Pi$) + H(2S) asymptote. The correlations with the strongly bound methylene molecule in its ground and first two excited states, as well as to the C($^3P, ^1D$) + H₂ dissociation channels, are indicated schematically in Fig. 17. The relative energetics are given in the figure caption.

There have been several theoretical studies of the CH + H $\leftrightarrow$ C + H₂ reaction [96–100], the first performed by Harding *et al.* [96]. These authors carried out quasi-classical trajectory calculations on a computed global ground-state PES and computed rate constants for the forward and reverse reactions. They found that the rate constants were nearly temperature independent. Petrongolo and coworkers [98–100] have focused on the inclusion of excited PESs in investigations of the CH + H reaction, the C(1D) + H₂ reaction, and CH + D $\rightarrow$ CD + H isotope exchange. In the case of the CH + H reaction, they carried out wave packet calculations on

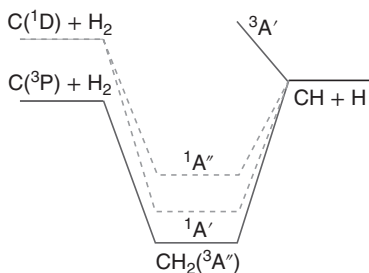


Figure 17. Schematic diagram of the potential energy surfaces of the CHH system. The triplet states are drawn with solid lines, while the singlet states with dashed lines. The lowest two states of methylene ($\tilde{X}^3B_2$ and $\tilde{a}^1A_1$) have well depths of 34,000 and 31,800 cm^{-1} , respectively, with respect to the CH + H asymptote. Reaction of CH with H is exoergic by 7900 cm^{-1} to form C(3P) + H_2 , but endoergic by 2000 cm^{-1} to form C(1D) + H_2 .

the ground $CH_2 \tilde{X}^3A''$ PES [99]. For the isotope exchange reaction, they included three PESs with the addition of Renner–Teller coupling.

Dagdigan [101] has calculated the four adiabatic PESs emanating from CH + H, fixing the CH bond length at its equilibrium value. Here, the explicitly correlated variant of the MRCI method [102–104] and aug-cc-pVTZ basis sets were employed. These PESs are appropriate for investigating inelastic CH + H collisions. Figure 18 presents contour plots. We see that three of these states have strongly attractive PESs, consistent with the diagram in Fig. 17. These PESs are in good agreement with the icMRCI PESs computed by Ben Abdallah *et al.* [105].

The PESs for the singlet states ($^1A'$ and $^1A''$) are repulsive near linear geometries, but attractive at intermediate values of θ , consistent with the bent equilibrium geometries of singlet methylene. The $^3A''$ state is strongly attractive for most geometries, except for $\theta = 0^\circ$ and 180° and $R > 4a_0$, for which there are local maxima in the potential. Dagdigan [101] investigated real and avoided crossings of states in linear and nonlinear geometries, respectively, and the local maxima are due to such crossings. The lowest of these (of height $\sim 600 \text{ cm}^{-1}$) is between the $^3A''$ component of the $^3\Pi$ state correlating with $CH(X^2\Pi) + H$ and the $^3\Sigma^-$ state correlating with the low-lying $CH(^4\Sigma^-)$ state for $\theta = 180^\circ$. As expected, the $^1A'$ and $^1A''$ states are degenerate at the linear geometries. However, this is not the case for the $^3A'$ and $^3A''$ states because of the crossing of states.

Dagdigan [101] has employed the PESs shown in Fig. 18 to compute cross sections for inelastic transitions in $CH(X^2\Pi)$ induced by collisions

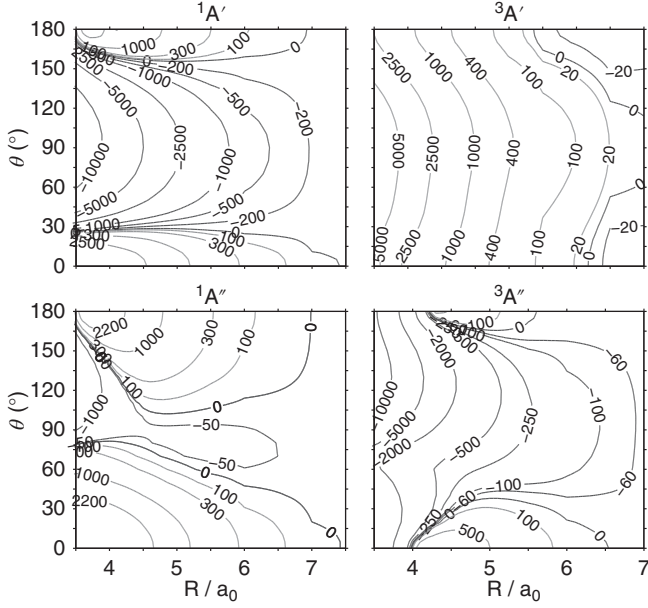


Figure 18. Contour plots (in cm^{-1}) of the CH-H PESs for the (top row) $^1A'$, $^3A'$, and (bottom row) $^1A''$, $^3A''$ states for the equilibrium CH bond length $r_e = 2.116a_0$. The angle $\theta = 0^\circ$ corresponds to linear CHH geometry.

with H atoms. Unlike the treatment of OH + H collisions by Alexander and coworkers [47, 56], a coupled, definite-parity scattering basis was employed in these calculations. Also, since only rotationally inelastic collisions are being considered, the CH bond length is not allowed to vary. These basis functions are defined as

$$|JMK\rho jF_i \varepsilon s_H j_{12}\rangle = 2^{-1/2} [|JM, +K, jF_i \varepsilon s_H j_{12}\rangle + \rho |JM, -K, jF_i \varepsilon s_H j_{12}\rangle] \quad (19)$$

where the parity index $\rho = \pm 1$. For $K = 0$, we have only $\rho = +1$:

$$|JM, K = 0, \rho = +1, jF_i \varepsilon s_H j_{12}\rangle = |JM, K = 0, jF_i \varepsilon s_H j_{12}\rangle \quad (20)$$

The signed- K , coupled basis functions in Eqs (19) and (20) are obtained by vector coupling the CH rotational angular momentum j and the H atom spin s_H to yield the coupled angular momentum j_{12} :

$$|JMKjF_i \varepsilon s_H j_{12}\rangle = \sum_{k, \sigma_H} (j k s_H \sigma_H | j_{12} K) |JMK\rangle |j k F_i \varepsilon\rangle |s_H \sigma_H\rangle \quad (21)$$

Here, $(\dots|..)$ is a Clebsch–Gordan coefficient [49]. We have the projections $k + \sigma_H = K$ along $\mathbf{R}$, so that the sum over k in Eq. (21) can be dropped. The projection of $\mathbf{j}_{12}$ along $\mathbf{R}$ equals K . The end-over-end rotational motion of the CHH complex is described by the wave function

$$|JMK\rangle = ([J]/8\pi^2)^{1/2} D_{MK}^J{}^*(\Omega) \quad (22)$$

The CH rotational/fine-structure wave functions are expressed in the body-frame as linear combinations of the Hund's case (a) wave functions

$$|j k \lambda \sigma \omega \epsilon\rangle = 2^{-1/2} ([j]/4\pi)^{1/2} \times \left[D_{k\omega}^{j*}(\phi, \theta, 0) |\lambda \sigma \omega\rangle + \epsilon D_{k,-\omega}^{j*}(\phi, \theta, 0) |j, -\lambda, -\sigma, -\omega\rangle \right] \quad (23)$$

The angles (θ, ϕ) denote the orientation of $\mathbf{r}$ in the body frame, and the rotational motion of CH in the body frame is described by the rotation matrix elements [49] in Eq. (23). The basis functions in Eqs (19) and (20) have the parity

$$\mathbf{i}_{\text{sp}} |JMK \rho j F_i \epsilon s_H j_{12}\rangle = \rho (-1)^{J+s_{\text{CH}}+s_H} |JMK \rho j F_i \epsilon s_H j_{12}\rangle \quad (24)$$

where $\mathbf{i}_{\text{sp}}$ is the inversion operator.

Since the diatomic bond length is held fixed here, the matrix elements of the electronic Hamiltonian H_{el} in Eq. (12) in the purely electronic basis $|\lambda \sigma s_H\rangle$ can be expanded in linear combinations of reduced rotation matrix elements $d_{m\mu}^l(\theta)$. As a consequence, the matrix elements of H_{el} in the scattering basis (Eqs (19) and (20)) can be evaluated by angular momentum algebra, unlike the situation for OH + H, described in Section IV.

The close-coupling equations are integrated in the scattering basis, starting at the capture radius. Since the $\text{C}(^3\text{P}) + \text{H}_2$ asymptote is significantly lower than $\text{CH} + \text{H}$ (see Fig. 17), we expect the $\text{CH}_2(^3\text{A}'')$ complex to decay predominantly to $\text{C}(^3\text{P}) + \text{H}_2$, and we need to consider only direct inelastic collisions in this case. The singlet $\text{C}(^1\text{D}) + \text{H}_2$ asymptote lies above $\text{CH} + \text{H}$, so that the CH_2 complex could, in principle, decay back to $\text{CH} + \text{H}$. We ignore this possibility here and assume that spin–orbit coupling in the complex will allow it to decay to $\text{C}(^3\text{P}) + \text{H}_2$. Hence, inelastic $\text{CH} + \text{H}$ cross sections are computed by considering only direct collisions.

Figure 19 presents integral cross sections for transitions out of the $n = 1 F_1 e/f$ levels to the $n' = 2 F_1 e/f$ and $F_2 e/f$ levels in collision with H atoms. As with the $\text{CH}-\text{H}_2$ cross sections (see Fig. 19), the $\text{CH}-\text{H}$ cross sections rise rapidly above the energetic threshold. The magnitude of the

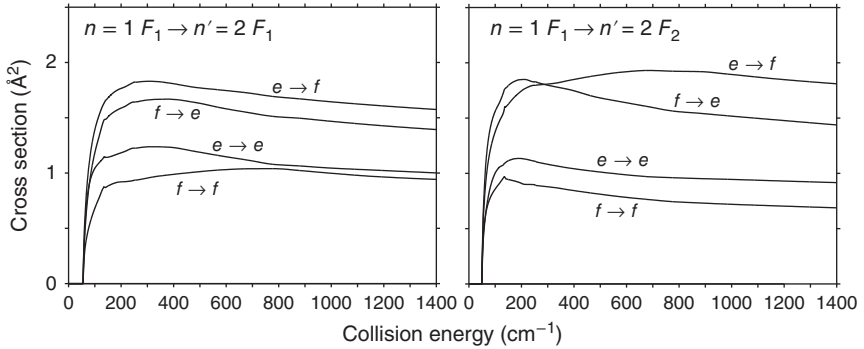


Figure 19. Integral cross sections as a function of the collision energy for collisions between the CH $n = 1 F_1 e/f$ Λ -doublet levels and H atoms for transitions to the $n' = 2 F_1 e/f$ and $F_2 e/f$ levels.

CH–H cross sections are smaller than the CH–H₂ cross sections. We also see in Fig. 19 that the CH–H cross sections generally decrease in size only very slowly with increasing collision energy, in contrast to the faster decrease in the CH–H₂ cross sections as a function of collision energy (see Fig. 17). This could be due to the fact that the CH₂ wells are deeper than the CH₃ well.

The Λ -doublet resolved $e \rightarrow e'$ cross sections for fine-structure-conserving and fine-structure-changing transitions to the F_1 and F_2 fine-structure levels, respectively, are very similar in magnitude to the corresponding $e' \rightarrow e$ cross sections. However, we see that the fine-structure-conserving $e \rightarrow e$ and $f \rightarrow f$ transitions have cross sections smaller than the corresponding $e \rightarrow f$ and $f \rightarrow e$ transitions.

Because of the astrophysical importance of CH–H collisions, rate constants for collision-induced transitions between the 16 lowest rotational/fine-structure levels of CH in collision with H atoms have been computed [101].

VII. H + O₂ TRANSPORT PROPERTIES

There has been considerable interest in computationally simulating combustion [106]. One important required ingredient for these simulations is a matrix of temperature-dependent and, where required, pressure-dependent rate constants. Considerable effort has been expended by many groups in the measurement of relevant rate constants and the construction of chemical models. (As an example, for the H₂–O₂ system, see the work of Burke *et al.* [107].)

Since combustion environments are not homogeneous, transport properties are also required for accurate simulations of flames and other combustion media. These have been conventionally estimated using isotropic Lennard-Jones (LJ) (12-6) potentials with the well depth and length parameters ϵ and σ , respectively, determined through combination rules for the like pairs [108]. In recent years, we have been engaged in the calculation of accurate transport properties of mainly small transient species with hydrogen atoms for which accurate PESs are available or can be calculated. The transport properties depend on angle-weighted moments of differential cross sections. However, the transport cross sections can be more efficiently computed as double sums, weighted by angular momentum coupling coefficients, of products of the collision S matrix elements (see, for example, [109]).

In some cases, we have found significant differences in transport properties computed conventionally and through quantum scattering calculations with accurate PESs [110]. To test whether these differences will make a significant difference in computed flame properties, we have compared calculated laminar flame speeds in one-dimensional combustion simulations using the two sets of transport properties. We have found differences in speeds of computed flames similar to differences found when different sets of rate constants are employed [111].

One of the collision pairs for which we carried out calculations of transport properties is $\text{H} + \text{O}_2$ [112]. As shown in Fig. 11, two states, namely $^2\text{A}''$ and $^4\text{A}''$, emanate from the $\text{H}(^2) + \text{O}_2(\text{X}^3\Sigma_g^-)$ asymptote. The former correlates with the deeply bound ground $\tilde{\text{X}}^2\text{A}''$ state of HO_2 , while the latter is repulsive. We employed the PES computed by Kłos *et al.* [71] for the $^2\text{A}''$ state and carried out a coupled-cluster [RCCSD(T)] calculation to determine the PES for the $^4\text{A}'$ state.

We carried out separate close-coupling calculations to treat collisions on the $^2\text{A}''$ and $^4\text{A}''$ PESs. The quantum statistical model was employed to treat the dynamics in the $^2\text{A}''$ state, while conventional inelastic scattering calculations were performed for the repulsive $^4\text{A}''$ state. We then weighted the cross sections with the 2:4 spin degeneracy to determine degeneracy-averaged collision properties for the overall interaction. Strictly speaking, one should include nonadiabatic (spin-orbit) interactions in the entrance channel to describe the separation of the incoming flux between the two states, but this was beyond the scope of the calculation.

We also see in Fig. 11 that at sufficiently high energies, the $\text{HO}_2(^2\text{A}'')$ complex can decay to channels other than $\text{H} + \text{O}_2(\text{X}^3\Sigma_g^-)$, namely

$\text{H} + \text{O}_2(a^1\Delta_g)$ and $\text{O} + \text{OH}$. The energies required to access the latter two channels are considerably higher than the energies required for the calculation of thermal rate constants.

For the $\text{H}-\text{O}_2$ collision pair, we did find that the transport properties computed in our quantum scattering calculations were significantly different in magnitude than those estimated using a LJ 12-6 isotropic potential. Figure 20 compares the $\text{H}-\text{O}_2$ diffusion coefficient obtained by these two methods.

Finally, it is interesting to compare rotationally inelastic scattering for this system with that for a collision pair for which the interaction has only a weakly bound van der Waals well and a repulsive PES for small R . Figure 21 presents cross sections for collision-induced transitions for the $\text{H}-\text{O}_2$ and $\text{H}-\text{N}_2$ collision pairs. The cross sections for $\text{H}-\text{N}_2$ were computed using a recent RCCSD(T) calculation of this PES [113]. We see in Fig. 21(a) that the final state distribution is broader for collisions on the $\text{H}-\text{O}_2$ $^2A''$ PES than on the $^4A''$ PES. Comparison of panels (a) and (b) of Fig. 21 reveals that the final state distribution for $\text{H}-\text{O}_2$ on the degeneracy-weighted PESs is very similar to that on the $^4A''$ PES alone; this is the result of the 2:1 spin-degeneracy weighting of the $^4A''$ as compared to the $^2A''$ cross sections. We see in Fig. 21(b) that the $\text{H}-\text{O}_2$ and $\text{H}-\text{N}_2$ cross sections have similar magnitude, but the $\text{H}-\text{N}_2$ final state distribution is narrower. We conclude by noting that there is no obvious

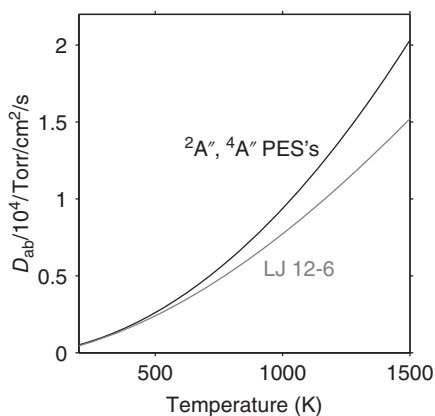


Figure 20. Diffusion coefficient for the $\text{H}-\text{O}_2$ system, computed from quantum scattering calculations (labeled as $^2A''$, $^4A''$ PESs) and from a two-center (atom-atom) model based on a LJ 12-6 potential. Reprinted with permission from [112]. Copyright 2014 American Chemical Society.

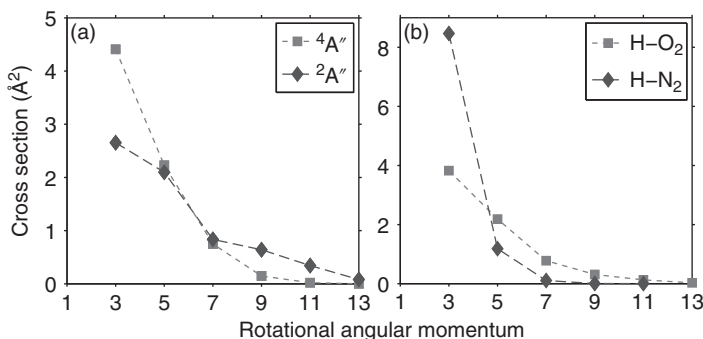


Figure 21. Cross sections for collision-induced transitions out of the lowest rotational level $n=1$ for $\text{H} + \text{O}_2$ and $\text{H} + \text{para-N}_2$ at a collision energy of 300 cm^{-1} . (a) Cross sections for $\text{H} + \text{O}_2$ scattering on the $4A''$ and $2A''$ PESs separately; (b) cross sections for $\text{H} + \text{N}_2$ and $\text{H} + \text{O}_2$, averaged over the degeneracies of the $4A''$ and $2A''$ PESs.

signature of the $\text{HO}_2(^2A'')$ deep well on rotationally inelastic scattering dynamics in $\text{H} + \text{O}_2$ collisions.

VIII. CONCLUSION

This review has highlighted the use of the quantum statistical method for the calculation of cross sections and rate constants for systems that possess one or more deep potential wells. Our particular focus has been inelastic scattering. The calculations reviewed here are rigorous within the assumption of statistical decay of the collision complex. To go beyond this approximation would require full reactive scattering calculations on multiple potential energy surfaces, a considerable computational challenge.

The quantum statistical method is not a panacea for the general calculation of cross sections for inelastic transitions in reactive systems. An example is nonreactive energy transfer in $\text{D} + \text{H}_2$ collisions [114], where full reactive scattering calculations were required. Note that here the reactant and product arrangements of the $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ reaction are separated by an energy barrier, so that one cannot apply statistical assumptions based on the existence of a transient complex.

The experimental determination of absolute cross sections and rate constants for collisions involving two open-shell species, particularly at state-to-state resolution, remains extremely challenging. Moreover, such measurements, even for the experimentally simpler investigation of

collisions of open-shell species with a closed-shell collision partner, can be carried out for only a limited range of collision energies and initial levels. Accurate close-coupling calculations based on state-of-the-art PESs provide a way to extend these measurements, for example for astrophysical modeling of excitation of radicals in interstellar media. The quantum statistical method offers a way to do this, with acceptable accuracy, for radical-radical systems where one or more of the PESs has a deep well.

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