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An *ab initio* quasi-diabatic potential energy matrix for $\text{OH}(^2\Sigma) + \text{H}_2$

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A diabatic potential energy matrix for three electronic states of OH_3 has been constructed by interpolation of multi-reference configuration interaction electronic structure data. The reactive, exchange and non-reactive quenching dynamics are investigated using surface hopping classical trajectories. Classical trajectory simulations show good agreement with cross molecular beam data for the $\text{OH}(^2\Sigma) + \text{D}_2 \rightarrow \text{HOD} + \text{D}$ reaction. © 2011 American Institute of Physics. [doi:10.1063/1.3664759]

I. INTRODUCTION

Chemical reaction dynamics is most commonly studied within the Born–Oppenheimer approximation.^{1–3} Here, the electronic Schrödinger equation is solved by modern *ab initio* quantum chemistry methods to give the electronic *adiabatic* state and energy at a given nuclear configuration. For a molecule containing N atoms, the resultant electronic energy is a $3N-6$ dimensional function of nuclear configurations. This is the potential energy surface (PES) that governs the motion of the atomic nuclei. For reactions involving more than three atoms, it is not feasible for a highly accurate *ab initio* calculation of the potential energy to be performed at every relevant molecular configuration. The PES must be approximated in some way. Modified Shepard interpolation of *ab initio* data has been shown to provide one satisfactory approach to PES approximation for reactions involving several atoms.⁴

However, the Born–Oppenheimer approximation may not be adequate. Many important chemical processes involve more than one electronic state and nonadiabatic dynamics. The nuclear wave functions for different adiabatic electronic states are coupled by so-called derivative coupling terms that arise from the action of the nuclear kinetic energy operator on the electronic wavefunction. It can be shown⁵ that the derivative coupling between two electronic states is inversely proportional to the difference of their electronic energies, becoming singular at an electronic degeneracy. Because of this singularity, the quantum dynamics of the nuclear motion is difficult to implement in the adiabatic basis. In addition, PES approximation is difficult because modified Shepherd interpolation cannot describe the characteristic conical shape of the PESs near such a degeneracy (a so-called conical intersection), nor the singularity in the coupling terms. To avoid these problems, the adiabatic electronic states might be (unitarily) transformed to a new set of states in such a way as to remove the singular derivative coupling, a so-called set of *diabatic* states. While the derivative coupling might

be removed, the transformed states no longer diagonalise the electronic Hamiltonian, so we no longer have a PES for each electronic state, but a diabatic potential energy matrix (DPEM), which couples nuclear motion in different diabatic states. Unfortunately, it is not actually possible to accomplish such a transformation exactly, for a finite set of states,⁶ essentially due to errors from the truncation of the (infinite) basis set of electronic states. Nevertheless, if a small set of adiabatic electronic states are not strongly coupled to the remaining infinite number of states, for all nuclear geometries of interest, then an approximate “quasi-diabatic” transformation is possible. In an earlier paper, the solution of several technical problems involved in achieving such a transformation and calculating the DPEM via Shepard interpolation was presented.⁷

In this paper, we present the first application of this methodology to the non-adiabatic dynamics of a bimolecular reaction involving four atoms in multiple (three) electronic states. The reactions studied herein arise from the collision of the excited ($^2\Sigma$) state of the OH radical with H_2 (or deuterated analogues). At low collision energies and low vibration/rotation excitation of the reactants, the following processes are energetically allowed (shown using D_2 for clarity):

Reaction (1.1) is simple non-reactive quenching to the ground state; (1.2) is reactive quenching; (1.3) is exchange with quenching; (1.4) is exchange without change of electronic state; and (1.5) is reactive substitution with quenching. The $\text{OH}(^2\Sigma)$ state lies about $32\,684\text{ cm}^{-1}$ above

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the $\text{OH}^2(\Pi)$ degenerate ground state. Throughout this paper, we will only be considering the spin-free non-relativistic molecular Hamiltonian, so that the ground state of OH is exactly doubly degenerate. Quenching of $\text{OH}^2(\Sigma)$ generates hot translation, vibration and rotation states in the products. These reactions (and isotopic analogues) have generated substantial experimental interest in recent years.^{8–17} Moreover, there has been significant theoretical interest in the electronic structure and conical intersections of this system,^{10,18,19} and in the general question of adiabatic to diabatic transformations (ADTs) in molecules with conical intersections.^{20–24} As a consequence, this system represents a benchmark test case for the development of theoretical reaction dynamics for polyatomic molecules in multiple electronic states.

Here, a global DPEM derived from the three lowest adiabatic electronic states of OH_3 is reported for the first time. The methodology for constructing adiabatic PES with modified Shepard interpolation employs classical trajectory dynamics to explore the chemically relevant molecular configurations. For DPEM, the construction methodology⁷ employs surface-hopping non-adiabatic classical dynamics to fill the same role. Hence, it is a simple matter to evaluate the dynamics of reactions (1.1)–(1.5) using such surface-hopping classical dynamics. We report cross sections and product energy distributions calculated in this way. A complete quantum dynamics study of reaction cross sections on such a DPEM is the subject of further work. However, both classical and quantum dynamics have been used to demonstrate that the interpolated DPEM is converged with respect to the size of the *ab initio* data set. Recently, adiabatic PES for two electronic states of OH_3 have been reported.²⁵ Classical trajectory simulations have been carried out on the ground state PES to model the dynamics after non-adiabatic surface-hopping was assumed to occur. Moreover, quantum dynamics for a five-dimensional (planar) two-state model of this system has recently been reported.²⁶ Here, we report a global full-dimensional DPEM for the lowest three electronic states and non-adiabatic dynamics that involves all three coupled states; making no assumptions about the non-adiabatic dynamics, beyond the use of a classical surface-hopping approach.

The paper is organised as follows. The diabatic representation is briefly reprised in Sec. II. The major steps required for the construction of a DPEM are summarised in Sec. III. Some additional details on the practical implementation of the previously published methodology are given in Appendices. Section IV presents some aspects of the final DPEM and evidence of convergence of the DPEM data set. The entire data set and software for evaluation of the DPEM is included in the supplementary material.²⁷ Section IV also presents the result of a classical trajectory study of the $\text{OH}^2(\Sigma) + \text{D}_2$ reaction. Some brief concluding remarks are given in Sec. V.

II. DIABATIC POTENTIAL ENERGY MATRICES

The nonrelativistic, spin-free, Hamiltonian for a molecule can be written as

$$H = -\frac{1}{2M}\nabla^2 + H_e, \quad (2.1)$$

where H_e is the usual electronic Hamiltonian. In atomic units, the unit of length is the bohr, the unit of mass is the electron mass, the nuclear coordinates are mass scaled Cartesians, and M represents the ratio of the atomic mass unit (amu) to the electron mass. The eigenfunctions of H_e are obtained from

$$H_e\psi_n(\mathbf{x};\mathbf{X}) = E_n(\mathbf{X})\psi_n(\mathbf{x};\mathbf{X}), \quad (2.2)$$

where $\mathbf{x}$ and $\mathbf{X}$ represent the electronic and nuclear coordinates, respectively, and $E_n(\mathbf{X})$ is the usual adiabatic PES for the n th electronic state. In the adiabatic basis, the total wavefunction is expanded as

$$\Psi(\mathbf{x};\mathbf{X}) = \sum_{n=1}^{nstates} \chi_n(\mathbf{X})\psi_n(\mathbf{x};\mathbf{X}) = \underline{\chi}^T(\mathbf{X})\underline{\psi}(\mathbf{x};\mathbf{X}). \quad (2.3)$$

Substituting this wavefunction into the Schrodinger equation for the Hamiltonian of Eq. (2.1) leads to

$$-\frac{1}{2M}[\nabla^2 + 2\mathbf{F} + \mathbf{G}]\underline{\chi} + \mathbf{E}\underline{\chi} = E_{tot}\underline{\chi}, \quad (2.4)$$

where $\mathbf{E}$ is the diagonal matrix of PES, and $\mathbf{F}$ and $\mathbf{G}$ are matrices of derivative couplings,

$$\begin{aligned} \mathbf{F}_{n,m} &= \int \psi_n(\mathbf{x};\mathbf{X}) \nabla \psi_m(\mathbf{x};\mathbf{X}) d\mathbf{x} \\ \mathbf{G}_{n,m} &= \int \psi_n(\mathbf{x};\mathbf{X}) \nabla^2 \psi_m(\mathbf{x};\mathbf{X}) d\mathbf{x}. \end{aligned} \quad (2.5)$$

These derivatives couplings can be singular at nuclear configurations where the adiabatic energies are degenerate and present numerical difficulties. To avoid these problems, a basis of *diabatic* states is defined by

$$\tilde{\psi}(\mathbf{x},\mathbf{X}) = \mathbf{A}^T(\mathbf{X})\underline{\psi}(\mathbf{x},\mathbf{X}), \quad (2.6a)$$

and

$$\tilde{\chi}(\mathbf{X}) = \mathbf{A}^T(\mathbf{X})\underline{\chi}(\mathbf{X}), \quad (2.6b)$$

where $\mathbf{A}(\mathbf{X})$ is the ADT matrix. If

$$\nabla \mathbf{A} \approx -\mathbf{F}\mathbf{A}, \quad (2.7)$$

then the nuclear Schrödinger equation simplifies to

$$\left[-\frac{1}{2M}\nabla^2 + \mathbf{D}\right]\tilde{\chi} = E_{tot}\tilde{\chi}, \quad (2.8)$$

where

$$\mathbf{D} = \mathbf{A}^T \mathbf{E} \mathbf{A}, \quad (2.9)$$

is a DPEM. The derivation from Eq. (2.1) to (2.9) is the standard procedure that is found in many places in the literature.^{6,20} There is no exact solution of Eq. (2.7), see Ref. 6. However, if an approximate solution of Eq. (2.7) is accurate near a conical intersection (where $\mathbf{F}$ is singular) then, importantly, $\mathbf{D}$ is a smooth, continuous function of the nuclear coordinates. In principle, the nuclear dynamics can be evaluated by solving Eq. (2.8) or its time-dependent equivalent.

From Eq. (2.9), it is clear that the eigenvalues of **D** are the PES of the corresponding adiabatic electronic states. The classical dynamics of the nuclei are commonly approximated by motion on these PES combined with “hops” from one PES to another moderated by the derivative coupling, which is also related to elements of **D** (as discussed below).²⁸

III. DPEM FOR OH₃

A. Construction of the DPEM

Since the DPEM is a smooth function of the nuclear coordinates, it can be expanded locally as a Taylor series. The DPEM at any place can be approximated as a weighted sum of these Taylor series from a scattered set of geometries⁷ (a modified Shepard interpolation²⁹),

$$\mathbf{D}(\mathbf{Z}) = \sum_{g \in G} \sum_{n=1}^{ndata} w[\mathbf{Z}; g \circ \mathbf{Z}(n)] \mathbf{D}[\mathbf{Z}; g \circ \mathbf{Z}(n)]. \quad (3.1)$$

Equation (3.1) is very similar in structure to that for modified Shepard interpolation of a single PES.⁴ This approach has also been applied to nonadiabatic dynamics for the two lowest states of H₃.^{30,31} Here **Z** represents a set of internal molecular coordinates (as detailed below). **Z**(*n*) represents the coordinates at a “data point” where *ab initio* calculations have been carried out which allow us to evaluate up to second order derivatives of **D**. *g* is an element of the symmetry group, *G*, and *g* ∘ **Z**(*n*) represents the data point which can be obtained by transforming **Z**(*n*) under the operation *g*. The symmetry group *G* is the complete nuclear permutation inversion (CNPI) group. Here that involves the six permutations of the H atoms coupled with inversion (a group of order 12). The *ab initio* data (energies, wavefunctions, and so on) evaluated at **Z**(*n*) can be transformed into the corresponding data at *g* ∘ **Z**(*n*), without additional *ab initio* calculations. This allows the calculation (as detailed below) of a local approximation to the DPEM at **Z**, **D**[**Z**; *g* ∘ **Z**(*n*)], based on *ab initio* data at *g* ∘ **Z**(*n*). These local approximations are combined in a weighted sum to give a global approximation to the DPEM. The “weight function”, *w*[**Z**; *g* ∘ **Z**(*n*)] is normalised,

$$\sum_{g \in G} \sum_{n=1}^{ndata} w[\mathbf{Z}; g \circ \mathbf{Z}(n)] = 1. \quad (3.2)$$

The weight function is largest when **Z** is “closest” to *g* ∘ **Z**(*n*) (see below).

1. Symmetry

In contrast to a simple PES, the DPEM is not invariant to operations such as the permutation of indistinguishable nuclei or inversion of the Cartesian coordinates, essentially because degenerate electronic wavefunctions transform non-trivially under these operations. This non-trivial symmetry at molecular geometries where electronic degeneracy occurs imparts global transformation characteristics to the DPEM. It is easier to understand the non-trivial symmetry of the DPEM in the context of a simpler two-state problem. Readers are referred to Sec. II F of Ref. 30 where we discuss the DPEM

for the two lowest energy adiabatic states of H₃. In this case the ADT matrix is a simple function of one rotation angle, and the relevant degenerate symmetry representation is the familiar E irreducible representation of the D_{3h} point group. There we show how the symmetry of the degenerate electronic states imposes a non-trivial symmetry on the DPEM in order that the total (electronic and nuclear) Hamiltonian remains totally symmetric with respect to the permutation of indistinguishable particles. The nontrivial symmetry of that 2 × 2 DPEM is also evident in the results presented by Abrol and Kuppermann for the adiabatic to diabatic transformation of these states in H₃.³² The particular, simpler, approach to the symmetry of the DPEM for H₃ was replaced in Ref. 7 by the general method we use here for three states of OH₃.

It has been shown that⁷

$$\mathbf{D}[\mathbf{Z}; g \circ \mathbf{Z}(n)] = \mathbf{M}^T(g) \mathbf{A}^T(n) \tilde{\mathbf{D}}[\mathbf{Z}; g \circ \mathbf{Z}(n)] \mathbf{A}(n) \mathbf{M}(g), \quad (3.3)$$

where **A**(*n*) is the ADT matrix at **Z**(*n*), **M**(*g*) is a “symmetry matrix” which transforms the diabatic states, and **D̃**[**Z**; *g* ∘ **Z**(*n*)] is a matrix of Taylor series expansions that does not depend on **A**(*n*). The detailed method employed for constructing **D̃**[**Z**; *g* ∘ **Z**(*n*)] from *ab initio* calculations is shown in Appendix A.

In the general approach, the required symmetry matrices, **M**(*g*), are not obtained from algebraic manipulations of tables of matrix representations for point groups, but are generated numerically using the automated methods of Ref. 7. This automated method requires that we find a configuration **Z**(1) for which the Taylor series **D**[**Z**; **Z**(1)] and **D**[**Z**; *g* ∘ **Z**(1)] are nearly equal at the midpoint, **Z** = (1/2)[**Z**(1) + *g* ∘ **Z**(1)]. The equality of these two instances of Eq. (3.3) is an equation for **M**(*g*). This approach requires that these geometries be close together in terms of their nuclear coordinates; a condition that is only satisfied if **Z**(1) is close to a geometry of high point-group symmetry. This near-high-symmetry configuration must also be near a conical intersection where the derivative coupling, **F**, is large and determines **M**(*g*) in a numerically stable procedure. Once, the set {**M**(*g*)} have been approximately determined in this way, the matrices are refined by demanding that they obey the CNPI group multiplication table (the group multiplication table is itself determined numerically from the matrices which represent permutations of the numbering of the atoms). The first data point chosen is therefore near to such a high symmetry geometry. The data contained in supplementary material²⁷ show that this molecular configuration has OH bond lengths of 1.748194, 1.761991 and 1.7736691 bohr, and HH bond lengths of 2.9213121, 2.9987561 and 2.944012 bohr, respectively. Although a systematic method for locating conical intersections has been reported,³³ **Z**(1) was determined simply by varying the OH and HH bond lengths, in C_{3v} symmetry, until a suitable conical intersection configuration was found. An arbitrary distortion of that geometry was introduced to ensure that all CNPI versions of **Z**(1) are distinct.

The {**M**(*g*)} depend on the particular choice of **Z**(1), and thereafter fix **A**(1). It may be more convenient to adjust the ADT matrices, {**A**(*n*)}, so that the ADT matrix approaches

the unit matrix in some region (say a reactant asymptote). This is easily accomplished, as described in Appendix B. The resultant matrices, $\{\mathbf{M}(g)\}$, for the three lowest energy states of OH_3 are given in the supplementary material.²⁷

The coefficients in the Taylor series, $\tilde{\mathbf{D}}$, are also obtained automatically from multi-reference configuration interaction (MRCI) *ab initio* calculations at any geometry (see Appendix A). Reference 7 (as modified here in Appendix C) described how to evaluate the Taylor series coefficients from *ab initio* calculations of the adiabatic state energies, energy gradients and the derivative coupling, $\mathbf{F}$. Here, these Taylor series coefficients are evaluated by finite difference, from the adiabatic state energies and the overlaps between the electronic wavefunctions at finitely displaced geometries.

2. Coordinates

The internal coordinates $\{\mathbf{Z}\}$ include the six reciprocal atom–atom distances,

$$Z_i = 1/\|\mathbf{x}(n) - \mathbf{x}(m)\|, i = 1, \dots, 6; \quad n = 1, \dots, 3, \quad m > n, \quad (3.4)$$

where $\{\mathbf{x}(n), n = 1, \dots, 4\}$ represent the Cartesian positions of the atoms. The set of coordinates is completed by the addition of a coordinate related to an out-of-plane angle. If $\mathbf{r}(1) = \mathbf{x}(2) - \mathbf{x}(1)$, $\mathbf{r}(2) = \mathbf{x}(3) - \mathbf{x}(1)$ and $\mathbf{r}(3) = \mathbf{x}(4) - \mathbf{x}(1)$, then

$$Z_7 = \frac{\mathbf{r}(1) \cdot [\mathbf{r}(2) \times \mathbf{r}(3)]}{\left[\sum_{n=1}^6 Z_i^{-1}\right]^4}. \quad (3.5)$$

The denominator in Eq. (3.5) ensures that all $\{Z_i\}$ have the same dimensions.

3. Weight functions

The weight functions in Eq. (3.1) are described in detail in Appendix E of Ref. 7. A slight modification of that approach has been employed to evaluate the Bayesian confidence lengths which appear in the weights: The average error in the gradient of the three adiabatic energies has been employed, in place of the error in the gradient of $\tilde{\mathbf{D}}$, in Eq. (E9) of Ref. 7.

4. ADT matrices

The set of ADT matrices, $\{\mathbf{A}(n)\}$, are evaluated using the method described in Appendix A of Ref. 7. The determination of the ADT matrices is achieved by imposing the constraint that the local Taylor series expansions of $\mathbf{D}$ in Eq. (3.3) must be consistent with the corresponding expansions from nearby data points (including all CNPI permutations of data points). As more and more data points are added to the data set, the distance between data points is reduced and the accuracy of the constraint improves. Hence, the set of ADT matrices converges as the size of the data set increases. The set of ADT matrices is transformed to be consistent with a unit matrix in one $\text{OH} + \text{H}_2$ asymptote (see Appendix B).

This completes the description of all the terms in Eq. (3.1).

B. Electronic structure calculations

All electronic structure calculations were carried out using the MOLPRO program package.³⁴ Over two thousand data points were required for sufficient accuracy in Eq. (3.1), so the choice of *ab initio* method employed reflects a balance between accuracy and computational cost. After considering a range of possible basis sets, we have used the Pople-type 6-311++G(2df,2pd) basis. Complete active valence space multi-configuration self-consistent field (MCSCF) calculations were carried out at each data point geometry. Since near degeneracy of adiabatic energies was anticipated, we used state averaging in these calculations. By carrying out trials at a number of geometries, it was determined that four-state-averaged calculations (with equal weights) gave convergence of the MCSCF wavefunction consistently (though not always). The MCSCF wavefunctions were then used as the basis for a MRCI calculation for the three lowest energy states. The converged MCSCF wavefunctions and geometries for each data point were stored. At each new data point geometry, the closest geometry in the MCSCF store was determined and that wavefunction was used as a starting guess for the new MCSCF calculation. A restricted Hartree–Fock (RHF) calculation was also carried out at the new geometry, and used to seed the MCSCF calculation. MRCI calculations for the energies at this geometry were carried out using both the “store-based” and “HF-based” MCSCF wavefunctions. We determined which MRCI calculation produced the lowest ground state energy. The corresponding MCSCF wavefunction was then used in the MRCI calculation for the data required for the data point. Since no analytic gradients were available for MRCI calculations, finite differences were used to evaluate the necessary second derivatives, as described in Appendix A. Each data point requires 43 “single point” energy and wavefunction overlap calculations (see Appendix A).

C. Data point selection

The selection of the location of data points in Eq. (3.1) was carried out using the Grow scheme⁴ with substantial modification, as described in Sec. IV of Ref. 7.

The first data point (which is used to numerically determine the symmetry matrices) was chosen to be a near C_{3v} symmetry configuration at which states 2 and 3 are near degenerate (as discussed above). Just as for the application of the grow scheme to adiabatic PES, an initial data set is required to provide a starting approximation to the energy surface (here a DPEM). Configurations in the vicinity of the first point were arbitrarily chosen as data points. Configurations corresponding approximately to points on a minimum energy path for the ground state reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ were included in the set. Calculations at the MCSCF level were carried out one at a time to determine configurations at which all three states were energetically accessible. This whole process resulted in approximately 100 initial data point

configurations. The MRCI calculations were carried out to evaluate the data required for the Taylor series expansions. The confidence lengths required for the weight functions were then determined.⁷ The self-consistent determination of the ADT matrices was then carried out.⁷ This produced an initial data set.

Automatic growth of the data set was then begun in an iterative process, using classical trajectories to sample the configuration space, in the usual Grow procedure. For the nonadiabatic dynamics of interest herein, the trajectory surface-hopping method²⁸ developed by Tully, which is based on the fewest switches algorithm, was used. Details can be found in Sec. IV B of Ref. 7 and in Appendix D herein. In each iteration, ten surface hopping trajectories were evaluated. All trajectories were initiated to simulate the collision of OH($^2\Sigma$) with H₂ (with zero-point-vibrational energy in both diatomics) with 5 mE_h of relative translational energy. A new data point was selected from molecular configurations encountered in these trajectories. The data points were chosen by alternating the “h-weight” based method and the variance sampling method (see Appendix D).⁴ The iterative exploration of the configuration space produces data point configurations as the automated procedure so chooses. Although we do not report explicit examples of conical intersections herein, many data points have nearly degenerate adiabatic energies, so that the eigenvalues of the interpolated DPEM may display conical intersections. More importantly, the classical dynamics involves surface hopping in that part of the full dimensional configuration space where the derivative coupling is sufficiently large; a region in which the adiabatic energies are sufficiently close to degenerate. The energies and geometries of all data points can be found in the full data set contained in the supplementary material.²⁷

During the iterative growth of the data set, the accuracy of the DPEM was examined by considering how accurately the adiabatic energies at each data point were estimated by Eq. (3.1) excluding that data point from the set. The data point with the least accurately estimated energies was determined. A new data point was then constructed at the mean position of that data point and its nearest neighbouring data point. This process was iterated until no large errors could be found.

Quantum wavepacket calculations (see Sec. IV for details) were then carried out for OH($^2\Sigma$) + H₂ with the total angular momentum set to zero. From these calculations and from slices through the adiabatic PES, regions of the configuration space where the adiabatic surfaces appeared to be sharply varying were determined. Data point locations in these regions were selected from the grids employed in the wavepacket calculations, and new data points were added to the set. Finally, this gave a set of 2246 data points.

This data set contained only sparsely scattered data in the OH($^2\Sigma$) + H₂ entrance channel. From slices through the adiabatic PES, it was determined that the OH($^2\Sigma$) + H₂ PES contained no barrier for optimal orientations of the reactants. For a barrierless reaction, the total cross section may be strongly influenced by the form of the PES at long-range separation of the reactants (ion-molecule reactions being an extreme example). Hence, to ensure that the long-range part of the DPEM is accurate, additional data points for OH...H₂ separations

between 7 and 14 bohr were added to the data set using an analytic fit to the long-range PES (see Appendix E for details). This produced a final data set of 2983 data points.

IV. RESULTS

A. Features of the interpolated DPEM

1. Asymptotes

The equilibrium bond length of H₂ in the entrance valley asymptote is 0.7434 Å (expt. 0.7414³⁵), and the harmonic frequency is 4382 cm⁻¹ (expt. 4401). The energy of OH($^2\Pi$) + H + H is 4.585 eV above that of equilibrium OH($^2\Pi$) + H₂. This implies a bond dissociation energy for H₂ of 4.315 eV, which is lower than the experimental value³⁶ of 4.477 eV. Nonetheless, dissociation of H₂ is not energetically accessible under the collision conditions considered herein. The equilibrium bond length of OH is 0.9719 Å ((expt. 0.9697 (Ref. 35)) for the $^2\Pi$ state and 1.0094 Å ((expt. 1.0121 (Ref. 35)) in the $^2\Sigma$ state. The corresponding harmonic frequencies are 3698 cm⁻¹ (expt. 3738) and 3228 cm⁻¹ (expt. 3179). The energy of OH + H₂ at the equilibrium geometry is -76.79496 E_h for the $^2\Pi$ state and higher by 4.147 eV in the $^2\Sigma$ state. This implies a ν_{00} excitation energy for OH of 4.115 eV, slightly above the experimental value of 4.017 eV.³⁵

The equilibrium geometry of H + H₂O has an OH bond length of 0.9600 Å, a HOH angle of 104.2° and an energy of -0.582 eV, relative to OH($^2\Pi$) + H₂. The geometry is very close to that for a very high level of theory, but the relative energy is higher; UCCSD(T)/aug-cc-pV5Z (based on a RHF reference function) gives -0.693 eV.³⁷ This error in the relative energy for the H + H₂O product is small compared to the total energy difference from the OH($^2\Sigma$) + H₂ reactants.

2. Conical intersections

Conical intersections can occur in a four dimensional subspace of the six dimensional space of internal coordinates for OH₃. Moreover, for configurations near this subspace, adiabatic energy levels may be sufficiently close that significant derivative coupling occurs between the states. Figure 1 provides a sketch of a few of the configurations in the data set at which states 2 and 3 are near degenerate and strongly coupled, to provide some indication of the variation.

Aside: Generally, molecular configurations of OH₃, contained in the data set or encountered in classical trajectories have no point group symmetry. When referring to the adiabatic states and their associated PES, the states are simply labelled as states 1, 2 and 3 in order of increasing energy.

The upper most configuration sketched in Figure 1, with near C_{3v} symmetry, is the first point in the data set which is used to evaluate the symmetry matrices. This configuration is about 132 kJ mol⁻¹ (1.37 eV) below the energy of equilibrium OH($^2\Sigma$) + H₂. The degeneracy between states 2 and 3 can occur from energies about 160 kJ mol⁻¹ below that of OH($^2\Sigma$) + H₂ to far above the reactant asymptote. At many such configurations, the energy of state 1 is also within 0.1–0.5 eV of state 3 and there is significant derivative coupling between these states. Hence, classical surface hopping can occur with

FIG. 1. This figure sketches four examples of configurations of OH_3 for which the two lowest excited electronic states are near-degenerate. None of these geometries has any exact point group symmetry, though the top most configuration is near to C_{3v} symmetry.

a very broad range of energies from state 3 to either state 2 or state 1. Figure 2 presents the results of a trajectory simulation of an $\text{OH}(^2\Sigma) + \text{D}_2$ collision at a relative translation energy of 15.5 kJ mol^{-1} (0.16 eV), with zero point energy in the reactants, zero rotational angular momentum and impact parameters up to 6 bohr. There we see the potential energy of state 3 at which the electronic state first hops to state 2 or to state 1. Clearly, hopping from states 3 to 2 is more likely (by about a factor of 3) than hopping from states 3 to 1. Note in particular, the broad range of energy. There is a peak in the energy distribution at around the reactant energy, consistent with the fact that all trajectories initially have potential energies near this value. Otherwise, the energy distribution is very broad, and low energy conical intersections are not particularly significant in this case.

FIG. 2. The distribution of the adiabatic energy of state 3 (relative to equilibrium OH and D_2) at which hopping first occurs out of state 3 in a trajectory simulation of $\text{OH}(^2\Sigma) + \text{D}_2$ (see text for details); (●) hopping to state 2, (○) hopping to state 1.

The broad energy range of surface hopping has a corresponding broad range of molecular configurations at which hopping occurs on the DPEM. For the same trajectory simulation as above, Figures 3 and 4 illustrate the configurations at which hopping first occurs in each trajectory (only 4079 of 23 434 trajectories undergo a surface hop). Figure 3 compares

FIG. 3. The shortest OD bond length is plotted against the shortest HD bond length for 4079 molecular configurations in a simulation of $\text{OH}(^2\Sigma) + \text{D}_2$ at which hopping first occurs from the initial adiabatic state 3.

FIG. 4. As in Figure 3, for the two OD bond lengths.

the minimum HD and OD bond lengths at these “first-hop” configurations. The bimodal distribution shows that most surface hopping occurs when D₂ approaches the oxygen side of OH, but that surface hopping can occur when D₂ approaches the hydrogen side of OH (see the bottom structure in Fig. 1). Figure 4 compares the two OD bond lengths at these “first-hop” configurations.

B. Convergence of the DPEM

Classical trajectory simulations of the reaction OH($^2\Sigma$) + D₂, studied experimentally by Davis and co-workers,¹⁷ were carried out to examine the convergence of the DPEM with the size of the data set. To minimise the statistical errors from Monte Carlo trajectory sampling, the classical dynamics were carried out for zero impact parameter (where the reaction probabilities are large). Figure 5 presents the probability of reaction for the dominant channels (1.1)–(1.3) at the collision energy of the cross molecular beam experiment (15.5 kJ mol⁻¹)¹⁷ and at a lower energy of 1.3 kJ mol⁻¹, versus the size of the data set. For each simulation, a percentage of the full set of data points were discarded at random. It is clear from Figure 5 that the classical reaction probabilities are reasonably constant when more than half the full data set is employed.

The quantum reaction probabilities show a very small variation with the composition of the data set. Figure 6 presents the results of quantum wavepacket calculations³¹ (at zero total angular momentum) for the probability of reactions (1.1) and (1.2) as a function of the collision energy, using the full data set and data sets with 5, 10 or 20% of the data points removed at random. It is clear that the quantum dynamics is converged with respect to the size of the data set over this energy range.

The complete data set and software required to evaluate the DPEM by Eq. (3.1) is contained in the supplementary material.²⁷

C. Classical simulations

A complete quantum dynamical study of this system is beyond the scope of this paper. However, some results of

FIG. 5. The classical probabilities for reactions (1.1)–(1.3) are shown as a function of the percentage of the full data set used in the simulation. All trajectories have zero impact parameter, zero point energy in the reactants, and no rotational angular momentum. For a relative translation energy of 15.5 kJ mol⁻¹, (×) denotes reaction (1.1), (+) denotes (1.2) and (Δ) denotes (1.3). For a relative translation energy of 1.3 kJ mol⁻¹, (●) denotes reaction (1.1), (○) denotes (1.2) and (◆) denotes (1.3). The error bars estimate two standard deviations arising from the finite Monte Carlo sampling.

FIG. 6. The quantum reaction probability at zero total angular momentum, for reactions (1.1) and (1.2), is shown as a function of the relative translational energy using the full data set (●), and data sets with 5% (○), 10% (◆) and 20% (×) of the data removed at random.

FIG. 7. The integral cross section for reactions (1.1)–(1.3) are shown as a function of the relative translation energy of the reactants. The initial conditions comprised zero point energy in the diatomic reactants with zero rotational angular momentum.

classical simulations are presented and compared to experimental data to indicate the utility of this DPEM. The classical cross sections for the reaction of $\text{OH}(^2\Sigma) + \text{D}_2$ have been evaluated for a series of relative translation energies between about 1 and 16 kJ mol^{-1} . Figure 7 presents the results for reactions (1.1)–(1.3). Reactions (1.4) and (1.5) were also observed in these simulations, but with very low (less than 0.1 $\text{\AA}^2$), and hence very uncertain, cross sections. We note that the cross section to form $\text{HOD} + \text{D}$ is relatively constant with energy. However, quenching to $\text{OH}(^2\Pi) + \text{D}_2$ and quenching with exchange display a tendency to rise with decreasing energy, at low energy.

The total cross section for all processes which remove the reactants is about 6.1 $\text{\AA}^2$ at 1.3 kJ mol^{-1} . Heard and Henderson¹⁶ reported that the total (thermal) quenching cross section for $\text{OH}(^2\Sigma) + \text{H}_2$, decreased from $11.8 \pm 0.9 \text{ \AA}^2$ at 200 K to $8.0 \pm 0.6 \text{ \AA}^2$ at 344 K. Given the apparent rise in cross section with decreasing energy, the total quenching cross section calculated herein is consistent with the observations in these experiments. We have not attempted to evaluate cross sections at lower energy, or at low temperatures. As part of constructing the DPEM in the asymptotic reactant valley (see Appendix E), we compared the eigenvalues of the interpolated DPEM with the energies of the fitted potentials at a large sample of configurations in the entrance channel. For this sample, the mean absolute difference in the adiabatic energies interpolated compared to the value given by Eq. (E1), was found to be about $5 \times 10^{-5} E_h$, which is about a factor of 10 smaller than the lowest relative translational energy in Figure 7. At much lower translational energy, interpolation error in the asymptote would be a larger fraction of the available energy, and might significantly affect the dynamics.

FIG. 8. The distribution of the relative kinetic energy for $\text{HOD} + \text{D}$ products is shown for reaction (1.2) at a relative translation energy of 15.5 kJ mol^{-1} . The histogram of trajectory data is shown with error bars that denote two standard deviations arising from the finite trajectory sampling. The open circles represent the distribution of Ref. 17, interpolated and scaled to the same bin size as the trajectory data.

Figure 8 presents the distribution of the relative kinetic energy of the HOD and D atom products at the experimental reactant collision energy of 15.5 kJ mol^{-1} , compared to the experimental data of Ref. 17. The experimental results correspond to the total of the two channels (lower and higher relative kinetic energies) assigned in Ref. 17. The results have been put on the same scale as the trajectory histogram simply by employing the same bin size for the relative kinetic energy distribution. Although there are differences between the trajectory and experimental distributions, both clearly show that the relative kinetic energy is low. The mean relative kinetic energy in the trajectory simulation is 66 kJ mol^{-1} , which represents only about 14% of the available energy released by the reaction. This is reasonably close to the experimental value of 85 kJ mol^{-1} , or 18% of the available energy.³⁸ Both distributions show that the kinetic energy released by the reaction is low, but the trajectory simulation produces a higher proportion of very low kinetic energy products than observed in the experiment.

Figure 9 presents the corresponding distribution of centre of mass scattering angles from the trajectory simulation and the experimental data of Ref. 17. Again, the experimental data corresponds to the total of two channels. The scattering angle was defined in the opposite sense in Ref. 17, but for both sets of data in Fig. 9, small angles correspond to the D atom forward scattered relative to the initial velocity of D_2 . The distribution $T(\theta)$ of Ref. 17 has been multiplied by $\sin(\theta)$ for direct comparison with the trajectory results. Clearly, the simulation of the product angular distribution is in very good agreement with the experimental data.

The dominant product channel for all collision energies studied herein is non-reactive quenching to $\text{OH}(^2\Sigma) + \text{D}_2$. Up to now, this product channel has not been studied in a cross molecular beam experiment (as in Ref. 17), but where

FIG. 9. The distribution of D + HOD scattering angles is shown for reaction (1.2) at a relative translation energy of 15.5 kJ mol⁻¹, with error bars that denote two standard deviations arising from the finite trajectory sampling. The open circles represent the distribution of Ref. 17 (see text for details).

D₂ and the HNO₃ precursor of OH($^2\Sigma$) were co-expanded in a supersonic nozzle.⁸ This experiment reported very different branching ratios from those calculated herein, including a large probability for reaction (1.5), and a different D atom velocity distribution from reaction (1.2) than that reported in Ref. 17. The reaction conditions in Ref. 8 are indicated as corresponding to a collision energy of about 0.05 eV (4.8 kJ mol⁻¹) or possibly a temperature of 150 K (1.2 kJ mol⁻¹). Our calculations indicate that the dynamics does not change dramatically over the energy range of 5–20 kJ mol⁻¹. If the conditions of Ref. 8 correspond to a collision energy of about 5 kJ mol⁻¹, then there is substantial disagreement between the dynamics calculated herein and the observations in Ref. 8. Alternatively, the disagreement may be due to the presence of a proportion of very low energy collisions under the conditions of Ref. 8. Unfortunately, we cannot simulate very low energy dynamics at present. In order to determine whether some aspects of the non-reactive dynamics near a collision energy of 15.5 kJ mol⁻¹ are similar to the experimental observations in Ref. 8, we have employed simple quasi-classical binning to estimate the final vibration-rotation energy distribution of the OH($^2\Pi$) products for the simulation of Figures 8 and 9 (see Figure 10). Despite the very different collision conditions, the vibration-rotation distribution of Fig. 10 is qualitatively similar to that observed in the low energy experiments of Dempsey *et al.*¹² The ground ($v = 0$) vibrational state is the dominant product in both calculation and experiment. The relative population of $v = 1$ is somewhat higher here than in the low energy experiment. The maximum in the rotational angular momentum (j) distribution occurs at around $j = 11$ here, compared to around $j = 15$ –16 in the low energy experiment, but the shapes of the distributions are similar.

The classical simulations reveal some interesting correlations between surface hopping and the formation of different products. For the simulations of Figs. 8–10, both the OH($^2\Pi$)

FIG. 10. The distribution of the rotational angular momentum in the OH($^2\Pi$) product from OH($^2\Sigma$) + D₂ at a collision energy of 15.5 kJ mol⁻¹ is shown. The classically binned vibrational energies correspond to vibrational quantum numbers of 0 (●), 1 (○), 2 (◆) and 3 (×). For clarity, error bars of one standard deviation, arising from the finite Monte Carlo sampling, are indicated for the ground vibrational state only.

+ D₂ and OD($^2\Pi$) + HD products have 41% occupancy in state 1 and 59% in state 2 (which are degenerate in the asymptote). The HOD + D product is 100% in state 1 (states 2 and 3 are energetically inaccessible). However, the first surface hops for trajectories which lead to OH($^2\Pi$) + D₂ are 79% into state 2 and only 21% into state 1. Apparently, subsequent hopping between states 2 and 1 brings the populations closer before the asymptote is reached. The first surface hops for trajectories which lead to OD($^2\Pi$) + HD are 96% into state 2. Conversely, the first surface hops for trajectories which lead to HOD + D are only 40% into state 2 (which must all hop to state 1 prior to reaching the asymptote). As Figure 3 showed, the first hop out of state 3 can occur when the minimum OD distance is greater or smaller than the minimum HD distance. When the HD distance is larger (approach of D₂ towards oxygen), 71% of hops are into state 2. However, when the HD distance is smaller, 99.5% of hops are into state 2.

Zhang *et al.*²⁶ have reported quantum cross sections for reactions (1.1) and (1.2) from a planar (five dimensional) two-state model. These calculations give reaction (1.2) to be more probable than non-reactive quenching, contrary to our calculation. However, this disagreement is not surprising in light of the discussion above, which shows that all three electronic states are involved in the full-dimensional dynamics.

V. CONCLUDING REMARKS

We have constructed an interpolated DPEM for the three lowest energy states of OH₃. The data and software to evaluate this DPEM are available in the supplementary material.²⁷

Both classical and quantum dynamics simulations of reactions (1.1)–(1.5) have been used to demonstrate that the DPEM is converged with respect to the size of the basis set: That is, the results of classical and quantum dynamical simulations are not substantially changed if only part of the data set is employed in the interpolation. We infer from this that additional *ab initio* data are not required for dynamics with collision energies in the range 1–16 kJ mol^{−1}.

This energy range includes the collision conditions relevant to the cross molecular beam experiments of Davis and co-workers.¹⁷ There appears to be substantial agreement between classical simulations on this DPEM and these experimental results. We have not examined the convergence of the DPEM at significantly lower energy. Preliminary calculations have shown that it is difficult and time-consuming to obtain converged quantum reaction probabilities below about 6 kJ mol^{−1}. Although the classical dynamics appears to be converged at a collision energy as low as 1.3 kJ mol^{−1}, we expect (from these preliminary calculations) that significant quantum effects occur below 6 kJ mol^{−1}. Hence, detailed examination of the reaction dynamics at energies below 6 kJ mol^{−1} must await more extensive quantum dynamics calculations. The classical dynamics suggests that the cross sections for non-reactive quenching and quenching with exchange may rise substantially as the energy falls below 3 kJ mol^{−1}. There is a great deal of experimental data from the work of Lester and co-workers.^{8,10–13,39,40} If the reaction conditions in these experiments involve very low energy collisions, then it is important to extend the dynamical calculations to lower energy. Unfortunately, the very low energy region is precisely where quantum dynamics calculations are most difficult, and where the accuracy of the DPEM is most uncertain. The uncertainty in the accuracy of the DPEM arises from two causes. As indicated above, there are interpolation errors in the DPEM, estimated to be about ±0.1 kJ mol^{−1} in the reactant entrance valley. These errors arise from the finite size of the data set, finite precision in the *ab initio* data and the quasi-diabatic nature of the DPEM (the neglect of so-called “non-removable” coupling between the adiabatic electronic states). The second cause of uncertainty arises from the fact that we have employed only a moderate sized basis set and active space in the *ab initio* calculations and that the state-averaged-MCSCF-MRCI method is not exact. Further work is required to establish what is the minimum energy at which reliable quantum dynamics can be obtained from this DPEM.

Finally, it is worth recalling that conical intersections in a four-atom system can occur in a high (four) dimensional space of molecular configurations. Surface hopping is likely to occur at molecular configurations that are near conical intersections. This means that surface hopping can occur over a wide range of molecular shapes and electronic energies, as demonstrated in Figures 2–4.

APPENDIX A: TAYLOR EXPANSION OF $\tilde{\mathbf{D}}$

A quasi-diabatic transformation based on overlaps of electronic wavefunctions is not new. However, a detailed description of how the DPEM is evaluated herein using this approach is necessary. Let ψ represent the adiabatic wave-

functions and $\tilde{\psi}$ represent the diabatic wavefunctions (see Eq. (2.6)), then at some Cartesian configuration, $\mathbf{X}$,

$$\tilde{\psi}(\mathbf{X}) = \mathbf{A}^T(\mathbf{X})\psi(\mathbf{X}). \quad (\text{A1})$$

Similarly, at a geometry displaced slightly from $\mathbf{X}$,

$$\tilde{\psi}(\mathbf{X} + \delta\mathbf{X}) = \mathbf{A}^T(\mathbf{X} + \delta\mathbf{X})\psi(\mathbf{X} + \delta\mathbf{X}). \quad (\text{A2})$$

The ADT is defined by imposing the following condition: that the diabatic wavefunctions change as little as possible with change in molecular configuration. To quantify this condition, we require that L be as large as possible, where

$$L = \sum_{n=1}^{N_{\text{states}}} \langle \tilde{\psi}_n(\mathbf{X} + \delta\mathbf{X}) | \tilde{\psi}_n(\mathbf{X}) \rangle, \quad (\text{A3})$$

is the sum of the overlaps of the diabatic wavefunctions with the corresponding wavefunction at a (slightly) displaced position. Using Eqs. (A1) and (A2), Eq. (A3) becomes

$$\begin{aligned} L &= \sum_{n=1}^{n_{\text{states}}} \sum_{i=1}^{n_{\text{states}}} \sum_{j=1}^{n_{\text{states}}} \langle A_{in}(\mathbf{X} + \delta\mathbf{X})\psi_i(\mathbf{X} + \delta\mathbf{X}) | A_{jn}(\mathbf{X})\psi_j(\mathbf{X}) \rangle \\ &= \sum_{n=1}^{n_{\text{states}}} \sum_{i=1}^{n_{\text{states}}} \sum_{j=1}^{n_{\text{states}}} A_{in}(\mathbf{X} + \delta\mathbf{X})A_{jn}(\mathbf{X}) \langle \psi_i(\mathbf{X} + \delta\mathbf{X}) | \psi_j(\mathbf{X}) \rangle \\ &= \sum_{n=1}^{n_{\text{states}}} \sum_{i=1}^{n_{\text{states}}} \sum_{j=1}^{n_{\text{states}}} A_{in}(\mathbf{X} + \delta\mathbf{X})A_{jn}(\mathbf{X})S_{ij}, \end{aligned} \quad (\text{A4})$$

where

$$S_{ij} = \langle \psi_i(\mathbf{X} + \delta\mathbf{X}) | \psi_j(\mathbf{X}) \rangle. \quad (\text{A5})$$

The value of each S_{ij} is obtained from the overlap of the MRCI wavefunctions given by the MOLPRO package (using the “*trans*” function with the BIORTH option). Now, we maximise L subject to the constraints that both $\mathbf{A}(\mathbf{X})$ and $\mathbf{A}(\mathbf{X} + \delta\mathbf{X})$ are unitary matrices. Introducing matrices Λ and Ω of Lagrange undetermined multipliers, we maximise L ,

$$\begin{aligned} L &= \sum_{n=1}^{n_{\text{states}}} \sum_{i=1}^{n_{\text{states}}} \sum_{j=1}^{n_{\text{states}}} A_{in}(\mathbf{X} + \delta\mathbf{X})A_{jn}(\mathbf{X})S_{ij} \\ &\quad - \sum_{i=1}^{n_{\text{states}}} \sum_{j=1}^{n_{\text{states}}} \Lambda_{ij} \left[\sum_{k=1}^{n_{\text{states}}} A_{ik}(\mathbf{X} + \delta\mathbf{X})A_{jk}(\mathbf{X} + \delta\mathbf{X}) - \delta_{ij} \right] \\ &\quad - \sum_{i=1}^{n_{\text{states}}} \sum_{j=1}^{n_{\text{states}}} \Omega_{ij} \left[\sum_{k=1}^{n_{\text{states}}} A_{ik}(\mathbf{X})A_{jk}(\mathbf{X}) - \delta_{ij} \right]. \end{aligned} \quad (\text{A6})$$

First, we evaluate the derivative of L with respect to $A_{pq}(\mathbf{X} + \delta\mathbf{X})$,

$$\begin{aligned} \frac{\partial L}{\partial A_{pq}(\mathbf{X} + \delta\mathbf{X})} &= \sum_{j=1}^{nstates} A_{jq}(\mathbf{X}) S_{pj} - \sum_{i=1}^{nstates} \sum_{j=1}^{nstates} \Lambda_{ij} \left[\sum_{k=1}^{nstates} \delta_{ip} \delta_{kq} A_{jk}(\mathbf{X} + \delta\mathbf{X}) + A_{ik}(\mathbf{X} + \delta\mathbf{X}) \delta_{jp} \delta_{kq} \right] \\ &= [\mathbf{S}\mathbf{A}(\mathbf{X})]_{pq} - \sum_{j=1}^{nstates} \Lambda_{pj} A_{jq}(\mathbf{X} + \delta\mathbf{X}) - \sum_{i=1}^{nstates} \Lambda_{ip} A_{iq}(\mathbf{X} + \delta\mathbf{X}) \\ &= [\mathbf{S}\mathbf{A}(\mathbf{X})]_{pq} - [\Lambda\mathbf{A}(\mathbf{X} + \delta\mathbf{X})]_{pq} - [\Lambda^T\mathbf{A}(\mathbf{X} + \delta\mathbf{X})]_{pq}. \end{aligned} \quad (\text{A7})$$

Therefore,

$$\frac{\partial L}{\partial A_{pq}(\mathbf{X} + \delta\mathbf{X})} = 0$$

implies

$$\mathbf{S}\mathbf{A}(\mathbf{X}) = [\Lambda + \Lambda^T]\mathbf{A}(\mathbf{X} + \delta\mathbf{X}). \quad (\text{A8})$$

Taking the transpose of (A8) gives

$$\mathbf{A}^T(\mathbf{X})\mathbf{S}^T = \mathbf{A}^T(\mathbf{X} + \delta\mathbf{X})[\Lambda + \Lambda^T]. \quad (\text{A9})$$

Multiplying Eq. (A8) by Eq. (A9) gives (by imposing the unitary constraints)

$$\mathbf{S}\mathbf{A}(\mathbf{X})\mathbf{A}^T(\mathbf{X})\mathbf{S}^T = [\Lambda + \Lambda^T]\mathbf{A}(\mathbf{X} + \delta\mathbf{X})\mathbf{A}^T(\mathbf{X} + \delta\mathbf{X})[\Lambda + \Lambda^T],$$

or

$$\mathbf{S}\mathbf{S}^T = [\Lambda + \Lambda^T]^2. \quad (\text{A10})$$

Thus,

$$[\Lambda + \Lambda^T] = (\mathbf{S}\mathbf{S}^T)^{1/2}, \quad (\text{A11})$$

and so from Eq. (A8)

$$\mathbf{A}(\mathbf{X} + \delta\mathbf{X}) = (\mathbf{S}\mathbf{S}^T)^{-1/2}\mathbf{S}\mathbf{A}(\mathbf{X}). \quad (\text{A12})$$

Equation (A12) is the central result that relates the ADT matrix at the displaced position to the ADT matrix at the original position. The DPEM at the displaced position is then,

$$\begin{aligned} \mathbf{D}(\mathbf{X} + \delta\mathbf{X}) &= \mathbf{A}^T(\mathbf{X} + \delta\mathbf{X})\mathbf{E}(\mathbf{X} + \delta\mathbf{X})\mathbf{A}(\mathbf{X} + \delta\mathbf{X}) = \mathbf{A}^T(\mathbf{X})\mathbf{S}^T \\ &\times (\mathbf{S}\mathbf{S}^T)^{-1/2}\mathbf{E}(\mathbf{X} + \delta\mathbf{X})(\mathbf{S}\mathbf{S}^T)^{-1/2}\mathbf{S}\mathbf{A}(\mathbf{X}), \end{aligned} \quad (\text{A13})$$

so that

$$\tilde{\mathbf{D}}(\mathbf{X} + \delta\mathbf{X}) = \mathbf{S}^T(\mathbf{S}\mathbf{S}^T)^{-1/2}\mathbf{E}(\mathbf{X} + \delta\mathbf{X})(\mathbf{S}\mathbf{S}^T)^{-1/2}\mathbf{S}. \quad (\text{A14})$$

Aside: The $\mathbf{S}$ matrix is close to the unit matrix, *except close to a conical intersection*. Therefore, $\mathbf{S}\mathbf{S}^T$ is also close to the unit matrix, and all the eigenvalues of $\mathbf{S}\mathbf{S}^T$ are close to one, *except close to a conical intersection*. This means that $(\mathbf{S}\mathbf{S}^T)^{-1/2}$ is well defined, *except close to a conical intersection*. So, unless we are very close to a conical intersection, we can evaluate $\tilde{\mathbf{D}}(\mathbf{X} + \delta\mathbf{X})$ at all the displaced positions we need in order to evaluate the first and second Cartesian derivatives of $\tilde{\mathbf{D}}(\mathbf{X})$ by finite differences.

The Cartesian derivatives of each element of $\tilde{\mathbf{D}}$ are transformed into derivatives with respect to local internal coordinates in essentially the same way as for an adiabatic PES,⁴ with minor modification. Briefly, for a molecule of N atoms, there are $3N-6$ internal coordinates. There are therefore $(3N-6)(3N-5)/2$ distinct second derivatives of each $\tilde{\mathbf{D}}_{ij}$ with respect to internal coordinates. The internal coordinates at some data point $\mathbf{X}(n)$ are defined by a linear combination of redundant internal coordinates. As for a PES, we take the reciprocal atom-atom distances as a (possibly redundant) set of internal coordinates. In addition, because the DPEM is not invariant to inversion of the Cartesian coordinates, we also include the $\binom{N}{4}$ possible out-of-plane angles (see Sec. III A of Ref. 7). The displacements, $\delta\mathbf{X}$, in Eq. (A14) correspond to the $(3N-6)(3N-5) + 1$ geometries needed to evaluate the value, gradient and second derivatives of $\tilde{\mathbf{D}}$ by central finite difference.

APPENDIX B: TRANSFORMING THE SYMMETRY AND ADT MATRICES

From Eqs. (3.1) and (3.3), the DPEM can be transformed by an arbitrary unitary matrix to give

$$\begin{aligned} \mathbf{B}^T\mathbf{D}(\mathbf{Z})\mathbf{B} &= \sum_{g \in G} \sum_{n=1}^{ndata} w[\mathbf{Z}; g \circ \mathbf{Z}(n)] \mathbf{B}^T \mathbf{M}^T(g) \mathbf{B} \mathbf{B}^T \mathbf{A}^T(n) \\ &\times \tilde{\mathbf{D}}[\mathbf{Z}; g \circ \mathbf{Z}(n)] \mathbf{A}(n) \mathbf{B} \mathbf{B}^T \mathbf{M}(g) \mathbf{B}. \end{aligned}$$

Defining

$$\mathbf{B}^T \mathbf{M}(g) \mathbf{B} \equiv \mathbf{M}'(g),$$

$$\mathbf{A}(n) \mathbf{B} \equiv \mathbf{A}'(n),$$

$$\mathbf{B}^T \mathbf{D}(\mathbf{Z}) \mathbf{B} \equiv \mathbf{D}'(\mathbf{Z}),$$

returns the DPEM to the usual form,

$$\begin{aligned} \mathbf{D}'(\mathbf{Z}) &= \sum_{g \in G} \sum_{n=1}^{ndata} w[\mathbf{Z}; g \circ \mathbf{Z}(n)] \mathbf{M}'^T(g) \mathbf{A}'^T(n) \\ &\times \tilde{\mathbf{D}}[\mathbf{Z}; g \circ \mathbf{Z}(n)] \mathbf{A}'(n) \mathbf{M}'(g). \end{aligned}$$

We can choose the arbitrary matrix $\mathbf{B}$ for convenience. For example, for OH + H₂, if the hydrogen atoms in H₂ are numbered atoms 3 and 4 in one asymptote, then we can

choose $\mathbf{B}$ such that

$$\mathbf{B}^T \mathbf{M} [g = (34)] \mathbf{B} = \mathbf{I}.$$

Assuming there is no conical intersection near this asymptote, the ADT matrices will approach the unit matrix in this region.

$$\begin{aligned} \mathbf{D}|_{\mathbf{X}=\mathbf{X}(n)} &= \mathbf{A}^T(n) \mathbf{E}|_{\mathbf{X}=\mathbf{X}(n)} \mathbf{A}(n) \\ \frac{\partial}{\partial X_a} \mathbf{D} \Big|_{\mathbf{X}=\mathbf{X}(n)} &= \mathbf{A}^T(n) \left(\frac{\partial}{\partial X_a} \mathbf{E} + [\mathbf{F}_a, \mathbf{E}]_- \right) \Big|_{\mathbf{X}=\mathbf{X}(n)} \mathbf{A}(n) \\ \frac{\partial^2}{\partial X_b \partial X_a} \mathbf{D} \Big|_{\mathbf{X}=\mathbf{X}(n)} &= \mathbf{A}^T(n) \left(\left[\frac{\partial}{\partial X_b} \mathbf{F}_a, \mathbf{E} \right]_- + \mathbf{F}_b \mathbf{F}_a \mathbf{E} + \mathbf{E} \mathbf{F}_a \mathbf{F}_b \right. \\ &\quad \left. + \left[\mathbf{F}_a, \frac{\partial}{\partial X_b} \mathbf{E} \right]_- + \left[\mathbf{F}_b, \frac{\partial}{\partial X_a} \mathbf{E} \right]_- - \mathbf{F}_a \mathbf{E} \mathbf{F}_b - \mathbf{F}_b \mathbf{E} \mathbf{F}_a + \frac{\partial^2}{\partial X_b \partial X_a} \mathbf{E} \right) \Big|_{\mathbf{X}=\mathbf{X}(n)} \mathbf{A}(n), \end{aligned}$$

where $[\mathbf{A}, \mathbf{B}]_- = \mathbf{AB} - \mathbf{BA}$.

APPENDIX D: TRAJECTORY DETAILS

1. Derivative coupling

Surface hopping trajectories were evaluated as described in Ref. 7. The atomic motion is governed by a single adiabatic PES (an eigenvalue of the DPEM) and a change of PES (surface hop) is determined by the derivative coupling between states. If $\mathbf{e}_k$ and $\mathbf{e}_j$ are eigenvectors of $\mathbf{D}(\mathbf{Z})$, then the component of the derivative coupling, $\mathbf{F}_{kj}$, between states k and j is given by

$$(\mathbf{F}_{kj})_\alpha = \frac{\mathbf{e}_k^T \frac{\partial \mathbf{D}}{\partial X_\alpha} \mathbf{e}_j}{E_k - E_j}. \quad (\text{D1})$$

However, extensive testing has shown that Eq. (D1) produces significant interpolation error in the evaluation of $\mathbf{F}_{kj}$, due to derivatives of the interpolation weights. Hence, Eq. (D1) has been replaced by

$$(\mathbf{F}_{kj})_\alpha = \frac{\mathbf{e}_k^T \mathbf{dD}_\alpha \mathbf{e}_j}{E_k - E_j}, \quad (\text{D2a})$$

where

$$\mathbf{dD}_\alpha = \sum_{g \in G} \sum_{n=1}^{ndata} w[\mathbf{Z}; g \circ \mathbf{Z}(n)] \frac{\partial \mathbf{D}[\mathbf{Z}; g \circ \mathbf{Z}(n)]}{\partial X_\alpha}. \quad (\text{D2b})$$

When a surface hop from state k to state j occurs, the atomic momenta are adjusted using the derivative coupling, $\mathbf{F}_{kj}$.^{41,42} The derivative coupling of Eq. (D2a) is minimally adjusted to ensure that the momentum of the molecular centre of mass and the total angular momentum are not changed by the hop.

APPENDIX C: TAYLOR EXPANSION OF $\tilde{\mathbf{D}}$ USING DERIVATIVE COUPLING

Some *ab initio* packages can provide the derivative coupling, $\mathbf{F}_{ij}$, between adiabatic states efficiently, using so-called analytic gradient techniques. Using this data, the DPEM can be evaluated as described in Ref. 7. Note, however, that Eq. (3.9) in Ref. 7 contains an error, and should be replaced by

2. Variance of the DPEM

In the iterative growth of the data set, new data points are chosen in each cycle of the iteration. The choice of a new data point was determined by the “h-weight” criterion⁴ every second cycle. In alternate cycles, the new data point was chosen to be the sampled trajectory configuration at which the variance in the DPEM was largest in magnitude. This variance is given by $\sigma(\mathbf{D})$,

$$\sigma(\mathbf{D}) = \sum_{g \in G} \sum_{n=1}^{ndata} w[\mathbf{Z}; g \circ \mathbf{Z}(n)] \|\mathbf{D}[\mathbf{Z}; g \circ \mathbf{Z}(n)] - \mathbf{D}(\mathbf{Z})\|^2. \quad (\text{D3})$$

APPENDIX E: LONG-RANGE PES

The interaction of OH with H_2 at large OH... H_2 separations can be approximated in terms of electrostatic, induction and dispersion interactions.⁴³ *Ab initio* calculations show that the splitting of the degeneracy of the lowest two electronic states is negligible when the smallest intermolecular distance exceeds about 7 bohr. Hence, in this asymptotic region, the energy of the two lowest energy states are taken to be equal. The major contributions to the total energy arise from (1) the quadrupole moment of H_2 interacting with the dipole and quadrupole moments of OH; (2) the dispersion interaction and (3) the OH and H_2 bond stretching energies. An appropriate potential energy function, $V(\mathbf{X})$, is therefore constructed as follows.

We assume that atom 1 (oxygen) is bonded to atom 2 in the OH + H_2 asymptote. Following the previous coordinate definitions (see Eqs. (3.4) and (3.5)), the OH bond vector is $\mathbf{r}(1)$ and the H_2 bond vector is $\mathbf{r}(6)$. The corresponding reciprocal bond lengths are Z_1 and Z_6 . The electrostatic

moments on OH and H₂ are taken to be at the centers of nuclear charge for each diatom, so that the interatomic vector **R** is given by

$$\mathbf{R} = \frac{1}{2} [\mathbf{x}(3) + \mathbf{x}(4)] - \frac{1}{9} [8\mathbf{x}(1) + \mathbf{x}(2)].$$

The asymptotic potential is then given (in atomic units) by

$$\begin{aligned} V(\mathbf{X}) = & c_0 + \sum_{n=1}^{N_b} c_n (Z_1 - Z_1^{eq})^n + \sum_{n=1}^{N_b} c_{N_b+n} (Z_6 - Z_6^{eq})^n \\ & + [c_{2N_b+1} + c_{2N_b+2}r(1) + c_{2N_b+3}r(6) + c_{2N_b+4}r(1)r(6)] \\ & \times \hat{r}_\alpha(1)T_{\alpha\beta\gamma} \left[\frac{3}{2}\hat{r}_\beta(6)\hat{r}_\gamma(6) - \delta_{\beta\gamma} \right] \\ & + [c_{2N_b+5} + c_{2N_b+6}r(1) + c_{2N_b+7}r(6) + c_{2N_b+8}r(1)r(6)] \\ & \times \left[\frac{3}{2}\hat{r}_\alpha(1)\hat{r}_\beta(1) - \delta_{\alpha\beta} \right] T_{\alpha\beta\gamma\delta} \left[\frac{3}{2}\hat{r}_\gamma(6)\hat{r}_\delta(6) - \delta_{\gamma\delta} \right] \\ & + \frac{c_{2N_b+9}}{R^6}, \end{aligned} \quad (\text{E1})$$

where $T_{\alpha\beta\gamma} = \nabla_\alpha \nabla_\beta \nabla_\gamma (1/R)$; $T_{\alpha\beta\gamma\delta} = \nabla_\alpha \nabla_\beta \nabla_\gamma \nabla_\delta (1/R)$, we employ the convention where repeated subscripts are summed in Eq. (E1), and $\hat{r}$ denotes a unit vector. We set $Z_1^{eq} = 0.545 \text{ bohr}^{-1}$ and $Z_6^{eq} = 0.710964 \text{ bohr}^{-1}$, and all lengths in Eq. (E1) are taken in bohr. After some preliminary investigation, we set $N_b = 8$, so that there are 26 unknown coefficients in Eq. (E1). The potential depends linearly on these coefficients. The *ab initio* energy of all three states was determined at a set of 189 geometries for which all intermolecular bonds exceeded 7 bohr, and which were scattered up to **R** values of about 14 bohr. The set included many geometries with stretched or compressed OH and H₂ bondlengths. The 26 unknown coefficients were least squares fit to these *ab initio* energies, using a singular value decomposition approach. An asymptotic potential was thereby derived for the highest adiabatic energy, $E(3)$, and for the average energy, $(1/2)[E(1) + E(2)]$. The average residual fitting error was approximately $1 \times 10^{-5} E_h$. Table S2 in the supplementary material²⁷ presents the fitted values of the coefficients.

Equation (E1) was employed to generate the three adiabatic energies at any geometry, with $E(1) = E(2)$. The overlap matrix, **S**, of Eq. (A5) was set to the unit matrix. The data required in Eq. (A14) can therefore be generated, so that a new Shepard interpolation data point can be constructed. In this asymptotic region, the ADT matrix is the unit matrix. Interpolation data points were generated in this asymptotic region as follows. The OH bond length was randomly selected from a uniform distribution in the interval 1.4–2.4 bohr. The H₂ bond length was randomly selected from a uniform distribution in the interval 1.1–1.8 bohr. The intermolecular separation, **R**, was randomly selected from a uniform distribution in the interval 7.0–14.0 bohr. The relative orientation of OH and H₂ was randomly selected. Thus a number (typically 1000) of geometries were generated. The adiabatic energies at each geometry were evaluated in two ways: from Eq. (E1) and by interpolation, using the current data set and Eq. (3.1). The geometry with the largest absolute difference between the

two values of $E(3)$ or $(1/2)[E(1) + E(2)]$ was chosen to be a new data point. Only random geometries at which the energies were experimentally accessible were considered for inclusion in the data set. The new data point was generated and included in the interpolation data set. The generation of random geometries and selection of the configuration with largest energy difference was repeated until 737 additional data points were generated. At this point, the average interpolation error for the adiabatic energies in this asymptotic region was estimated, from a large sample of random configurations, to be below $5 \times 10^{-5} E_h$. By comparison, the total zero-point vibrational energy in this region is about $1.5 \times 10^{-2} E_h$.

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