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Ab initio potential energy surface for the reactions between H₂O and H

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Interpolated *ab initio* potential energy surfaces which describe abstraction and exchange reactions in collisions of hydrogen and water are reported. The electronic structure calculations are performed at the QCISD(T) level of theory, with an additivity approximation. A sufficiently large basis set is required to describe the Rydberg character of the electronic state for molecular configurations which are important for the exchange process. Classical and quantum dynamics calculations on the surfaces are presented. © 2000 American Institute of Physics. [S0021-9606(00)30923-0]

I. INTRODUCTION

The reaction between a hydrogen atom and water,

$$H+H_2O \rightarrow OH+H_2, \tag{1.1}$$

has been the subject of considerable experimental and theoretical interest.¹ Experimental studies have considered the temperature² and energy³ dependence of the rate coefficient. The reaction became a focus of attention when it was shown by Crim and co-workers and Zare and co-workers^{4,5} to have a rate constant that depended strongly on the initial vibrational state of the water molecule. In particular, the branching ratio between reactions (1.2),

$$H + HOD \rightarrow OH + HD,$$
 (1.2a)

$$H + HOD \rightarrow OD + H_2,$$
 (1.2b)

was shown to vary substantially with initial excitation of the OH or OD stretching modes in HOD.^{4,5} Recent experiments have also considered the competition between these reactions and collision-induced vibrational relaxation.^{6,7} To add further complexity to this system, various exchange/abstraction reactions can compete with the simple abstraction reaction,⁸

$$H+D_2O \rightarrow HOD+D,$$
 (1.3)

$$H+D_2O \rightarrow OH+D_2. \tag{1.4}$$

Up to now, no potential energy surface (PES) has been available to provide the foundation for accurate theoretical investigations of *all* the reactions (1.1) to (1.4). The initial *ab initio* work on the OH₃ system was performed by Walch and Dunning.⁹ These authors found that the saddle point to the reaction,

$$OH + H_2 \rightarrow H_2 O + H, \tag{1.5}$$

was a planar *cis*-HOH–H configuration. Schatz and Elgersma¹⁰ then approximately fitted an analytical potential function to this and their own *ab initio* data. This analytic

surface, or a modified form of it, has since been used in numerous quantum mechanical scattering calculations to study reaction (1.5) and, to a lesser extent, reaction (1.1). More recently, Alagia *et al.*¹¹ reported the dynamics of the reaction

$$OH+D_2 \rightarrow DOH+D.$$
 (1.6)

This work includes the highest level ab initio calculations to have been reported on this system to date. An analytic PES was fitted to 640 energies evaluated using an internally contracted multireference configuration interaction with Davidson correction procedure (CMRCI+Q) for molecular configurations which were constrained to be planar, in which the OH bond length was constrained, and which were chosen to lie close to the minimum energy path (MEP) for reaction (1.6). This PES is very accurate in an important fourdimensional region of the configuration space, and may accurately describe reaction (1.6). More recently, Ochoa de Aspuru and Clary developed a new functional form for this surface based on the same *ab initio* data.¹² However, both these surfaces are not based on ab initio data in much of the configuration space required to describe reactions (1.1) to (1.4).

In this paper we present potential energy surfaces that are given by an interpolation of QCISD(T) level ab initio data at geometries scattered in a sufficiently large region of configuration space that reactions (1.1) to (1.4) should be adequately described. However, these surfaces do not describe molecular configurations in much of the OH+H₂ region of the surface. Unfortunately, in the entrance channel of reaction (1.5) there is a second low-lying electronic state. These two low-lying states are nearly degenerate (split by less than 2 kJ mol⁻¹) until the H₂ is quite close to OH (when the forming OH bond is about 2.6 Å long). The theoretical and practical consequences of the ensuing breakdown in the Born-Oppenheimer approximation in this region of configuration space are discussed in more detail below. For those regions of configuration space where adiabatic dynamics is clearly applicable, we report here the most accurate PES for

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the full dimensional OH_3 system to date. The PES is an interpolation of high-level *ab initio* data distributed throughout the full six-dimensional configuration space. The interpolated PES incorporates not only the *ab initio* energies at each of the data points, but also the gradients and second derivatives of the energies with respect to the six internal degrees of freedom.

In order to compute the required gradients and second derivatives in a feasible time, we have employed an additive approximation to correct the QCISD(T) energies, gradients, and second derivatives for basis set inadequacy, in a similar manner to that employed in G2(MP2) calculations.¹³ The inaccuracy of the resultant PES is primarily due to the use of this additivity approximation. A very simple ansatz is then used to evaluate a second PES based on data in which the energy at each data point is given by the exact QCISD(T) value for a large basis set, although the gradients and second derivatives at each data point rely on the additivity approximation.

Some results of exact quantum scattering calculations of the collision of H and H_2O (at zero total angular momentum) on these PES are presented to demonstrate the convergence of these interpolated surfaces. The results of classical calculations of the reaction cross sections are also reported.

The paper is set out as follows. Section II describes the methods employed in this work. The electronic structure method employed to construct the full PES is presented and compared, at certain stationary points on the surface, with various levels of *ab initio* theory and with results obtained by other workers. Calculations are also presented to show the presence of two low-lying electronic states in much of the OH+H₂ valley, and to indicate the region in which an isolated ground-state PES can be constructed. The form of the interpolated PES is briefly described, and various computational details regarding the iterative construction of the PES are presented. Section III presents the PES surfaces and describes the need for extra diffuse basis functions to accurately describe reaction (1.3). Section IV presents the results of dynamical studies of reactions (1.1) and (1.3) to indicate the convergence of the interpolated PES. A brief summary and discussion concludes the paper.

II. METHODS

In this section, the method for iteratively developing an interpolated PES is briefly presented. The current methodology has been presented in detail elsewhere.

A. Form of the PES

The PES is given by an interpolation of Taylor expansions centered at data points scattered throughout the configuration space of the system.^{14–19} For the molecule considered here, the PES can be constructed using the inverse interatomic distances, $\mathbf{Z} = \{1/R_1, 1/R_2, \ldots, 1/R_6\}$, as coordinates. The potential energy, *V*, at a configuration, **Z**, in the vicinity of a data point, $\mathbf{Z}(i)$, can be expanded as a Taylor series to second order, T_i ,

$$T_{i}(\mathbf{Z}) = V[\mathbf{Z}(i)] + \sum_{k=1}^{6} \left[Z_{k} - Z_{k}(i) \right] \frac{\partial V}{\partial Z_{k}} \bigg|_{\mathbf{Z} = \mathbf{Z}(i)}$$
$$+ \frac{1}{2!} \sum_{k=1}^{6} \sum_{j=1}^{6} \left[Z_{k} - Z_{k}(i) \right] [Z_{j} - Z_{j}(i)]$$
$$\times \frac{\partial^{2} V}{\partial Z_{k} \partial Z_{j}} \bigg|_{\mathbf{Z} = \mathbf{Z}(i)} + \cdots .$$
(2.1)

If the required energy and derivatives have been evaluated at each of N_d molecular configurations, a modified Shepard interpolation^{20,21} gives the potential energy at any configuration **Z** as a weighted average of the Taylor series about all N_d data points and their symmetry equivalents,¹⁸

$$V(\mathbf{Z}) = \sum_{g \in G} \sum_{i=1}^{N_d} w_{g \circ i}(\mathbf{Z}) T_{g \circ i}(\mathbf{Z}).$$
(2.2)

The weight function, w_i , gives the contribution of the *i*th Taylor expansion to the potential energy at the configuration **Z**. In Eq. (2.2), *G* denotes the symmetry group of the molecule; in this case *G* is S_3 , the group of permutations of the three hydrogens. Here, $g \circ i$ denotes that the *i*th data point, **Z**(*i*), is transformed by the group element *g*. The sum over $g \in G$ means that all permutationally equivalent data points are included in the data set.²² The form of the weight function, w_i , has been discussed in detail elsewhere.^{18,19,23} We have used a "two-part" weight function which is derived via a Bayesian analysis of the data set. All the details are as previously reported.¹⁹

B. Iterative development of the PES

The location of the data points in Eq. (2.2) has been determined using the iterative methods developed previously;^{14,15,18} an initial set of data points was chosen to lie on or near the reaction path for reaction (1.1), and new data points (chosen from the paths of classical trajectories) were iteratively added to the set until the PES was held to be "converged." In earlier studies, convergence of this type of PES has been established by performing large-scale classical simulations of the reaction(s) of interest periodically during the "growth" of the data set. When the observable properties of interest, e.g., a rate coefficient, do not change with increasing data set size, the PES is taken to be converged. Recently, we have demonstrated that this type of interpolated PES converges in that the quantum probability of reaction converges to the exact value as the size of the data set increases.24

The methods for choosing a new data point at each iteration have been discussed in detail elsewhere. Here we have used both "variance sampling" ¹⁸ and "h weight" methods^{14,15} alternatively for each additional data point.

The distribution of data points chosen is influenced by the distribution of configurations sampled by the classical trajectories. The initial conditions for these trajectories principally determine the energy range of the data points, and bias the relative frequency with which different regions of configuration space are sampled. Each new data point is chosen from a sample of molecular configurations encountered

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during a classical simulation of the reaction. Here we consider two slightly different types of classical simulation, where the classical trajectories are initiated at either (a) separated reactants for reaction (1.1), or (b) at the saddle point for reaction (1.1). For the separated reactants, H₂O was given various fixed vibrational energies with coordinates and momenta corresponding to a microcanonical distribution. The H₂O molecule was initially randomly oriented and given zero rotational angular momentum, an impact parameter of zero relative to the H atom, and an initial separation relative to H of $10-12a_0$. For case (b), the OH₃ molecule was given various fixed vibrational energies with coordinates and momenta corresponding to a microcanonical distribution, subject to the constraint that the forming OH bond be 2.554 68 $\pm 0.05a_0$. The OH₃ moiety has zero angular momentum.

C. Ab initio methods for reaction (1.1)

It has been demonstrated previously,²⁵ that in order to achieve accuracy for the barrier height for reaction (1.1), very high levels of ab initio theory are required. Our method for constructing a full-dimensional PES requires energies, gradients, and second derivatives of the potential at many molecular configurations. At present there are no *ab initio* program packages available to calculate all of these quantities analytically at the required levels of theory. The CPU time necessary to numerically evaluate these quantities is very high. However, the success of "additive" methods, such as G2 and G2(MP2), for determining the energetics of numerous chemical systems, suggests a resolution of this difficulty. The utility of these methods is to significantly reduce CPU time by performing a number of relatively low-level ab initio calculations in order to approximate the energy that would be obtained from a single high-level calculation.

The basic idea behind the additivity ansatz used here is an assumption that a basis set correction for a high level treatment of electron correlation can be obtained from the basis set correction for a lower level treatment of electron correlation. The high and low level configuration interaction (CI) methods we have chosen are the same as G2(MP2), i.e., QCISD(T) and MP2, respectively. Thus, the additivity approximation is given by

E[QCISD(T)/large basis]

$$\approx E[QCISD(T)/moderate basis] + \Delta_{basis},$$
 (2.3a)

where

$$\Delta_{\text{basis}} = E[\text{MP2/large basis}] - E[\text{MP2/moderate basis}].$$
(2.3b)

In order to determine the appropriate basis sets, the relative energies of the reactants and products and the barrier to reaction for (1.1) have been compared at the MP2 and QCISD(T) levels of theory using the GAUSSIAN94 and GAUSSIAN98 suite of programs.^{26,27} The basis sets employed were varied in a consistent manner from 6-31G(*d*) through to 6-311++G(3*df*,3*pd*) and aug-cc-pVTZ, for a fixed set of geometries. Illustrative results are displayed in Table I. Results for UCCSD(T) calculations with a very large basis set are also shown in Table I to indicate the best available

TABLE I. Comparison of the energy at stationary points on the PES for reaction (1.1), using the QCISD(T) method and the corresponding additivity approximation, Eq. (2.3).

Structure ^a	Moderate basis	Large basis	Additive energy ^b kJ mol ⁻¹	QCISD(T) energy ^c kJ mol ⁻¹
Abstraction saddle	6-311G(d,p)	6-311+G(3df,2p)	97.2	90.1
		6-311+G(2df,2pd)	94.7	88.8
		6-311 + + G(2df, 2pd)	94.5	88.6
		6-311 + + G(3df, 2pd)	95.3	89.0
		6-311 + + G(3df, 3pd)	95.3	88.8
		aug-cc-pVTZ	92.7	85.8
		aug-cc-pV5Z ^d	•••	89.5
$OH+H_2$	6-311G(d,p)	6-311+G(3df,2p)	67.5	63.0
		6-311+G(2df,2pd)	68.4	65.0
		6-311 + + G(2df, 2pd)	68.3	64.9
		6-311 + + G(3df, 2pd)	68.9	65.2
		6-311 + + G(3df, 3pd)	69.0	65.5
		aug-cc-pVTZ	66.6	63.0
		aug-cc-pV5Z ^d		66.7

^aStructures were obtained by constraining the structure planer and performing a full optimization at the CCSD(T)/6-311++G(d,p) level.

^bEnergies relative to H_2O+H , using Eq. (2.3).

 $^{\rm c} {\rm Energies}$ relative to ${\rm H_2O+H},$ using single-point energies at the QCISD(T)/ large basis level.

^dEnergies relative to H₂O+H, using UCCSD(T)/[aug-cc-pV5Z on oxygen, pV5Z on hydrogen]. These energies were evaluated using the MOLPRO suite of programs (Ref. 28).

theoretical estimates. From these results, the optimal choice for the moderate and large bases were taken to be 6-311G(d,p) and 6-311+G(2df,2pd), respectively. This choice reflects a balance between CPU time and accuracy. It is clear from Table I that the error due to the additivity approximation is of the order of 3-6 kJ mol⁻¹ for the QCISD(T)/6-311+G(2df,2pd) level of theory in the region of the MEP for reaction (1.1).

The saddle point and asymptotic geometries were then reoptimized at the level of theory given by Eq. (2.3). The saddle point configuration is represented in Fig. 1. A barrier of 94.9 kJ mol⁻¹ for reaction (1.1) was obtained at these optimized geometries. The electronic energy difference between equilibrium reactants and products is 68.4 kJ mol⁻¹ under this approximation. In order to determine the most reliable theoretical estimate of the barrier for reaction (1.1) to date, we performed a UCCSD(T)/O-aug-cc-pV5Z, (H-ccpV5Z) calculation using the geometries for OH,H₂,H₂O, and the saddle point from our additivity calculations. The MOLPRO suite of programs²⁸ was used for these particular



FIG. 1. A schematic representation of the structure of the saddle point for the abstraction reaction (1.1), evaluated using the additivity approximation of Eq. (2.3) with the 6-311G(d,p) and 6-311+G(2df,2pd) basis sets. The bond lengths are given in Angstrom and the bond angles are given in degrees.

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TABLE II. Properties of the OH₃ potential energy surfaces of Schatz and Elgersma (Ref. 10), Alagia et al. (Ref. 11), and this work.

Property	SE fit ^a	CMRCI+Q ^b	This work	Experimental value		
H ₂ O properties						
$r_{\rm OH}/a_0$	1.808	1.815	1.814	1.811 ^c		
∠HOH/deg	104.6	104.29	104.0	104.3 ^c		
$\omega_1/\mathrm{cm}^{-1}$	3864	3828	3841	3825 ^c		
$\omega_2/\mathrm{cm}^{-1}$	1687	1647	1660	1654 ^c		
$\omega_3/\mathrm{cm}^{-1}$	3975	3935	3950	3936 ^c		
OH properties						
$r_{\rm OH}/a_0$	1.863	1.838	1.835	1.832 ^d		
$\omega_e/\mathrm{cm}^{-1}$	3624	3733	3754	3738 ^d		
H ₂ properties						
$r_{\rm OH}/a_0$	1.429	•••	1.403	1.401 ^d		
$\omega_e/\mathrm{cm}^{-1}$	4261		4421	4401 ^d		
Saddle point properties						
$r_{\rm OH}/a_0$	1.86	1.836	1.834			
$R_{\rm OH-H2}/a_0$	2.31	2.562	2.555			
$\angle H_c H_b O/deg$	163.4	161.47	164.0			
$\angle H_bOH_a/deg$	116.3	97.10	96.2			
$\tau(H_aOH_bH_c)/deg$	180	0	0			
ω_1 (torsion)/cm ⁻¹	830	487	486			
$\omega_2/\mathrm{cm}^{-1}$	573	576	582			
$\omega_3 $ (H ₂ O bend)/cm ⁻¹	857	1072	1062			
ω_4 / cm ⁻¹	1920	2609	2585			
$\omega_5/\mathrm{cm}^{-1}$	3542	3729	3758			
$\omega_i/\mathrm{cm}^{-1}$	1526 <i>i</i>	1197 <i>i</i>	1336 <i>i</i>			
Energy relative to $OH+H_2/kJ \text{ mol}^{-1}$	25.5	24.2	26.5			

^aSee Table II of Ref. 10.

^bSee Table I of Ref. 11.

^cReference 30.

^dReference 31.

calculations. The barrier obtained at this level of theory was 89.5 kJ mol⁻¹, and the energy difference from equilibrium reactants to products was 66.8 kJ mol⁻¹. It is worth noting that the additive approach saves more than an order of magnitude in CPU time compared to a direct calculation of the PES data points at the QCISD(T)/6-311+G(2df,2pd) level.

The vibrational energy levels of OH, H₂, and H₂O have been calculated on this surface, which enabled us to calculate the enthalpy of reaction (1.1) at 0 K: $\Delta H(0K) = 61.8$ kJ mol⁻¹. This value compares very well with the experimental value of 61.3 ± 1.2 kJ mol⁻¹.²⁹

Table II compares some of the properties of stationary points on the OH₃ surface obtained with this additivity approach to those reported by Alagia et al.¹¹ and Schatz and Elgersma.¹⁰ It is clear from Table II that our results agree well with the high level calculations of Alagia et al.

The PES construction method used herein requires the first and second derivatives of the energy at each data point. From Eq. (2.1), it is apparent that we therefore require the first and second derivatives of the MP2/6-311G(d,p), MP2/6-311+G(2df, 2pd), and QCISD(T)/6-311G(d, p) energies at each data point. Analytic first and second derivatives of the MP2 energies were evaluated using the GAUSSIAN94 suite of programs.²⁶ The corresponding derivatives of the QCISD(T)/6-311G(d,p) surface were obtained



FIG. 2. The energy of OH₃, evaluated using Eq. (2.3) and relative to that of OH+H₂, is shown for configurations on a planar minimum energy path leading to the saddle point of Fig. 1. The energy of the $A'(\bullet)$ and $A''(\circ)$ states are shown as functions of the forming O . . . H bond length. The lines are merely visual aids.

from central differences of 43 single-point energy calculations. It is important to note that accurate derivatives could only be obtained when both the self-consistent field (SCF) wave function and QCISD iteration were very tightly converged; the electron density in the SCF procedure was converged to 10^{-12} , and the QCISD energy was converged to 10^{-12} .

D. Domain of the PES

We have evaluated the PES throughout much of the configuration space in which the potential energy is no more than about 260 kJ mol^{-1} above the energy of separated H₂O+H. However, we have not evaluated the PES in much of the OH+H₂ region of the surface for the following reasons.

The electronic ground state of OH is ${}^{2}\Pi$. Thus, when $({}^{1}\Sigma_{a}^{+})H_{2}$ is infinitely separated from OH there exists a spatial double degeneracy. Except for collinear geometries, this degeneracy is lifted as H2 approaches OH. Geometries on the minimum energy path (MEP) for reaction (1.1), for example, possess only C_s symmetry. In this case, the two states which correlate with the asymptotic ${}^{2}\Pi$ state are labeled A' and A", depending on whether the unpaired electron lies in a molecular orbital in the plane of OH_3 or not, respectively. The A' state correlates with the ground state of the H₂O+H products.

Figure 2 shows the energy [as given by Eq. (2.3)] of the two electronic states originating from the ${}^{2}\Pi$ state of OH, as H₂ approaches OH along this MEP until the saddle point has been reached. Figure 3 is an enlargement of this energy profile which clearly indicates that the splitting of these two states does not reach 1.5 kJ mol⁻¹ until the H₂ is quite close to the OH (when the forming O-H bond is about 2.6 Å



FIG. 3. An enlargement of Fig. 2 which more clearly shows the energy splitting of the $A'(\Phi)$ and $A''(\bigcirc)$ states.

long). The energy splitting of these two states then rises rapidly to about 105 kJ mol⁻¹ at the saddle point. The relative stability of the A'' state "early" along the MEP is evident in Fig. 3. Clearly, this near degeneracy, and reversal in the expected relative stabilities, persists over a large region of configuration space in the OH+H₂ channel. For nonplanar, C_1 symmetry, configurations in the OH+H₂ valley, the two potential energy surfaces cannot cross, but must form a complicated pattern of avoided crossings. For geometries in which the H₂ is closer to the H atom in OH than to the O atom, the splitting between the two states is much smaller than that indicated in Figs. 2 and 3. The two states remain degenerate for all collinear configurations in the OH+H₂ entrance channel.

Hence, it not clear that the dynamics of $OH+H_2$ can be very accurately described using a single Born-Oppenheimer surface. No exact nonadiabatic quantum reaction dynamics has yet been reported for a system of more than three atoms. Therefore, at this time, calculation of both low-lying electronic surfaces, and the nonadiabatic matrix elements coupling them, does not appear to be warranted. In addition, there are practical difficulties associated with constructing ab initio PES in the OH+H2 region with single determinant methods (as used herein): For configurations that possess no symmetry, it is generally not possible to converge the SCF wave function because the first excited electronic surface lies very close to the ground-state surface. Such difficulties can be overcome through the use of state-averaged CMRCI+Q or CASPT2 methods. Alagia et al.¹¹ have shown that the MRCI+Q method, with a sufficiently flexible basis set, can achieve the required accuracy for electronic states in this system, at least for planar geometries. However, at present there are no program packages available that provide analytic gradients or second derivatives at the CRMCI+Q level of theory. Hence, at least 43 single-point energy calculations must be performed in order to obtain the first and second derivatives of the energy which are required for each data point in the interpolated PES described below. Such calculations are far too computationally expensive at present.

It is for these reasons that the PES reported herein describes the entrance channel for H_2O+H up to the saddle point and only a little further into the $OH+H_2$ channel. It was found that convergence of the SCF wave functions required in these calculations could be achieved if the middle length OH interatomic distance was not permitted to exceed $3.5a_0(1.85 \text{ Å})$. Moreover, data points were generally added in the region where the longest interatomic distance did not exceed about $15a_0(7.9 \text{ Å})$. These two criteria define the domain of the OH₃ PES constructed in this work.

Quantum reaction dynamics calculations indicate that this is a sufficiently large domain of configuration space to describe reactions (1.1) to (1.3), though it is not possible to evaluate the final state distribution of $OH+H_2$ products.

III. POTENTIAL ENERGY SURFACES

In light of the results shown in Table I and the discussion above, a PES was developed using the additivity approximation with the 6-311G(d,p) and 6-311 + G(2df,2pd) basis sets. However, the iterative construction procedure explores the energetically available configuration space, sometimes "discovering" regions not previously considered.³² In this case the region involved in the exchange reaction (1.3) was explored, and an inadequacy in the adopted basis sets was revealed. More accurate PES were then developed.

A. An additivity based surface for reaction (1.1)

A PES was developed with data point energy *E*, E = E[QCISD(T)/6-311G(d,p)] + E[MP2/6-311+G(2df,2pd)] - E[MP2/6-311G(d,p)].(3.1)

The data set was initiated with 25 points on a MEP for reaction (1.1), with no data far into the $OH+H_2$ valley, as discussed above. The data set was then grown to 776 data points; 358 data points were added using trajectories initiated at the saddle point of Fig. 1, and 393 points were added using trajectories initiated at H+H2O. The vibrational energy of OH₃ initiated at the saddle point varied between about 40 and 140 kJ mol⁻¹. For trajectories initiated at H+H₂O, the vibrational energy of H₂O was varied between about 68 and 100 kJ mol⁻¹, while the relative translational energy was varied between about 68 and 142 kJ mol⁻¹. This surface is denoted as PES1. The distribution of the potential energy over the 776 data points in PES1 is shown in Fig. 4. This figure indicates the type of energy distribution that results from the automated PES construction. The distribution has a mean of 123 kJ mol⁻¹ and a standard deviation of 51 kJ mol⁻¹.

1. Accuracy of the interpolation

The 'interpolation accuracy' of any PES is difficult to describe, since the absolute error in the interpolation formula varies throughout the space of internal coordinates. The rel-



FIG. 4. The distribution of the energy of data in PES1 is shown as a histogram constructed with a bin size of 20 kJ mol⁻¹. The energies are given relative to that of H+H₂O.

evant "effective accuracy" is best measured by the convergence of observable properties calculated using the PES, as considered in the next section. However, a crude estimate of the accuracy of the interpolation formula, Eq. (2.2), has been obtained for this surface by generating a sample of molecular configurations and comparing the energy given by Eq. (2.2)with that given directly by Eq. (3.1) for each configuration. From trajectories initiated at the saddle point for reaction (1.1), 192 configurations were selected at random. A random sample of 150 configurations was obtained from trajectories initiated at H+H₂O. The energy range of the total sample of 342 configurations was 159.1 kJ mol⁻¹. The small size of the sample reflects the computational expense of the *ab initio* calculations required. The average interpolation error was found to be 0.38 kJ mol⁻¹, the median error was 0.16 kJ mol^{-1} , and the maximum error was 5.1 kJ mol^{-1} . The average error represents about 0.2% of the energy range of the sample. These interpolation errors are consistent with those obtained for other reactions involving four atoms,¹⁹ and are well below the error inherent in this level of *ab initio* theory.

2. Inaccuracy for exchange

Classical simulations of reaction (1.1) were carried out using PES1. These simulations showed that the hydrogen exchange process analogous to reaction (1.3) occurred much more readily than the abstraction reaction (1.1). In order to examine the energetics in the relevant region of configuration space, the saddle point for this exchange reaction was determined by optimization at the UCCSD (T)/6-311+ +G(d,p) level of theory. The structure of a nearby energy minimum was also optimized. These structures are depicted in Fig. 5. The accuracy of Eq. (3.1) was investigated for these stationary points. Table III presents a comparison of the energies of these configurations in the "exchange region" at various levels of *ab initio* theory. Comparison of



FIG. 5. A schematic representation of the structures of a C_s symmetry saddle point for the exchange reaction (1.3), and a nearby potential energy minimum of C_{3V} symmetry. There are three equivalent C_s saddle points on the surface. The bond lengths are given in Angstrom and the bond angles are given in degrees for structures optimized at the UCCSD(T)/6-311 + +G(d,p) level of theory and on the interpolated surface denoted PES2 (in brackets).

Tables I and III shows clearly that the relative accuracy of different basis sets for configurations relevant to reaction (1.1) is quite different to the relative accuracy of different basis sets for configurations relevant to reaction (1.3). Table III shows that a slightly larger basis set, 6-311+ + G(3*df*,2*pd*), is required for reasonably accurate evaluation of the energy at the QCISD(T) level of theory in the exchange region.

This somewhat anomalous basis set effect is due to the unusually diffuse character of the ground electronic state of H₃O in the vicinity of the C_{3V} minimum.^{33,34} In this region of configuration space, H₃O is a "Rydberg radical," loosely described as a stable OH₃⁺ cation plus an electron. Although

TABLE III. Comparison of the energy at the stationary points for reaction (1.3), calculated using the QCISD(T) method and the corresponding additivity approximation, Eq. (2.3).

Structure ^a	Moderate basis	Large basis	Additive energy ^b kJ mol ⁻¹	QCISD(T) energy ^c kJ mol ⁻¹
Exchange saddle	6-311G(<i>d</i> , <i>p</i>)	6-311+G(3df,2p)	114.2	112.6
		6-311+G(2df,2pd)	109.6	108.1
		6-311 + + G(2df, 2pd)	86.5	82.2
		6-311 + + G(3df, 2pd)	88.1	87.8
		6-311 + + G(3df, 3pd)	86.4	85.9
		aug-cc-pV5Z ^d	•••	91.0
Exchange minimum	6-311G(d,p)	6-311+G(3df,2p)	125.9	124.0
		6-311+G(2df,2pd)	121.0	119.0
		6-311 + + G(2df, 2pd)	78.8	76.2
		6-311 + + G(3df, 2pd)	80.5	77.9
		6-311 + + G(3df, 3pd)	78.7	76.1
		aug-cc-pV5Z ^d		86.4

^aStructures were obtained by performing a full optimization at the CCSD(T)/6-311++G(d,p) level.

^bEnergies relative to H₂O+H, using Eq. (2.3).

 $^{\rm c} Energies$ relative to H_2O+H, using single-point energies calculated at the QCISD(T)/large basis level.

^dEnergies relative to H₂O+H, using UCCSD(T)/(aug-cc-pV5Z on oxygen, pV5Z on hydrogen). These energies were evaluated using the MOLPRO suite of programs.

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this description is more appropriate to excited electronic states, some part of this Rydberg character is also evident in the ground electronic state. Hence, accurate energies for these configurations can only be obtained with basis sets which contain very diffuse functions on both the hydrogen and oxygen atoms. It is interesting to note that the energy of the exchange saddle point, relative to the reactants, is reasonably well described at the MP2 level of theory for sufficiently large basis sets, in contrast to the abstraction saddle point where the UQCISD(T) level of theory was required.

Hence, while the PES derived using Eq. (3.1) is accurate in the vicinity of the minimum energy path for the abstraction reaction, it is not sufficiently accurate for configurations associated with the exchange reaction. In particular, the energy of the saddle point for exchange is significantly overestimated by Eq. (3.1).

B. An additivity based surface for reactions (1.1) and (1.3)

From Tables I and III, it is apparent that a PES more accurate than that given by Eq. (3.1) could be based on Eq. (3.2),

$$E = E[QCISD(T)/6-311G(d,p)] + E[MP2/6-311++G(3df,2pd)] - E[MP2/6-311G(d,p)].$$
(3.2)

Table III suggests that Eq. (3.2) underestimates the saddle point energy, relative to reactants, by only about 3 kJ mol⁻¹. The energy of the nearby C_{3V} symmetry minimum appears to be underestimated by about 6 kJ mol⁻¹ at this level of theory.

The difference between Eqs. (3.1) and (3.2) across the relevant configuration space has been investigated by evaluation of Eq. (3.2) at each of the data points in PES1. This showed that the energy of approximately 75% of the data points was only marginally effected by this expansion of the basis set. For this 75% of the data points, the energy change was in the range 3.65 ± 0.5 mhartree. Since a constant energy shift has no physical significance, the basis set expansion produces an effective variation of only ± 0.5 mhartree in these 578 data points. Figure 6 depicts the location of the data points in PES1 for which the 6-311 + G(3df, 2pd)basis set shifts the energy by more or less than ± 0.5 mhartree from the mean. This figure shows that, with a few exceptions, only data points in the vicinity of the exchange saddle point and C_{3V} minimum are significantly shifted in energy.

All data points in PES1 for which Eqs. (3.1) and (3.2) differ by more than ± 0.5 mhartree from the mean were eliminated from the data set. For the remaining 578 data points, the value of the energy of each data point was replaced by that given by Eq. (3.2). Note that the gradients and second derivatives at each data point, evaluated from Eq. (3.1), were retained. However, since the relative energy shift of data points in neighboring regions should be quite small,



FIG. 6. The location of configurations in the data of PES1 which are discarded (\bullet) and retained (\bigcirc) in PES2 is depicted as a projection onto the plane of the two longest OH bond lengths for each configuration. The symmetry of the data set is indicated by the inclusion of both permutations of the axes for each data point.

the inconsistency of the energy at each data point with the corresponding gradients and second derivatives should be insignificant.

Seven configurations describing well-separated H and H₂O with stretched and compressed OH bonds were added to the data set to ensure accurate description of the asymptotic reactants. The iterative growth of the PES was then initiated from this set of 585 configurations using trajectories initiated at H+H₂O: 50 data points were added using trajectories with approximately 96 kJ mol⁻¹ vibrational energy and 96 kJ mol^{-1} relative translational energy; 36 data points were added using trajectories with approximately 50 kJ mol⁻¹ vibrational energy and 184 kJ mol⁻¹ relative translational energy, and a further 50 data points using trajectories with approximately 210 kJ mol⁻¹ relative translational energy. Finally, the data set was grown to 827 points using trajectories initiated at both H+H₂O and the abstraction saddle point with total energies between 195 and 265 kJ mol⁻¹ above the equilibrium H₂O+H asymptote. We denote this surface as PES2.

Figure 7 depicts the distribution of data for PES2 in the region of strong interaction of the fragments. It is clear that PES2 is based on data which is scattered throughout the regions where both reactions (1.1) and (1.3) take place. Figure 8 shows the distribution of the energies of the data in PES2. Comparison of Figs. 4 and 8 shows that PES2 has a very similar overall distribution of data point energies to PES1, despite the lower energy of points in the exchange region. The mean and standard deviation of the distribution in Fig. 8 are lower than the corresponding values for Fig. 4 by only about 1 kJ mol⁻¹.

Figure 5 also depicts the structures of the exchange saddle point and local minimum as determined on PES2. The saddle point has an energy of 88.0 kJ mol⁻¹ relative to equilibrium reactants and vibrational frequencies of 3403, 3326, 1521, 922, 723, and 1769*i* cm⁻¹. The local minimum has an energy of 80.5 kJ mol⁻¹ relative to equilibrium reactants and



FIG. 7. The location of configurations in the data of PES2 (•) is depicted as a projection onto the plane of the two longest OH bond lengths for each configuration. The symmetry of the data set is indicated by the inclusion of both permutations of the axes for each data point. The locations of two equivalent saddle points for abstraction (\blacksquare) and two equivalent saddle points for exchange (\Box) (see Figs. 1 and 5) are indicated.

vibrational frequencies of 2916, 2298, 2298, 1374, 1374, and 886 cm^{-1} .

C. An approximate QCISD(T)/6-311++G(3df,2pd)surface

It is apparent from Tables I and III that the major limitation on the accuracy of PES2 is due to the use of the additivity approximation of Eq. (3.2). In particular, the additivity approximation appears to overestimate the height of the barrier to the abstraction reaction by about 5.5 kJ mol^{-1} . Since the best theoretical estimates give the abstraction and exchange barrier heights equal to within 1 kJ mol⁻¹, this additivity error in PES2 may be significant.



FIG. 8. The distribution of the energy of data in PES2 is shown as a histogram constructed with a bin size of 20 kJ mol⁻¹. The energies are given relative to that of H+H₂O.



FIG. 9. The distribution of the energy difference between data in PES3 and PES2 (\bullet) is shown as a histogram constructed with a bin size of 1 kJ mol⁻¹. Similarly, the distribution of the interpolated energy difference between PES3 and PES2 is shown for a sample of molecular configurations obtained from trajectories initiated at H+H2O (O) and at the saddle point for abstraction (\times) .

In order to investigate the importance of the error due to the additivity approximation, PES2 has been modified in a very simple fashion. We have seen that in constructing PES2, it was possible to merely shift the energy of the first 578 data points to account for a small basis set modification, leaving the energy gradients and second derivatives at these points unchanged. The smooth evolution of classical trajectories on this modified PES is consistent with very small errors in the interpolated gradient for this PES. The accuracy of this approximation to the data is likely due to the fact that the variation in the energy shifts is small, of the order of ± 1 kJ mol⁻¹. Although the error due to additivity can be several kJ mol⁻¹, a new PES was constructed by simply replacing the energy of each data point by the QCISD(T)/6-311 + +G(3df, 2pd) value. This surface is denoted as PES3.

The question naturally arises as to whether the energy shifted data in PES3 produces significant errors in the interpolation, particularly in the interpolated gradient of the PES. The differences in the energy and gradient between PES2 and PES3 have been examined as follows. A classical simulation of the collision of H and H₂O (with approximately zero-point energy) at a translational energy of about 1.8 eV has been carried out, and a sample of 2570 configurations encountered in these trajectories was recorded. Trajectories initiated at H+H₂O rarely cross the abstraction saddle point toward OH+H₂, so a sample of 1563 configurations was also obtained from trajectories initiated at this saddle point.

Figure 9 presents a histogram of the distribution of energy difference between PES3 and PES2 for the 2570 "H+H₂O trajectory configurations," the corresponding histogram for the 1563 "saddle point trajectory configurations," and the corresponding histogram of the energy difference between PES3 and PES2 at the 827 data points. It is clear that the histograms for the data set and the 1563 "saddle point trajectory configurations" are bimodal, while the other is not. This indicates that distinctly larger energy differences are associated with configurations encountered in the abstraction saddle region.

However, the differences between PES3 and PES2 are found to effect the potential gradients of both samples of "trajectory configurations" in a similar way. First, we have found that the *average* magnitude of the Cartesian gradient, $\|\nabla V\|$, increases by only 0.3% for PES3 relative to PES2 for both sets of sampled configurations. Moreover, the average relative change in the Cartesian gradient, δ ,

$$\delta = \frac{\langle \|\nabla V_{\text{PES3}} - \nabla V_{\text{PES2}}\|\rangle}{0.5 \langle \|\nabla V_{\text{PES3}}\| + \|\nabla V_{\text{PES2}}\|\rangle},\tag{3.3}$$

is about 2.6% in both samples. The standard deviations about the mean δ are 5.6% for the first trajectory sample and 6.8% for the sample weighted toward the abstraction region. It is worth remembering that the interpolation formula, Eq. (2.2), for a finite data set, does not give the exact gradient at any configuration other than at a data point. Even when the PES has apparently converged sufficiently to reproduce the observables measured, there is usually an average residual relative error in the Cartesian gradient of several percent. Hence, although the energy substitution which produces PES3 from PES2 has introduced "gradient noise" in PES3, the level of noise is not large compared to the error expected to arise from the interpolation procedure.

IV. CONVERGENCE OF DYNAMICAL PROPERTIES

In order to indicate the convergence of the interpolated PES, we present some results for the reaction dynamics on these surfaces. Since the PES were constructed using classical dynamics, it is important to demonstrate that the calculated classical reaction dynamics would not change if the data set were "grown" larger.

The classical simulations of H+H₂O collisions were carried out using standard methods. Since the domain of the PES excludes the OH+H₂ product, trajectories were terminated, and counted as OH+H2 product, if the breaking OH bond exceeded $3.5 a_0$. Figure 10 presents the calculated cross section for the exchange of two hydrogen atoms in the collision of H with H₂O, as a function of the size of the data set, for both PES2 and PES3. This figure is derived using sets of 4000 trajectories in which the maximum impact parameter was $1.8 a_0$, the relative translational energy was 173.7 kJ mol⁻¹ (1.8 eV), and the H₂O molecule has a microcanonical vibrational energy distribution of 49.9 kJ mol⁻¹ (approximating the zero-point energy) and no rotational angular momentum. Since the region of configuration space important for exchange is populated with few if any data in the first 585 points, it is not surprising that the cross section is not converged for fewer than several hundred data points. The accuracy of the additivity approximation of Eq. (3.2) in the exchange region is reflected in the similarity of the cross sections for PES2 and PES3.

Figure 11 presents the cross section for the abstraction reaction (1.1) as a function of the size of the data set for both



FIG. 10. The classical cross section for the exchange reaction is shown for PES2 (\bigcirc) and PES3 (\bigcirc) as a function of the size of the data set. The error bars correspond to two standard deviations.

PES2 and PES3. The trajectory samples are the same as those used for Fig. 10. The relatively large error bars in Fig. 11 are a reflection of the very small cross section for this process. Within this uncertainty, the abstraction cross sections appear to be converged. PES3 might be expected to produce a larger cross section for reaction (1.1) than PES2, since the energy for PES3 lies below that of PES2 near the saddle point for abstraction. Given the very low probability of the abstraction reaction, quantum dynamics is required to accurately quantify this property for PES2 and PES3.

The initial state selected time-dependent wave packet (ISSTDWP) method has been used to calculate the total reaction probabilities for both abstraction and exchange reactions for PES2 and PES3 over a range of relative translational energy. The ISSTDWP method has been discussed in detail in previous publications.^{35–37} A more detailed examination of the quantum dynamics on these surfaces will be



FIG. 11. The classical cross section for the abstraction reaction is shown for PES2 (\bigcirc) and PES3 (\bigcirc) as a function of the size of the data set. The error bars correspond to two standard deviations.

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FIG. 12. The quantum probability for the abstraction reaction (1.1), for zero total angular momentum and ground-state reactants, is shown as a function of the relative translational energy of H and H₂O. The results shown were evaluated with PES3 (\bullet), and with PES2 including 500 data points (----), 650 data points (----), and all 827 data points (----).

reported later. Since there is no ab initio data point in the OH+H2 channel where the breaking OH bond distance exceeds $3.5 a_0$, the interpolated PES is only accurate up to and slightly beyond that line. Therefore, an absorption potential was used to absorb the wave function starting from r(OH)= $3.3 a_0$ before it moved into the OH+H₂ region. The total reaction probabilities for abstraction and exchange processes were measured at $r(OH) = 3.0 a_0$, where the reaction flux for these two processes is already quite well separated for the collision energies investigated. Using this approach, we consider the convergence of the reaction probability with the number of data points. However, since part of the configuration space has few if any data in the first 585 points, we have constructed two new partial data sets as follows. About 50 data points on the minimum energy path and at the H+H₂O asymptote have been combined with data points chosen at random from the total data set to give data sets of 500 and 650 points. Figure 12 presents the abstraction reaction probability as a function of translational energy, calculated with these 500, 650, and all 827 data points of PES2. The convergence of the reaction probability is clear. Hence, one can infer that the interpolation error in PES2 is sufficiently small to allow accurate calculation of even very small total reaction probabilities. For comparison, Fig. 12 also shows the abstraction reaction probability calculated for PES3. The lower abstraction barrier for PES3 is reflected in a significantly larger probability for abstraction. Finally, Fig. 13 presents the exchange reaction probability as a function of translational energy, calculated with the same 500, 650, and all 827 data points of PES2. The reaction probability is again clearly converged. Since the additivity approximation is quite accurate in the exchange region of the surface, it is not with PES3 (\bullet), and with PES2 including 500 data points (----), 650 data points (----), and all 827 data points (----).

FIG. 13. The quantum probability for the exchange reaction, for zero total

angular momentum, and ground-state reactants, is shown as a function of the

relative translational energy of H and H₂O. The results shown were evaluted

surprising that the reaction probability for PES3 (also shown in Fig. 13) is very close to that for PES2.

V. SUMMARY AND DISCUSSION

We have presented an interpolated surface, PES2, for H₃O which uses an additivity assumption to approximate the energy of this system at the QCISD(T)/6-311++G(3df,2pd) level of *ab initio* theory. Comparison with experimental and other theoretical results in Table II shows that this surface is accurate at the few molecular configurations where comparison is possible.

The QCISD(T) treatment of electron correlation is generally held to provide a reliably accurate description in situations where multiconfiguration methods are not essential. For OH₃, this caveat limits the PES to the $H+H_2O$ entrance valley, to the region where exchange takes place, and to the immediate vicinity of the saddle point for the abstraction reaction. Much of the product, $OH+H_2$, region of the surface has not been described. In this region there are two low-lying electronic states, so that separation of electronic and nuclear motion may not be appropriate.

We have discovered that very diffuse basis functions are required on both the oxygen and hydrogen atoms in order to accurately describe the "exchange region" of the surface where the OH_3 molecule has a Rydberg-like electronic structure. Interestingly, in this region, electron correlation is reasonably described using the MP2 level of *ab initio* theory. On the other hand, while a reasonably accurate description of the abstraction saddle point region can be obtained without such diffuse basis functions, the higher QCISD(T) treatment of electron correlation is essential there.





Classical and quantum dynamics have been used to demonstrate that PES2 is converged with respect to the size of the data set for the abstraction reaction (1.1) and for the exchange reaction (1.3), for a reactant translational energy of at least 1.8 eV. The surface was "grown" using trajectories with vibrationally excited reactants, so that the surface may also adequately describe collisions between H and H₂O with about 4000 cm⁻¹ of vibrational excitation.

We have not observed the combined exchangeabstraction reaction (1.4) in classical simulations at the energies considered. This reaction has not been examined with quantum dynamics as yet.

The principal source of inaccuracy in PES2 appears to be the use of the additivity approximation of Eq. (3.2). This results in an overestimation of the barrier to abstraction of several kJ mol⁻¹. A crude attempt to remove this source of error was made by substitution of the exact QCISD(T)/6-311++G(3df,2pd) energies at each data point, while retaining the first and second derivatives obtained with the additivity approximation. This surface, PES3, has a lower barrier for reaction (1.1) which results in a higher probability for the abstraction reaction on this surface, compared to that for PES2. However, the additivity approximation is more accurate in the reactant and exchange regions, so that the probability for exchange is very similar for PES2 and PES3. The classical and quantum dynamics calculations on PES3 give no indication that the simple energy substitution has introduced large errors in the gradient of PES3.

It is interesting to note that, coincidentally, the barrier heights for reactions (1.1) and (1.3) are very similar. Nevertheless, the exchange reaction is about two orders of magnitude more probable than the abstraction reaction in the energy range of Figs. 12 and 13. The probability of exchange is characterized by a rich "resonance structure" as a function of the translational energy of the reactants. This may be due to the presence of a local minimum in the PES for an OH_3 structure of C_{3V} symmetry. Future work will include a more detailed examination of this quantum scattering, including the dependence of the reactants.

The data files and all software required to evaluate PES2 and PES3 for OH₃, and the PES for other systems, are available via the Internet and anonymous ftp: (http://www.rsc.anu.edu.au/RSC/ChemResearch/Groups/DD-home. html and ftp://rsc.anu.edu.au/pub/collins/).

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- ¹J. M. Bowman and G. C. Schatz, Annu. Rev. Phys. Chem. 46, 169 (1995).
- ²J. V. Michael and J. W. Sutherland, J. Phys. Chem. **92**, 3853 (1988).
- ³ A. Jacobs, H. Volpp, and J. Wolfrum, J. Chem. Phys. **100**, 1936 (1994).
- ⁴F. F. Crim, J. Phys. Chem. **100**, 12725 (1996).

- ⁵M. J. Bronikowski, W. R. Simpson, and R. N. Zare, J. Phys. Chem. **97**, 2204 (1993).
- ⁶G. Hawthorne, P. Sharkey, and I. W. M. Smith, J. Chem. Phys. **108**, 4693 (1998).
- ⁷P. Barnes, P. Sharkey, I. R. Sims, and I. W. M. Smith, Faraday Discuss. **113**, 167 (1999).
- ⁸R. A. Brownsword, M. Hillenkamp, T. Laurent, R. K. Vatsa, H. Volpp, and J. Wolfrum, Chem. Phys. Lett. **259**, 375 (1996).
- ⁹S. P. Walch and T. H. J. Dunning, J. Chem. Phys. 72, 1303 (1980).
- ¹⁰G. C. Schatz and H. Elgersma, Chem. Phys. Lett. **73**, 21 (1980).
- ¹¹ M. Alagia, N. Balucani, P. Casavecchia, D. Stranges, G. G. Volpi, D. C. Clary, A. Kliesch, and H. Werner, Chem. Phys. **207**, 389 (1996).
- ¹²G. Ochoa de Aspuru and D. C. Clary, J. Phys. Chem. A **102**, 9631 (1998).
 ¹³L. A. Curtiss, K. Raghavachari, and J. A. Pople, J. Chem. Phys. **98**, 1293 (1993).
- ¹⁴J. Ischtwan and M. A. Collins, J. Chem. Phys. **100**, 8080 (1994).
- ¹⁵ M. J. T. Jordan, K. C. Thompson, and M. A. Collins, J. Chem. Phys. **102**, 5647 (1995).
- ¹⁶ M. J. T. Jordan, K. C. Thompson, and M. A. Collins, J. Chem. Phys. **103**, 9669 (1995).
- ¹⁷ M. J. T. Jordan and M. A. Collins, J. Chem. Phys. 104, 4600 (1996).
- ¹⁸K. C. Thompson and M. A. Collins, J. Chem. Soc., Faraday Trans. 93, 871 (1997).
- ¹⁹ R. P. A. Bettens and M. A. Collins, J. Chem. Phys. **111**, 816 (1999).
- ²⁰ R. Farwig, in *Algorithms for Approximation*, edited by J. C. Mason and M. G. Cox (Clarendon, Oxford, 1987), p. 194.
- ²¹P. Lancaster and K. Salkauskas, *Curve and Surface Fitting, An Introduc*tion (Academic, London, 1986), Chap. 10.
- ²² M. A. Collins and K. C. Thompson, in *Chemical Group Theory: Techniques and Applications*, edited by D. Bonchev and D. H. Rouvray (Gordon and Breach, Reading, 1995), p. 191.
- ²³ K. C. Thompson, M. J. T. Jordan, and M. A. Collins, J. Chem. Phys. 108, 8302 (1998).
- ²⁴M. A. Collins and D. H. Zhang, J. Chem. Phys. **111**, 9924 (1999).
- ²⁵E. Kraka, J. Gauss, and D. Cremer, J. Chem. Phys. 99, 5306 (1993).
- ²⁶ GAUSSIAN94, Revision A. 1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1995.
- ²⁷ GAUSSIAN98, Revision A. 6, G. W. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1998.
- ²⁸ H. Werner, P. J. Knowles, J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, and R. Lindh, MOLPRO, Version 96.1.
- ²⁹ M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Chem. Ref. Data 14, 1 (1986).
- ³⁰G. Herzberg, *Molecular Spectra and Molecular Structure*. II (Krieger, Florida, 1991), p. 282 and p. 489.
- ³¹K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ³² R. P. A. Bettens and M. A. Collins, J. Chem. Phys. **108**, 2424 (1998).
- ³³M. Luo and M. Jungen, Chem. Phys. **241**, 297 (1999).
- ³⁴M. N. Glukhovtsev, J. Mol. Struct. **357**, 237 (1995).
- ³⁵D. H. Zhang and J. Z. H. Zhang, J. Chem. Phys. **101**, 1146 (1994).
- ³⁶D. H. Zhang, J. C. Light, and S. Y. Lee, J. Chem. Phys. **109**, 79 (1998).
- ³⁷D. H. Zhang and S. Lee, J. Chem. Phys. **110**, 4435 (1998).