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The interaction of OH(X^2Π) with H_2: Ab initio potential energy surfaces and bound states

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For the interaction of OH(X^2Π) with H_2, under the assumption of fixed OH and H_2 bond distances, we have determined two new sets of four-dimensional ab initio potential energy surfaces (PES’s). The first set of PES’s was computed with the multi-reference configuration interaction interaction method [MRCISD+Q(Davidson)], and the second set with an explicitly correlated coupled cluster method [CCSD(T)-F12a] sampling the subset of geometries possessing a plane of symmetry. Both sets of PES’s are fit to an analytical form suitable for bound state and scattering calculations. The CCSD(T) dissociation energies (D_0) of the OH–para-H_2 and the OH–ortho-H_2 complexes are computed to be 36.1 and 53.7 cm^{-1}. The latter value is in excellent agreement with the experimental value of 54 cm^{-1}. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4900478]

I. INTRODUCTION

There has been considerable interest in the dynamics of the OH–H_2 system. One important reason is that the OH + H_2 → H_2O + H reaction is one of the simplest four-atom reactions.1,2 The OH(X^2Π)–H_2 system is also of astrophysical importance.3,4

Loomis and Lester have stabilized the weakly bound OH(X^2Π)–H_2/D_2 complexes,5 reporting binding energies of, for H_2, 54 cm^{-1} and, for D_2, >66 cm^{-1}, which they assigned to the OH–ortho-H_2 and OH–para-D_2 complexes, respectively.6 Subsequently, Lester and co-workers have observed and analyzed the rotational structure of these complexes.7–9

Andersen et al.10,11 first determined relative inelastic cross sections of OH j = 3/2 F_j (with equal populations in both Λ-doublet levels) in collisions with H_2 and D_2. Later, Schreel and ter Meulen12 measured Λ-doublet resolved inelastic cross sections for OH–H_2, using an electrostatic hexapole as a state selector for OH. Recently, Kirste et al.13 used a Stark decelerator14 to measure the energy dependence of inelastic cross sections for transitions out of the upper j = 3/2 F_j Λ-doublet level of OH in collisions with D_2.

Here we report two accurate sets of OH(X^2Π)–H_2 potential energy surfaces (PES’s) for the study of both bound states and inelastic collisions. Because of its orbital degeneracy, two PES’s are needed to describe the interaction of OH with a closed-shell collision partner.15

To treat the dynamics of the OH–H_2 system, it is most convenient to describe the interaction of the collision partner in terms of the two components (with body-frame projections Λ = ±1 of the electronic orbital angular momentum) of OH(X^2Π). These “definite-Λ” states are linear combinations of Cartesian basis functions, |Π_j⟩ (with electronic occupancy π_x π_y π_z) and |Π_j⟩ (with electronic occupancy π_x^2 π_y^2), which are eigenfunctions of the operator corresponding to the reflection of the spatial coordinates of all the electrons in a plane through the OH axis.

In this Cartesian basis, the wave functions for the supermolecular system of OH and a structureless atom are eigenfunctions of the same reflection operator, and correspond to two states of differing reflection symmetry (A’ and A’’). The electronic energies of these two states correspond to interaction potentials which are conventionally labelled V_{A’} and V_{A’’}. In the definite-Λ basis, the matrix of the electronic Hamiltonian is a full 2×2 matrix, with elements which are one-half of the sum and difference of V_{A’} and V_{A’’}.16

In general the tetratomic OH–H_2 system is nonplanar. There will be still two electronic states, which we can express as linear combinations of the two Cartesian basis functions: |Π_j⟩ and |Π_j⟩. The matrix of the electronic Hamiltonian can be diagonalized in this “diabatic” basis, at each geometry, by a rotation of the adiabatic wave functions through a single “mixing angle.”

Two strategies have been previously employed to treat this: the first is to sample only OH–H_2 geometries that have a plane of symmetry, in which case the wave functions for the two electronic states have differing reflection symmetries. This allows the two PES’s, which correspond to the lowest states of A’ and A’’ symmetry, to be calculated separately using conventional quantum chemical approaches. This strategy was adopted by Kochanski and Flower (KF),17 who used
self-consistent field (SCF) calculations with a perturbation theory approximation to include electron correlations, and later by Miller et al. (MCKW)\textsuperscript{18} in coupled electron pair approximation (CEPA) calculations.

Alternatively, one can obtain the mixing angle directly in the \textit{ab initio} calculations. This strategy was implemented by Offer and van Hemert (OVH),\textsuperscript{15} using the multi-configuration self-consistent field (MCSCF) method with corrections for the dispersion interaction.

The PES’s mentioned above have been tested by comparison with experimental studies of rotationally inelastic scattering and the determination of OH–H\textsubscript{2} bound state energies. Both the KF and MCKW PES’s gave state-to-state inelastic cross sections in good agreement with the experiments by Andersen et al.,\textsuperscript{12} although the agreement was better for cross sections in which OH remains in its initial (\textit{F\textsubscript{1}}) spin-orbit manifold.\textsuperscript{18–20} Cross sections computed from the OVH PES’s agree well with the later scattering experiments of Schreel and ter Meulen.\textsuperscript{12,21} The KF and MCKW PES’s predict dissociation energies (\textit{D\textsubscript{0}}) of the OH–ortho-H\textsubscript{2} complex of 42.2 and 85.4 cm\textsuperscript{-1}, respectively.\textsuperscript{18,22} These numbers are only in semi-quantitative agreement with the experimental value of 54 cm\textsuperscript{-1}.

It is probable that these disagreements reflect inaccuracies in the PES’s, either because the \textit{ab initio} calculations sampled a small number of geometries, or because of a simplistic (by today’s standards) treatment of electron correlation.

The two strategies mentioned above have their own shortcomings. In the first approach, one samples a very limited number of orientations. The second tack requires \textit{ab initio} methods that can compute excited-state energies accurately, which is less cost-effective. In this paper, we present two high-quality sets of OH–H\textsubscript{2} PES’s, one based on a multi-reference configuration interaction [MRCISD+Q(Davidson)] method and the other based on an explicitly correlated coupled cluster method with single-, double-, and (perturbatively) triple-excitations [RCCSD(T)-F12a]. In a similar vein, Dobryn et al.\textsuperscript{23} combined RCCSD(T) and MRCI methods to construct PES’s to describe the Cl(\textit{2}\textsuperscript{P}) + HCl → CIH + Cl(\textit{2}\textsuperscript{P}) reaction.

This paper is organized as follows: In Sec. II, we present the theory for the analytical expansion of the OH–H\textsubscript{2} PES’s in a definite-\Lambda basis. In Sec. III, we describe our treatment in developing the PES’s. We show that despite its incomplete angular sampling, the CCSD(T) PES’s are more accurate. Features of the PES’s and comparison with previous PES’s are also illustrated in Sec. III. We present bound-state calculations for the OH–H\textsubscript{2} complex with our PES’s in Sec. IV. A discussion in Sec. V concludes this paper. Further technical details are available in the supplementary material.\textsuperscript{24}

**II. THEORY**

The theoretical framework for the PES’s describing the interaction of a diatomic molecule in a \textit{2}\textsuperscript{\Pi} electronic state, like OH(\textit{X}\textsuperscript{2}\textit{\Pi}), and another diatomic molecule in a \textit{1}\textsuperscript{\Sigma}\textsuperscript{+} electronic state has been described previously.\textsuperscript{15,19,25} In this section, we summarize and clarify the previous treatments.

![FIG. 1. The definition of the coordinate system describing the interaction between OH and H\textsubscript{2}. The OH moiety lies in the XZ plane, with \(\theta_{O} = 0\) corresponding to the H-atom of the OH pointing toward the H\textsubscript{2} moiety.](Image)
must be independent of the sign of \( m \). Consequently, we can restrict the sum over \( m \) to positive semi-definite values and use a symmetry property of the Clebsch-Gordan coefficient to write the diagonal matrix elements \( V_d \) as

\[
V_d = \sum_{l_1,l_2} V_{l_1l_2}^{(0)}(R) \sum_{m=0} \langle l_1m,l_2,-m|0\rangle (1 + \delta_{m0})^{-1}
\times \left[ e^{-im\phi}\phi + (-1)^{l_1+l_2} e^{-im\phi}\right] d^{l_1}_{m0}(\theta_O) d^{l_2}_{-m,0}(\theta_H). \tag{2}
\]

Wormer and co-workers have used the invariance of the Hamiltonian with respect to time-reversal to show that only terms with even values of \( l_1 + l_2 + l \) occur in the expansion of the diagonal matrix elements with \( \Lambda' = \Lambda \).\textsuperscript{25} Hence the electronic Hamiltonian will be invariant with respect to a reflection in the \( XZ \) plane in Fig. 1 (\( \phi_{\text{HT}} \rightarrow -\phi_{\text{HT}} \)). Under this constraint, the sum of exponentials in Eq. (2) is proportional to \( \cos (m\phi_{\text{HT}}) \), which allows us to write \( V_d \) as

\[
V_d = \sum_{l_1,l_2} V_{l_1l_2}^{(0)}(R) \sum_{m=0} \langle l_1m,l_2,-m|0\rangle (2 - \delta_{m0})^{1/2}
\times d^{l_1}_{m0}(\theta_O) d^{l_2}_{-m,0}(\theta_H) \cos (m\phi_{\text{HT}}).
\tag{3}
\]

Since the diagonal elements of a Hermitian matrix must be real, and since all the terms in this equation except the \( V_{l_1l_2}^{(0)} \) expansion coefficients are real, it follows that also these coefficients must be real.

C. Off-diagonal (\( \Lambda' \neq \Lambda \)) matrix elements

The reader can easily deduce from the work of Wormer and co-workers\textsuperscript{25} [see their Eqs. (30) and (31)] that the expansion coefficients in Eq. (1) obey the symmetry relation

\[
V_{l_1l_2}^{(-2)}(R) = (-1)^{l_1+l_2+l} V_{l_1l_2}^{(2)}(R).
\tag{4}
\]

Because the matrix of the Hamiltonian must be Hermitian, Eq. (4) implies that the \( V_{l_1l_2}^{(\pm 2)} \) expansion coefficients must be real.

We designate the off-diagonal \( V_{\Lambda'=1,\Lambda=-1}(R, \theta_O, \theta_H, \phi_{\text{HT}}) \) PES as \( V_o \),

\[
V_o = \sum_{l_1,l_2} V_{l_1l_2}^{(2)}(R) \sum_m \langle l_1m,l_2,-m|0\rangle e^{-im\phi_{\text{HT}}} d^{l_1}_{m0}(\theta_O) d^{l_2}_{-m,0}(\theta_H). \tag{5}
\]

The off-diagonal potential for the interaction of a linear molecule in a \( \Pi \) electronic state with a closed-shell diatomic exhibits the same lowering of an underlying symmetry, reflected by the appearance of expansion terms with odd \( l_1 + l_2 + l \), as the interaction of a nonlinear polyatomic with a closed-shell diatomic.\textsuperscript{27,28} Consequently, in fitting our \textit{ab initio} interaction energies, we did include the flexibility of both even and odd values of \( l_1 + l_2 + l \) for the off-diagonal matrix elements.

D. Normalization

The individual \( \{|l_1, l_2, l\} \) basis functions in the expansions in Eqs. (2) and (5) are not normalized with respect to integration over \( \theta_O, \theta_H, \) and \( \phi_{\text{HT}} \). Comparable expansions in orthonormal bases are

\[
V_d = (8\pi)^{-1/2} \sum_{l_1,l_2} B_{l_1l_2}(R) [(2l_1 + 1)(2l_2 + 1)]^{1/2}
\times \sum_{m=0} \langle l_1m,l_2,-m|0\rangle (2 - \delta_{m0})^{1/2}
\times d^{l_1}_{m0}(\theta_O) d^{l_2}_{-m,0}(\theta_H) \cos m\phi_{\text{HT}}, \tag{6}
\]

and

\[
V_o = (8\pi)^{-1/2} \sum_{l_1,l_2} F_{l_1l_2}(R) [(2l_1 + 1)(2l_2 + 1)]^{1/2}
\times \sum_m \langle l_1m,l_2,-m|0\rangle e^{-im\phi_{\text{HT}}} d^{l_1}_{m0}(\theta_O) d^{l_2}_{-m,0}(\theta_H). \tag{7}
\]

Examination of the magnitude of these \( B_{l_1l_2} \) and \( F_{l_1l_2} \) coefficients will provide the most meaningful insight into the importance of individual terms. Note that the earlier treatment of collisions between a \( ^2\Pi \) molecule and a structureless atom\textsuperscript{16,20} used an unnormalized basis.

E. Adiabatic and quasi-diabatic bases

\textit{Ab initio} calculations give electronically adiabatic states. For a four-atom \( ^2\Pi-^1\Sigma^+ \) system in geometries in which there is a reflection plane that lies in the \( XZ \) or \( YZ \) plane, the electronic wave functions will belong to different irreducible representations \( A' \) and \( A'' \) in \( C_2 \) symmetry. We will designate these states as \( |\Pi_{\text{u}}\rangle \) and \( |\Pi_{\text{g}}\rangle \), in which the Cartesian index designates the singly-filled \( \pi \) lone-pair orbitals on the OH molecule, i.e., \( |\Pi_{\text{u}}\rangle \sim \pi^1_x \pi^1_y \) and \( |\Pi_{\text{g}}\rangle \sim \pi^2_x \pi^2_y \). Because these two Cartesian states belong to different irreducible representations, they are not mixed by the OH–H\(_2\) interaction. In these geometries, the Cartesian states are then the electronically adiabatic states and their energies, the electronically adiabatic energies.

Consider now an arbitrary OH–H\(_2\) geometry, in which there are no symmetry elements save the identity operator (\( C_1 \) symmetry). In an \textit{ab initio} calculation, it is possible to rotate the orthogonal \( \pi \) molecular orbitals so that one lies in the \( XZ \) plane and the other, perpendicular to this plane. In our specific application, the molecular orbitals from a complete active space, self-consistent field (CASSCF) calculation are rotated to achieve maximum overlap with the CASSCF orbitals for the OH–H\(_2\) system at the same geometry except for \( \phi_{\text{HT}} = 0 \).

We use these rotated orbitals to define two state functions \( \pi^1_x \pi^1_y \) and \( \pi^2_x \pi^1_y \). These will be mixed by the Hamiltonian. Diagonalization will give rise to two electronically adiabatic states, which we designate as \( |u\rangle \) (upper) and \( |l\rangle \) (lower). These are \( 2 \times 2 \) linear transformations of the two Cartesian states, namely,

\[
\begin{pmatrix}
|u\rangle \\
|l\rangle
\end{pmatrix} = \begin{pmatrix}
\cos \chi & \sin \chi \\
-\sin \chi & \cos \chi
\end{pmatrix}
\begin{pmatrix}
|\Pi_{\text{u}}\rangle \\
|\Pi_{\text{g}}\rangle
\end{pmatrix} = C^T \begin{pmatrix}
|\Pi_{\text{u}}\rangle \\
|\Pi_{\text{g}}\rangle
\end{pmatrix}, \tag{8}
\]
where $\chi$ is the so-called “mixing angle.” This latter depends on the OH–H$_2$ geometry, just as the potential energy surfaces.

The $2 \times 2$ basis in terms of the rotated $\pi$ orbitals defines what are called “quasi-diabatic” (or, more simply, “diabatic”) states.\textsuperscript{30,31} In this diabatic basis, the matrix of the interaction Hamiltonian $\hat{H}_{int}$ is\textsuperscript{15,25}

\[
\begin{pmatrix}
V_{xx} & V_{xy} \\
V_{yx} & V_{yy}
\end{pmatrix} = C \begin{pmatrix}
V_d & 0 \\
0 & V_u
\end{pmatrix} C^T
\]

\[
= \begin{pmatrix}
V_d & \frac{1}{2}V_u - \frac{1}{2}\chi
\\
\frac{1}{2}V_u & V_u + \frac{1}{2}\chi
\end{pmatrix},
\]

(9)

where $V_{d,u}$ is a shorthand notation for $\langle \Pi_d | \hat{H}_{int} | \Pi_u \rangle$, and $V_d$ and $V_u$ are the adiabatic interaction energies. This equation should be compared with Eq. (3) of Ref. 15, which gives the relation between the definite-$\Lambda$ diabatic and adiabatic states.

As with the one-electron molecular orbitals, the definite-$\Lambda$ states are linear combinations of the Cartesian states, namely,

\[
|\Pi_{\pm\Lambda} \rangle = \mp 2^{-\frac{1}{2}}(|\Pi_+ \rangle \pm i |\Pi_- \rangle).
\]

(10)

Wormer and co-workers have shown [see Eq. (4) of Ref. 25] that in the definite-$\Lambda$ basis the diagonal potential is

\[
V_d = \frac{1}{2}(V_u + V_u),
\]

and the off-diagonal potential is

\[
V_o = \frac{1}{2}(V_u - V_u)(\cos 2\chi - i \sin 2\chi).
\]

(12)

For any OH–H$_2$ geometry in which the XZ plane is a plane of reflection symmetry $V_{xy}$ and $V_{yx}$ vanish. For these geometries, the diagonal potentials are identical to the adiabatic potentials $V_d$ and $V_u$, and it follows that

\[
V_d = \frac{1}{2}(V_{xx} + V_{yy}),
\]

(13)

and

\[
V_o = \frac{1}{2}(V_{xy} - V_{yx}).
\]

(14)

Equations (13) and (14) are equivalent to the “sum” and “difference” PES’s usually used in describing the interaction between a $^2\Sigma$ atom and a structureless atom.\textsuperscript{16,29,32}

F. Symmetry restrictions

The symmetry of the potential with respect to interchange of the two hydrogen atoms and to reflection in the XZ plane (Fig. 1) allows us to restrict the $ab$ initio calculations to a subspace of the complete coordinate space grid. As a consequence, in the $ab$ initio calculation of the potential energy surfaces, we can restrict ourselves to the subspace $0 \leq \theta_H \leq \pi/2$ and $0 \leq \phi_H \leq \pi$.

G. Limiting geometries

When the OH molecule lies along the Z axis, $\theta_O = 0$ or $\pi$. The two adiabatic potential energies, $V_d$ and $V_u$, will obviously be independent of $\phi_H$.

When the H$_2$ molecule is in the XZ plane, i.e., $\phi_H = 0$, or $\theta_H = 0$ or $\pi$, $|\Pi_+ \rangle$ and $|\Pi_- \rangle$ will be symmetric and antisymmetric, respectively, with respect to reflection in the XZ plane. Since the identification of $V_d$ and $V_u$ with $V_{xx}$ and $V_{yy}$ is different for $\theta_H = 0$ and $\pi$, we have $\chi = 0$ and $\pi/2$ for these two values of $\theta_H$. For both cases, the off-diagonal potential $V_o$ is real.

When the OH molecule lies along the Z axis, the OH–HH system is always planar. However, the CASSCF orbitals are rotated to achieve maximum overlap with those from a calculation in which the XZ plane (Fig. 1) defines the plane of reflection symmetry. Because the system is planar, there is no additional coupling between the two states. In the case where $\theta_O = 0$ the mixing angle $\chi$ is equal to $\phi_H$, while for $\theta_O = \pi$ we have $\chi = -\phi_H$.\textsuperscript{15,25}

Finally, in linear geometries (both polar angles 0 or $\pi$), the degeneracy of the two $\Pi$ states of OH is not lifted. The two adiabatic states of the complex are degenerate.

III. POTENTIAL ENERGY SURFACES

A. MRCI calculations

We used the MOLPRO program suite\textsuperscript{33} to determine the two lowest adiabatic energies of the OH–H$_2$ complex, $E_i$ and $E_u$, as well as the mixing angle $\chi$. For each geometry, we first performed a CASSCF calculation, with 1 core orbital and 7 active orbitals, and the augmented correlation-consistent polarized quadruple zeta (aug-cc-pVQZ) basis.\textsuperscript{34} As discussed in Sec. II E, the resulting orbitals were rotated to maximize the overlap with CASSCF orbitals from a calculation with $\phi_H = 0$ and the other coordinates unchanged.

With configuration state functions built from these diabatic orbitals, we then performed an internally contracted, multi-reference configuration interaction calculation including all single and double excitations (ic-MRCISD) to determine the two adiabatic energies. The CI calculation included 7 active orbitals and 210 external orbitals. We used the cluster corrected energies of Langhoff and Davidson.\textsuperscript{35} These MRCI calculations were carried out on a four-dimensional ($R$, $\theta_O$, $\phi_H$, $\phi_d$) grid (see Fig. 1).

We assumed that the OH and HH bond distances remain fixed at the average value of $r$ in the $v = 0$ vibrational levels [$r_0 = 1.8509a_0$ for OH (Ref. 36) and $r_0 = 1.448736a_0$ for H$_2$ (Ref. 37)]. The MRCI method is not size-extensive, i.e., the calculated energy of the OH-H$_2$ complex does not precisely equal the sum of the energies of OH and H$_2$ when the distance $R$ goes to infinity. Therefore, we obtained the interaction energy at a given geometry from the expression

\[
V_{\text{MRCI}}(R, \Omega) = E_{\text{MRCI}}(R, \Omega) - E_{\text{MRCI}}(R = 100a_0, \Omega),
\]

(15)

where $\Omega$ denotes the three angles. Finally, the quasi-diabatization procedure in MOLPRO was used to compute $\chi(R, \Omega)$ from analysis of the CI coefficients.\textsuperscript{38,39} We did not use the alternative, but computationally more cumbersome, approach of diabatization by integration of calculated nonadiabatic coupling matrix elements.
The angular grid included 845 orientations, with 11 values of \( \theta \), defined by \( \cos \theta = -1 \) to 1 in steps of 0.2, 6 values of \( \phi \), defined by \( \cos \phi = 0 \) to 1 in steps of 0.2, and 13 values of \( \phi' \) from 0 to \( \pi \) in steps of \( \pi/12 \). This choice of grid provides a uniform sampling of the differential solid angle.

The potential in the definite-state was calculated. We used the scaled triples correction\(^{42} \) as implemented in MOLPRO.\(^{33} \) In these RCCSD(T) calculations, we used the counterpoise method to estimate the basis set superposition error (BSSE),\(^{40} \) in which we subtract the energies of the fragments computed in the (supermolecular) atomic orbital basis. The interaction energy is

\[
V_{\text{CCSD(T)}}(R, \Omega) = E_{\text{CCSD(T)}}^{(\text{OH} \cdots \text{HH})}(R, \Omega) - E_{\text{CCSD(T)}}^{(\text{OH})}(R, \Omega) - E_{\text{CCSD(T)}}^{(\text{HH})}(R, \Omega).
\]

### B. CCSD(T) calculations

We also carried out restricted explicitly correlated coupled-cluster calculations with single-, double-, and (perturbatively) triple-excitations [RCCSD(T)-F12a].\(^{41,42} \) The advantage of a coupled-cluster method is that one can recover more of the correlation energy. The disadvantage is that it is difficult to determine the energy of the second adiabatic state, except in high-symmetry geometries where the wave functions for the two states belong to different irreducible representations.

We performed RCCSD(T)-F12a calculations with the augmented correlation-consistent triple-zeta basis (aug-cc-pVTZ)\(^{34,43,44} \) supplemented with mid-bond functions (3s3p2d2f/1g1h) at the following high-symmetry OH–H₂ geometries: (1) \( \phi_H = 0 \) or 180°, and a grid including 11 values of \( \theta_O \) (0°, 20°, 40°, 60°, 80°, 90°, 100°, 120°, 140°, 160°, and 180°) and 7 values of \( \theta_H \) (0°, 22.5°, 30°, 45°, 60°, 67.5°, and 90°); (2) \( \phi_H = 90°, \theta_O = 0° \) or 180°, and \( \theta_H \) with each of the 7 values above; and (3) \( \phi_H = 90°, \theta_H = 0° \) or 90°, and \( \theta_O \) with each of the 11 values above excluding 0° and 180°. We note that many of the geometries listed above are equivalent, e.g., all geometries in set (2) and (3) are equivalent to some geometries in set (1). However, we used the interaction energies of all these geometries in fitting the PES’s. This choice of angles gives rise to 186 orientations, of which 131 are unique.

For 90% of all these geometries the existence of a plane of symmetry allows us to determine RCCSD(T) energies for the lowest states of both \( A' \) and \( A'' \) symmetry. These energies correspond to \( V_{ax} \) and \( V_{yy} \) depending on the chosen plane of symmetry. The potential in the definite-A symmetry was computed with Eqs. (13) and (14). The grid in the OH–H₂ distance \( R \) consisted of 39 values ranging from 3.5 \( a_0 \) to 30 \( a_0 \).

We used the scaled triples correction\(^{42} \) as implemented in MOLPRO.\(^{33} \) In these RCCSD(T) calculations, we used the counterpoise method to estimate the basis set superposition error (BSSE),\(^{45} \) in which we subtract the energies of the fragments computed in the (supermolecular) atomic orbital basis. The interaction energy is

\[
V_{\text{CCSD(T)}}(R, \Omega) = E_{\text{CCSD(T)}}^{(\text{OH} \cdots \text{HH})}(R, \Omega) - E_{\text{CCSD(T)}}^{(\text{OH})}(R, \Omega) - E_{\text{CCSD(T)}}^{(\text{HH})}(R, \Omega).
\]

### C. Additional calculations

To check the accuracy of our MRCI and RCCSD(T) calculations, we carried out additional computations, with various basis sets and methodologies, for T-shaped geometry at several values of the intermolecular separation \( R \), ranging from the repulsive region to that of the van der Waals well. The two sections of Table I present the results of these additional calculations.

We can draw a number of conclusions from Table I. In the MRCI calculations, there is little difference in the interaction energies when only two electronic states [the two components of OH(X²Π)], rather than the first three states [OH(X²Π + A²Σ⁺)], are optimized. Second, CBS extrapolation with an active space including the O 3s and 3p orbitals yields only a slightly smaller value for the repulsive potential. Finally, use of an explicitly correlated F12 basis gives results similar to the CBS extrapolation.

Calculations with full triples (CCSDT)\(^{46} \) give results very similar to those with perturbative inclusion of triples. Unfortunately, it is not possible to perform CCSDT calculations with larger basis sets, nor does a F12 version of the CCSDT code currently exist.

Expanding the calculations to allow core-valence correlation has little effect upon the computed interaction energies. Also, explicit inclusion of scalar relativistic effects (using the Douglas-Kroll Hamiltonian)\(^{47} \) also does not significantly affect the results; this is expected since oxygen is a light atom.

In our calculations, we kept the OH and H₂ bond distances fixed at \( r_0 \). A better approximation would be to calculate the PES at several values of the bond distances and then average over the ground vibrational wave functions for both species. We see in Table I that vibrationally averaging over \( r(H_2) \) has little effect. Vibrational averaging over \( r(OH) \) leads to only a slight increase in the repulsive interaction.

Present computational resources do not permit full-triples calculations (CCSDT), or those involving vibrational averaging, for the more than \( \sim 6000 \) points used to determine the RCCSD(T)-F12 potential. Notwithstanding, from Table I we would not anticipate a significant difference in the calculated interaction energies.

### D. Fitting the PES’s

The phase of the CI wave functions is not defined uniquely in the CI calculation. Consequently the signs of the mixing angle \( \chi \), as well as of the real and/or imaginary part of the off-diagonal potential, may vary inconsistently from point to point. To compensate for this uncertainty in sign, we first fitted our CCSD(T) \textit{ab initio} potential to a small set of angular basis functions. This fitted potential was then used to resolve ambiguities in the signs of the MRCI off-diagonal functions. Manual inspection confirmed smoothness in the off-diagonal PES. Unfortunately, for a few geometries, \( V_{\alpha} \) is very close to zero (\(| V_{\alpha} | < 0.05 \text{ cm}^{-1} \)), preventing the determination of a consistent sign for these points.

The fitting procedure was as follows: We first set upper limits of 9 and 6 for, respectively, \( l_1 \) and \( l_2 \). The subsequent
expansion contains 126 terms for $V_d$ and 198 terms for $V_o$. We then carried out a least-squares fit of the sign-corrected MRCI interaction energies at $R = 5 \ a_0$ (a point in the repulsive region of the PES where we do not anticipate that the important expansion coefficients will be changing sign) to Eqs. (6) and (7). All terms with expansion coefficients of absolute value greater than 1.5 cm$^{-1}$ were retained. This corresponds to 39 terms for $V_d$ and 15 terms for $V_o$. In the latter case, 3 of the terms have odd values of $(l_1 + l_2 + f)$.

We used this (39/15)-term fitting scheme and Eqs. (6) and (7) to fit both the MRCI and the CCSD(T) PES’s. Figure 2 displays the root-mean-square deviation (RMS) of the fits to $V_d$ and $V_o$ as a function of $R$. Overall, we see the fit is good, and the RMS is well below 1 cm$^{-1}$ for $R \geq 6 \ a_0$. Because, in general the off-diagonal potential is smaller in magnitude, the RMS for $V_o$ is smaller. We will discuss this further in Sec. III F.

At short range, $V_d$ of the CCSD(T) potential has a larger rms. This is reasonable since the terms we used in the fit were optimized for the MRCI PES’s. For $V_o$ and $V_d$ at long range, the CCSD(T) PES’s have smaller RMS. The RMS for the MRCI PES’s generally remains a constant ($0.05-0.1 \ cm^{-1}$) for $R \geq 8 \ a_0$. This is a measure of the precision of our MRCI calculations.

To estimate the systematic error of the CCSD(T) PES’s due to the restriction of the angular sampling to high symmetry points, we also created test $V_d$ and $V_o$ PES’s using only the MRCI points whose molecular geometry has a plane of symmetry [referred to in the following as the MRCI-HS

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(high-symmetry) PES’s). Out of the 858 orientations for each \( R \), there are 153 that have a plane of symmetry. Fitting just these points, by means of the same procedure as described above, we obtain the MRCI-HS PES’s.

The three sets of OH–H\(_2\) PES’s, in the form of expansion coefficients as a function of \( R \), can be obtained from the supplementary material.\(^{24}\)

### E. Extrapolation of the PES’s

#### 1. Short range

The calculated PES’s were limited to \( R \geq 3.5\, a_0 \), which is sufficiently small for scattering and bound-state calculations. Inside this value of \( R \), the expansion coefficients are held constant to their values at \( 3.5\, a_0 \). We note that a few expansion coefficients, of relatively small magnitude, do not vary smoothly for \( R \leq 4.25\, a_0 \).

#### 2. Long range

The CCSD(T) PES’s were extrapolated by a least-squares fit of a few \textit{ab initio} points at large \( R \) to the form

\[
V_{l_1l_2}^{\text{ext}}(R) = \sum_i C_i R^{-n_i}. \tag{17}
\]

Here \( V_{l_1l_2}^{\text{ext}} \) represents an extrapolated \( B \) or \( F \) coefficient, \( C_i \) is a fitted parameter, and \( n_i \) is the appropriate power in the standard long-range expansion of the multipole-multipole electrostatic, the dispersion, and the induction interactions.\(^{48, 49}\) We included only the smallest one or two values of \( n_i \leq 11 \) in modeling the induction and dispersion terms. Care was taken to choose a proper range of \( R \) values for this long-range fit so that none of the expansion coefficient would be artificially large at \( R = 200\, a_0 \).

The MRCI PES’s were extrapolated by a slightly different method since the \textit{ab initio} points are less precise at long-range. We employed a multipole expansion method similar to that described in Ref. 25 to model the long-range electrostatic interaction in terms of the multipole moments of the separate OH and H\(_2\) molecules. The relevant theory as well as the calculated multipole moments are included in the additional technical details which are available in the supplementary material.\(^{24}\)

We included in this expansion only the dipole, quadrupole, and octupole moments of OH, and the quadrupole moment of H\(_2\). For the diagonal PES, we can thus estimate the OH-dipole/H\(_2\)-quadrupole (\( B_{123}, R^{-4} \)), the quadrupole-quadrupole (\( B_{224}, R^{-5} \)), and the OH-octupole/H\(_2\)-quadrupole (\( B_{325}, R^{-6} \)) interactions. Since there is no dipole moment between the \( \Lambda = \pm 1 \) and \( \Lambda = \mp 1 \) states of OH, for the off-diagonal PES we included just the quadrupole-quadrupole (\( I_{224}, R^{-5} \)) and the OH-octupole/H\(_2\)-quadrupole (\( I_{325}, R^{-6} \)) terms.

For these multipole-multipole interactions, the \( V_{l_1l_2f}^{(\Lambda'-\Lambda)} \) expansion coefficients are proportional to the products of the corresponding OH and H\(_2\) moments, multiplied by \( R^{-l'-1} \). We then subtracted these electrostatic expansion coefficients from the coefficients obtained by fitting the MRCI \textit{ab initio} points to Eq. (17). The difference potential was then extrapolated to long range with Eq. (17), using the same method as used in extrapolating the CCSD(T) PES’s. The values of \( n_i \) in Eq. (17) corresponding to the already modeled electrostatic interaction were excluded.

We obtain the final MRCI expansion coefficients by smoothly switching, as \( R \) approaches \( 16\, a_0 \), between the fit to the \textit{ab initio} points at short range and the extrapolated expansion coefficients at long range, for the \( \{l_1l_2l_3l_4\} = 123, 224, \) and 325 terms. For the other \( \{l_1l_2l_3\} \) terms with known inverse \( R \) dependences we extrapolated by smoothly switching at \( R = 16\, a_0 \) to Eq. (17), or, if not, to an exponential decay.

In the case of the CCSD(T) expansion coefficients, which are smoothly varying out to \( R = 30\, a_0 \), we did not switch to the known multipole-multipole terms. For \( R > 30\, a_0 \), we just extrapolated by Eq. (17) for the terms with a known inverse \( R \) dependence, or by an exponential decay.

The MRCI-HS PES’s were extrapolated with the same procedure and parameters as for the full MRCI PES’s.

### F. Fitted potential energy surfaces

#### 1. Expansion coefficients

Figure 3 shows several radial cuts of \( V_d \) for the MRCI and CCSD(T) PES’s at \( \theta_0 = 90^\circ \) and \( \phi_H = 0^\circ \). These correspond to planar geometries with H\(_2\) perpendicular to \( R \). Three values of \( \theta_0 \) (\( 0^\circ \), \( 90^\circ \), and \( 180^\circ \)) were chosen. For comparison, we also show comparable radial cuts of the CEPA MCKW PES’s (adapted from Ref. 18).

The MRCI and the CCSD(T) PES’s agree very well. Of the three orientations plotted, only the \( \theta_0 = 0^\circ \) curve shows a significant well, which corresponds to a T-shaped geometry with the H-end of the OH pointing to H\(_2\). The minima on these curves are also the global minima of \( V_d \), whose positions and depths are tabulated in Table II. The geometry of these global minima are a consequence of both the dipole-quadrupole interaction and the quadrupole-quadrupole interaction. The signs of both quadrupole moments are positive, which implies that there is an excess of positive charge at both ends of each molecule and of negative charge in the middle.

**FIG. 3.** The diagonal potential \( V_d \) as a function of intermolecular distance for various \( \theta_0 \) with \( \theta_H = 90^\circ \) and \( \phi_H = 0^\circ \), obtained from the CCSD(T) PES’s (solid lines), the MRCI PES’s (dotted lines), and the MCKW PES’s (dashed lines). The MRCI and CCSD(T) curves are nearly identical to within the resolution of the plot.
Therefore, the quadrupole-quadrupole interaction favors a T-shaped geometry.

Both minima are significantly more attractive than predicted by the MCKW PES’s (see Table II). This is not unexpected, since the MCKW \textit{ab initio} calculations were based on the CEPA method which gives a less complete recovery of electron correlation and, hence, a shallower van der Waals well. Second, the monomer bond lengths were slightly different. Here, for both OH and H$_2$ we used the average value of $r$ in the ground vibrational level, namely, $\langle r \rangle_{v=0}$ for both OH and H$_2$, as recommended by Faure et al.$^{50}$ Since $\langle r \rangle_{v=0}$ is larger than $r_r$, the polarizability and the electrostatic moments of the monomer fragments will be larger, so that the long-range interaction will be stronger.

We display the larger fitted expansion coefficients as a function of $R$ in Figs. 4 and 5 for the MRCI, MRCI-HS, and CCSD(T) PES’s. The difference between the expansion coefficients of the MRCI PES’s and MRCI-HS PES’s are insignificant. Consequently, restricting the angular sampling in the CCSD(T) \textit{ab initio} calculations to geometries with a plane of symmetry will not lead to significant error in the fitted CCSD(T) PES.

As a justification of the use of only the points with high symmetry, we performed some full close-coupling scattering calculations for several rotationally inelastic transitions of OH in collisions of H$_2$ $j = 0, j = 1, \text{and } j = 2$, at collision energies ranging from 70 to 150 cm$^{-1}$. We found that the state-to-state cross sections computed with the MRCI and the MRCI-HS PES’s differ by no more than $\sim$2%, comparable to the precision of the scattering calculations ($\sim$1%). For calibration, the maximum difference between cross sections computed on the MRCI and CCSD(T) PES’s is 8%. Also, we see from Table II that OH--H$_2$ dissociation energies computed with MRCI and MRCI-HS PES’s differ by only $\sim$0.3 cm$^{-1}$. We will further show the OH--H$_2$ bound state energies and spectroscopic constants computed from these two sets of PES’s in Sec. IV.

We thus assert that our CCSD(T) set of PES’s, determined at points with a plane of symmetry, is the most accurate currently available for OH--H$_2$. Inclusion of triple excitations

<table>
<thead>
<tr>
<th>PES</th>
<th>$R_0$ (a$_0$)</th>
<th>$D_0$ (cm$^{-1}$)</th>
<th>$D_0$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OH–H$_2$</td>
<td>OH–D$_2$</td>
<td>OH–D$_2$</td>
</tr>
<tr>
<td></td>
<td>para</td>
<td>ortho</td>
<td>para</td>
</tr>
<tr>
<td>KF$^a$</td>
<td>5.90</td>
<td>248.8</td>
<td>53.7</td>
</tr>
<tr>
<td>MCKW$^b$</td>
<td>6.08</td>
<td>188.1</td>
<td>28.6</td>
</tr>
<tr>
<td>MRCI$^c$</td>
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<td>219.6</td>
<td>38.7</td>
</tr>
<tr>
<td>MRCI-HS</td>
<td>6.05</td>
<td>219.6</td>
<td>38.7</td>
</tr>
<tr>
<td>CCSD(T)$^c$</td>
<td>6.02</td>
<td>219.5</td>
<td>36.1</td>
</tr>
<tr>
<td>Expt.$^d$</td>
<td>54</td>
<td>&gt;66</td>
<td></td>
</tr>
</tbody>
</table>

$^a$PES’s reported in Ref. 17, and bound states in Ref. 22.
$^b$Reference 18.
$^c$This work, CCSD(T) calculations restricted to the “high-symmetry” (HS) geometries in which there exists a plane of symmetry.
$^d$Reference 6.

FIG. 4. Larger $B_{1/1/1}$ expansion coefficients for the diagonal potential $V_d$ as a function of intermolecular distance $R$ for the CCSD(T) (solid lines) and MRCI (dashed lines) PES’s. The corresponding expansion coefficients for the MRCI-HS PES (dotted lines) are indistinguishable from the dashed lines. The upper panel shows the $B_{1/1/1}$ terms which go asymptotically to multipole-multipole electrostatic interactions; the lower panel displays other coefficients.

FIG. 5. Larger $F_{1/1/1}$ expansion coefficients for the off-diagonal potential as a function of intermolecular distance $R$ for the CCSD(T) PES’s (solid lines), MRCI PES’s (dashed lines), and the MRCI-HS PES’s (dotted lines, barely visible due to the overlap with the dashed lines). The top panel shows $F_{1/1/1}$ coefficients that have contributions from multipole-multipole interactions; the bottom panel displays other coefficients.
allows a more complete recovery of electron correlation than in the MRClSD+Q calculations. Use of the CCSD(T)-F12a method with an aug-cc-pVTZ basis is expected to be more accurate than a standard (without explicit correlation) CCSD(T) calculation with a larger aug-cc-pVQZ basis. In addition, the CCSD(T) calculations are faster. Also, whenever there is a plane of symmetry, the diabatic coupling \( V_{xx} \) vanishes, so that the determination of the diagonal \( V_{xx} \) and off-diagonal \( V_{xy} \) PES’s from the \( V_{xx} \) and \( V_{xy} \) Cartesian PES’s is straightforward by means of Eqs. (13) and (14).

The top panels of Figs. 4 and 5 show coefficients with \( l = l_1 + l_2, l_1 \geq 1 \), and \( l_2 \geq 2 \), to which the multipole-multipole electrostatic interactions make significant contributions at long range. For the diagonal potential, the \( B_{123} \) (OH-dipole/H\(_2\)-quadrupole, \( R^{-4} \) dependence) and the \( B_{224} \) (quadrupole-quadrupole, \( R^{-5} \) dependence) terms dominate the PES at medium to long range. In this range the only comparable non-multipole contribution is the isotropic \( B_{000} \) term, which is a reflection of the \( R^{-6} \) dispersion interaction. As seen in the lower panel of Fig. 5, the largest non-multipole contribution is the \( F_{202} \) term, which is a difference between the dispersion interaction between \( H_2 \) and OH in its \( \pi_0^2 \pi_1 \) and \( \pi_0 \pi_1^2 \) Cartesian states.

We discussed in Sec. II C, the appearance of terms in the expansion of the off-diagonal potential \( V_{xy} \) corresponding to an odd sum of the indices \( \{l_1, l_2, l\} \). For the electrostatic interactions between the two fragments, the indices obey the relation \( l_1 + l_2 = l \), so they do not give rise to terms with odd \( (l_1 + l_2 + l) \). The induction, dispersion, and overlap interactions are not subject to this restriction. Thus, for these interactions there arise terms with \( l_1 + l_2 \neq l \), both with odd and even \( (l_1 + l_2 + l) \). For this reason, and guided by Green’s investigation of similar terms in the expansion of the interaction between a non-linear polyatomic and a diatomic, we included terms with odd \( (l_1 + l_2 + l) \) in our fit. The largest of these was the \( F_{223} \) term (see Fig. 5). As can be seen, this term is quite small except at small values of \( R \).

2. Anisotropies

At small \( R \), the anisotropy of both the diagonal and the off-diagonal PES’s is more complex than predicted by a simple multipole-multipole model. A number of expansion terms make important contributions. When \( H_2 \) is in the lowest rotational level \( (j = 0) \), its wave function is spherically symmetric. The \( \text{OH–}H_2(j = 0) \) PES is a function of only \( R \) and \( \theta \), and can be obtained by an equal-weight averaging over all orientations \( (\theta_{\text{H}} \text{ and } \phi_{\text{H}}) \) of the \( H_2 \) moiety. Figure 6 compares the \( \text{OH–}H_2(j = 0) \) PES with the \( V_{sum} \) PES’s for \( \text{OH–He} \) \( ^{33} \) and \( \text{OH–Ne} \).

The anisotropies of these PES’s are very similar. All three have global minima at \( \theta_{\text{O}} = 0^\circ \) and \( R \sim 6.5 a_0 \). Although \( \text{OH–}H_2 \) is isoelectronic with \( \text{OH–He} \), the \( \text{OH–}H_2(j = 0) \) minimum is more than three times deeper than the \( \text{OH–He} \) minimum, and the interaction is more repulsive at short range. Both differences are reasonable. For \( H_2 \) in \( j = 0 \), the charge distribution is spherical so that there will be no multipole moments. Hence, the dominant attractive contribution is the dispersion interaction. Because the charge distribution of \( H_2 \) is more polarizable than that of He, the \( \text{OH–}H_2 \) attractive interaction will be larger. Similarly the size of an \( H_2 \) molecule, even averaged over orientation, will be larger than that of the isoelectronic He atom. Thus, we expect a somewhat steeper repulsive wall. In reality, the \( \text{OH–}H_2(j = 0) \) PES’s appears more similar to that of \( \text{OH–Ne} \).

Figure 7 displays contour plots of the off-diagonal \( \text{OH–}H_2(j = 0) \) PES and the \( V_{\text{dif}} \) PES’s for \( \text{OH–He} \) and \( \text{OH–Ne} \). The \( V_{\text{dif}} \) (or \( V_{\text{dif}} \)) PES’s are the half difference between the PES’s corresponding to interaction of a collision partner with OH \( (\pi_0^2 \pi_1) \) and \( (\pi_0 \pi_1^2) \). This will vanish in linear geometry, where the two electron occupancies are degenerate, and reach a maximum at \( \theta_{\text{O}} \sim 90^\circ \) where the spherical partner is pointed at either a singly filled or doubly filled OH \( \pi \) orbital. Overall, \( V_{\text{dif}} \) is smaller magnitude than \( V_{\text{dif}} \). We thus expect it to play a less important role in scattering and bound-state calculations.

Figure 8 presents contour plots of \( V_{xy} \) and \( V_{xy} \) in the OH molecule frame similar to plots given by OvH (Fig. 3(a) of Ref. 15). In these plots, the center of mass of the OH molecule defines the origin. The OH molecule lies on the \( z \) axis with the H atom on the positive direction. The \( \text{OH–}H_2 \) separation is \( (x^2 + y^2)^{1/2} \), and the orientation of the OH molecule in the space-fixed frame defined in Fig. 1 is \( \theta_{\text{H}} = \tan^{-1}(x/z) \). The orientation of the \( H_2 \) molecule is fixed at \( \{\theta_{\text{H}}, \phi_{\text{H}}\} = \{27.46^\circ, 45^\circ\} \). Overall, our PES’s and those of OvH show a very similar dependence on the OH–HH distances and
on the orientation of the OH moiety. For both sets of PES’s, \(V_d\) has an attractive well on the oxygen side of OH, and \(|V_o|\) is slightly asymmetric about the \(x = 0\) axis.

Our CCSD(T) calculations sampled only high-symmetry geometries while the OvH PES’s are fits to \(ab\) \(initio\) calculations which sampled non-planar geometries. Thus the great qualitative similarity in the OvH and CCSD(T) PES’s confirms that sampling only high-symmetry geometries will provide an excellent description of the OH–H\(_2\) system. The OvH PES’s were computed with a SCF dispersion method, which yields a deeper well at this H\(_2\) orientation compared with our more accurate method.

Contour plots showing the dependence of \(V_o\) and \(V_d\) on \(\theta_o\) and \(\theta_H\) for \(\phi_H = 0^\circ\) and \(90^\circ\) at \(R = 6 \, a_0\) are presented in Figs. 9 and 10, respectively. At medium to long range, the interaction between the OH dipole (negative at the O end) and the HH quadrupole (positive at the ends, negative in the middle) will dominate the interaction. The interaction will be most attractive when the OH approaches the H\(_2\) in T-shape geometry with the H-end of the OH closer to the H\(_2\) (\(\theta_o = 0^\circ\), \(\theta_H = 90^\circ\), T-shape OH–HH). In addition to this global minimum, there are local minima in linear HO–HH geometry, in which the negative end of the OH dipole approaches the positive ends of the HH quadrupole (\(\theta_o = 180^\circ\), \(\theta_H = 90^\circ\), linear HO–HH).

Figure 10 presents contour plots of the off-diagonal potential \(V_o\). The minima and the maxima of \(\Re(V_o)\) and \(\Im(V_o)\) are all located at \(\theta_o = 90^\circ\). At this value of \(\theta_o\), one lobe of the \(\pi_s\) orbital of OH points to H\(_2\), and thus will maximize the difference between the energies of the \(\pi_s^2\) and \(\pi_s\) electron occupancies. When \(\phi_H = 0^\circ\), \(\Im(V_o)\) vanishes by symmetry, while the real and imaginary parts of \(V_o\) have comparable magnitudes when \(\phi_H = 90^\circ\).

When \(\phi_H = 90^\circ\), \(\exp(\text{i}m\phi_H) = \text{i}^m\) and \(\cos(\text{i}m\phi_H)\) vanishes unless \(m\) is even. Since the index \(l_2\) is also even (because of the permutation symmetry of the HH moiety), one can show that the diagonal potential [Eq. (3)] and the real part of the off-diagonal potential [Eq. (5)] is unchanged when \(\theta_H\) is replaced by \(\pi - \theta_H\). In contrast, the imaginary part of the off-diagonal potential changes sign when \(\theta_H\) is replaced by \(\pi - \theta_H\). Thus \(V_d\) and \(\Re(V_o)\) should be symmetric, while \(\Im(V_o)\) should be antisymmetric, about \(\theta_H = 90^\circ\). This prediction is borne out by the right panel of Fig. 9, and the middle and right panels of Fig. 10.

Finally, we compare in Fig. 11 at \(R = 15 \, a_0\) contour plots of the contribution to \(V_d\) of just the terms which correlate at long-range to the lower-order multipole-multipole interactions (\(B_{123}, B_{224},\) and \(B_{325}\)) and the full fitted CCSD(T) PES’s. The electrostatic interactions were computed from the multipole moments listed in Table I of the supplementary material. Overall, consideration of just the electrostatic interactions represents well the angular dependence and magnitude of the PES. Notwithstanding, the CCSD(T) PES’s is
less repulsive at all orientations than that predicted by with the electrostatic interactions alone. We infer that there are still non-trivial contributions from induction and dispersion at this large value of \( R \). We thus believe that a full calculation of the long-range potential will be more accurate than relying on electrostatics alone.

We note that Wormer et al.\textsuperscript{25} used electrostatic interactions only in extrapolating their OH–HCl PES. Notably, though, the OH-HCl PES is dominated by the strong \( R^{-3} \) dipole-dipole interaction which is absent for OH–H\(_2\).

Although we did not use the multipole moments in extrapolating the CCSD(T) PES, fits of the CCSD(T) potentials are practically identical. We list in Tables III and IV the energies of the bend-stretch states. The bound-state energies were also computed independently using another program described in Ref. 57. The results obtained from the two calculations are practically identical.

### IV. BOUND-STATE CALCULATIONS

#### A. Theory and method

The Hamiltonian for the OH–H\(_2\) system with fixed bond lengths can be written as

\[
\hat{H} = -\frac{1}{2\mu R} \frac{\partial}{\partial R^2} R + \hat{H}_0 + \hat{H}_1 = \frac{\hat{L}^2}{2\mu R^2} + V(R, \theta_H, \phi_H),
\]

where \( \mu \) is the OH–H\(_2\) reduced mass, \( \hat{H}_0 \) and \( \hat{H}_1 \) are the rotational Hamiltonians of OH and H\(_2\), respectively, \( \hat{L} \) is the orbital angular momentum of the complex, and \( V \) is the interaction potential.

We construct a set of basis functions from the product of stretching functions and angular functions and use a set of distributed Gaussians to span the \( R \)-space. The construction of the rotational basis functions, which can also be used for scattering calculations, is discussed in detail in the supplementary material.\textsuperscript{24}

We employed the following parameters for \( \hat{H}_0 \): the rotational constant \( B \), the spin-orbit constant \( A \), and the \( \Lambda \) doubling parameters \( p \) and \( q \) for the \( \nu = 0 \) level of OH. The values of these parameters were taken from Mélen et al.\textsuperscript{54} and the matrix elements of \( \hat{H}_0 \) were defined by Kotlar et al.\textsuperscript{55} For \( \hat{H}_1 \) we use the rotational constants \( B \) of H\(_2\) and \( D_2 \) averaged over the \( \nu = 0 \) probability distributions (59.322 and 29.9043 cm\(^{-1}\), respectively).

The expression for the matrix elements of the interaction potential in this angular basis is given in the supplementary material.\textsuperscript{24} We used our Hibridon\textsuperscript{56} suite of programs, recently extended to handle the OH–H\(_2\) system, to construct and diagonalize the Hamiltonian matrix to determine the energies of the OH–H\(_2\) bend-stretch states. The bound-state energies were also computed independently using another program described in Ref. 57. The results obtained from the two calculations are practically identical.

#### B. Results

We list in Tables III and IV the energies of the bend-stretch levels of the OH–H\(_2\) complex calculated with the CCSD(T) PES’s for total angular momenta \( J = 1/2 \) and 3/2. In computing these energies, we included all angular basis functions with \( j_1 \leq 13/2 \) and \( j_2 \leq 5 \) and \( \leq 4 \) for \textit{ortho} and \textit{para} H\(_2\), respectively. The stretch basis (the expansion in the OH–H\(_2\) distance) was 41 equally spaced Gaussian functions spanning the range \( 4 \alpha_0 \leq R \leq 16 \alpha_0 \). The computed bound state energies are converged to \( \sim 0.01 \) cm\(^{-1}\).

We have inspected the wave functions for each bound level and assigned OH–H\(_2\) stretching quantum numbers \( \nu \) and the body-fixed projection \( P \) of the angular momentum of the complex \( J \). \( P \) was assigned using the vector model of angular momenta similar to the method described in Ref. 22.
Overall, we find that the computed bound level energies are in qualitative agreement with the values reported by Miller et al.\textsuperscript{18, 22} The number of bound levels is similar, the zero point energies are large, and for both $J = 1/2$ and $3/2$ the binding energies for OH–ortho-H$_2$ are greater than for the para--H$_2$ complex.

The stronger binding with ortho-H$_2$ is a general phenomenon for all H$_2$ complexes.\textsuperscript{18, 22, 58–63} The para–H$_2$ molecule is spherically symmetric and cannot orient to sample the most attractive orientations (at least without mixing in higher $j = 2$ rotational level). Alternatively, because of this spherical symmetry, the $j = 0$ state of H$_2$ lacks a quadrupole moment. Thus, the long-range quadrupole-quadrupole attraction does not contribute in the interaction of OH with H$_2$(j = 0).

In Sec. III F 1, we discussed whether restricting the angular sampling to geometries with a plane of symmetry would lead to significant error in the fitted PES. The differences between the expansion coefficients for the MRCl and MRCl-HS PES’s were found to be insignificant. Moreover, there were only minimal differences between state-to-state cross sections computed with these two PES’s. As a further check on the validity of considering interaction energies only for geometries with a plane of symmetry, we compare the energies of bend-stretch levels computed with these two PES’s. Table V presents comparison of the energies of the lower $J = 1/2$ and $3/2$ bound levels computed with the MRCl and MRCl-HS PES’s. We see that the energies computed with the MRCl PES’s are slightly lower than the MRCl-HS values, but only by a fraction of a wavenumber ($\Delta E < 0.3$ cm$^{-1}$). This provides additional justification for using only geometries that have a plane of symmetry in our fit. This restriction permits the use of RCCSD(T) calculations of the interaction energies.

### Table III. $J = 1/2$ bound levels (in cm$^{-1}$) of OH–H$_2$ for the CCSD(T) PES. Also shown are assignments of the stretching quantum numbers.$^a$

<table>
<thead>
<tr>
<th>$\rho = +1^b$</th>
<th>$\rho = -1^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>Energy</td>
</tr>
<tr>
<td>OH--para-H$_2$</td>
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<tr>
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<tr>
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<tr>
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<td>-7.43</td>
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<tr>
<td>7</td>
<td>-6.52</td>
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<tr>
<td>8</td>
<td>-3.74</td>
</tr>
<tr>
<td>9</td>
<td>-1.42</td>
</tr>
</tbody>
</table>

$^a$The zero of energy is the energy of separated OH(2$^1$Pi, $j = 3/2$ $F_r(e) + H_2(j)$, where $j = 0$ and 1 for para-- and ortho-H$_2$, respectively. Levels with energy $> -1$ cm$^{-1}$ are not listed.

$^b$Symmetry index for the complex. The overall parity of the bend-stretch wave function equals $\rho(-1)^{j-1/2}$.

### Table IV. $J = 3/2$ bound levels (in cm$^{-1}$) of OH–H$_2$ predicted for the CCSD(T) PES. Also shown are assignments of the stretching quantum numbers and approximate values of $P$.\textsuperscript{a,b}

<table>
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</thead>
<tbody>
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<td>Energy</td>
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<tr>
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<tr>
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<td>13</td>
<td>-2.12</td>
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<tr>
<td>14</td>
<td>-2.08</td>
</tr>
</tbody>
</table>

$^a$The zero of energy is the energy of separated OH(2$^1$Pi, $j = 3/2$ $F_r(e) + H_2(j)$, where $j = 0$ and 1 for para-- and ortho-H$_2$, respectively. Levels with energy $> -1$ cm$^{-1}$ are not listed.

$^b$Symmetry index for the complex. The overall parity of the bend-stretch wave function equals $\rho(-1)^{j-1/2}$.

$^c$Strong Coriolis coupling prevents the assignment of the body-frame projection $P$.\textsuperscript{a}

### Table V. The lower $J = 1/2$ and $3/2$ bound levels (in cm$^{-1}$) of OH–H$_2$ predicted the MRCl and MRCl-HS PES’s.$^a$

<table>
<thead>
<tr>
<th>$\rho = +1^b$</th>
<th>$\rho = -1^b$</th>
</tr>
</thead>
<tbody>
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<td>J = 1/2</td>
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<tr>
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<td>J = 3/2</td>
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<tr>
<td>3</td>
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<tr>
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<td>J = 3/2</td>
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</tr>
<tr>
<td>3</td>
<td>-41.27</td>
</tr>
</tbody>
</table>

$^a$The zero of energy is the energy of separated OH(2$^1$Pi, $j = 3/2$ $F_r(e) + H_2(j)$, where $j = 0$ and 1 for para-- and ortho-H$_2$, respectively.

$^b$Symmetry index for the complex. The overall parity of the bend-stretch wave function equals $\rho(-1)^{j-1/2}$.\textsuperscript{a}
We see in Tables III–V that there are significant parity splittings in the energies of the bend-stretch levels. Green and Lester$^{64}$ and Dubernet et al.$^{65}$ have employed a perturbation theory to determine the $J$-dependence of the bend-stretch energies and parity splittings, which can be expressed for $P = 1/2$ bend levels as

$$BJ(J + 1) + \frac{p}{2} p(J + 1/2),$$

where $B$ is the rotational constant of the complex and $p$ is the parity splitting parameter of that particular bend level. As expected from the analysis in the above cited studies,$^{64,65}$ the parity splittings are much larger for $P = 1/2$ levels than for $P = 3/2$ levels.

We have fit the $J$ and parity dependence of the computed energy of the lowest bend-stretch level ($P = 1/2$) of OH–ortho-H$_2$ to Eq. (19). Table VI compares the rotational constant and parity splitting parameter for this bend-stretch level, determined both experimentally and theoretically. As expected from the small differences between the MRCI and MRCl-HS bend-stretch energies, the derived spectroscopic constants computed with these two PES’s are in good agreement. We also see that there are only slight differences in the parameters computed with the CCSD(T) and MRCI PES’s. By contrast, the agreement of our computed spectroscopic constants with those reported experimentally,$^7$ which were obtained from fitting $J = 1/2$ and $J = 3/2$ level energies derived from the spectrum, is less satisfactory. Our values for $B$ and $p$ are, respectively, smaller and larger than the experimental values. The differences lie outside the experimental error bars. The spectroscopic constants computed with the less sophisticated MCKW PES’s are in better agreement with experiment. We note that the Coriolis coupling in the $J = 3/2$, $P = 1/2$ levels we used in deriving spectroscopic constants are weak.

Calculation of the bend-stretch energies allows us to predict the zero-point corrected dissociation energy $D_0$. These values are presented in Table II. Our predicted well depths ($D_0$) are ca. 31 cm$^{-1}$ larger than predicted for the MCKW PES’s. However, this difference is compensated somewhat by the larger curvature of our PES’s in the region of the well (see the blue lines in Fig. 3). Thus the zero-point-corrected dissociation energies ($D_0$) are only 8 cm$^{-1}$ (MRCI) and 11 cm$^{-1}$ [CCSD(T)] larger than the values computed for the MCKW PES’s.

The $D_0$ values obtained from our CCSD(T) PES’s, 36.1 cm$^{-1}$ and 53.7 cm$^{-1}$ for OH–para-H$_2$ and OH–ortho-H$_2$, respectively, are both in good agreement with the MRCI values (Table II). We note that our computed $D_0$ for OH–ortho-H$_2$ is in excellent agreement with the experimental value of 54 cm$^{-1}$. We have also computed the bound states for OH–ortho-D$_2$ and OH–para-D$_2$ with the CCSD(T) PES’s, and obtained $D_0$ values of 51.4 cm$^{-1}$ and 67.5 cm$^{-1}$. These values are Δ~7 cm$^{-1}$ larger than those obtained with the MCKW PES.$^9$ The lower limit of the OH–para-D$_2$ binding energy determined via electronic spectroscopy is 66 cm$^{-1}$, which is again in excellent agreement with our prediction.

### V. CONCLUSION

We have presented here two sets of OH($X^2\Sigma^+$)–H$_2$ PES’s, calculated using the MRClSD+Q (Davidson) and the CCSD(T)-F12a methods. Comparison of the full MRClSD+Q PES’s with a fit to a subset of points determined at geometries with at least one plane of reflection symmetry shows that sampling based on this subset of points provides a very accurate, but much less computationally demanding, representation of the OH–H$_2$ PES’s. For these points with symmetry we can then use the CCSD(T)-F12a method, which is more accurate and, in addition, computationally faster. We expect this strategy to be useful in developing PES’s for similar systems involving a $^2\Pi$ molecule and a $^1\Sigma^+$ molecule, such as NO($X^2\Pi$)–H$_2$.

We have performed calculations of the bend-stretch levels of the binary OH–H$_2$ complex for both the para and ortho nuclear spin modifications. The dissociation energies ($D_0$) predicted by fits to the MRCI and the CCSD(T) points differ by less than 2 cm$^{-1}$, and agree extremely well with the experimental estimate.$^6$ This agreement is a measure of the accuracy of our PES’s, especially for the depth and shape of the attractive well.

Comparison of inelastic OH–H$_2$ scattering cross sections with experiment would constitute a further test of our PES’s. This comparison would be most sensitive to the PES’s near the onset of the repulsive well. Collisions of OH with H$_2$ have been well studied.$^8,12$ Most recently, use of a Stark decelerator$^{13,66}$ has permitted the determination of the relative magnitude of state-resolved OH$j \rightarrow j'$ transitions in collisions with D$_2$ and H$_2$ over a wide range of collision energies. Comparable scattering calculations are in progress and will be reported soon.

### ACKNOWLEDGMENTS

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