



Quantum wave packet calculation of the $O(^3P) + H_2$ reaction on the new potential energy surfaces for the two lowest states

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ABSTRACT

New accurate potential energy surfaces (PESs) for the lowest states ($^3A''$ and $^3A'$) of the $O(^3P) + H_2$ reaction are proposed using an *ab initio* multireference configuration interaction method (MRCI) with Davidson correction and a large orbital basis set (aug-cc-pv5z). The many-body expansion procedure is employed to describe the analytical PES function. The topographical features of the new global PESs are presented and compared with previous surfaces. The quantum reaction scattering dynamics calculations are carried out over the collision energies range of 0.3–1.0 eV on the new PESs. The integral cross-sections and rate coefficients for the title reaction were calculated. The calculated coefficients are lower than the experimental ones at the low temperature.

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1. Introduction

The reaction of $O(^3P) + H_2$ has been widely studied due to its importance in combustion processes and atmospheric reaction [1–3]. Both theoretical and experimental studies were performed on this reaction as shown by the variety of potential energy surfaces (PESs) and dynamics calculations [4–37] and the wealth of experimental reaction rate constants [9,35,36,38–41].

It is known that the PES provides information on the interaction of a reactive system at a molecular level. Various theoretical methods were used to improve the accuracy of the potential energy surfaces. Early, Johnson and Winter [4] presented the London–Eyring–Polanyi–Sato (LEPS) potential energy surfaces using LEPS function with a single adjustable Sato parameter. The PES for the $^3A''$ state of the $O(^3P) + H_2$ reaction was computed using a first order configuration interaction (FO-CI) wave function by Howard et al. [1]. The PES based on the polarization configuration interaction (POL-CI) method was performed by Walch et al. [6]. The chemically accurate potential energy surfaces for the lowest electronic states of the $O(^3P) + H_2$ system were reported by Rogers et al. [15]. Later, Brandao et al. [19] presented a new potential energy surface using *ab initio* data calculated by Rogers et al. [15]. That was done by employing a DMBE formalism that uses a semiempirical description of long-range interactions.

In this work, we present the new PESs for the two lowest states ($^3A''$ and $^3A'$) of the reaction $O(^3P) + H_2$ from accurate *ab initio* data,

employing the many-body expansion in the Aguado–Paniagua function form [42].

The remainder of the paper is outlined as follows. In Section 2, the *ab initio* calculations and the construction of the new PESs of the reaction are described in detail. Section 3 describes the dynamics calculations based on the new PESs. Comparisons with the experimental measurements are also made. Finally, conclusions are presented in Section 4.

2. PES construction

The new 3D adiabatic PESs have been computed using complete active space self-consistent field (CASSCF) [43,44] and internally contracted multireference configuration interaction (MRCI) [45,46] wave functions. All *ab initio* calculations have been performed with the MOLPRO [47] package of *ab initio* programs. The aug-cc-pv5z basis set of Dunning was employed. In both the CASSCF and MRCI calculations, nine valence electrons were included in the 11 active orbitals ($9a' + 2a''$), consisting of the H 1s orbital and the 2s, 2p, 3s, 3p, 4s orbital of the O atom. The remaining orbital was kept doubly occupied. In the CASSCF and MRCI calculations, equal weights were assigned to each of the three states ($1^3A''$, $1^3A'$, $2^3A''$) in the state-averaging calculations. In addition, the multireference Davison correction (+Q) [48] was included to compensate for the effect of higher order correlation.

The *ab initio* energies have been calculated with the grid points generated by $0.6 \leq r_{H_2}/a_0 \leq 8.0$, $1.0 \leq R_{O-H_2}/a_0 \leq 14.0$ and $0.0 \leq \theta^\circ \leq 90$ for O– H_2 geometries, and $0.8 \leq r_{OH}/a_0 \leq 3.0$, $1.5 \leq R_{H-OH}/a_0 \leq 10.0$ and $0.0 \leq \theta^\circ \leq 180$ for H–OH geometries; r , R and θ are the atom–diatom Jacobi coordinates, and the r grids are

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Table 1
Diatomic data.

	This work	GLDP	Experiment
E_{OH} (kcal/mol)	106.6	107.0	106.6
E_{HH} (kcal/mol)	109.3	109.4	109.5

non-uniform scale, more grids are in the vicinity of equilibrium distances of OH and H₂.

The *ab initio* energy points have been chosen to be fitted to analytical forms for use in the scattering calculations. For the analytical representation of the PES, we chose the many-body expansion in the Aguado–Paniagua [42] function form.

$$V_{ABC}(R_{AB}, R_{AC}, R_{BC}) = V_A^{(1)} + V_B^{(1)} + V_C^{(1)} + V_{AB}^{(2)}(R_{AB}) + V_{AC}^{(2)}(R_{AC}) + V_{BC}^{(2)}(R_{BC}) + V_{ABC}^{(3)}(R_{AB}, R_{AC}, R_{BC}) \quad (1)$$

The one-body term $V_A^{(1)}, V_B^{(1)}, V_C^{(1)}$ is the energy of the separated atom and taken to be zero. The two-body terms are written as follows:

$$V^{(2)} = C_0 \frac{\exp(-\alpha R)}{R} + \sum_{l=1}^M c_l \rho^l \text{ with } \rho = R \exp(-\beta R) \quad (2)$$

where R corresponds to the bond length of the diatomic systems involved. *Ab initio* points for each of diatomic are fitted to the 11th order polynomial ($M = 11$). For the diatomic potential of OH, about 50 points were used to determine the parameters in Eq. (2). The root-mean-square (rms) error was 0.0062 kcal/mol. Similarly, for the HH potential, about 58 points were used and the corresponding rms error was 0.0099 kcal/mol. The dissociation energies

Table 2
Abstraction Saddle-point position and barrier height.

	${}^3A''$				${}^3A'$		
	AP	GLDP	RMOS	BMS1	AP	GLDP	RMOS
R_{HH} (bohr)	1.677	1.706	1.635	1.742	1.685	1.705	1.669
R_{OH} (bohr)	2.280	2.300	2.350	2.273	2.301	2.309	2.243
E (kcal/mol)	13.40	13.04	13.26	13.08	13.42	13.22	13.44

are shown in Table 1, which are basically coincident with the experimental results.

The three-body terms are written as a polynomial

$$V_{ABC}^{(3)}(R_{AB}, R_{AC}, R_{BC}) = \sum_{ijk} d_{ijk} \rho_{AB}^i \rho_{AC}^j \rho_{BC}^k \quad (3)$$

Here the indices i, j , and k vary from zero to a maximum value and i, j, k satisfy the following conditions: $i + j + k \leq M$ and $i + j + k \neq i \neq j \neq k$. There are two identical atoms in the present case ($B = C$), we have $d_{ijk} = d_{jik}$, $\rho_{AB} = \rho_{AC}$. For $M = 11$, there are 140 linear parameters to be determined.

We constructed a globally smooth PES using the procedure described by Aguado and Paniagua [42]. Compared to the above computed *ab initio* value, the rms error was 0.24 kcal/mol and the maximum energy deviation was 1.56 kcal/mol on the ${}^3A''$. For ${}^3A'$, the rms error was 0.27 kcal/mol and the maximum energy deviation was 2.5 kcal/mol. Fig. 1 shows contour plots of the four approaches of H to OH for the ground state ${}^3A''$ expressed in internal coordinates, the O–H–H angles are 180°, 135°, 90°, and 45°. Obviously, there is a barrier at the collinear geometry and

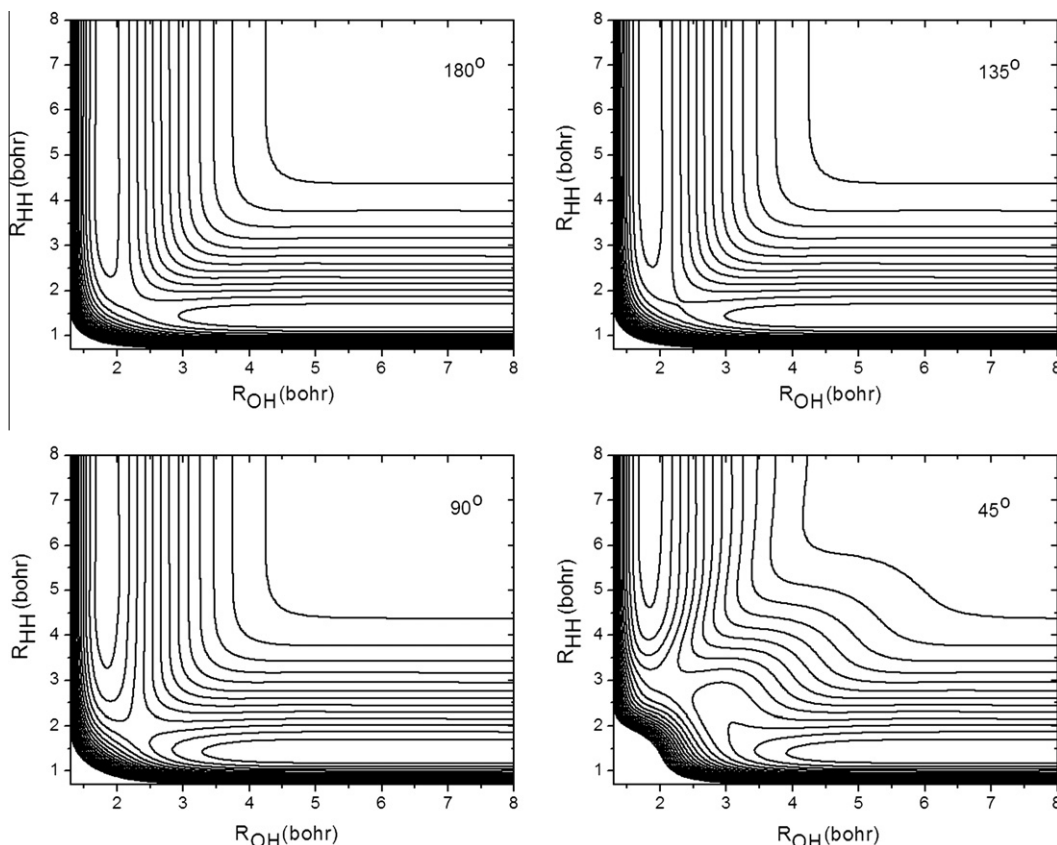


Fig. 1. Contour plots of the PES on the ground state ${}^3A''$ for the four different O–H–H angles in internal coordinates 180°, 120°, 90° and 30°. (Energies here are given in kcal/mol, and interatomic distances in bohr.)

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