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New *ab initio* Potential Energy Surfaces for $\text{Cl}(^2\text{P}_{3/2}, ^2\text{P}_{1/2})+\text{H}_2$ Reaction[†]

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New global three dimensional potential energy surfaces for the $\text{Cl}+\text{H}_2$ reactive system have been constructed using accurate multireference configuration interaction calculations with a large basis set. The three lowest adiabatic potential energy surfaces correlating asymptotically with $\text{Cl}(^2\text{P})+\text{H}_2$ have been transformed to a diabatic representation, which leads to a fourth coupling potential for non-linear geometries. In addition, the spin-orbit coupling surfaces have also been computed using the Breit-Pauli Hamiltonian. Properties of the new potential are described. Reaction dynamics based on the new potential agrees with the recent experimental results quite well.

Key words: Potential energy surface, Multi-reference configuration interaction, Spin-orbit coupling, Non-adiabatic effect

I. INTRODUCTION

The reaction $\text{Cl}(^2\text{P})+\text{H}_2\rightarrow\text{HCl}+\text{H}$ is one of the most widely studied elementary chemical reactions and has been the object of both theoretical and experimental studies for over a century [1,2]. Several years ago, many dynamic features of this reaction have been elucidated in a series of crossed-molecular beam experiments [3–6]. Particularly, Liu and coworkers obtained striking results for the relative reactivity of the two different spin-orbit (SO) states of the Cl atom, indicating considerably larger reactive cross sections for the spin-orbit excited $^2\text{P}_{1/2}$ state [4–6]. These results were in contrast with the Born-Oppenheimer (BO) approximation. This breakdown of BO approximation can be explained only by postulating that nonadiabaticity in the $\text{Cl}+\text{H}_2$ reaction is quite different from that in other reactions such as $\text{F}+\text{D}_2$ reaction [7]. The dramatic discrepancies between the experimental results and our customary knowledge confused scientists for many years.

Theoretically, a number of semi-empirical potential energy surfaces (PESs) have been constructed long before, such as GSW [8], GQQ [9], and G3 [10] potentials. The first high-quality fully *ab initio* PES was computed for the ground state by Bian and Werner (called BW2) [11] using multi-reference configuration interaction method with a very large basis set. This ground state surface was found to be very accurate in reproducing some important experimental results, such as the

$\text{DCl}+\text{H}/\text{HCl}+\text{D}$ branching ratio [12] and the increase of the reactive cross section as a function of the initial rotational excitation [13]. But in view of the challenging experimental results measured by Liu *et al.*, such a single-surface approach was inadequate. Therefore, three lowest adiabatic PESs and spin-orbit coupling surfaces for the entrance channel of the reaction were computed by Capecchi and Werner (called CW) [14] based on previous BW2 PES. Dynamic calculations based on the CW PESs have been carried out in recent years [15–19] along with some experiments [18,19] in order to resolve this disagreement. All of these results indicated that the breakdown in the BO approximation was small and the excited spin-orbit state plays only a minor role in the reaction. However, the experimental resolution was insufficient to separate unambiguously products formed by reaction of Cl^* from those formed by Cl. Very recently, Yang and coworkers have investigated this reaction using a high-resolution crossed molecular-beam method [20], and the experimental results were in excellent agreement with quantum scattering calculations based on the new PESs and CW set of PESs. This study resolved the previous disagreement between theory and experiment. In this paper, we will present details of our calculations and the features of the new PESs.

II. CALCULATIONAL DETAILS

The diabatic representation of this system has been described in detail in Ref.[14]. Briefly, the three lowest electronic states of the ClH_2 system are correlated with the asymptotic P_x , P_y , and P_z -states of the Cl-atom respectively. In the two-state approximation, the two adiabatic A' states can be described as mixtures of two diabatic states, denoted as Σ and Π_x , the dia-

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batic and adiabatic A'' states are identical. Through a transformation matrix \mathbf{U} , which is determined by a nonadiabatic mixing angle θ ,

$$\mathbf{U} = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix} \quad (1)$$

the three adiabatic states can be expressed as [14],

$$\begin{aligned} |1A'\rangle &= |\Sigma\rangle \cos \theta + |\Pi_x\rangle \sin \theta \\ |2A'\rangle &= -|\Sigma\rangle \sin \theta + |\Pi_x\rangle \cos \theta \\ |1A''\rangle &= |\Pi_y\rangle \end{aligned} \quad (2)$$

In our calculations, the diabatic states were obtained from the adiabatic ones by the inverse transformation.

All calculations of in this work were carried out with the MOLPRO package of *ab initio* programs [21]. The three lowest adiabatic states $1A'$, $2A'$, and $1A''$ for the ClH_2 system have been computed by means of the internally-contracted multi-reference configuration-interaction method (IC-MRCI) [22,23] with complete active space self consistent field (CASSCF) [24,25] reference wave functions. Through various test calculations, the augmented correlation consistent polarized valence quadruple zeta (aug-cc-pVQZ) basis was used for Cl and aug-cc-pV5Z basis [26] for H to produce accurate endothermicity. A full valence active space was used in the CASSCF reference wave functions with nine electrons in six active orbital. The active space included the 3s and 3p orbital of Cl and the 1s orbital of H. The orbital were optimized in the state-averaged CASSCF calculations for the three states with equal weights. The inner shell orbital including the Cl 2s and 2p orbital were correlated in the final MRCI calculation, only the 1s orbital of Cl was kept frozen. In the MRCI calculations of the two $2A'$ states, internally contracted configurations were generated from both reference states and were used in the CI wavefunctions for both states. This guarantees a balanced treatment of both states even in the region of avoided crossings or conical intersections [27]. The Davidson correction (+Q) was applied to account for the effect of higher excitations and to reduce the size consistency error [28].

In order to cover the global potential energy surface for the ClH_2 system, *ab initio* calculations were performed at about 12×10^3 geometries. The ClH_2 system is described in the yz -plane in inner coordinates, the distance between Cl and one H atom ranging from 1.9 bohr to 18.0 bohr with 31 points, the distance between two H atoms ranging from 0.8 bohr to 15.0 bohr with 24 points, and the Cl–H–H bond angle ranging from 0° to 180° at every 10° .

To transform the calculated adiabatic potential surfaces to a quasi-diabatic representation, the mixing angle were obtained by MRCI calculations using a smaller basis set with satisfactory accuracy. The augmented correlation consistent polarized valence triple zeta (aug-cc-pVTZ) basis was used, and the angle was computed

by the following formula [29],

$$\theta = \arcsin \frac{\sum_{\Pi} (C_i^{(1)})^2}{\sum (C_i^{(1)})^2} \quad (3)$$

where $C_i^{(1)}$ designates the expansion coefficients of the adiabatic wave function of the lower A' state in the MRCI calculations. The first sum extends only over those configurations which have Π symmetry in $C_{\infty v}$ geometry.

In addition, the spin-orbit coupling surfaces have been computed using the (unperturbed) MRCI wavefunctions and Breit-Pauli Hamiltonian, as described in detail elsewhere [30]. Different from potential energy calculations, aug-cc-pV5Z and aug-cc-pVQZ basis set for Cl and H atom were used, respectively. Overall we selected more than 4×10^3 points in the same coordinates with PES calculations. Finally, a three-dimensional cubic spline interpolation was employed to yield the global PESs (both diabatic and adiabatic) for this system.

III. RESULTS AND DISCUSSION

In order to demonstrate the quality of the *ab initio* potentials, we present a comparison of experimental and theoretical values for diatomic molecules in Table I. As can be seen, the predicted endothermicity for the $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ abstraction reaction is much improved, which is within 0.42 kJ/mol of the experimentally-derived value.

TABLE I Comparison of calculated and experimental properties of the diatomic molecules (r_e in bohr, D_e and ΔE in kJ/mol, all values are without spin-orbit couplings).

Surface	$r_e(\text{HCl})$	$r_e(\text{H}_2)$	$D_e(\text{H}_2)$	$D_e(\text{HCl})$	ΔE
BW1 [11]	2.411	1.402	108.93	106.29	11.03
BW2 [11]	2.410	1.401	109.67	107.09	10.78
This work	2.408	1.401	109.50	107.43	8.65
Expt. [32]	2.409	1.401	109.47	107.30	9.07

In the entrance channel, the three computed states correlate asymptotically with $\text{Cl}(^2\text{P}) + \text{H}_2$. The triatomic system is also described in Jacobi coordinates (R, r, α) , where R is the distance between Cl and the center of mass of H_2 , r is the H_2 bond distance, and α is the angle between \mathbf{R} and \mathbf{r} . Due to the quadrupole-quadrupole interaction of the H_2 molecule and the Cl atom, the $^2\Pi$ state is more attractive than the $^2\Sigma^+$ state at asymptotic range and collinear geometries. This situation is reversed in T-shaped geometries, where the 2A_1 state, correlating with the diabatic $^2\Sigma^+$ state, is more attractive than the 2B_1 and 2B_2 states, which correlate with the diabatic Π_x and Π_y states respectively. This leads to a crossing of the diabatic $^2\Sigma^+$ and

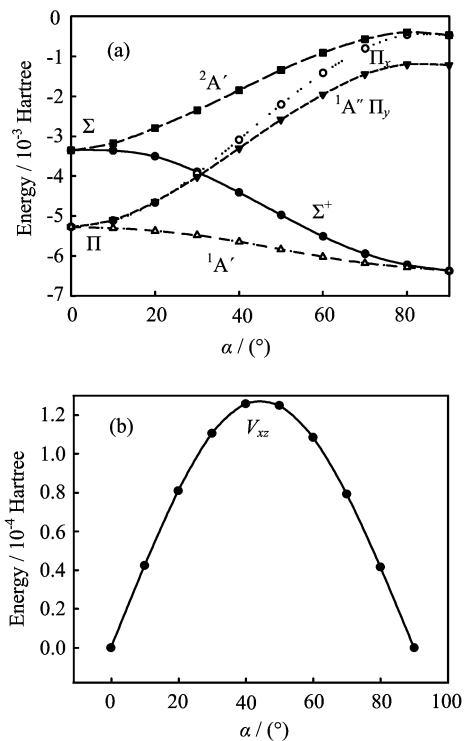


FIG. 1 (a) Curves of adiabatic and diabatic potentials as a function of the Jacobi angle α , for $R=6.5a_0$ and $r=1.4a_0$. (b) Similar curve for the coupling potential V_{xz} as a function of α , for $R=6.5a_0$ and $r=1.4a_0$. All energies are relative to the $\text{Cl}(^2\text{P})+\text{H}_2$ asymptote.

TABLE II Comparison of barrier properties for $\text{Cl}+\text{H}_2$ abstraction reaction. Bond distance R in bohr, bond angle θ in ($^\circ$), and barrier height E_c in kJ/mol.

Surface	R_{HCl}	R_{HH}	θ_{ClHH}	E_c
Without SO^{a}				
GQQ [9]	2.710	1.850	180	32.19
G3 [10]	2.648	1.870	180	32.94
BW2[11]	2.704	1.854	180	31.81
CW [14]	2.704	1.854	180	31.77
This work	2.707	1.836	180	29.26
With SO^{b}				
CW [14]	2.704	1.854	180	35.32
This work	2.707	1.837	180	32.69

^a Barrier height without inclusion of the spin-orbit coupling, the zero of energy is defined here as $\text{Cl}+\text{H}_2$ ($r=r_e$).

^b Barrier height with inclusion of the spin-orbit coupling, the zero of energy is defined here as $\text{Cl}(^2\text{P}_{3/2})+\text{H}_2$ ($r=r_e$).

Π_x potentials at an intermediate angle α . In Fig.1(a), the diabatic and adiabatic potentials are presented as a function of the Jacobi angle α in Fig.1(b), and the coupling potential V_{xz} is also shown in the lower panel. The figure is similar to the Fig.6 in Ref.[14], indicating that the nonadiabaticity of JX PESs is similar to that

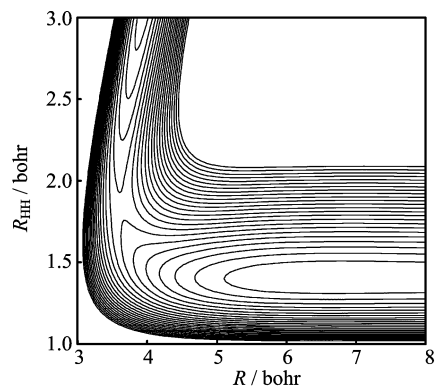


FIG. 2 Contour plot of the lowest adiabatic potential of JX PESs as a function of Jacobi coordinates R and α in collinear geometries, the zero of energy is defined by $\text{Cl}(^2\text{P}_{3/2})+\text{H}_2$ ($r=r_e$).

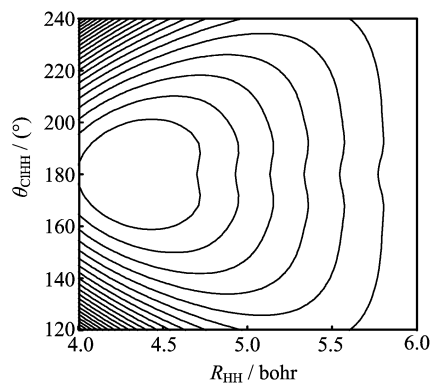


FIG. 3 Contour plot of the $\text{Cl}+\text{H}_2$ reaction in the exit region as a function of the internal coordinates R_{HH} and θ_{ClHH} .

of CW PESs.

The barrier height on the JX PES is 29.26 kJ/mol, a bit less than the value of 31.77 kJ/mol on the CW PES. Including spin-orbit coupling leads to an increase of the barrier height by 3.43 kJ/mol (about 1/3 of the asymptotic splitting of the $\text{Cl}(^2\text{P}_{1/2})$ and $\text{Cl}(^2\text{P}_{3/2})$ states). The transition state geometries and barrier heights on the previous PESs and ours are summarized in Table II. Figure 2 presents a contour plot of the lowest adiabatic potential of JX PESs in collinear geometry. Compared with the CW PESs, the two PESs are very similar except for the disagreement in the barrier height. The accuracy of the barriers on the CW and JX PESs could be ascertained by comparison with higher-level calculations, in a manner similar to the recent investigation of the barrier in the $\text{F}+\text{H}_2$ reaction by Werner, Kallay and Gauss [31].

We present a contour plot as a function of R_{HH} and θ_{ClHH} in the exit channel in Fig.3. Both the BW2 and new surfaces have a shallow well in this region. For JX PES, the minimum is collinear and lies at $R_{\text{HCl}}=2.41a_0$ and $R_{\text{HH}}=4.29a_0$. Compared to the BW2 PES ($R_{\text{HCl}}=2.41a_0$ and $R_{\text{HH}}=4.77a_0$), the distance of

two H atoms is a little shorter. The well depth is 1.67 kJ/mol relative to the HCl+H asymptote, slightly lower than that for the BW2 PES (1.88 kJ/mol). These small differences may affect a little on the rotational product distributions.

IV. CONCLUSION

New *ab initio* potential energy surfaces for the three lowest adiabatic states of Cl($^2P_{3/2}$, $^2P_{1/2}$)+H₂ reaction have been developed with a very large basis set. The predicted endothermicity for the Cl+H₂→HCl+H abstraction reaction agrees with the experimental value better than that of CW PESs. The barrier height on the new potential is a bit less than the previous CW potential and this is a key distinguish of the two set of PESs. Except that, the nonadiabatic couplings in the two set of PESs are very similar. The scattering calculations based on a time-independent expansion of the scattering wavefunction have been carried out on the two set of PESs, respectively. The predicted ratio [20] of the reactivity of the two spin-orbit states (Cl($^2P_{1/2}$) and Cl($^2P_{3/2}$)) which measures the degree of breakdown in the BO approximation is little changed from one set of PESs to the other. These results are in excellent agreement with the available experimental results.

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