

## ARTICLE

## Theoretical Study on Reaction Mechanism of Aluminum-Water System

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A theoretical study on the reaction of aluminum with water in the gas phase was performed using the hybrid density functional B3LYP and QCISD(T) methods with the 6-311+G(d,p) and the 6-311++G(d,p) basis sets. The results show that there are three possible reaction pathways that involve four isomers, seven transition structures, and two possible products for the reaction of aluminum with water. The two most favorable reaction pathways were found, whose intermediates and products agreed quite well with experimental results. The enthalpy and Gibbs free energy change of the reaction between Al and H<sub>2</sub>O at 298 and 2000 K were calculated. Some results are also in good agreement with the previous calculations or experimental results.

**Key words:** Aluminum, Water, Reaction mechanism, Hybrid density functional theory

## I. INTRODUCTION

Aluminum and water as propellants have been proposed for application in both space [1,2] and underwater propulsion [3,4]. The research was initiated in the 1940s and continued in the early 1960s. For propulsion systems, if the reaction takes place between metal fuels and water, the specific impulse will be remarkably increased. The reaction of metal and H<sub>2</sub>O applied as the energy of propulsion has a notable volume energy density because it does not bear the weight of water under the water propulsion system. However, because of the higher melting and boiling point of Al and its oxide coating, the reaction activity of Al-H<sub>2</sub>O is lower. Moreover, the start-up of reaction Al-H<sub>2</sub>O is more difficult. These facts indicate that it is enormously difficult to make the Al-H<sub>2</sub>O propulsion system usable in practice unless nano-sized Al particles are used. As for the energetic density, the amounts of producing gas, the stability of storing, price, and so on, the reaction of Al with H<sub>2</sub>O is the best in metal-fuels system. Furthermore, the reaction of Al-H<sub>2</sub>O with high energetic density can attain better propulsion performance.

For the high heat of combustion of Al with various oxidizers that are encountered in practical applications, a considerable number of studies, such as the ignition temperature of Al in kinds of gases [5,6] and combustion characteristics [7,8], have been published, especially concerning the flame characteristics of Al combustion [9,10]. In order to improve the propulsion performance for the reaction of Al with H<sub>2</sub>O, and make the reaction proceed, a great deal of work has been carried out [11-18], such as the reaction of different sizes of Al with H<sub>2</sub>O, and the addition of Mg or Li powder into Al

powder.

However, there are few studies on the reaction mechanism of Al with H<sub>2</sub>O. To reveal the detailed reaction mechanism and to enrich data concerning the vapor phase reaction of Al-H<sub>2</sub>O system, here we study the reaction mechanism of Al with H<sub>2</sub>O by a theoretical method. In addition, the enthalpy and the free energy changes of reaction at 298 and 2000 K are also calculated, respectively.

## II. THEORETICAL CALCULATIONS

All geometry optimizations were carried out with the hybrid density functional B3LYP method [19] with the 6-311+G(d,p) basis set [20,21]. Vibrational frequencies were calculated at the same level to verify the nature of the corresponding stationary point and to determine the zero-point vibrational energy (ZPE) and the thermodynamic contributions to the enthalpy and free energy of the reaction. The intrinsic reaction coordinate (IRC) calculations [22-24] were performed to ensure that a given transition state connects the desired reactant and product.

The energies of the stationary points corresponding to the reactants, products, intermediates and transition states (TS) were calculated at the QCISD(T)/6-311++G(d,p) level. All of these calculations were performed with the GAUSSIAN 98 program package [25].

## III. RESULTS AND DISCUSSION

## A. The energy minima

The optimized geometries of the reactants, intermediates, transition states and products involved in the reaction of Al with H<sub>2</sub>O are shown in Fig.1. The most important feature of the potential energy surface of the reaction Al-H<sub>2</sub>O is the nascent association minimum

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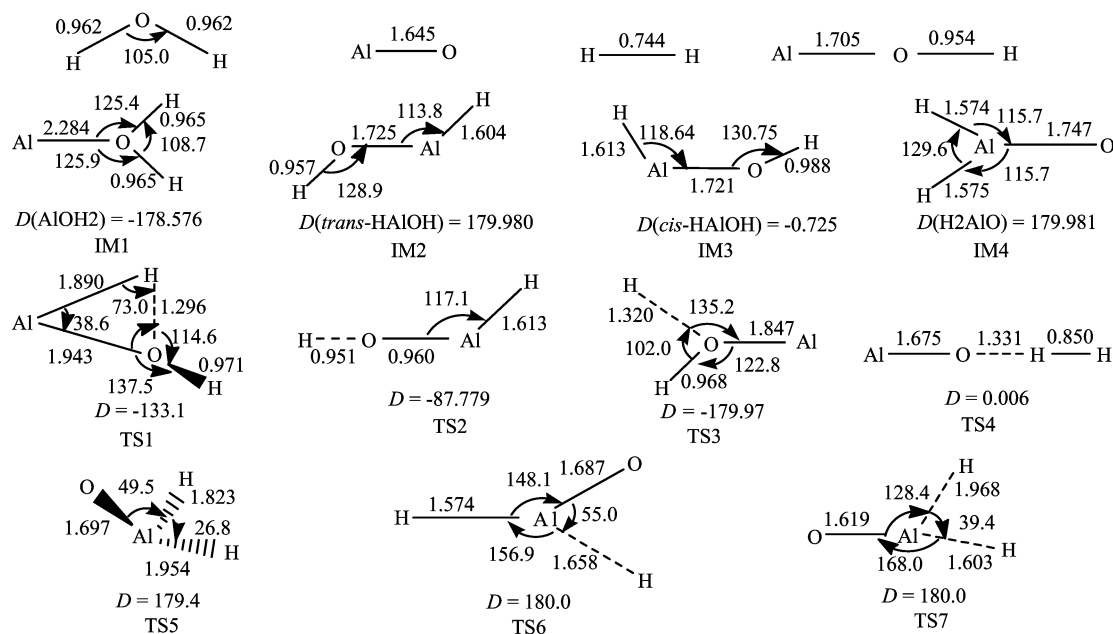


FIG. 1 Optimized structures of reaction, products, intermediates, and transition states for all reactions at B3LYP/6-311+G(d,p) level. Bond lengths are in Å, and bond angles are in ( $^{\circ}$ ).

IM1. In IM1, the forming Al–O bond length is 2.284 Å and other two O–H bond lengths are 0.965 Å which is only 0.003 Å longer than those in the H<sub>2</sub>O molecule. The energy of IM1 relative to that of the reactants is 26.92 kJ/mol at the QCISD(T) level.

The isomeric structure IM2 (−170.79 kJ/mol) is considerably more stable than IM1, which is formed through the isomerization of IM1 via a transition state TS1. TS1 is formed by the shifting of the H atom from the O to the Al atom. The Al–O–H bond angle bends from 125.4° in IM1 to 68.4° in TS1. The breaking O–H bond length increases from 0.965 Å in IM1 to 1.296 Å in TS1 and the forming Al–H bond length is 1.890 Å. The relative energy of TS1 is 30.31 kJ/mol.

The isomeric structure IM3 with relative energy of −166.53 kJ/mol is nearly as stable as IM2 and it can be formed through the isomerization of IM2 via a transition state TS2. TS2 is formed by the H atom transferring from one side of the O atom to another side. The Al–O–H bond angle bends from 128.9° in IM2 to 179.9° in TS2. The O–H bond length decreases from 0.957 Å in IM2 to 0.951 Å in TS2. The relative energy of TS2 is located at −158.97 kJ/mol, still much lower than that of the reactants Al–H<sub>2</sub>O, so that the rearrangement process is in principle possible. The conformers of IM2 and IM3 are shown in Fig.1, which, depending on the orientation of H atom with respect to another H atom, are denoted hereafter as IM2 (*trans*) and IM3 (*cis*). These minima are found to be 143.12 and 139.61 kJ/mol more stable than IM1, respectively.

In addition, the measured vibrational frequencies of products HAlOH from the reaction of Al atom with H<sub>2</sub>O [26] is shown in Table I. For the H–O stretch

TABLE I Measured vibrational frequencies of HAlOH isolated in an argon matrix ( $\text{cm}^{-1}$ ) [26]

	HAlOH	AlOH
H–O stretch	3743	3790
Al–H stretch	1743.3	–
HAIO bending	605.4	–
Al–OH stretch	817.9	810.3

in IM1, our calculated result (shown in Table II) is 3770.18  $\text{cm}^{-1}$  which is in line with experimental result 3743  $\text{cm}^{-1}$  as shown in Table I. In IM3, the Al–H stretch is 1765.59  $\text{cm}^{-1}$  and the experimental value is 1743.4  $\text{cm}^{-1}$ . For HAIO bending and Al–OH stretch in IM2 and IM3, the calculated results are 616.07, 598.29, 800.55, and 816.35  $\text{cm}^{-1}$ , respectively, which are also in agreement with the experimental results 605.4 and 817.9  $\text{cm}^{-1}$ , respectively. This suggests that the experimentally observed HAlOH is from the compounds of IM1, IM2, and IM3.

## B. Reaction mechanism

The overall energy profile based on the QCISD(T)/6-311+G(d,p) level is depicted in Fig.2. The vibrational frequencies are summarized in Table II at the B3LYP level for the reactants, intermediate complexes, transition states and products, and Table III summarizes the calculated electronic energies.

### 1. Reaction pathways of IM1

The Al atom reacts directly with the H<sub>2</sub>O molecule by using the O atom of the H<sub>2</sub>O molecule to form an inter-

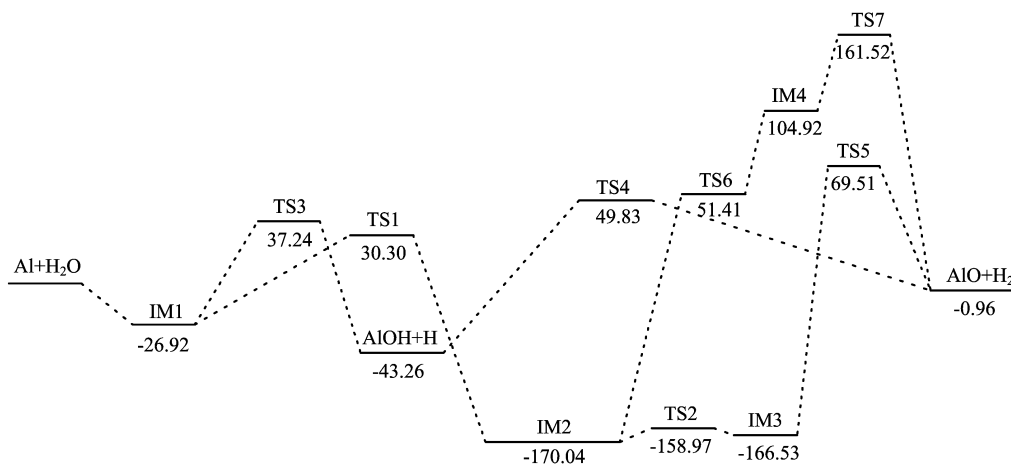


FIG. 2 The relative energy profile for the Al-H<sub>2</sub>O system at the QCISD(T)/6-311++G(d,p) level of theory (unit in kJ/mol).

TABLE II Vibrational frequencies calculated at B3LYP/6-311+G(d,p) level of theory for reactants, intermediate complexes, and transition states involved in Al-H<sub>2</sub>O reaction

Species	Frequency/cm <sup>-1</sup>
Al	0
H <sub>2</sub> O	1604.07, 3815.30, 3919.10
IM1	187.56, 190.31, 261.23, 1599.87, 3770.18, 3877.88
IM2	414.95, 510.50, 616.07, 800.55, 1809.68, 3939.44
IM3	363.50, 436.37, 598.29, 816.35, 1765.59, 3914.70
IM4	401.87, 592.96, 703.64, 786.60, 1963.60, 1979.98
TS1	1310.92i, 302.90, 454.16, 696.20, 1202.10, 3705.04
TS2	377.23i, 145.41, 572.36, 849.26, 1755.90, 4047.24
TS3	1587.23i, 301.57, 492.39, 605.84, 989.03, 3746.85
TS4	983.31i, 145.80, 826.74, 887.33, 943.38, 2420.44
TS5	1050.81i, 527.08, 801.81, 1018.85, 1506.17, 2272.81
TS6	1230.16i, 437.50, 493.79, 872.26, 1693.82, 1967.05
TS7	1389.16i, 294.13, 466.61, 613.68, 1029.60, 1873.03
AlOH	248.27, 806.72, 3983.71
AIO	924.66
H <sub>2</sub>	4419.16

TABLE III Zero-point energies (ZPE, in kJ/mol), reaction and activation energies ( $E$ ), and ZPE-corrected energies ( $E_{ZPE}$ ), for the reaction between Al and H<sub>2</sub>O

Compounds	ZPE	$E$ /Hartree	$E_{ZPE}$ /(kJ/mol)	
			RE1	RE2
H <sub>2</sub> O+Al	55.80	-318.2042105	0.0	0.00
IM1	59.06	-318.2157285	-26.96	
IM2	48.36	-318.2661992	-170.04	-158.67
IM3	47.19	-318.2644083	-166.53	
IM4	38.41	-318.157586	104.92	105.42
TS1	38.00	-318.1858629	30.30	
TS2	44.06	-318.260336	-158.97	
TS3	36.66	-318.1827085	37.24	
TS4	31.22	-318.1761265	49.83	
TS5	36.62	-318.1703928	69.51	
TS6	32.65	-318.1757849	51.41	54.18
TS7	25.54	-318.1311051	161.52	
AlOH+H	30.10	-318.2108996	-43.26	
AIO+H <sub>2</sub>	31.94	-318.1954796	-0.96	

RE1, at QCISD(T) level. RE2, at CCSD(T) level.

mediate IM1. This process is found to be a barrierless association reaction and exothermic by 26.92 kJ/mol. This shows that IM1 is a more stable activated complex. The IM1 molecule then breaks into AlOH+H via the O-H cleavage transition state TS3. The AlOH molecule has been observed experimentally by Oblath and Gole [27]. They reported the minimal AlOH emission with zero AIO emission in their low-temperature pure Al-H<sub>2</sub>O experiments. They found that AlOH emission is not characterized by vibrational transition bands, but is instead dominated by a broad rotational-relaxation profile that smears across the entire visible spectrum. At the same time, they have suggested that emission from excited HAIOH may be responsible for

the continuum resulting from the reaction of Al with H<sub>2</sub>O in the gas phase. Hauge *et al.* also found that Al-H<sub>2</sub>O reacts to form the divalent HAIOH species and that photolysis of HAIOH yields AlOH [26]. Jones *et al.* found a large amount of continuum AlOH emission by visible wavelength emission spectra recorded using a spectrometer coupled to a streak camera [28]. Our calculations are in good agreement with the possible emitter formation mechanisms speculated by Oblath and Gole [27] according to the observed experimental results for the Al-H<sub>2</sub>O system. However, the AlOH is not the final product, and the reaction of AlOH with H proceeds via the O-H bond cleavage transition state TS4 and produce products AIO and H<sub>2</sub>. The barrier

TABLE IV Calculated gas phase heats of reaction at 298 and 2000 K (in kJ/mol)

Reaction	$\Delta H$ (298 K)	$\Delta G$ (298 K)	$\Delta H$ (2000 K)	$\Delta G$ (2000 K)
Al+H <sub>2</sub> O→IM1	-30.72	-7.27	-24.08	107.93
IM1→AlOH+H	-8.23	-12.04	-1.00	-47.90
AlOH+H→AlO+H <sub>2</sub>	30.76	11.45	22.86	-89.58
IM1→IM2	-153.87	-148.43	-148.22	-162.89
IM2→IM3	4.31	3.76	4.89	-0.54
IM3→AlO+H <sub>2</sub>	172.09	144.08	165.24	-15.84
IM2→IM4	138.78	138.40	142.29	134.72
IM4→AlO+H <sub>2</sub>	37.62	9.45	27.84	-151.11

height of TS3 relative to IM1 is 64.16 kJ/mol, and TS4 relative to AlOH+H is 93.09 kJ/mol.

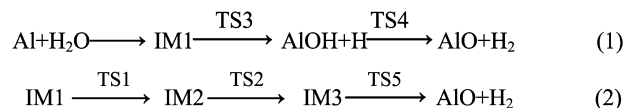
The next pathway involves the isomerization of IM1 in which one of the H atoms on the O atom is shifted to the Al atom to form another intermediate IM2 via a transition state TS1. The isomerization barrier height is 57.22 kJ/mol, which is 6.94 kJ/mol lower than TS3. It can be seen from Fig.2 that IM2 is 143.12 kJ/mol more stable than IM1, i.e. IM2 has higher internal energy, so many decomposition channels of IM2 would be open.

## 2. Reaction pathways of IM2

Starting from IM2 there are two reaction pathways. As shown in Fig.2, the most feasible channel for IM2 is the formation of IM3 via a transition state TS2 with the lowest barrier, 11.08 kJ/mol. The H atom of O-H attacking the Al atom can form IM3. Then IM3 can further decompose to AlO+H<sub>2</sub> via a transition state TS5. TS5 is formed by the H atom shifting from the O atom to the Al atom in IM3. Then the broken AlOH bonds can form AlO+H<sub>2</sub> in TS5. The barrier height of TS5 is 236.04 kJ/mol.

The second reaction process of IM2 is very interesting. IM2 can isomerize to IM4 via a transition state TS6 with a barrier of 221.46 kJ/mol. The forming H-Al bond length is 1.658 Å in TS6. IM4 further decomposes to AlO+H<sub>2</sub> via TS7. In TS7, the breaking Al-H bond lengths are elongated to 1.968 and 1.603 Å, respectively, and the Al-O distance is shortened from 1.747 Å in IM4 to 1.619 Å in TS7. The relative energies of TS6, IM4 and TS7 are 51.41, 104.92, and 161.52 kJ/mol, respectively. In this work, we also carried out additional calculations in some cases using CCSD(T)//6-311++G(d,p) methods to verify the energetics obtained by the QCISD(T)//6-311++G(d,p) method. The relative energies of IM2, TS6, and IM4 are -166.20, 54.17, and 105.42 kJ/mol, respectively. It appears clear that the high barrier height for this process makes it not important for this reaction system.

In summary, the studies of all possible reaction channels indicate the mechanism of the reaction between Al and H<sub>2</sub>O. The most probable production channels are shown as follows:



It can be seen that AlO and H<sub>2</sub> are the final products in the reaction of Al with H<sub>2</sub>O. The product of AlO has been observed elsewhere [5,27-29]. In 1993, McCleant *et al.* studied the reaction of Al (<sup>2</sup>P<sub>0</sub>) with H<sub>2</sub>O over an extended temperature range [30]. They proposed that the reaction occurs according to the following two-step mechanisms. One channel gives AlOH via the intermediate HAlOH, and the other channel yields AlO. However, they do not give the structures of intermediates, the specific reaction channels and the final products. In the present work, density functional theory was used to determine the geometries of intermediates in our calculations. Furthermore, the intermediates have been observed in experiments. At the same time, the specific channels of reaction for Al with H<sub>2</sub>O are found, and the final products are given.

It should be pointed out that in the reaction system of Al-H<sub>2</sub>O, the reaction mechanism is important. It could be useful in providing a probable help to remove the oxide coating of Al, and improve the reaction activity of Al with H<sub>2</sub>O. Finally, it might be used to solve the start-up issues of a reaction system of Al-H<sub>2</sub>O.

## C. The reaction thermodynamics of Al with H<sub>2</sub>O

The enthalpies and the free energies of the reaction for Al with H<sub>2</sub>O at 298 and 2000 K are shown in Table IV. It can be seen from Table IV that  $\Delta H$  changes very little over this temperature range. The  $\Delta H$ (298 K) of Al+H<sub>2</sub>O→IM1 in our calculation is -30.72 kJ/mol, which is in good agreement with the previously calculated result of -33.44 kJ/mol for Al+H<sub>2</sub>O→AlOH<sub>2</sub> [31-33]. For Al+H<sub>2</sub>O→IM2, the  $\Delta H$ (298 K) between the products and the reactants is -184.59 kJ/mol which is also in line with previously results of -183.92 kJ/mol of Al+H<sub>2</sub>O→HAlOH [32-34]. For Al+H<sub>2</sub>O→AlOH+H and Al+H<sub>2</sub>O→AlO+H<sub>2</sub>, the calculated results of  $\Delta H$ (298 K) are -38.96 and -8.19 kJ/mol, respectively. Mallard reported the experimental results of  $\Delta H$ (298 K) for reactions Al+H<sub>2</sub>O→AlOH+H and Al+H<sub>2</sub>O→AlO+H<sub>2</sub> are

−50.16 and −20.90 kJ/mol [35]. The calculated results are very consistent with the experimental results. For the free energies of the reaction at 298 and 2000 K, unlike  $\Delta H$ , however, it can be seen from Table IV that  $\Delta G(2000\text{ K})$  can differ quite considerably from  $\Delta G(298\text{ K})$ .  $\Delta G$  changes largely as the temperature changes.

#### IV. CONCLUSION

The reaction system of Al with H<sub>2</sub>O was studied at the B3LYP/6-11+G(d,p)//QCISD(T)/6-311++G(d,p) level. The vibrational frequencies and reaction thermodynamics were calculated and the reaction mechanism was fully investigated. The reaction of Al with H<sub>2</sub>O leads to final products AlO and H<sub>2</sub>. The most favorable pathways are the ones labeled (1) and (2) above. Moreover, the intermediates and products of the two reaction pathways have been found by experimental results, so this proves that the two reaction pathways are feasible.

#### V. ACKNOWLEDGMENT

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