



# Ab initio study on isotope exchange reactions of H<sub>2</sub> with surface hydroxyl groups in lithium silicates

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## Abstract

Effects of Al atoms on the hydrogen exchange reactions of hydrogen molecules with surface hydroxyls in silicates are investigated by ab initio calculations at the HF/6-31G\*\* and MP2/6-31G\*\* levels with the model clusters H<sub>3</sub>SiOH and H<sub>3</sub>Si(OH)Al(H)<sub>2</sub>OSiH<sub>3</sub>. The direct interaction of Al atoms with surface hydroxyl is found to bring about the lowering in the potential energy barrier of exchange reactions between H<sub>2</sub> and H<sub>3</sub>SiOH. The lowering is explained by the changes of the reaction mechanism and the weakening of the O–H bond in surface hydroxyl by the interaction of Al atoms.

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## 1. Introduction

The ease of tritium release is an important performance factor of ceramic tritium breeding materials such as Li<sub>2</sub>O, Li<sub>4</sub>SiO<sub>4</sub>, and Li<sub>2</sub>TiO<sub>3</sub> in D–T fusion reactors. The tritium generated by the <sup>6</sup>Li(n,α)<sup>3</sup>H reactions mainly exists as hydroxyl group of –OT on the surface of breeding materials [1]. The tritium is released through the isotopic exchange reaction with various gases such as H<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, etc., which are added to helium sweep gas [2–5].

Some improvements of breeding materials have been done to enhance the tritium release at low temperature. Addition of catalytically active metals, such as Al, Mg, Pt, etc., to the breeding materials have been indicated to promote the tritium release at low temperatures [2,3,6].

Recently, we have investigated the influence of trivalent elements, such as B, Al, and Ga, on the properties of surface hydroxyls in lithium silicate by ab initio molecular orbital calculations [7,8], and have also reported the effects of the Al atoms on the formation and de-

sorption reactions of H<sub>2</sub>O molecules from surface hydroxyl groups in silicates [9]. However, there is little study on the mechanism of isotopic exchange reactions between the tritium forming surface hydroxyl and the gases included in the sweep gas. In this study, in order to obtain a basic knowledge of the tritium release from lithium silicate, isotopic exchange reactions of hydrogen molecule with surface hydroxyl in silicates are investigated using ab initio molecular orbital calculations. Especially, we present the effect of the doping of Al atoms on the exchange reactions.

## 2. Method

To investigate the effect of Al atoms on the hydrogen exchange reaction between molecular hydrogen and surface hydroxyl of silicate, we have used the method of computational quantum chemistry to determine the minimum energy geometries of adsorption complexes and transition state (TS) structures. Silanol (H<sub>3</sub>SiOH) is chosen as the simplest molecular model of the free surface hydroxyl of silicate. This simplest molecular model has been used in previous work [10] to represent the free hydroxyl of silicate. H<sub>3</sub>Si(OH)Al(H)<sub>2</sub>OSiH<sub>3</sub> is adopted as a model of the surface hydroxyl in silicate glasses containing Al atoms. These cluster models represent the

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local surface structures of silicate glasses formed in pure and Al-doped lithium silicates by the nature of radiation [8].

All calculations have been performed at ab initio level with the Gaussian 98 program [11]. Basis sets adopted for all the atoms are 6-31G\*\*, i.e., split-valence basis set including p- and d-type polarization functions for the hydrogen and the heavy atoms, respectively. Full geometry optimizations have been carried out at the Hartree–Fock (HF) level by analytical gradient techniques [12], and have been also done using the Møller–Plesset second-order perturbation theory (MP2), which accounts for electron correlation [13]. No symmetry constraints have been assumed in the geometry optimization. The vibrational frequencies have been calculated using analytical second derivatives of the total energy in each case to ensure that the stationary points are local minima on the potential energy surface. The transition states reported here have been confirmed to have one imaginary frequency. The unscaled frequencies have been used in the calculations for the vibrational zero-point energy (ZPE) correction. Atomic charges have been obtained from a Mulliken population analysis [14]. The intrinsic reaction coordinates have been calculated in order to check and obtain reaction energy profiles.

### 3. Results and discussion

#### 3.1. Reaction of H<sub>2</sub> with H<sub>3</sub>SiOH

The process of hydrogen exchange reaction of H<sub>2</sub> with H<sub>3</sub>SiOH is represented in Fig. 1 along with the

geometrical parameters. Table 1 gives atomic charges and energies of primary structures involved in the exchange reaction. The geometrical parameters of the H<sub>3</sub>SiOH cluster (1a) are consistent with the previous theoretical values at the same levels [15].

In the hydrogen exchange reaction, the hydrogen atom in the H<sub>2</sub> molecule is exchanged for one hydrogen of the surface hydroxyl via the TS (1b) with a symmetric four-membered ring reaction center. Here, the hydrogen atoms (H1, H2) connecting to the oxygen atom of the surface hydroxyl are charged positively, and the hydrogen atom (H3) is charged negatively. After that, a new H<sub>2</sub> molecule is formed.

For this reaction, the HF and MP2 potential energy barriers, which are determined as the differences between the total energy of the transition states and the sum of the total energies of H<sub>3</sub>SiOH cluster and H<sub>2</sub> molecule, are calculated to be 88.07 and 72.61 kcal mol<sup>-1</sup>, respectively. The energy barrier calculated for H<sub>3</sub>SiOH at the MP2 level in this study is almost equal to that for FOH [16]. The exchange reaction of H<sub>2</sub> with FOH takes place through a four-membered ring transition state as well as the exchange reaction of H<sub>2</sub> with H<sub>3</sub>SiOH. And also, the strength of the OH bond in FOH is almost equal to that in H<sub>3</sub>SiOH. For the isotope exchange between D<sub>2</sub> and the OH groups of varying acidity of the molecular fragments X–OH (X = Li, H, F), the energy barriers have been presented to be consistent with the strengths of the OH bond in the XOH molecule [16]. At the MP3/6-31G\*\*//6-31G\*\*, the energy barriers have been calculated for X = H and X = F to be 88 and 75 kcal mol<sup>-1</sup>, respectively [16]. The agreement on the energy barrier between FOH and H<sub>3</sub>SiOH is consistent with the

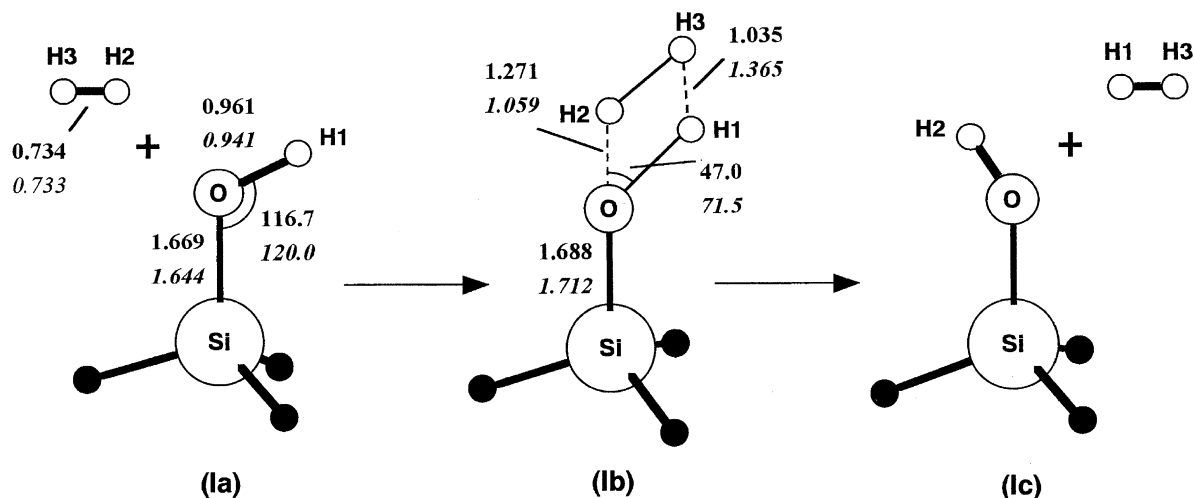


Fig. 1. Structures calculated for the hydrogen exchange reaction of molecular hydrogen (H<sub>2</sub>) with isolated surface OH group of silicates: (1a) silanol and H<sub>2</sub> molecule; (1b) TS for exchange reaction; (1c) silanol and H<sub>2</sub> molecule after exchange reaction. Bond lengths are in Å and bond angles are in degrees. Italic values are from the HF/6-31G\*\* optimization, while others are from the MP2/6-31G\*\* optimization.

Table 1

Atomic charges and energies of stationary-point structures involved in the hydrogen exchange reaction of molecular hydrogen with isolated surface OH group of silicates

	Ia		Ib	
	HF	MP2	HF	MP2
$q(\text{Si})$	0.988	0.988	0.977	0.997
$q(\text{O})$	-0.754	-0.764	-0.674	-0.884
$q(\text{H1})$	0.353	0.355	0.334	0.346
$q(\text{H2})$			0.334	0.346
$q(\text{H3})$			-0.508	-0.236
$E_c$	-366.141921	-366.426774	-367.132741	-367.468761
$E_{\text{ZPE}}$	0.041305	0.040001	0.051705	0.050540
$E_t$	-366.100615	-366.386773	-367.081036	-367.418221
$\Delta E_{\text{rel}}$	0.0	0.0	88.07	72.61

Electronic energy  $E_c$ , zero-point energy  $E_{\text{ZPE}}$  and total energy  $E_t$  in Hartree. Relative energy  $E_{\text{rel}}$  in kcal mol<sup>-1</sup>. Energies calculated for H<sub>2</sub> molecule at the HF/6-31\*\* level are as follows:  $E$ , -1.131334;  $E_{\text{ZPE}}$ , 0.010560;  $E_t$ , -1.120774. Energies calculated for H<sub>2</sub> molecule at the MP2/6-31G\*\* level are as follows:  $E$ , -1.157661;  $E_{\text{ZPE}}$ , 0.010501;  $E_t$ , -1.147161.

deprotonation energies for FOH (391 kcal mol<sup>-1</sup>) [16] and for H<sub>3</sub>SiOH (370–390 kcal mol<sup>-1</sup>) [17,18], which correspond to the strength of the OH bond [8,19].

### 3.2. Reaction of H<sub>2</sub> with H<sub>3</sub>Si(OH)Al(H)<sub>2</sub>OSiH<sub>3</sub>

The structural changes in the hydrogen exchange reaction between H<sub>2</sub> and H<sub>3</sub>Si(OH)Al(H)<sub>2</sub>OSiH<sub>3</sub> are shown in Fig. 2 along with some of the geometrical parameters. Table 2 gives atomic charges and energies of primary structures involved in this exchange reaction. The geometrical parameters of the H<sub>3</sub>Si(OH)Al(H)<sub>2</sub>OSiH<sub>3</sub> cluster (IIa) are in good agreement with the previous theoretical values of the H<sub>3</sub>Si(OH)Al(H)<sub>2</sub>OSiH<sub>3</sub> cluster at the HF level [20] and of the H<sub>3</sub>Si(OH)Al(OH)<sub>2</sub>OSiH<sub>3</sub> cluster at the HF and MP2 levels [21]. The potential energy barriers at HF and MP2 levels are calculated to be 42.69 and 29.52 kcal mol<sup>-1</sup>, respectively. The MP2 energy barrier is comparable to the experimental value of 24

kcal mol<sup>-1</sup>, which has been obtained for an H-CaY zeolite [22].

The mechanism of the hydrogen exchange is quite different from the simple silicate model described above. In the TS (IIb), the reaction center is a symmetric six-membered ring including two Al–O bonds, while the TS (Ib) has a four-membered ring without Al–O bond. As shown in Fig. 2, the hydrogen exchange is accompanied by the alternation of the bonding character of the two Al–O bonds. One is the coordination and the other is the ordinary Al–O single bond. This concerted alternation of the Al–O bonds must reduce the potential energy barrier for the hydrogen exchange drastically, as mentioned in the Section 3.3.

### 3.3. Reaction energy profiles

In Fig. 3, the energy profile of the hydrogen exchange reaction of H<sub>2</sub> with H<sub>3</sub>SiOH is compared with

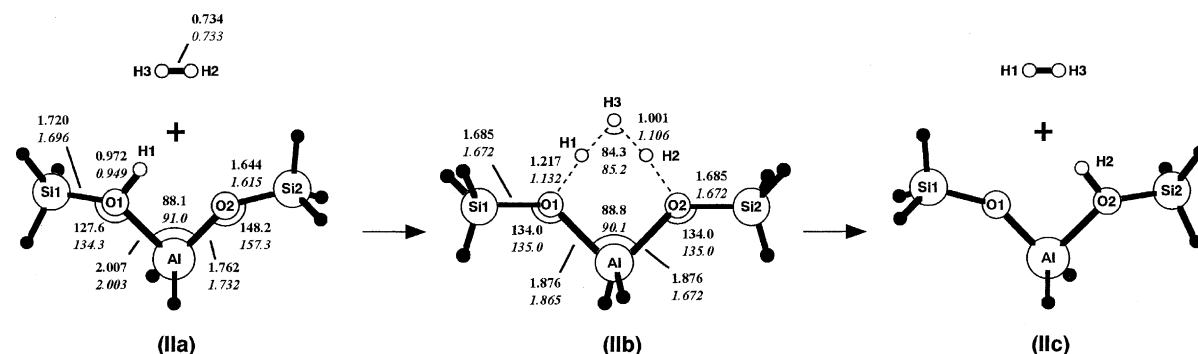


Fig. 2. Structures calculated for the hydrogen exchange reaction of molecular hydrogen (H<sub>2</sub>) with surface OH group of silicates containing Al atom: (IIa) surface OH group of silicates containing Al atom and H<sub>2</sub> molecule; (IIb) TS for exchange reaction; (IIc) surface OH group of silicates containing Al atom and H<sub>2</sub> molecule after exchange reaction. Bond lengths are in Å and bond angles are in degrees. Italic values are from the HF/6-31G\*\* optimization, while others are from the MP2/6-31G\*\* optimization.

Table 2

Atomic charges and energies of stationary-point structures involved in the hydrogen exchange reaction of molecular hydrogen with surface OH group of silicates containing Al atoms

	IIa		IIb	
	HF	MP2	HF	MP2
$q(\text{Si1})$	1.025	1.023	1.037	1.043
$q(\text{Si2})$	1.014	1.023	1.037	1.043
$q(\text{Al})$	0.941	0.948	0.976	0.982
$q(\text{O1})$	-0.824	-0.836	-0.942	-0.983
$q(\text{O2})$	-0.936	-0.965	-0.942	-0.983
$q(\text{H1})$	0.406	0.416	0.356	0.348
$q(\text{H2})$			0.356	0.348
$q(\text{H3})$			-0.341	-0.229
$E_c$	-974.853528	-975.484489	-975.918485	-976.597178
$E_{ZPE}$	0.090216	0.087929	0.102425	0.100500
$E_t$	-974.763312	-975.396560	-975.816060	-976.496678
$\Delta E_{rel}$	0.0	0.0	42.69	29.52

Electronic energy  $E_c$ , zero-point energy  $E_{ZPE}$  and total energy  $E_t$  in Hartree. Relative energy  $E_{rel}$  in kcal mol<sup>-1</sup>. Energies calculated for H<sub>2</sub> molecule at the HF/6-31\*\* level are as follows:  $E$ , -1.131334;  $E_{ZPE}$ , 0.010560;  $E_t$ , -1.120774. Energies calculated for H<sub>2</sub> molecule at the MP2/6-31G\*\* level are as follows:  $E$ , -1.157661;  $E_{ZPE}$ , 0.010501;  $E_t$ , -1.147161.

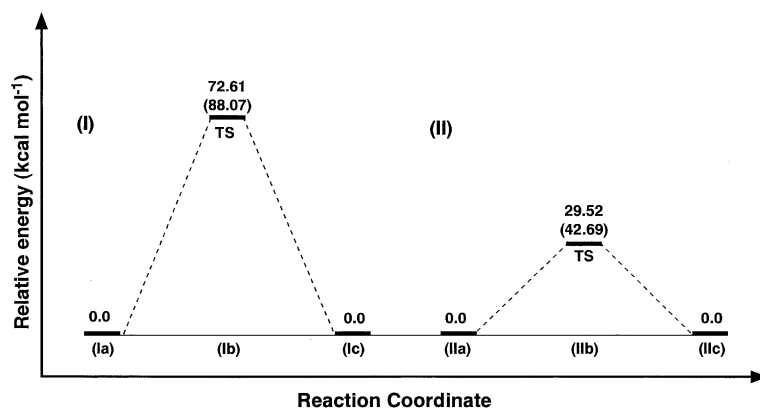


Fig. 3. MP2/6-31G\*\* reaction profiles for the hydrogen exchange reactions of hydrogen molecule with surface hydroxyl group of: (I) the model for pure silicate; (II) the model for the Al-doped silicate. The values in parentheses are calculated at HF/6-31G\*\* level. TS stands for the transition state.

that of H<sub>2</sub> with H<sub>3</sub>Si(OH)Al(H)<sub>2</sub>OSiH<sub>3</sub>. The potential energy barrier for the exchange reaction of H<sub>2</sub> with H<sub>3</sub>Si(OH)Al(H)<sub>2</sub>OSiH<sub>3</sub> is calculated at MP2 level to be 29.5 kJ mol<sup>-1</sup>, which is about 41% of that for the exchange reaction of H<sub>2</sub> with H<sub>3</sub>SiOH. This drastic reduction of the barrier height is mainly ascribed to the mechanistic changes noted above. Those are the concerted alternation of the Al–O bonds and the six-membered ring structure in (IIb), which is stereochemically less constrained than the four-membered ring structure in (Ib). Also, the decrease in energy barrier is associated with the changes in the strength of the O–H bond and an ionicity of the surface hydrogen caused by the interaction of Al atoms to the surface hydroxyl.

The strength of the O–H bond is estimated with the overlap bond population, which is considered as a

measure of bond strength [23], and the ionicity of the surface hydrogen is done with its atomic charge. The overlap population of O1–H1 bond in the structure (IIa) is calculated to be 0.296 at MP2 level. This value is smaller than that of the overlap population of O–H1 bond in the structure (Ia), which is calculated to be 0.313 at MP2 level. The positive charge on H1 in the H<sub>3</sub>Si(OH)Al(H)<sub>2</sub>OSiH<sub>3</sub> cluster is larger than that on H1 in the H<sub>3</sub>SiOH cluster (see Tables 1 and 2). The increase in ionicity of the surface hydrogen atom leads to the decrease in the deprotonation energy, which corresponds to the bond strength [7,8]. These changes due to the interaction of Al atoms are interpreted by the transfer of an electron from surface hydrogen in the direction of an Al atom because the AlH<sub>2</sub>O group operates as an electron acceptor in the H<sub>3</sub>Si(OH)Al(H)<sub>2</sub>OSiH<sub>3</sub>

cluster [24]. The decrease in the overlap population and the increase in the ionicity mean that the O–H bond is weakened by the interaction of the Al atom. From a strength relation of the O–H bond in the XO<sub>2</sub> molecule with the potential energy barrier [16], it is considered that the weakening of the O–H bond due to the interaction of the Al atom causes the lowering in the potential energy barrier in the hydrogen exchange reaction.

The reaction energy profiles shown in Fig. 3 are very useful from the experimental point of view, since the interaction of Al atoms with the surface hydroxyl groups are found to play a significant role in the exchange reactions of a hydrogen molecule on the surface of silicates. The present calculations have shown the lowering in the potential energy barrier of the hydrogen exchange reaction by adding Al. In fact, in the tritium release experiment using helium sweep gas containing hydrogen, the tritium release from the Al-doped lithium silicate has been confirmed to increase in quantity at low temperature [2]. The lowering in the potential energy barrier due to the effects of the Al-atom doping is considered to improve the tritium release performance from the Al-doped lithium silicate at low temperature.

#### 4. Conclusions

In this study, the hydrogen exchange reactions of surface hydroxyls in silicate and silicate containing Al atoms with hydrogen molecules are investigated by ab initio calculations at the HF and MP2 levels with the model clusters H<sub>3</sub>SiOH and H<sub>3</sub>Si(OH)Al(H)<sub>2</sub>OSiH<sub>3</sub>. The direct interaction of Al atoms with the surface hydroxyl is found to bring about the lowering in potential energy barrier of exchange reactions between H<sub>2</sub> and H<sub>3</sub>SiOH. The lowering in the energy barrier is ascribed to the changes of the reaction mechanism and the weakening of the O–H bonds in surface hydroxyl due to the interaction with Al atoms.

#### Acknowledgement

We gratefully acknowledge the interest and encouragement presented from Dr A. Iwamoto.

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