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Molecular orientation dependence of ortho-para H_2 conversion on $Fe(OH)_3$ cluster induced by hyperfine contact interaction

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Abstract. We investigate the molecular orientation dependence of the *(o)rtho-(p)ara* H_2 conversion on $Fe(OH)_3$ cluster. Taking Fermi's contact interaction as perturbation, we find that the *o-p* H_2 conversion yield for the molecular orientation angle $\theta = 10°$ with respect to the surface normal is larger than that for $\theta = 70°$.

PACS. 31.70.Hq Time-dependent phenomena: excitation and relaxation processes, and reaction rates

1 Introduction

$Fe(OH)_3$ is known to be a good catalyst for the *o-p* H_2 conversion [1–3] and has been used widely in the industry to overcome problems related to storing liquid hydrogen [3]. Although the experiment of *o-p* H_2 conversion on $Fe(OH)_3$ catalyst has been done by Buyanov in 1960 [1], the detailed mechanism as to how this material can induce *o-p* H_2 conversion has not yet been understood. One major hurdle to a theoretical explanation of the mechanism of *o-p* H_2 conversion in Buyanov's experiments is that the structure of the $Fe(OH)_3$ could not be determined using X-ray and electron photographs [1,2]. Efforts to determine the structure of $Fe(OH)_3$ are now being done by many researchers [4–6].

In the last ten to twenty years, we have seen great progress in computational physics. Through first principles calculations, we can now determine the structure of many materials and directly relate these to experimental results with a high degree of accuracy. In particular, it is now possible to theoretically explore the structure of $Fe(OH)_3$ and even simulate catalytic processes involving its interaction with H_2, e.g., the *o-p* H_2 conversion process.

In our previous studies we have investigated the effect of the molecular orientation on the *o-p* H_2 conversion on metal oxide surfaces and metal surfaces [7–9,11]. We found that the *o-p* H_2 conversion yield for a H_2 in a perpendicular orientation with respect to the metal oxide and metal surfaces is larger than that in a parallel orientation. One may ask, however, whether the same conclusion hold for other surfaces/catalysts. To answer this, we investigate in this paper, the molecular orientation dependence of *o-p* H_2 conversion yield on a cluster system i.e., $Fe(OH)_3$ cluster.

To understand the effect of molecular orientation on the *o-p* conversion of the interaction between H_2 and $Fe(OH)_3$ cluster, we calculate the *o-p* H_2 conversion yield for the molecular orientation angle $\theta = 10°$ and $\theta = 70°$. The azimuthal orientation of H_2 on the surface is not considered in this paper since the results from our previous studies showed that the effect of this orientation to the *ortho-para* H_2 conversion yield is small [11].

2 Model interaction between H_2 and $Fe(OH)_3$ cluster

The stable structure of $Fe(OH)_3$ [Fig. 1a] and the relative configuration between interacting H_2 and $Fe(OH)_3$ is shown in Figure 1b. We assume that H_2 sits on top of the Fe atom of $Fe(OH)_3$ and θ is the H_2 molecular orientation angle with respect to the surface normal of $Fe(OH)_3$, while Z is the distance from the H_2 center-of-mass (CM) to the $Fe(OH)_3$ surface. The stable structure of $Fe(OH)_3$ is determined by an optimization calculation using Gaussian 03 [12] via a series of density functional theory (DFT) based total energy calculations [13], adopting Becke's three-parameter functional [14], Perdew and Wang's gradient-corrected correlation functional [15], and Dunning [16], Hay and Wadt's basis sets [17]. The obtained structure of $Fe(OH)_3$ is comparable with previous

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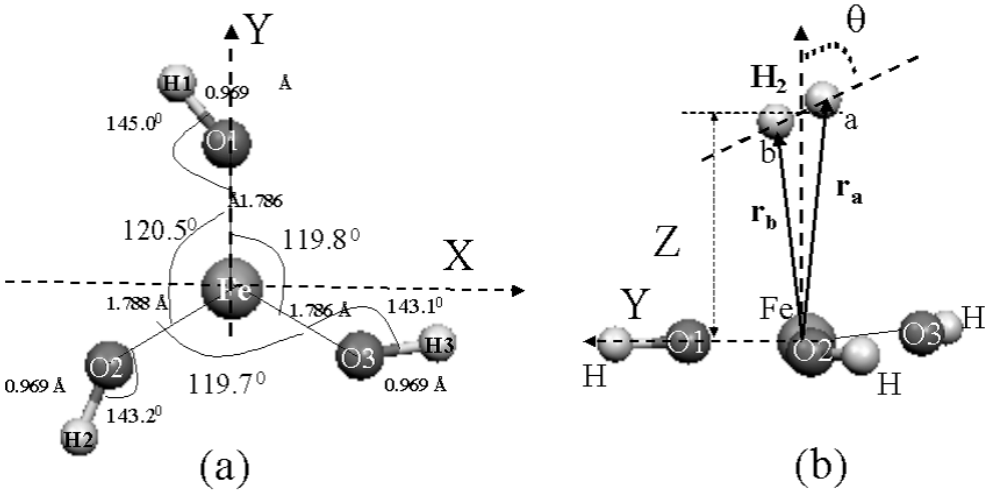

Fig. 1. (a) The structure of Fe(OH)$_3$ cluster. The structure is obtained by optimization calculation using Gaussian 03 [12]. (b) The relative configuration between interacting H$_2$ and Fe(OH)$_3$. The H$_2$ is sitting on top of the Fe ion of Fe(OH)$_3$ with the H$_2$ center-of-mass (CM) distance Z from the Fe(OH)$_3$ surface and θ is its molecular orientation angle with respect to the surface normal. $\mathbf{r}_\mathrm{a}$ and $\mathbf{r}_\mathrm{b}$ are the position vectors of protons a and b with respect to the Fe ion, respectively.

results [4,18]. The ground state of Fe(OH)$_3$ has $S = 5/2$ (S is the total spin).

The $\langle \mathbf{S}\cdot\mathbf{S}\rangle/\hbar$ values ($\mathbf{S}$ is the electron spin operator) is examined, and compared to the $S(S + 1)$ values for each total spin of the Fe(OH)$_3$ system, to check for spin contamination. In the ground state of the Fe(OH)$_3$ system the $S(S + 1)$ value is 8.76 with spin contamination around 0.1%. It is much smaller than the allowable maximum value of 10% [19].

In our previous study [20], we have investigated the behavior of H$_2$ when it adsorbs on Fe(OH)$_3$. We considered cases such as whether H$_2$ on Fe(OH)$_3$ is stable or not and whether H$_2$ undergoes dissociation or not. We have shown the potential energy surface (PES) of an adsorbed H$_2$ on Fe(OH)$_3$ for the H$_2$ molecular orientation angle $\theta = 10°$ and for the H$_2$ molecular orientation angle $\theta = 70°$. For the case when the H$_2$ molecular orientation angle is $\theta = 10°$, there is a potential well at $Z = 4.2$ Å with a depth of around 4.4 meV. The H–H bond-length of H$_2$ $r = 0.74$ Å at $Z = 4.2$ Å corresponds to the gas-phase equilibrium internuclear distance. For the case when the H$_2$ molecular orientation angle is $\theta = 70°$, we find the bottom of the well at $Z = 3.0$ Å and $r = 0.74$ Å with a depth of around 17.7 meV.

When the H$_2$ gets closer to the surface, e.g., $Z = 2.0$ Å, for the H$_2$ molecular orientation angle $\theta = 10°$, the H–H bond-length slightly shortens to 0.72 Å as a result of increasing Coulomb repulsion against the surface. The energy to bring H$_2$ to this position is around 0.63 eV. On the other hand, when the $\theta = 70°$, r increases to 0.76 Å as a result of increasing electron density between H$_2$ and Fe(OH)$_3$ and energy to bring H$_2$ to this position is 0.20 eV. This situation shows that in the adsorption of H$_2$ on the Fe(OH)$_3$, the initial translational energy of H$_2$ is stable at around 0.63 eV and H$_2$ does not undergo dissociation.

3 Molecular orientation dependence of ortho-para H$_2$ conversion yield

The molecular orientation dependence of the *o-p* H$_2$ conversion yield of H$_2$ on Fe(OH)$_3$ is investigated using the anti-symmetric part of the hyperfine contact interaction [2,7]. We can write the anti-symmetric part of the hyperfine contact interaction (H_{HC}) between each electron spin and two H$_2$ nuclear spins by [2,7]

$$H_{HC} = \lambda_C \sum_{\alpha=1}^{N} \mathbf{S}_\alpha \cdot (\mathbf{I}_\mathrm{a} - \mathbf{I}_\mathrm{b})[\delta(\mathbf{r}_\mathrm{a} - \mathbf{r}_\alpha) - \delta(\mathbf{r}_\mathrm{b} - \mathbf{r}_\alpha)]. \quad (1)$$

Here, $\mathbf{I}_\mathrm{a}$ and $\mathbf{I}_\mathrm{b}$ are the operators for the nuclear spin of the two protons a and b of H$_2$. $\delta(\mathbf{r}_\mathrm{a} - \mathbf{r}_\alpha)$ and $\delta(\mathbf{r}_\mathrm{b} - \mathbf{r}_\alpha)$ represent the Dirac operators. $\mathbf{r}_n$ (n = a, b) and $\mathbf{r}_\alpha$ are the proton and electron coordinates with respect to the Fe ion, respectively. $\mathbf{S}_\alpha$ is the electron spin operator and λ_C is the hyperfine contact constant.

The *o-p* H$_2$ conversion yield can be written as

$$W_{\Psi_f \leftarrow \Psi_i}(Z) \propto |\xi(Z)|^2, \quad (2)$$

where

$$\xi(Z) = \langle \Psi_{el}(\mathbf{r}_\alpha, Z)|\langle \chi_p|H_{HC}|\chi_o\rangle|\Psi_{el}(\mathbf{r}_\alpha, Z)\rangle. \quad (3)$$

$\xi(Z)$ is the hyperfine contact interaction that contributes to the *o-p* H$_2$ conversion yields where has been chosen for $\theta = 70°$ and for $\theta = 10°$. $|\Psi_{el}(\mathbf{r}_\alpha, Z)\rangle$ is the unperturbed wave function for the electron system obtained from Gaussian 03. The H$_2$ nuclear spin wave function of the *o*-H$_2$ can be expressed as

$$|\chi_o\rangle = \left\{ \begin{array}{l} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle \end{array} \right\}, \quad (4)$$

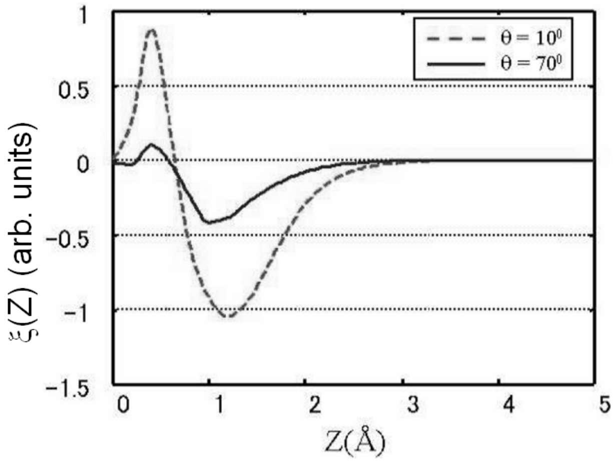

Fig. 2. The matrix element of the hyperfine contact interaction $\xi(Z)$ for $\theta = 10°$ and $\theta = 70°$ as a function of the H_2 CM distance from the $Fe(OH)_3$ surface.

and for p-H_2 can be expressed as

$$|\chi_p\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \quad (5)$$

Figure 2 shows the matrix element of the hyperfine contact interaction $\xi(Z)$ for $\theta = 10°$ and $\theta = 70°$. We can see that $\xi(Z)$ for $\theta = 10°$ is larger than that for $\theta = 70°$. The strong dependence on the H_2 molecular orientation angle θ is due to the antisymmetric part of the hyperfine contact interaction in equation (1). The maxima and minima for $\theta = 10°$ are found at $Z = 0.5$ Å and $Z = 1.2$ Å, respectively, whereas the maxima and minima for $\theta = 70°$ are found at $Z = 0.5$ Å and $Z = 1.0$ Å, respectively. These extrema correspond to the maximum contacts between the nuclear spin of H_2 and the electron spin density distribution of $Fe(OH)_3$–H_2 system.

4 Summary

To obtain general conclusion of the effect of molecular orientation on the o-p H_2 conversion on surfaces, we have investigated the molecular orientation dependence of o-p H_2 conversion on a cluster surface. As a first step we considered $Fe(OH)_3$ cluster known to be a good catalyst for the o-p H_2 conversion. We optimized the structure of $Fe(OH)_3$ cluster using density functional theory (DFT)-based total energy calculations. By considering hyperfine contact interaction we calculated the o-p H_2 conversion yield as for the H–H molecular orientation $\theta = 70°$ and $\theta = 10°$. On the basis of the calculated results, we found that the o-p H_2 conversion yield for the molecular orientation angle $\theta = 10°$ with respect to the surface normal is larger than that for $\theta = 70°$.

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