Ortho-para conversion of hydrogen molecules on 
Cr₂O₃(0001)/Cr(110) surfaces

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Abstract. The Cr₂O₃(0001) surface can be terminated by Cr ions, which are either antiferromagnetically or ferromagnetically ordered. Ortho-para (o-p) conversion of H₂ and para-ortho (p-o) conversion of D₂ were investigated on such Cr₂O₃(0001)/Cr(110) surfaces by resonance-enhanced multiphoton ionization combined with photostimulated desorption. The natural conversion time of H₂ and D₂ was estimated to be 210 ± 22 s and 538 ± 57 s, respectively. The mechanism of the hydrogen nuclear-spin flip is discussed in terms of the magnetic structure of the Cr₂O₃(0001) surface.

1. Introduction

Hydrogen molecules consisting of two identical nuclei exist in nuclear-spin modifications of ortho and para species. Due to the nuclear-spin coupling, ortho-H₂ has the total nuclear spin (I) of I=1, while para-H₂ has I=0. Ortho- and para-D₂, on the other hand, have I=0, 2 and I=1, respectively [1, 2]. The ortho-para (o-p) conversion accompanied by nuclear-spin flip is forbidden in gas phase with a conversion time of longer than 10⁸ s because of the small coupling terms related to the nuclear spins [1]. The H₂ o-p conversion has been experimentally investigated on a variety of magnetic materials [3, 4]. The H₂ o-p conversion is reported to be accelerated as the amount of magnetic impurity is increased and also the magnetic moment gets larger [3, 4]. Despite much efforts, unfortunately, the detailed mechanism of the o-p conversion and the relation with the surface magnetism have not been well understood, because the sample surfaces were not well-characterized in most studies.

In our previous study [5], we have investigated the effects of O₂ molecules on the hydrogen o-p conversion. The o-p conversion was considerably accelerated with increasing O₂ coverage, indicating that the electronic spins of O₂ ³Σ are preserved on a Ag surface at low temperature. With the aid of Monte Carlo simulations, we have estimated the conversion time in the vicinity of O₂ to be 8.3 and 53.4 s for H₂ and D₂, respectively.

Cr₂O₃ is an insulating antiferromagnetic material. The spins at Cr ions in the Cr₂O₃ bulk are antiferromagnetically ordered below its Neel temperature of 308 K [6, 7]. Recent studies have shown that Cr₂O₃ ultra-thin films grow epitaxially on Cr(110) by direct oxidation with a saturation thickness of about 4 nm [8, 9]. The surface of Cr₂O₃/Cr(110) is terminated by a half
of the Cr ions in a Cr layer of the corundum structure and strongly relaxed compared to the ideal
bulk structure [10]. Naively, the surface Cr ions are expected to be ferromagnetically ordered,
which remains to be solved. Possible magnetic and electronic phase transitions, furthermore,
make this surface attractive and interesting [11, 12].

In the present paper, we report o-p conversion of H2 and p-o conversion of D2 on a single-
crystal film of Cr2O3 grown on Cr(110) [9, 12] with a laser technique. The conversion time of H2
and D2 was estimated to be 210 and 538 s, respectively. Compared with the conversion times
on diamagnetic Ag [13, 14, 15] and O2-adsorbed Ag surfaces [5], the conversion mechanism and
surface magnetism of the Cr2O3(0001) surface are discussed.

2. Experiment
The experimental setup used in the present study was the same as those used in previous work
[14]. Briefly, a single-crystal Cr2O3(0001)/Cr(110) surface was prepared by direct oxidation of a
clean Cr(110) surface in an ultra-high vacuum (UHV). A chromium metal single-crystal surface
with the (110) orientation was cleaned by argon ion bombardment at 780 K and annealing
at 1000 K until a 1×1 low-energy electron diffraction (LEED) pattern was observed. After
oxidation of the surface, a hexagonal LEED pattern corresponding to the Cr2O3(0001) surface
was observed [9, 12]. The thickness of the Cr2O3(0001) film was estimated to be about 5 nm.
After transfer of the sample through the air to the cold stage of the apparatus for the conversion
experiment, the sample was cleaned by heating in the UHV chamber. The clean surface of the
Cr2O3(0001) film was almost intact during the transfer and restored in the UHV chamber.

The o-p (p-o) conversion of H2 (D2) was measured by resonance-enhanced multiphoton
ionization (REMPI) combined with photostimulated desorption (PSD) [14]. The sample was
exposed to 60 L of H2 (D2) at 7 K by backfilling the chamber. Both H2 and D2 were molecularly
physisorbed on the surface. Since o-H2 (p-D2) and p-H2 (o-D2) are in the rotational states with
odd and even rotational quantum numbers (J), respectively, they fall into their ground states of
J=1 and J=0 at this temperature, respectively [5]. The ortho-para ratio of adsorbed H2 (D2)
was measured with a pump-probe technique. The pump laser pulse with a wavelength of 193
nm (2.2 mm in diameter, laser fluence of 86 µJ/cm2/pulse) induced desorption of small amount
of adsorbed H2 (D2), and subsequently, the probe laser pulse J-state-selectively ionized the
desorbed H2 (D2) in a REMPI scheme via the E,F 1Σg+ states [16]. This allows us to distinguish
the nuclear-spin state of H2 (D2). For the REMPI measurement, lasers with a wavelength
of 201 nm and an energy of 120-360 µJ/pulse were focused at a distance of 10 mm in front of
the sample with a delay time of 20 µs from the pump pulse. The ion intensity was normalized
to the REMPI laser intensity following the relation between the laser fluence and the ion yield
[14]. In the present paper, several data sets of the J=0 and J=1 signals were acquired under
identical conditions, and the ratios of the averaged intensities (J=1/J=0) are plotted in Figs. 1 and 2.

3. Results and Discussion
Figure 1(a) shows the J=1 to J=0 ratio of H2 on Cr2O3(0001)/Cr(110) measured by REMPI-
PSD as a function of time. The J=1 and J=0 intensities were measured alternately every 80 s
after the H2 dosage with a pump laser fluence of 86 µJ/cm2/pulse. The J=1/ J=0 ratio decreases
with increasing time. As discussed in our previous paper [14], this decrease represents the o-p
conversion naturally occurring on the surface. After a fit of these data points to an exponential
function (Cexp(-t/τ)), where C and τ are fit parameters, the conversion time τ was estimated
to be 210 ± 22 s.

Figures 1(b)-(d) show evolution of the J=1/J=0 ratio measured at higher pump laser fluences
of 65-194 µJ/cm2/pulse. In our previous studies, the o-p conversion was found to be accelerated
on Ag at higher laser fluences. Compared to the Ag surface, however, the acceleration of the
The $J=1$(ortho) to $J=0$(para) ratio of $\text{H}_2$ on $\text{Cr}_2\text{O}_3$(0001)/Cr(110) surfaces as a function of time. (a) The natural conversion was probed every 80 s. The o-p conversion was probed under continuous laser irradiation of 193 nm with fluences of (b) 65, (c) 129, (d) 194 $\mu\text{J/cm}^2$.

Figure 1. The $J=1$(para) to $J=0$(ortho) ratio of $\text{D}_2$ on $\text{Cr}_2\text{O}_3$(0001)/Cr(110) surfaces as a function of time. The p-o ratio was probed under continuous laser irradiation of 193 nm with fluences of (a) 65, (b) 134, (c) 189, (d) 344 $\mu\text{J/cm}^2$.

Figure 2. The $J=1$(para) to $J=0$(ortho) ratio of $\text{D}_2$ on $\text{Cr}_2\text{O}_3$(0001)/Cr(110) surfaces as a function of time. The p-o ratio was probed under continuous laser irradiation of 193 nm with higher laser fluences of 134-344 $\mu\text{J/cm}^2$. As $\text{H}_2$ o-p conversion, photoacceleration of $\text{D}_2$ p-o conversion was not so prominent as that on Ag.

In the following, we discuss the mechanism of the o-p (p-o) conversion on $\text{Cr}_2\text{O}_3$(0001)/Cr(110) and the magnetic structure of the $\text{Cr}_2\text{O}_3$(0001) surface on the basis of the above experimental results. The structure of $\text{Cr}_2\text{O}_3$ is the corundum type, where Cr and O layers are alternately stacked in the c-axis direction. Each $\text{Cr}^{3+}$ ion is in the $^4\text{A}_{2g}$ state having a spin of 3/2 [17]. The $\text{Cr}^{3+}$ ion spin is antiferromagnetically ordered in the c-direction as well as within the Cr layer [18]. On the $\text{Cr}_2\text{O}_3$(0001)/Cr(110) surface, half of the $\text{Cr}^{3+}$ ions terminate the surface to avoid divergence of the electrostatic surface potential [11].

In our previous work [5], we have examined the o-p (p-o) conversion of $\text{H}_2$ (D$_2$) on clean Ag and O$_2$-covered Ag surfaces. The o-p (p-o) conversion of $\text{H}_2$ (D$_2$) on Ag was dramatically accelerated by co-adsorption of O$_2$ molecules. The origin of such acceleration was attributed to the spatially inhomogeneous magnetic field on the position of the two nuclear spins of $\text{H}_2$ (D$_2$) and the conversion time in the vicinity of O$_2$ was estimated to be 8.3 and 53.4 s for $\text{H}_2$ and D$_2$, respectively.

The present conversion times of 210 and 538 s for $\text{H}_2$ and D$_2$ on $\text{Cr}_2\text{O}_3$ are slightly shorter than those on Ag. Nonetheless, the values are much longer than those in the vicinity of O$_2$. In the present experimental condition, Molecular hydrogen is physisorbed on surfaces via the van der Waals interaction where orbital mixing between the hydrogen and substrate is negligibly
small. Therefore, the substrate electronic levels do not substantially affect the o-p conversion of physisorbed hydrogen, while the surface magnetism is expected to influence the conversion to a greater degree. If the Cr ion spins of the Cr$_2$O$_3$(0001) surface were antiferromagnetically coupled, strongly inhomogeneous magnetic field would be formed near the surface and the o-p (p-o) conversion time would be of the order of 10 s as obtained for the O$_2$-covered Ag surface. We therefore argue that the Cr ion spins in the Cr$_2$O$_3$(0001) surface are ferromagnetically ordered yielding a rather homogeneous magnetic field.

On an atomic scale, however, a weakly inhomogeneous magnetic field might be present near the surface Cr ions even if the Cr spins are ferromagnetically ordered. When we model the Cr$_2$O$_3$ surface as spins regularly arrayed with a distance of 3 Å, numerical calculations show that the magnetic-field gradient on this surface is 1/5 - 1/50 as small as that due to the dipolar field of a single spin corresponding to O$_2$ on Ag. These results are qualitatively consistent with the difference of the conversion time between the Cr$_2$O$_3$(0001) surface and the O$_2$-adsorbed-Ag surface.

It is worth noting that the o-p (p-o) conversion accompanies the rotational-energy dissipation of hydrogen molecules as well as the nuclear-spin flip. Both o-H$_2$ and p-D$_2$ are in the $J=1$ state, whereas p-H$_2$ and o-D$_2$ are in the $J=0$ state at low temperature. The rotational energies of o-H$_2$ and p-D$_2$ are 14.7 and 7.35 meV, respectively, which should be dissipated into either surface or molecule degrees of freedom upon o-p (p-o) conversion. According to photo absorption and neutron scattering studies, the exchange interaction energy of the Cr ion spin is about 30 meV [19], and the resulting spin-wave energy is of the order of 1-50 meV [18]. The rotational energies of o-H$_2$ and p-D$_2$ are well compared with these magnetic energy scales of Cr$_2$O$_3$, and possibly dissipated into magnetic degrees of freedom.

In conclusion, we have investigated the o-p conversion of H$_2$ and p-o conversion of D$_2$ on a single-crystal film of Cr$_2$O$_3$ grown on Cr(110) with a laser technique of resonance-enhanced multiphoton ionization. The conversion time of H$_2$ and D$_2$ was estimated to be 210 and 538 s, respectively. The results suggest that the Cr spins of the Cr$_2$O$_3$(0001)/Cr(110) are ferromagnetically ordered yielding a weak inhomogeneous magnetic field, which could be effective for the hydrogen spin flip. The rotational energy of H$_2$ and D$_2$ is possibly accommodated by the magnetic transitions of Cr$_2$O$_3$.

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