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Effects of coadsorbed O_2 on hydrogen ortho-para conversion on Ag surfaces

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Ortho-para (o-p) conversion of H_2 and para-ortho (p-o) conversion of D_2 were investigated on a Ag surface coadsorbed with O_2 by resonance-enhanced multiphoton ionization combined with photostimulated desorption. Compared with a bare Ag surface, both H_2 o-p conversion and D_2 p-o conversion were accelerated on O_2-covered surfaces, and the conversion time was found to decrease with increasing O_2 coverage. In order to analyze the conversion kinetics, Monte Carlo simulations taking account of hydrogen diffusion on the surfaces were performed and compared with the experimental data. The conversion time of H_2 and D_2 in the vicinity of adsorbed O_2 was estimated to be 8.3 and 53.4 s, respectively. The isotope dependence of the conversion is discussed.

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I. INTRODUCTION

Molecular hydrogen (deuterium) exists in two nuclear modifications of ortho and para species. Due to the symmetry of the total wave function with respect to the permutation of the two nuclei, ortho-H_2 (o-H_2) [para-D_2 (p-D_2)] having the total nuclear spin $I=1$ ($I=1$) is in the rotational state with odd rotational quantum numbers (J), while para-H_2 (p-H_2) [ortho-D_2 (o-D_2)] of $I=0$ ($I=2$ or 0) has even J.[1,2] The ortho-para (o-p) conversion is so slow in the gas phase with a conversion time of the order of 10^8-10^{10} s because of the small coupling terms related to the nuclear spins.[1] As intuitively expected, the o-p conversion is promoted under the presence of magnetic materials. Spatially inhomogeneous magnetic field might be induced near the magnetic materials, which is effective for the nuclear-spin flip. While a theoretical formula was derived for the o-p conversion due to collision with a paramagnetic substance,[3] the H_2 o-p conversion has been experimentally investigated on a variety of magnetic materials.[4–6] The H_2 o-p conversion is reported to be accelerated as the amount of magnetic impurity is increased and also the magnetic moment gets larger.[4,6] The homogeneous gas-phase conversion catalyzed by paramagnetic gas molecules and the conversion catalyzed by paramagnetic ions in aqueous solution could be explained by the Wigner[3] theory. Despite much efforts, unfortunately, the detailed mechanism of the o-p conversion has not been well understood because the sample surfaces were not well characterized in most studies. Furthermore, the rotational-energy relaxation, which is essentially important in the o-p [para-ortho (p-o)] conversion, has not been so seriously considered.

The hydrogen o-p conversion has also been observed on diamagnetic surfaces such as Ag,[7,8] Cu,[9,10] and graphite.[11] The conversion mechanism on these surfaces has theoretically been proposed to be the Coulomb-contact model.[12] This model is a second-order perturbation theory where electrons are virtually transferred from metal substrates to the adsorbed H_2 (D_2) as an intermediate state followed by nuclear-spin flip of the hydrogen molecule through the hyperfine contact interaction.[12] Photoacceleration of the o-p conversion furthermore suggested that the electron transfer is important for the o-p (p-o) conversion of H_2 (D_2).[13,14]

O_2 molecules have two unpaired electrons in the antibonding orbitals of $2p\pi^*$ revealing a diradical nature. When molecular O_2 is adsorbed on a metal surface, two possible adsorption states exist:[15] (1) physisorbed state, which is neutral O_2, and (2) chemisorbed state, which is either superoxolike O_2^- or peroxolike O_2^{2-}. Depending on the charged state, the spin state is expected to change from a triplet to doublet and singlet. The adsorption state can be controlled by the surface temperature, e.g., O_2 molecules are physisorbed below ~40 K on Ag(110) and ~50 K on Ag(111), whereas physisorbed O_2 is partially chemisorbed and partially desorbed upon heating at ~40–170 K.[15] On an O_2-covered surface, the hydrogen o-p conversion might be affected depending on the spin state of adsorbed O_2. It is expected that the triplet state is most effective for the o-p conversion.

In the present paper, we have investigated the effect of adsorbed O_2 on the hydrogen o-p conversion in a submonolayer regime. The o-p (p-o) conversion was found to be accelerated as the O_2 coverage was increased. With the aid of Monte Carlo simulations, the effects of hydrogen diffusion on the conversion kinetics were examined, and the conversion times in the vicinity of adsorbed O_2 were evaluated.

II. EXPERIMENT

The experimental setup is the same as those used in previous work.[13,14] Briefly, a Ag film deposited on a Cu block was used as the sample surface. Ag of ~5 nm (purity ≥99.99%) was deposited in an ultrahigh vacuum (UHV) chamber (2×10^{-8} Pa) with a W filament at a substrate temperature of 6.8 K followed by annealing of the film at 300 K. Ag forms islands with an average size of 50 nm consisting of an average terrace width of 6 nm as characterized by scanning tunnel microscope (STM) in a separate chamber. The sample was surrounded by a radiation shield attached to a cold stage kept at 40 K. Before each measurement, the sample was exposed to O_2 at 6.8 K by backfilling the chamber. The O_2 coverage was estimated from the impinging rate of O_2 on the assumption that the sticking probability is unity on the shield surface as well as the sample surface.[16,17] At an O_2 pressure of P, the impinging rate Γ is expressed by

$$\Gamma = \frac{AP}{\sqrt{2\pi mkT}}, \tag{1}$$

where T is the gas temperature, m is the mass of O_2, k is the Boltzmann constant, and A is the solid-angle correction factor. Since the sample was surrounded by the radiation shield attached to the cold stage, O_2 can be accessible to the sample surface through a limited space of small apertures for the Ag source and laser light introduction. From the sizes, distances, and directions of the apertures from the sample in the present apparatus, the solid-angle correction factor (A) was evaluated at about 0.06. By defining 1 monolayer $(\mathrm{ML}) = 1.38 \times 10^{19}/\mathrm{m}^2$ here on the assumption that the sample surfaces mainly consist of Ag(111), an O_2 dose of 1 L $(1.33 \times 10^{-4}\ \mathrm{Pa\,s})$ measured by the B-A gauge attached to the UHV chamber then corresponds to 0.016 ML.

After an O_2 dose, the sample was exposed to 30 L of H_2 (D_2) at 6.8 K by backfilling the chamber, where H_2 and D_2 were molecularly physisorbed on the surface. At this temperature, o-H_2 and p-D_2 are in the $J=1$ state, while p-H_2 and o-D_2 are in the $J=0$ state. To monitor the ortho-para ratio of adsorbed H_2 (D_2), a small amount of H_2 (D_2) was desorbed by irradiation of a pulsed laser light [photostimulated desorption (PSD)] with a wavelength of 193 nm (2.2 mm in diameter and laser fluence of 120 $\mu\mathrm{J/cm}^2$ per pulse) at an incidence angle of 81°. The desorbed H_2 (D_2) molecules from the surface were state-selectively detected by the (2+1) resonance-enhanced multiphoton ionization (REMPI) via the $E,F\ {}^1\Sigma_g^+$ states.[18] For the REMPI measurement, laser pulses with a wavelength of 201 nm and an energy of 120–360 μJ per 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.[13,14] After each experiment, both hydrogen and oxygen molecules were desorbed from the surface by heating the sample up to room temperature. After the heat treatment, the o-p conversion time without O_2 exposure was confirmed to be identical to the value obtained on a freshly prepared Ag surface. This indicates that an oxygen-free surface was restored by heating the sample at room temperature. This is consistent with previous reports that O_2 dissociation probability is extremely small and physisorbed O_2 is almost completely removed from the surface above 300 K.[15]

As reported in previous papers,[13,14] the $J=1$ and $J=0$ intensities probed by this REMPI combined with PSD are proportional to the coverages of these two species on the surface. The desorption signal in the $J=1$ state was observed to decrease with increasing time mainly due to the o-p (p-o) conversion of H_2 (D_2), whereas the $J=0$ signal remained almost constant or gradually decreased as a function of time due to desorption. 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.

III. RESULTS

Figure 1 shows the $J=1$ (ortho) to $J=0$ (para) ratio of H_2 on O_2-covered Ag surfaces monitored by REMPI PSD as a function of time. The $J=0$ and $J=1$ intensities were measured alternately every few hundreds of seconds after the H_2 dosage. The $J=1/J=0$ ratio decreases with increasing time. Open circles in Fig. 1 denote the data taken for Ag without O_2 dosage, which represents the o-p conversion naturally occurring on the bare Ag surface. After a fit by an exponential function $[C\exp(-t/\tau)]$, where C and τ are fit parameters, the conversion time τ was estimated to be 610 ± 90 s. Filled circles, open squares, filled squares, and open triangles in Fig. 1 show the time evolution of the $J=1/J=0$ ratio of H_2

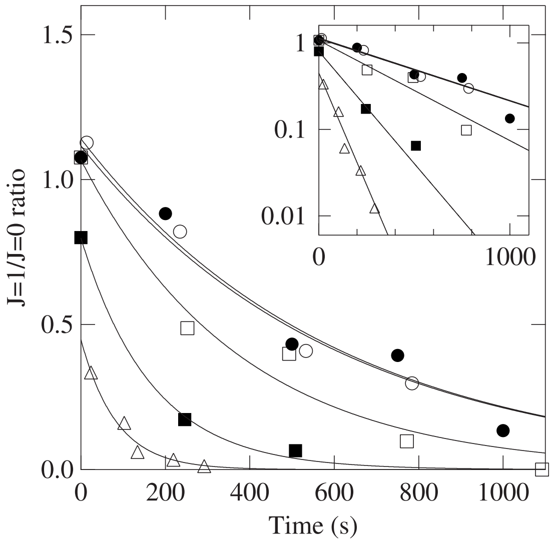

FIG. 1. Time evolution of the $J=1/J=0$ ratio of H_2 on Ag surfaces with O_2 coverages of 0 (open circles), 0.0004 (filled circles), 0.002 (open squares), 0.005 (filled squares), and 0.01 (open triangles) ML. The $J=0$ and $J=1$ intensities were measured by REMPI PSD alternately every few hundreds of seconds after H_2 dosage.

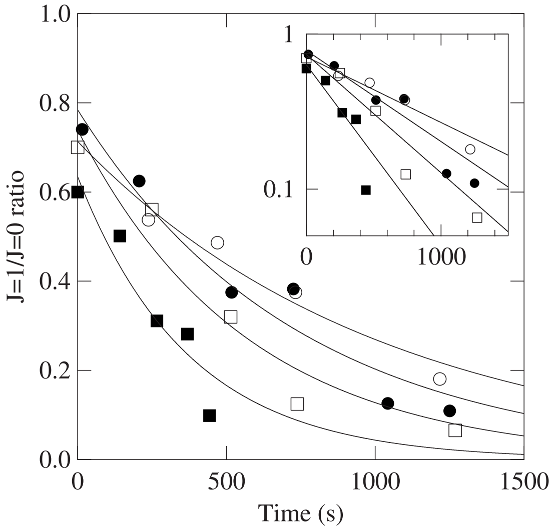

FIG. 2. Time evolution of the $J=1/J=0$ ratio of D_2 on Ag surfaces with O_2 coverages of 0 (open circles), 0.005 (filled circles), 0.01 (open squares), and 0.015 (filled squares) ML. The $J=0$ and $J=1$ intensities were measured by REMPI PSD alternately every few hundreds of seconds after D_2 dosage.

on Ag surfaces covered with the O_2 coverages of 0.0004, 0.002, 0.005, and 0.01 ML, respectively. Compared with the Ag clean surface, the o-p ratio obviously decays faster as the O_2 coverage is increased.

Figure 2 shows the $J=1$ (para) to $J=0$ (ortho) ratio of D_2 on the Ag surface with various amounts of O_2 measured by REMPI PSD as a function of time. Similarly to H_2, the $J=1/J=0$ ratio of D_2 decreases exponentially. From a fit of the data by an exponential function, the p-o conversion time on bare Ag is estimated to be 1030 ± 170 s. With O_2 dosages of 0.005, 0.01, and 0.015 ML, the $J=1/J=0$ ratio was found to decrease faster, indicating that adsorbed O_2 promotes the p-o conversion.

IV. DISCUSSION

Both H_2 o-p conversion and D_2 p-o conversion were accelerated by O_2 coadsorption. According to previous studies, O_2 molecules are physisorbed below ~40 K on Ag(110) and ~50 K on Ag(111).[15] In a physisorbed state where the molecules are adsorbed at a relatively distant position from the surface via the van der Waals interaction, the electrons in the π^* orbitals of O_2 are expected to remain unpaired. Thus, the acceleration of the o-p (p-o) conversion is caused by the unpaired spins of O_2. The unpaired spin produces the dipolar magnetic field, which has a r^{-3} dependence where r is the distance from the spin. The dipolar field is spatially inhomogeneous, which is effective for the nuclear-spin flip of hydrogen molecules.

Because the O_2 coverage is in a submonolayer regime in the present experiments, the o-p (p-o) conversion of adsorbed H_2 (D_2) takes place via two mechanisms. If H_2 (D_2) stays far from adsorbed O_2, the effect of the O_2 spin is negligible so that adsorbed H_2 (D_2) undergoes o-p (p-o) conversion through interaction with the substrate Ag. The conversion mechanism on Ag is proposed to be the Coulomb-contact model, and the conversion time (τ_1) is 610 and 1030 s for H_2 and D_2 as estimated in Figs. 1 and 2, respectively. If H_2 (D_2) is in the vicinity of the adsorbed O_2, on the other hand, the o-p (p-o) conversion can be promoted by the magnetic-dipole interaction. This conversion time is defined as τ_2.

In the conversion process on the O_2-covered surface, an important factor is the diffusion of hydrogen molecules on the surface. Even if H_2 (D_2) is initially adsorbed at a site far from preadsorbed O_2, H_2 (D_2) possibly diffuses on the surface to approach O_2, resulting in facile conversion due to the O_2 spin. In order to gain the kinetic behavior of the o-H_2 (p-D_2) coverage on the surface based on the two conversion mechanisms, Monte Carlo simulations have been performed with surface diffusion taken into consideration. Figure 3 shows the model adopted in the calculations; $n \times n$ lattice points represent the substrate sites, and the blue triangle at the center of this square lattice represents adsorbed O_2. This means that the O_2 coverage is $1/n^2$ (ML) and that the O_2 location is fixed on the surface on the assumption that O_2 is immobile. The nearest- and next-nearest-neighbor sites denoted by red circles are assumed to be the sites where H_2 (D_2) o-p (p-o) conversion is accelerated by O_2. On this model substrate, a hydrogen molecule was randomly adsorbed at a site on the substrate and allowed to diffuse randomly on the surface between adjacent sites with a hopping rate of ν. During the diffusion, the molecule undergoes conversion with conversion probabilities of $1/\tau_1$ and $1/\tau_2$ on the bare substrate (black-dotted sites) and in the vicinity of O_2 (blue-triangled and red-circled sites), respectively. For the molecule motion on this model substrate, a periodic boundary condition was adopted in both x and y directions. To simulate the conversion kinetics, the time required until the conversion took place was recorded for 10^4 individual events. From the histogram of the time required until the conversion, the time evolution of the number of molecules that survived the conversion (survival rate) was plotted as a function of time, which can be compared with the experimental data. In all calculations, τ_1 and τ_2 were tentatively set at 1000 and 10 s, respectively, and the hopping rate ν and n representing the O_2 coverage were varied.

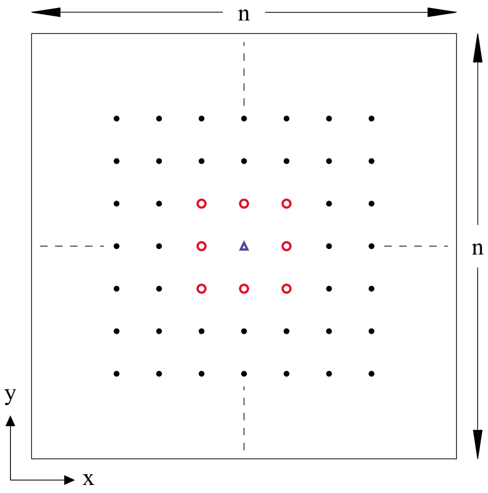

FIG. 3. (Color online) Lattice model for the Monte Carlo simulations; $n \times n$ lattice points denote substrate sites, and the blue triangle at the center of this square lattice represents adsorbed O_2. The nearest- and next-nearest-neighbor sites denoted by the red circles are assumed to be the sites where H_2 (D_2) o-p (p-o) conversion is accelerated by O_2.

In Fig. 4(a), the survival rate is shown as a function of time at four n values of 31, 15, 9, and 7 with ν fixed at 0.001 s^{-1}. These n values correspond to the O_2 coverages of 0.001, 0.004, 0.012, and 0.02 ML, respectively. As n is decreased, the survival rate decreases faster. At this ν value, furthermore, the results reveal a double exponential decay, as confirmed by reasonable fits by a sum of two exponential functions. The decay times obtained from the fits almost coincide with the conversion times of τ_1 and τ_2. Since the hopping rate is smaller than $1/\tau_1$, the conversion occurs independently on the two regions with respective conversion times revealing a double exponential feature.

Figures 4(b) and 4(c) show the time evolution of the survival rate at hopping rates of 0.1 and 1000 s^{-1}, respectively. Similar to Fig. 4(a), the survival rate decreases faster with decreasing n. Whereas the decay curves in Fig. 4(c) were well expressed by a single-exponential function, the curves in Fig. 4(b) reveal a double exponential feature not fitted by

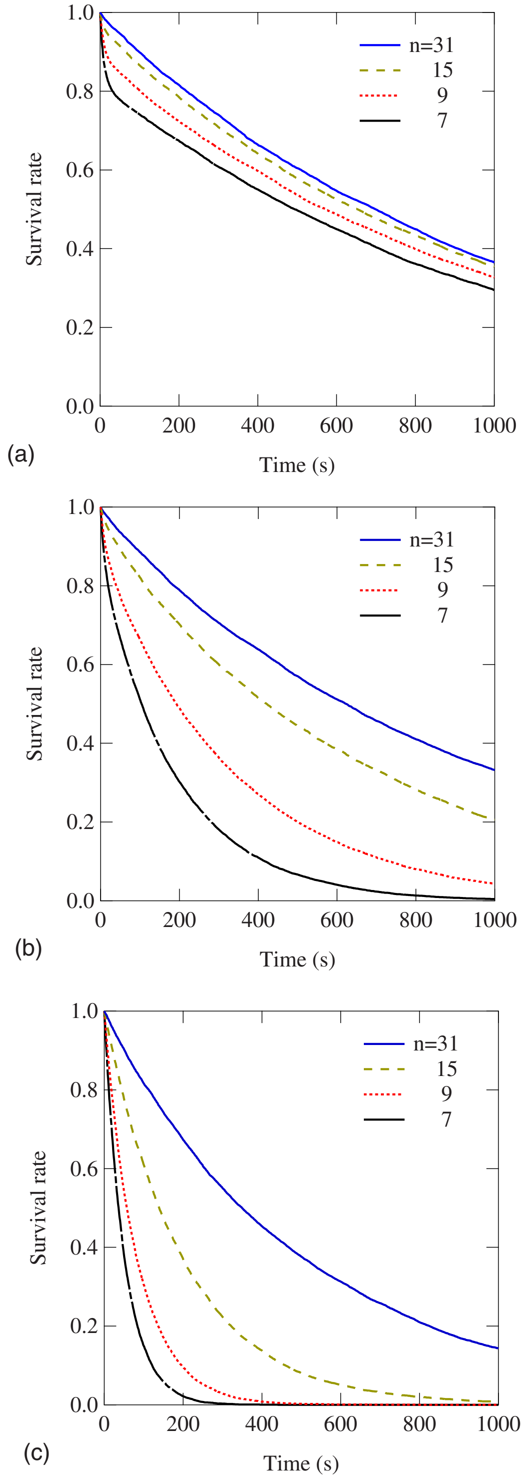

FIG. 4. (Color online) Survival rate as a function of time at four n values of 31, 15, 9, and 7 with hopping rates (ν) of (a) 0.001, (b) 0.1, and (c) 1000 s^{-1}.

a single-exponential decay. In contrast to Fig. 4(a), the decay times obtained by fits with a sum of two exponential functions are different from τ_1 and τ_2. The decay times obtained from a fit were 193.4 and 12.3 s for $n=7$. This is because the diffusion time is comparable with the conversion times. The single-exponential character revealed in Fig. 4(c), on the other hand, is corroborated by considering the time scale of the diffusion and conversion. The diffusion length of a molecule within a time period of Δt is expressed by $\sqrt{\nu\Delta t}$ in the unit of the lattice distance. The time scale of the diffusion over the $n\times n$ area is therefore given by $2n^2/\nu$. When $\nu=1000\ \mathrm{s}^{-1}$, the diffusion time is shorter than the o-p conversion times in all cases of n. This suggests that the molecule coverage is kept equal between the bare surface (black dots) and the vicinity of O_2 (the blue triangle and red circles). When a single-exponential function was fitted to the simulation data in Fig. 4(c), it was found that the decay rates were well expressed by the mean conversion probability $(1/\tau)$ given by

$$\frac{1}{\tau}=\frac{(1-\theta N)}{\tau_1}+\frac{\theta N}{\tau_2}. \qquad (2)$$

Here, θ indicates the O_2 coverage and N denotes the number of sites in the vicinity of O_2 where the conversion is accelerated.

The insets of Figs. 1 and 2 show semilogarithmic plots of the $J=1/J=0$ ratio of H_2 and D_2, respectively. It seems that the data points are on straight lines, suggesting that the decays are expressed by a single-exponential function. In Fig. 4, the simulations showed that there exist three regimes for the conversion kinetics depending on the hopping rate. Although fits by the double exponential curve as displayed in Fig. 4(b) cannot be unambiguously excluded due to the uncertainty and limited number of the data points, we discuss the o-p conversion mechanism in the following by assuming that the kinetics follows the single-exponential decay. The single-exponential feature corresponds to the case where the hydrogen diffusion is much faster than the conversion times. From the fitting analysis of the data in Figs. 1 and 2 with a single-exponential function, the effective conversion time of H_2 is estimated to be 604 ± 77, 375 ± 49, 170 ± 27, and 74 ± 5 s at O_2 coverages of 0.0004, 0.002, 0.005, and 0.01 ML, respectively, and the effective p-o conversion time of D_2 is derived as 664 ± 93, 528 ± 78, and 270 ± 67 s at O_2 coverages of 0.005, 0.01, and 0.015 ML, respectively. The uncertainties are the standard deviations of the fit results for the several data sets.

Figure 5 shows the variations in the effective conversion times for H_2 and D_2 as a function of the O_2 coverage. From the fits by Eq. (2) as indicated by solid curves in Fig. 5, τ_2 of H_2 and D_2 is estimated to be 8.3 ± 1.2 s and 53.4 ± 9.3 s, respectively, with an assumption of $N=7$ [(111) is assumed to be mainly exposed]. As expected, the conversion time near the adsorbed O_2 is considerably shorter than those on the bare Ag surface.

In the vicinity of magnetic impurities, the nuclear-spin flip can be induced by the dipolar magnetic field due to impurity spins. The o-p conversion in the collisional process with an impurity spin was theoretically investigated on the basis of the time-dependent perturbation theory.[3] A crude approximation of this treatment was that the collisional time is assumed to be sufficiently short and the rotational-energy release is not explicitly taken into consideration. A more rigorous calculation was performed by taking account of the interaction with the translational motion of hydrogen as a rotational-

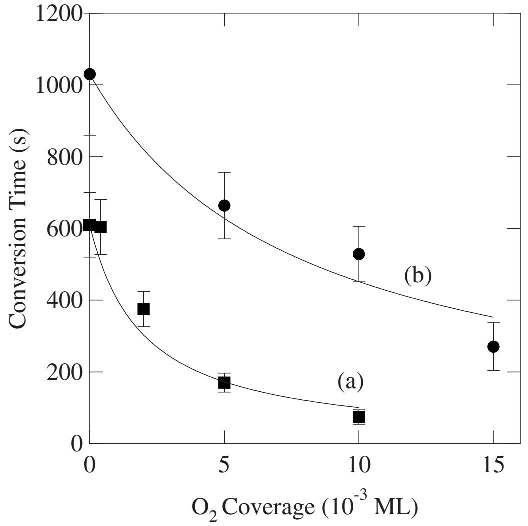

FIG. 5. Variations in τ for (a) H_2 and (b) D_2 as a function of the O_2 coverage. Solid curves are fits by Eq. (2).

energy relaxation channel.[19,20] The calculated conversion time for D_2 is 117 s,[20] which is in reasonable agreement with the experimental τ_2 value of 53.4 s in the present work.

Finally, isotope dependence of the conversion time is discussed. As shown in Figs. 1 and 2, the natural conversion times of H_2 and D_2 on bare Ag are 610 and 1030 s, respectively, i.e., the conversion time ratio for D_2 and H_2 is 1.7. On the other hand, the ratio of τ_2 corresponding to the conversion time near O_2 is 6.4 ± 1.9, which is substantially larger than 1.7. The magnetic interaction Hamiltonian setting off the nuclear-spin flip is proportional to the nuclear g factor (g_I), which is a common feature for both magnetic-dipole interaction and hyperfine contact interaction. The square of the matrix element related to the nuclear-spin flip, when averaged over the initial states and summed over the final states, is then calculated to be proportional to $\frac{g_I^2}{3}$ and $2g_I^2$ for H_2 and D_2, respectively, reflecting the initial- and final-state degeneracies.[20] Considering $g_I=5.59$ for proton and 0.857 for deuteron, both magnetic-dipole and hyperfine contact interactions are larger for H_2 than D_2 by a factor of 7.1. The ratio of τ_2 for D_2 and H_2 obtained in the present analysis is similar to the interaction strength 7.1. In contrast to this, the conversion time ratio is appreciably smaller on bare Ag. On bare Ag, the conversion mechanism has been discussed to be the Coulomb-contact model in which electron transfer between the substrate and hydrogen is involved. In our previous work,[14] we discussed the isotope dependence on bare Ag in terms of electron transfer and/or rotational-energy dissipation. We suggested that the probability of electron transfer or rotational-energy release is larger for D_2 than H_2, resulting in deviation of the conversion time ratio from 7.1. In this regard, it is worth emphasizing that the conversion time ratio between D_2 and H_2 can be a signature of the conversion mechanism.

In conclusion, the o-p conversion of H_2 and p-o conversion of D_2 on Ag coadsorbed with O_2 were investigated by the REMPI-PSD technique. Both o-p and p-o conversions were found to be accelerated as the O_2 coverage was increased. With the aid of Monte Carlo simulations taking account of hydrogen diffusion, the conversion kinetics is analyzed on the basis of two conversion mechanisms. The conversion time of H_2 and D_2 in the vicinity of adsorbed O_2 was estimated to be 8.3 and 53.4 s, respectively.

As a future prospect, temperature dependence of the conversion time would be interesting and informative. By comparing with the simulation results, the diffusion coefficient of hydrogen on surfaces could be obtained.

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