

Photostimulated Desorption and Ortho-Para Conversion of H₂ on Ag Surfaces

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Photostimulated desorption and change of the ortho-para ratio of H₂ physisorbed on Ag at 7 K are reported. After pump laser excitation at 193 nm neutral H₂ desorbing in a nonthermal process is state selectively detected by resonance-enhanced multiphoton ionization. At weak pump laser fluence the natural ortho-para conversion of H₂ on Ag was monitored to proceed with a conversion time of ~ 780 s, which is in good agreement with predictions based on an electron-exchange-hyperfine-contact model. With increasing pump laser fluence, the ortho-para ratio decreases faster, suggesting photoassisted ortho-para H₂ conversion.

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Molecular hydrogen consists of two protons with nuclear spins $1/2$ and is classified into ortho and para species, according to the total nuclear spin of 1 and 0, respectively. Since the Pauli principle dictates that the total wave function be antisymmetric with respect to the exchange of the two nuclei, the ortho and para species correspond to rotational states with odd and even quantum numbers (J), respectively. One particular consequence for molecular hydrogen is that due to the necessity of nuclear spin inversion, transitions between the ortho and para states are strictly forbidden in the gas phase. Through interaction with magnetic materials, however, the ortho-para (o-p) conversion is considerably promoted. In pure solid ortho H₂ the magnetic field represented by neighboring ortho H₂ induces a slow o-p conversion proceeding at a rate of 1.9%/h [1].

On solid surfaces, on the other hand, previous studies with high-resolution electron energy loss spectroscopy (EELS) have shown that H₂ physisorbed on Ag [2,3], Cu [4–6], and graphite [7] surfaces do undergo o-p H₂ conversion, although these surfaces are nonmagnetic. In these experiments, ortho and para H₂ are distinguished by energy loss peaks corresponding to the rotational excitations from $J = 1$ to 3 and from $J = 0$ to 2, respectively. Although the small o-p ratio observed on Cu(100) was first attributed to a J -dependent sticking coefficient of H₂, this effect has later been shown to be negligible [8]. On the basis of the EELS observations, the o-p conversion was concluded to occur rather fast on the above surfaces: Ortho H₂ is converted at the instant of adsorption or within 1–2 min residence on both Ag films and Ag(111) [2]. On Cu(100) the conversion rate has been reported to vary from slower than 1%/min [4] to one monolayer per 5 min [6], depending on the sample preparation. A theoretical study has shown that direct interaction of substrate electrons and the adsorbed H₂ leads to a conversion time in the order of hours [9]. Later, Ilisca proposed a theoretical model for the fast o-p conversion on nonmagnetic metal surfaces, which involves a virtual electron transfer from the metal substrates to the adsorbed H₂, followed by

spin conversion through hyperfine-contact interaction. This hyperfine-Coulomb excitation model predicted an o-p conversion time on the order of 1–10 min [10,11].

In this Letter, we report o-p conversion of H₂ on Ag surfaces with a different experimental approach. We performed photostimulated desorption (PSD) experiments of H₂ physisorbed on Ag by ultraviolet (UV) photons with a J -state selective detection technique. Thereby the change of the H₂ o-p ratio on the surface could be monitored in real time during the conversion process. Under weak pump laser fluence, we find that the natural conversion proceeds on Ag with a time constant of ~ 780 s. At higher pump laser fluences, faster decrease of the o-p ratio is observed, suggesting that o-p H₂ conversion can be accelerated by photostimulation.

The sample in the present work was a 30 nm thick Ag film deposited on a Cu block in ultrahigh vacuum (2×10^{-8} Pa) from a W filament loaded with Ag wire (purity $> 99.99\%$) at a substrate temperature of 7 K. Although previous studies on H₂ molecularly adsorbed on Ag films and on Ag(111) found no significant difference in the corresponding EELS spectra [2], indicating that defects play a minor role for o-p H₂ conversion on these surfaces, the film was annealed at 300 K after deposition. The sample was surrounded by a radiation shield (50 K) to suppress the heat load from the chamber walls at room temperature (90% of the total solid angle was shielded): Infrared radiation has been reported to induce desorption of physisorbed H₂ [12–14]. Before each measurement, the sample was exposed to 30 L of normal H₂ at 7 K by backfilling the chamber. Multilayer H₂ condensation is unlikely in view of the vapor pressure of solid H₂ [12], and therefore the H₂ coverage is considered to be in the monolayer regime. To induce desorption of adsorbed H₂, a 2×10 mm² area of the sample surface was irradiated by 193 nm photons (6.4 eV) generated by an ArF excimer laser at an incidence angle of 80° from the surface normal. The desorbed H₂ molecules were J state selectively detected by (2 + 1) resonance-enhanced multiphoton ionization (REMPI) via the E , F $^1\Sigma_g^+$ states. The

REMPI laser pulses with a wavelength of ~ 201 nm and an energy of $400 \mu\text{J}/\text{pulse}$ were focused at a distance of 10 mm in front of the sample, and the ionized H_2 was detected by a microchannel plate attached to the radiation shield. In the given pulse energy range the ion yield increased with the REMPI laser fluence to the 1.5th power because of saturation of the intermediate state [15], hence the ion intensity was normalized accordingly. It should be noted that the gas-phase ratio of $(J = 1)/(J = 0)$ measured by REMPI near the sample surface during H_2 dosage was about 2.2, while it is expected to be 3 in thermal equilibrium with the shield at 50 K. The reason for this deviation is not yet clear, but a lower $(J = 1)/(J = 0)$ ratio may result from o-p conversion during scattering of H_2 at the shield surface. As described later, pump laser excitation induces o-p conversion as well as desorption of adsorbed H_2 . This suggests that the para desorption signal contains contributions from the photoconverted ortho H_2 . However, the initial $(J = 1)/(J = 0)$ ratio measured by the REMPI-PSD technique right after adsorption was the same as the gas-phase value. Therefore, the REMPI signal in the present study mainly reflects the actual ortho and para H_2 concentrations on the surface, which is due to the large PSD cross section compared with the photoconversion cross section.

The physisorbed H_2 desorbs under pump laser irradiation, and the desorption signal intensity decreases gradually as a function of irradiation time. From the initial decay of the desorption yield, a PSD cross section of $\sim 10^{-16} \text{ cm}^2$ was estimated. Figure 1 shows time of flight (TOF) spectra for $J = 0$ (para) and $J = 1$ (ortho) states. Each spectrum was averaged over four independent scans measured at a pump laser fluence of $7.5 \mu\text{J}/\text{cm}^2$ under an ambient H_2 pressure of $3 \times 10^{-6} \text{ Pa}$ to establish a constant H_2 coverage. Both spectra fit well to the sum of two Maxwell-Boltzmann distributions, the translational temperature of the fast peak being 11 K. This parameter is close to the sample temperature of 7 K, which might suggest thermal desorption. However, the TOF spectrum does not vary with pump laser fluence, while the desorption yield increases linearly with the pump laser fluence up to $\sim 200 \mu\text{J}/\text{cm}^2$. In addition, the temperature rise of the sample is estimated to be lower than 0.6 K assuming a triangular temporal shape for the pump laser pulse [16]. Therefore, we conclude that the photoinduced H_2 desorption at 193 nm is a nonthermal process. It is noted that the translational temperature of the slow component is as low as 2 K.

In contrast, the desorption yield was found to be J state dependent, as shown in Fig. 2, where the H_2 yield was measured by alternately probing the $J = 0$ and $J = 1$ states. The measurement was carried out 600 s after H_2 dosage with a pump laser fluence of $40 \mu\text{J}/\text{cm}^2$ and a repetition rate of 1 Hz. Each data point is an average of 10–20 laser shots. The desorption signals in $J = 0$ and $J = 1$ decrease with increasing laser exposure, indicating

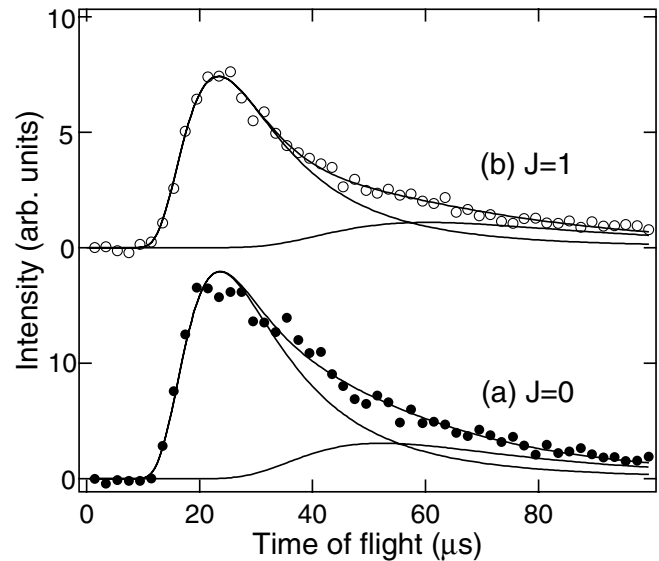


FIG. 1. TOF spectra of H_2 in (a) $J = 0$ and (b) $J = 1$ states desorbed from an Ag surface at a sample temperature of 7 K with a pump laser wavelength of 193 nm. The pump laser fluence was $7.5 \mu\text{J}/\text{cm}^2$, and the distance between the probe laser and the sample was 10 mm. The measurements were performed about 1200 s after the H_2 dosage where the o-p ratio was about 0.5. The solid curves are fits to a sum of two Maxwell-Boltzmann distributions.

depletion of the H_2 coverage on the Ag surface. The intensity of the $J = 1$ state decays clearly faster than that of $J = 0$ and it is evident that the initial ortho-para ratio larger than unity decreases to 0.2 at $t = 1600$ s. This might point towards a larger PSD cross section for $J = 1$ than for $J = 0$. However, the TOF spectra for the $J = 0$

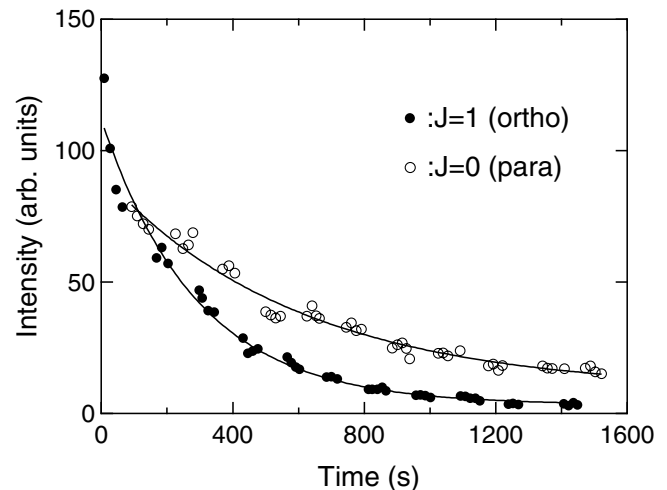


FIG. 2. H_2 yield in $J = 0$ and $J = 1$ desorbed from an Ag surface as a function of irradiation time with a pump laser wavelength of 193 nm at a repetition rate of 1 Hz. The sample temperature was 7 K and the pump laser fluence was $40 \mu\text{J}/\text{cm}^2$.

and $J = 1$ states shown in Fig. 1 are identical, suggesting that the same mechanism is operative for the PSD of both J states. Although we cannot unambiguously exclude the possibility of J -dependent PSD cross sections, we suggest at this stage that the difference in the decay rate is caused by ortho-para conversion taking place simultaneously on the surface.

In order to determine the natural o-p conversion rate for H_2 on Ag, the variation of the o-p H_2 ratio was probed at a cycle of 60 s by the REMPI-PSD technique at a low pump laser fluence of $10 \mu\text{J}/\text{cm}^2$, as shown in Fig. 3(a). To minimize the exposure, the sample was irradiated with pump laser pulses at 2 Hz for only 20 s during each cycle, 10 s for each J -state detection. The effect of the laser irradiation on the o-p H_2 ratio is negligible under these conditions: Filled squares in Fig. 3 denote the o-p H_2 ratios measured 600, 1200, and 2400 s after H_2 dosage on a nonirradiated sample, which are in good agreement with Fig. 3(a). It should be noted that the para H_2 intensity gradually decreases with a time constant of about 2000 s even under low pump conditions. When we did the same experiment on a para rich surface, the para H_2 intensity was also found to decrease with the same time constant within our experimental accuracy. This suggests that the effects of infrared radiation from the chamber walls are not negligible in the present experiments inducing desorption of H_2 from the surface. By correcting for this infrared radiation effect, it was found that o-p conversion does not increase the surface density of para H_2 , indicating that the converted ortho H_2 does not remain on

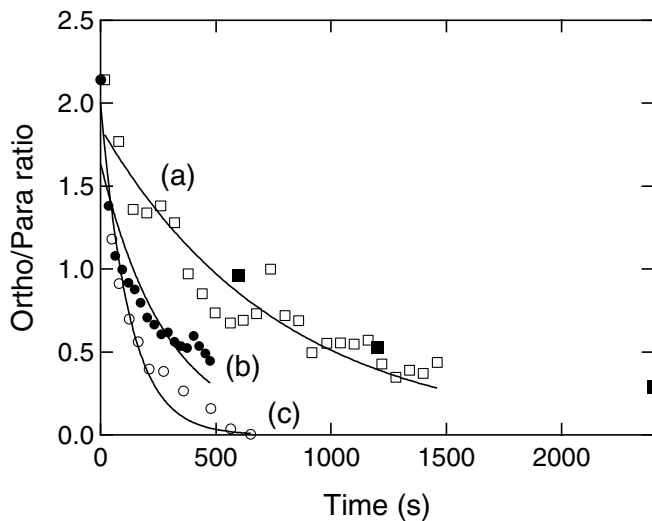


FIG. 3. Evolution of the ortho-para ratio as a function of time as measured by REMPI-PSD. The ortho-para ratio was measured by alternately probing $J = 0$ and $J = 1$ with a pump laser wavelength of 193 nm at a repetition rate of 2 Hz. The sample temperature was 7 K and the pump laser fluence was (a) 10, (b) 150, and (c) $250 \mu\text{J}/\text{cm}^2$. Filled circles denote the o-p H_2 ratios measured 600, 1200, and 2400 s after H_2 dosage on a non-irradiated sample.

the surface but desorbs from the surface probably due to heat emission originating from the rotational energy released in the o-p conversion. If the converted ortho H_2 desorbs from the surface, the evolution of the o-p ratio in Fig. 3(a) corresponds merely to o-p conversion. We estimate the conversion time τ to be 780 ± 70 s by fitting the o-p ratio data to the form $A \exp(-t/\tau)$. This conversion time corresponds to the natural conversion process arising from the interaction of H_2 with the Ag substrate. According to theoretical studies [9,10], conversion via direct interaction with the substrate electrons takes ~ 10 h, while indirect conversion mechanisms involving virtual electron transfer between the substrate and physisorbed H_2 followed by hyperfine-contact interaction occur on a scale of 100 s. Two types of intermediate states are considered for the electron exchange, neutral and charge transfer, and the conversion time on Ag(111) is calculated to be 420 and 120 s, respectively [11]. The experimentally measured value in the present work is apparently in good agreement with the indirect mechanism via the neutral intermediate.

Figures 3(b) and 3(c) show the change of the ortho-para ratio probed by REMPI-PSD at higher pump laser fluences of 150 and $250 \mu\text{J}/\text{cm}^2$, respectively, where the sample was continuously irradiated at 2 Hz. Obviously, the decay proceeds much faster than in the natural o-p H_2 conversion represented by Fig. 3(a). As discussed above, we consider that the faster decay is not due to the J -dependent PSD cross section but that the o-p conversion can be photoaccelerated on the surface. From the decay curves of Figs. 3(b) and 3(c), we estimate the photo-induced conversion cross section to be 0.7 ± 0.3 and $1.4 \pm 0.3 \times 10^{-17} \text{ cm}^2$, respectively, where the ortho H_2 is assumed to desorb after conversion without staying on the surface as a para H_2 . It is worth noting that in this system photons cause a nuclear spin flip, an event that is strictly forbidden for dipole transitions.

According to the exchange-contact model, the conversion probability (W) is expressed as follows [10,17]:

$$W \propto \left| \sum_I \frac{\langle \Psi_f | H_{HC} | \Psi_I \rangle \langle \Psi_I | H_C | \Psi_i \rangle}{E_i - E_I} \right|^2. \quad (1)$$

Ψ_i , Ψ_I , and Ψ_f are the initial, intermediate, and final state wave functions, respectively. E_i and E_I are the initial and intermediate energies. H_C and H_{HC} represent the Coulomb and hyperfine-contact interactions, respectively. As is apparent from the formula, the conversion probability increases as the energy difference between the initial and intermediate states decreases.

A promising candidate for the intermediate state is the affinity level of H_2 . The electron affinity level of H_2 in the gas phase is located ~ 2.3 eV above the vacuum level with a broad width of ~ 2.5 eV, which is known as a shape resonance with designation $2^2\Sigma_u^+$ [18]. On the other hand, the work function of the Ag(111) surface is 4.7 eV. When

H_2 is in the physisorption well of a metal surface, the affinity level shifts downward by ~ 1 eV due to the image-charge effect. As a consequence, the energy separation between the H_2 affinity level and the Ag Fermi level becomes ~ 6 eV, which is accessible by the photon energy of 6.4 eV. Therefore, the electron transfer probability can be expected to be promoted, thereby enhancing the o-p conversion process. We also note that the excited-state wave function is spatially more extended compared to the electronic ground state, which may further contribute to a more efficient electron transfer to the physisorbed H_2 . This mechanism is supported by a previous theoretical study reporting that optical excitation of substrate electrons to the image-charge state of a surface promotes the o-p H_2 conversion [19].

One interesting question concerns energy conservation. The 15 meV rotational energy possessed by ortho H_2 must dissipate into other degrees of freedom upon conversion to para H_2 . Two possible channels are the translational motion of H_2 and the substrate electron/phonon system. In the former case, the TOF spectrum of $J = 0$ can be expected to reveal an extra component with additional 15 meV energy, which would correspond to a TOF of $\sim 8 \mu\text{s}$. Since the cross section of PSD is 1 order of magnitude higher than that of photostimulated o-p conversion, the intensity of such a high-velocity component can be expected to be smaller than 10% of the main TOF peak. Nevertheless, the TOF spectrum of $J = 0$ in Fig. 1 is identical to that of $J = 1$, and no additional peak is observed. Therefore, we conclude that the entire rotational energy is not transferred to the H_2 translational motion, but the substrate degrees of freedom are also responsible for the energy dissipation.

Finally we briefly comment on the conversion times reported in earlier EELS studies [2]. As mentioned above, o-p conversion on Ag was reported to take place immediately upon adsorption or, at most, within 1–2 min residence time on the surface. This is apparently much shorter than the natural conversion time measured in the present work. To achieve a high cross section for rotational excitation in the EELS measurements [2], a primary electron energy of 3 eV was used, which lies in the shape resonance of H_2 . As pointed out in theoretical studies [10,17] and also indirectly supported by the photostimulated o-p conversion rate observed in the present paper, such a resonance may efficiently promote o-p conversion.

We suggest that EELS experiments at different electron energies out of resonance with H_2 could produce different o-p conversion kinetics.

In conclusion, we have investigated the H_2 o-p conversion on Ag by the REMPI-PSD technique. Physisorbed H_2 was nonthermally desorbed by laser irradiation at 193 nm with a translational temperature of 11 K for both $J = 0$ and $J = 1$ states. The natural o-p conversion time on the Ag surface was determined to be 780 s in good agreement with predictions based on the hyperfine-Coulomb excitation model. The o-p conversion was found to be promoted by the 193 nm laser photons with a cross section on the order of 10^{-17} cm^2 .

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