

Direct measurement of fast ortho-para conversion of molecularly chemisorbed H₂ on Pd(210)H. Ueta^{1,*}, Y. Sasakawa,² D. Ivanov², S. Ohno,² S. Ogura², and K. Fukutani^{1,2,*}¹Advanced Science Research Center, Japan Atomic Energy Agency (JAEA), 2-4 Shirakata, Tokai, Ibaraki 319-1195, Japan²Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

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Ortho-para conversion of molecularly chemisorbed H₂ on a Pd(210) surface at a surface temperature of 50 K is reported. A combination of a pulsed molecular beam, photostimulated desorption, and resonance-enhanced multiphoton ionization techniques was used for probing the change in the rotational states of molecularly chemisorbed H₂ on the surface. Our result shows that fast ortho-para conversion of chemisorbed H₂ occurs. The conversion time was experimentally determined to be about 2 s, which is in good agreement with a previous theoretical calculation. This agreement supports that the ortho-para conversion mechanism of the molecularly chemisorbed H₂ on Pd(210) is a two-step process based on the hyperfine-Coulomb excitation.

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Two nuclear-spin modifications exist for H₂, i.e., *ortho*-H₂ (*o*-H₂) and *para*-H₂ (*p*-H₂). Due to quantum-mechanical symmetry restrictions, the rotational (quantum number *J*) states of molecular hydrogen couple with its nuclear-spin states. *o*-H₂ and *p*-H₂ with parallel and antiparallel proton spins have odd and even rotational states, respectively, which can be characterized by rotational spectroscopy. Interconversion between these two species, *ortho-para* (*o-p*) conversion of H₂, is of great interest not only from a fundamental point of view but also in industrial applications such as H₂ liquification and storage. While for an isolated H₂ molecule the *o-p* conversion is forbidden, it is reported that the conversion is promoted on various surfaces [1,2]. In most of past studies on *o-p* conversion at surfaces, H₂ in the physisorption state via the van der Waals interaction was focused, in which the molecule is in a nearly-free rotational state. The rotational state and *o-p* conversion have been probed by either electron energy loss spectroscopy or a combination of H₂ desorption with the resonance-enhanced multiphoton ionization (REMPI) technique. In addition to the typical adsorption schemes of H₂, i.e., dissociative chemisorption and molecular physisorption, a novel adsorption of molecular chemisorption, where strong chemical hybridization between H₂ and a surface sets in, has been recognized to occur on various surfaces [3–7].

Recently, the rotational state and *o-p* conversion of H₂ in the molecular chemisorption state on Pd(210) acquired much attention [8–10]. Using rotational-state-selective temperature-programmed desorption (RS-TPD) a difference in the desorption energy between H₂(*J* = 1) and H₂(*J* = 0) was found, which was ascribed to confinement of H₂ in the highly anisotropic potential of the molecularly chemisorbed state [8]. Although determination of the *o-p* conversion time was also attempted, due to the limited time resolution of the RS-TPD

technique, it was not possible to track the change in the rotational-state population of H₂ at a surface residence time shorter than ~100 s, and no significant change in the *o-p* ratio was observed at a residence time of 150–2000 s, indicating a fast *o-p* conversion. Theoretical calculations [8] supported this interpretation by a calculated conversion time of ~2 s based on the two-step process via the Coulomb and Fermi contact interactions which was originally proposed for a physisorption system [11]. To verify the validity of this conversion mechanism in a chemisorption system, unambiguous experimental evidence of fast *o-p* conversion is highly desirable. In addition, while such rapid *o-p* conversion has been reported on Cu(510) under H₂ adsorption-desorption equilibrium condition where the conversion and the subsequent desorption of *p*-H₂ is balanced by adsorption of *o*-H₂ [12], a more direct measurement of the conversion time is still challenging.

In this Rapid Communication, we report an experimental verification of fast *o-p* conversion with the determination of conversion time of about 2 s for the system of molecularly chemisorbed H₂ on Pd(210). To probe the population in the rotational states and evaluate their time evolution we developed a pulsed H₂ beam apparatus combined with photostimulated desorption (PSD) and REMPI techniques. Reasonable agreement between our result and previous theoretical calculations suggests the occurrence of fast conversion via the two-step mechanism [11].

The experiments were carried out in an ultrahigh vacuum (UHV) chamber at a base pressure of 3.0 × 10^{−8} Pa with a doubly differentially pumped molecular beam source. The Pd(210) surface was cleaned by repeated cycles of Ar⁺ sputtering at room temperature and annealing at a surface temperature (*T*_s) of 1100 K, and oxygen exposure at *T*_s = 700–750 K followed by cooling in H₂. The sample could be cooled to 40 K by a closed-cycle He cryostat. The surface crystallographic order was checked by low-energy electron diffraction. Upon exposure of the clean surface to H₂, H₂ molecularly chemisorbs on the surface following dissociative chemisorption, which was confirmed by observing an

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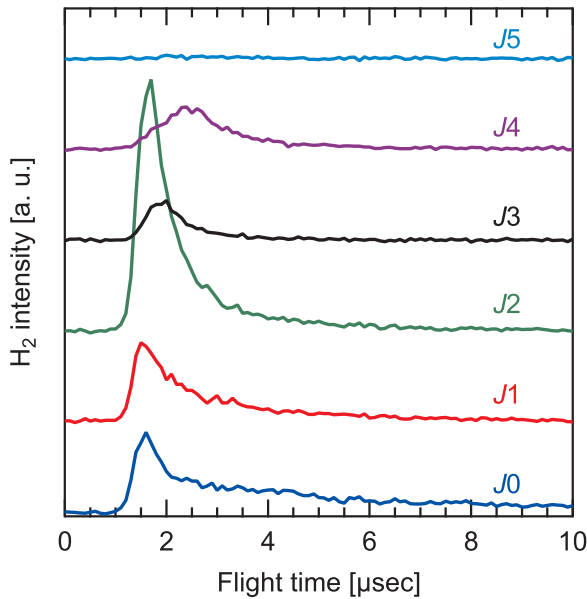


FIG. 1. TOF spectra of photodesorbed H_2 in $J = 0-5$ from a Pd(210) surface at $T_s = 50$ K after 6 Langmuir of normal H_2 exposure. The distance between the REMPI laser and the sample was 5 mm. The spectra were acquired by collecting the H_2^+ signal while changing the delay time between the PSD and REMPI lasers.

H_2 desorption signal in the temperature range of 50–100 K corresponding to the desorption of molecularly chemisorbed H_2 [5]. The chemisorbed H_2 molecules were detected by a combination of PSD and (2+1) REMPI techniques via the $E, F \ ^1\Sigma_g^+$ states [13,14]. The PSD was caused by irradiation of a slightly focused pulsed laser light at a wavelength of 532 nm and a laser fluence of 19 mJ/cm². The PSD laser irradiated the sample at an incidence angle of 25° from the surface normal with an irradiated area of about 3×4 mm². The desorbed H_2 molecules were J -state selectively detected by REMPI. The REMPI laser wavelength was fixed at the resonance of ~ 201 nm for the ionization of H_2 ($v = 0, J$). The ionized H_2 molecules were detected by a microchannel plate (MCP). Both PSD and REMPI lasers were run at a repetition rate of 10 Hz. All experiments in the present Rapid Communication were performed at $T_s = 50$ K. While the H absorption is known to occur for Pd surfaces [15–17], this process is kinetically hindered on Pd(210) at $T_s = 50$ K [7]. Thus, a potential influence of subsurface H in the present results can be excluded.

Figure 1 shows the time-of-flight (TOF) spectra for photodesorbed H_2 in the direction of 20° from the surface normal after 6 Langmuir (1 Langmuir = 1.33×10^{-4} Pa s) of normal H_2 exposure via background dosing. Unlike the physisorption systems in previous reports in which the lowest para ($J = 0$) and ortho ($J = 1$) states were only detected [13,14], in the present system significant intensities in the $J = 0-4$ states were detected. It is apparent that the intensity in $J = 2$ is the highest among $J = 0-4$. Additionally, we observed that the peak position in Fig. 1 shifts to the longer TOF with increasing J . It is worth noting that the thermal equilibrium population of isolated H_2 molecules in $J \geq 2$ states in the gas phase is negligible at a temperature of 50 K.

To monitor the time evolution of the population in each H_2 rotational state, we combined a pulsed molecular beam (MB) and the PSD-REMPI detection scheme. A schematic diagram of our experimental setup and pulse sequence driving the MB and two lasers is shown in Fig. 2. To guarantee the molecular chemisorption of incident H_2 occurs, we initially prepared an H-covered surface by 0.2 Langmuir of H_2 exposure before the MB-PSD-REMPI measurement. First a single H_2 pulse is sent to the surface with an incidence angle of 70° from the surface normal, and then after a certain period of delay time (t_{res}) the PSD laser irradiates the surface, and H_2 photodesorbed in the direction of 20° from the surface normal was ionized state selectively by REMPI laser focused at a distance of 5 mm from the sample surface. Since the depth of focus of the lens for the REMPI laser is estimated to be longer than 10 mm, the PSD signal in a wide range of desorption angle was detected in the present setup. For the time evolution measurement, the delay time between the two laser pulses was adjusted to the time when the desorbed hydrogen signal takes a maximum intensity for each J state. Note that the intensities of the J states shown in Fig. 4 do not correspond to the true J -state distribution due to the different TOF distribution between the J states. In Fig. 2, t_{res} corresponds to the residence time of H_2 on the surface. By varying t_{res} , therefore, the time evolution of the J -state distribution can be monitored. The arrival time of the H_2 MB pulse at the surface was accurately confirmed by measuring the ion signal with the REMPI laser set in the collinear direction with the MB. The pulsed MB was operated with a backing pressure of 5.9 bars and a valve opening time of 5 ms. With this setup, the time evolution of the *o*- and *p*- H_2 can be measured with a time resolution of about 5 ms. The velocity of the incident H_2 beam has been measured to be 2770 m/s by means of a Doppler technique [18]. It leads to the H_2 translational energy of 79 meV. To ensure the stability of the laser intensities, the PSD laser injection to the sample was controlled by a mechanical shutter as shown in the pulse sequence of Fig. 2, while the laser was continuously run. The REMPI laser was also run synchronously with the PSD laser during the measurement. The timing of the pulsed-valve opening and injection of two lasers as well as the opening of a mechanical shutter was controlled by electric pulses.

Figure 3 shows a series of the averaged $J = 1$ REMPI signals for residence times of 0.4, 1, 3, and 20 s after a single pulse of H_2 was deposited at $t = 0$. The signal intensity is zero until $t = t_{res}$, which means the signal due to the scattering of MB is negligibly small because the REMPI laser is continuously run throughout the measurement. At $t = t_{res}$, where the PSD laser starts to irradiate the surface by shutter opening, the signal intensity sharply rises. With shorter t_{res} , the intensity quickly decreases followed by a gradual decrease. With longer t_{res} , on the other hand, the intensity gradually decreases without a fast-decay component. The fast decay is caused by *o*-*p* conversion as detailed below, and the slow decay represents the H_2 coverage loss due to PSD. From the slow decay, the coverage loss of molecularly chemisorbed H_2 is estimated to be about 25% during PSD for 30 s. This coverage loss is replenished by the next MB pulse, and several cycles of MB-PSD-REMPI measurements were repeated for each t_{res} as shown in the inset of Fig. 3. The area intensities for the REMPI signals within 0.6 s after shutter

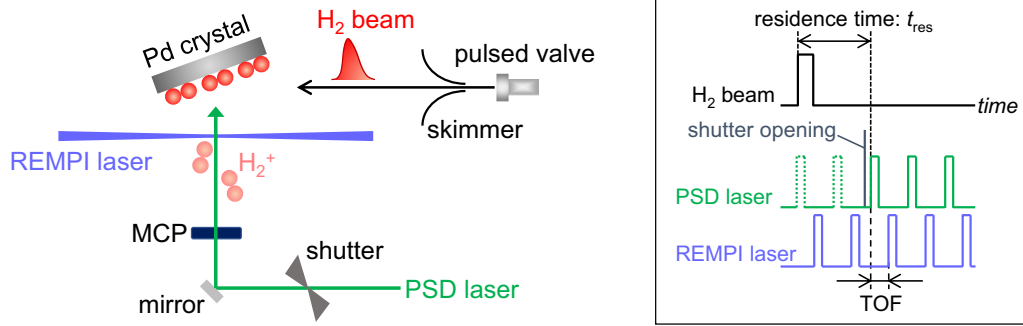


FIG. 2. Schematic diagram of the experimental setup and pulse sequence driving the molecular beam and two lasers for the *o-p* conversion measurement. An H_2 beam pulse is formed in a pulsed molecular beam expansion. After a skimmer H_2 passes through a differential-pumping stage (not shown) and enters a UHV chamber. After a certain period of delay time (residence time) following the H_2 deposition, the PSD laser at a repetition rate of 10 Hz photodesorbs H_2 on the surface for 30 s (green line). The PSD laser irradiation onto the surface is controlled by mechanical shutter opening/closing. The photodesorbed H_2 is state-selectively ionized by REMPI (light-purple line) and detected by an MCP. The delay time between the PSD and REMPI laser pulses corresponds to the TOF.

opening were collected to analyze the time evolution of the H_2 population in each rotational state, because the conversion time was found to be about 2 s as shown later. The area intensities at several J states are plotted as a function of t_{res} in Fig. 4. As shown in Fig. 1, the intensity of photodesorbed H_2 in the $J = 2$ state is the highest over entire t_{res} , and a clear intensity change was found for $J = 0$ and $J = 1$; the $J = 1$ intensity decreases while the $J = 0$ intensity increases by approximately the same amount. On the other hand, the changes in other J states are less drastic. A gradual increase with some fluctuations in the intensity for the $J = 2$ state and a slight decrease in the intensity for the $J = 3$ state, respectively, with increasing t_{res} were observed, while the intensity for the $J = 4$ state is nearly constant over entire t_{res} . These results imply that the rotational-state distribution of H_2 photodesorbed from the chemisorbed state apparently varies with time. Here, the rotational-state distribution is discussed in terms of *o*- and *p*- H_2 species. In Fig. 5, *o*- H_2 (sum of

$J = 1$ and $J = 3$) and *p*- H_2 (sum of $J = 0$, $J = 2$, and $J = 4$) intensities obtained from Fig. 4 are plotted as a function of t_{res} . While the sum of the *o*- H_2 and *p*- H_2 intensities is constant within the experimental accuracy, as the residence time on the surface increases, the intensity for *o*- H_2 decreases and that for *p*- H_2 increases, definitely indicating the occurrence of the *o-p* conversion. Note that the observed initial *o-p* ratio was smaller than 3, although normal H_2 with an *o-p* ratio of 3 was used as the incident beam. This is due to the fact that the surface is partially precovered with H_2 in addition to H prior to the impingement of MB H_2 . Also H_2 molecular chemisorption probability may potentially depend on the H_2 rotational state

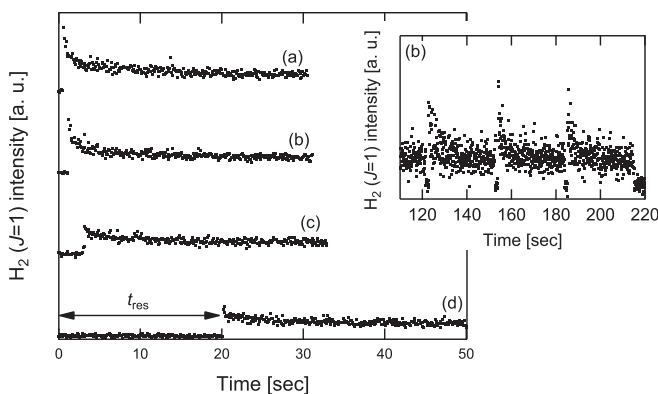


FIG. 3. Intensities of photodesorbed H_2 for $J = 1$ detected by REMPI at different residence times: $t_{\text{res}} =$ (a) 0.4 s, (b) 1 s, (c) 3 s, and (d) 20 s. These data points were obtained by averaging over the data from repeated measurements. The origin of the time axis corresponds to the opening of the pulsed valve of the molecular beam source. The representative of individual data of $t_{\text{res}} = 1$ s is shown in the inset.

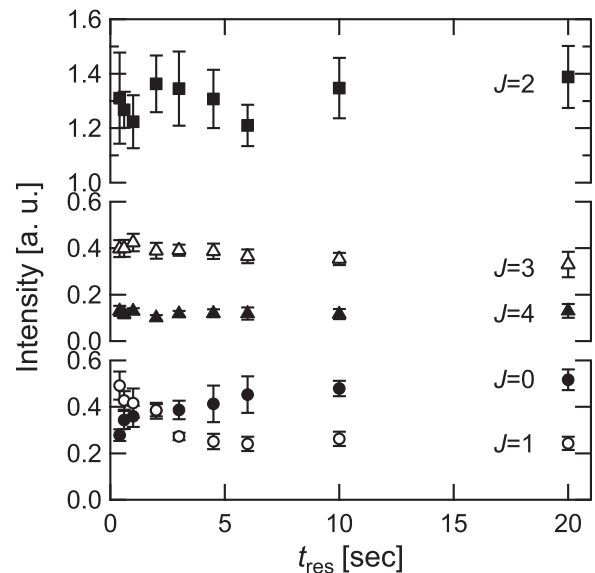


FIG. 4. Time evolution of the photodesorbed H_2 intensities derived from the area intensities for the REMPI signals within 0.6 s after shutter opening, for $J = 0$ (filled circle), 1 (open circle), 2 (filled square), 3 (open triangle), and 4 (filled triangle). The error bars represent the standard deviation of several measurements. For clarity, the data sets for the $J = 2$, 3, and 4 are plotted separately from those of $J = 0$ and $J = 1$.

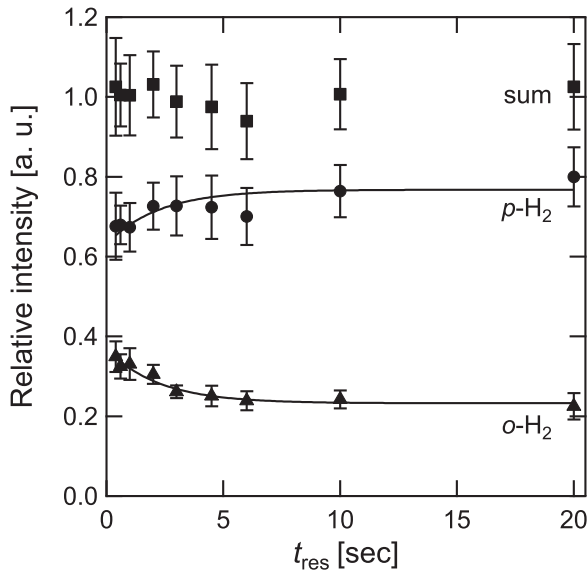


FIG. 5. Time evolution of the photodesorbed H_2 intensities for $o\text{-H}_2$ (triangle), $p\text{-H}_2$ (circle), and their sum (square). $o\text{-H}_2$ and $p\text{-H}_2$ intensities are derived from the summation of $J = 1$ and $J = 3$, and of $J = 0$, $J = 2$, and $J = 4$ intensities shown in Fig. 4, respectively. The solid line for $o\text{-H}_2$ is a fit using an exponential function, and that for $p\text{-H}_2$ is based on the parameters obtained from the fitting of the $o\text{-H}_2$ data.

as previously reported for H_2 dissociation on $\text{Pd}(111)$ [19], which would affect the initial o - p ratio. The conversion time can be determined to be 2.2 ± 1.2 s by fitting the data for $o\text{-H}_2$ with a single exponential function. This conversion time is remarkably short compared with those previously reported for physisorption systems; the conversion time was hundreds to thousands of seconds [20–24]. A similar value of around 1 s was obtained from the analysis based on the adsorption-desorption equilibrium for the H_2 adsorbed on the step site of $\text{Cu}(510)$ [12]. Using RS-TPD and its kinetic simulations, the conversion time of H_2 on $\text{Pd}(210)$ was estimated to be of the order of 1 s [8]. In contrast to these studies, the present study unambiguously concludes the conversion time is 2.2 ± 1.2 s and this value is in agreement with the theoretically estimated conversion time of ~ 2 s [8] based on the two-step mechanism involving electron exchange between the adsorbed H_2 and the Pd surface and the Fermi hyperfine contact interaction [1]. Note that the theoretical conversion time was obtained for H_2 at the stable position and orientation. The molecular motion such as rotation and zero-point vibration [9,10] has to be considered for an accurate estimation. Nevertheless, the present agreement supports that the two-step model is operative for the o - p conversion of chemisorbed H_2 on $\text{Pd}(210)$. As discussed by Svensson and Andersson [12], the observed fast conversion may be a general feature, which is associated with the short H_2 -metal bond length. For $\text{H}_2/\text{Cu}(510)$, the H_2 -Cu bond length was calculated to be 1.8 Å [25]. A similar bond length was also reported for $\text{H}_2/\text{Pd}(210)$ [9,26]. When the H_2 -metal bond length is short, the electron exchange processes between H_2 and the surface due to Coulomb and hyperfine interactions are enhanced in the two-step model, which leads to fast o - p conversion. Note that nearly equilibrated values

of o - and $p\text{-H}_2$ intensities at $t_{\text{res}} = 20$ s in Fig. 5 are 0.2 and 0.8 respectively, which are different from that of the RS-TPD experiment [8]. This could be due to the fact that in contrast to our measurement at $T_s = 50$ K, the data obtained by RS-TPD involves thermal desorption of H_2 at about 75 K, which inevitably leads to a higher $o\text{-H}_2$ population.

As the origin for the presence of high J states, the following two contributions are considered. Firstly, the H_2 adsorption state is discussed. Previous studies reported that the H_2 adsorption potential for $\text{Pd}(210)$ is highly anisotropic [8,9]. The calculated potential energy curves show a deep potential well for the orientation with the H_2 molecular axis in the parallel orientation, while it shows a shallow well for the perpendicular orientation, which means the potential is highly anisotropic. This anisotropic potential induces lifting of the rotational-state degeneracy. The lowest $o\text{-H}_2$ in the adsorption state is doubly degenerate ($m = \pm 1$), while gas-phase $J = 1$ H_2 is triply degenerate. Hence, the adsorbate H_2 is in a sort of two-dimensional rotor state [26,27], and the eigenstate in the adsorbed H_2 cannot be described by the gas-phase rotational state. The rotational wave function of adsorbed H_2 can be expressed by linear combination of those of a free molecule [10]. In that case, it would be conceivable that photodesorbed H_2 exists in high J states reflecting the wave function of adsorbed H_2 states. Secondly, the observation of the high J states may be associated with the photodesorption process. We consider that the desorption of adsorbed H_2 is induced by electronic transition. While several models for photodesorption were proposed in the past, in general, adsorbed molecules gain the energies in translational and internal degrees of freedom during the excitation and deexcitation processes between an excited state and the ground state. Although the amount of energy transfer to the molecular motion depends on the shape and the lifetime of the excited state relevant to the photodesorption, the desorption process potentially results in the occupation of high J states. To completely understand the desorption process, further experimental and theoretical studies are necessary, which will be the subject of a future study.

An interesting result in the present study is the time evolution of the H_2 population in high J states: In contrast to the changes in the $J = 0$ and 1 states, the intensities of the $J \geq 2$ states are almost constant. The rotational distribution within $p\text{-H}_2$ and $o\text{-H}_2$ would not change as a function of t_{res} , because the rotational distributions are expected to quickly reach the thermally equilibrium state after H_2 adsorption from MB, aside from the o - p conversion. Previous experimental and theoretical studies revealed that the configuration of the H_2 adsorption well depends on the local atomic H coverage in the vicinity of the step edge Pd atom where H_2 adsorbs. While the anisotropic potential is retained up to an atomic H coverage of two monolayers per surface unit cell, its anisotropy weakens with increasing H coverage [5,9,26]. This indicates that neighboring H atoms affect the adsorbed H_2 wave functions and its conversion, and the rotational distribution and conversion rate might depend on the local hydrogen coverage. Thus, the time evolution of the rotational distribution observed in Fig. 4 is possibly ascribed to the difference in the local hydrogen coverage.

In the present study, we were able to probe the population change in the H₂ rotational states in a subsecond time resolution and experimentally demonstrate the fast *o-p* conversion of molecularly chemisorbed H₂ on Pd(210) using a combination of MB and PSD-REMPI techniques. Verification of the conversion model by the present study pushed forward our understanding of the *o-p* conversion on surfaces.

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