3–5 Insight into Designing Highly Efficient *Ortho-Para* Hydrogen Conversion Catalysts
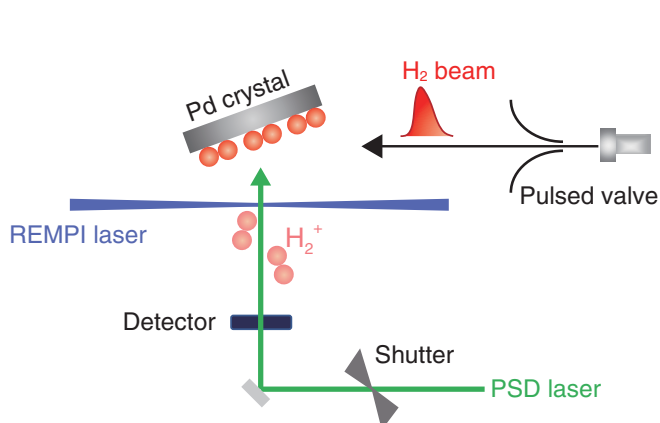## －Demonstration of Fast *Ortho–Para* Conversion of H_2 on a Stepped Surface－

Fig.3-10 Development of a measurement method for surface adsorbed H_2 *ortho*-to-*para* (*o-p*) conversion time based on a combination of a pulsed molecular beam, photo-stimulated desorption (PSD), and resonance-enhanced multiphoton ionization (REMPI) techniques

First, a pulsed H_2 beam is sent to the surface, and then after a certain period of delay time the PSD laser irradiates the surface, and the photodesorbed H_2 is ionized state-selectively by the REMPI laser. Changing the delay time between the H_2 beam and PSD laser allows us to track the change in the nuclear-spin state of H_2 with surface adsorption time.

Fig.3-11 Time evolution of the photodesorbed H_2 intensities for *o*-H_2, *p*-H_2, and their sum

As the residence time on the surface increases, the intensity of *o*-H_2 decreases whereas that of *p*-H_2 increases. The conversion time is determined to be 2.2 ± 1.2 s by fitting the data for *o*-H_2 with a single exponential function.

Hydrogen is promising as a clean energy source that does not produce greenhouse and harmful gases. Two nuclear-spin modifications exist for H_2: *ortho*-H_2 (*o*-H_2) and *para*-H_2 (*p*-H_2). When liquefying and storing hydrogen, it is necessary to para-hydrogenate the *o*-H_2 before liquefaction because liquefying hydrogen gas containing *o*-H_2 mixed in it causes heat generation due to the rotational energy of *o*-H_2. This phenomenon is called the boil-off problem. Although it is known that *ortho*-to-*para* (*o–p*) conversion occurs on solid surface, the conversion is not efficient. In addition, the detailed conversion mechanism still remains unclear at present. Therefore, unraveling the conversion mechanism and developing a highly efficient conversion catalyst based on this knowledge are crucial to utilize hydrogen as an energy source.

In most of the past studies on *o–p* conversion on solid surfaces, H_2 in the physisorption state was focused. However, it is known that a unique molecular chemisorption of H_2 occurs on some stepped surfaces in addition to the typical adsorption scheme of physisorption. The previous studies indicate that the *o–p* conversion of molecularly chemisorbed H_2 is faster than that of physisorbed one. However, because of the limited time resolution of the measurement techniques used, it was difficult to probe the *o-p* conversion. Thus, a direct measurement of the conversion time was not possible. Against this background,
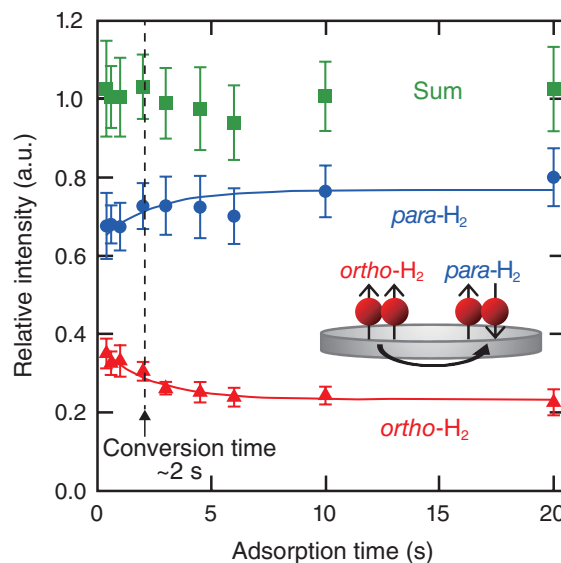
we recently developed a new method to determine the *o–p* conversion time by using a combination of a pulsed molecular beam, photostimulated desorption, and resonance-enhanced multiphoton ionization techniques. In this method, the time resolution was improved by about two orders of magnitude (Fig.3-10). We successfully tracked the change in the H_2 nuclear-spin state and experimentally determined the *o–p* conversion time of the molecularly chemisorbed H_2 on palladium (Pd) (210) face at a surface temperature of 50 K to be about 2 s (Fig.3-11). This value is 2–3 orders of magnitude smaller than those reported for physisorption systems, implying that the *o–p* conversion occurs rapidly. H_2 molecularly chemisorbs on top of the step-edge Pd atom. This fast conversion of H_2 in the molecular chemisorption state is a result of the strong interaction between H_2 and the Pd substrate which is ascribed to the unique step surface structure. The present study indicates the importance of the surface structure in *o–p* conversion and is expected to lead to the design of highly efficient conversion catalysts.

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Reference
Ueta, H. et al., Direct Measurement of Fast Ortho-Para Conversion of Molecularly Chemisorbed H_2 on Pd(210), Physical Review B, vol.102, issue 12, 2020, 121407(R), 5p.