Rotational state and ortho-para conversion of H_2 on solid surfaces

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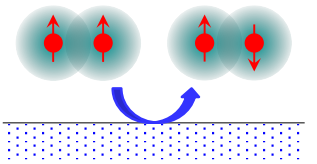


KF, TS, Prog. Surf. Sci. 88 (2013) 279.

Spin-isomers: rotational state

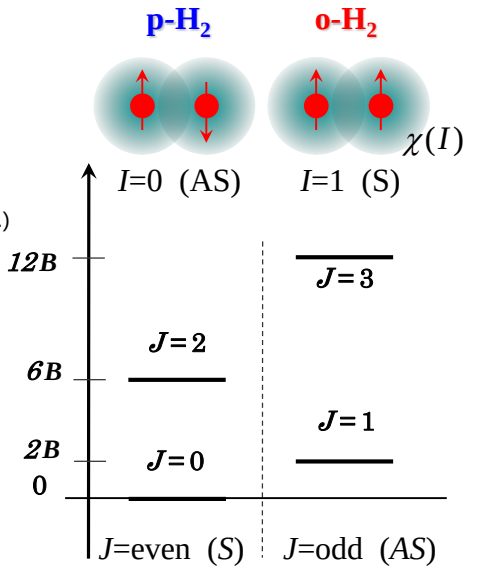
Conversion time in gas phase

$\tau(gas) \approx 10^{20}$ s （> 13.7 by）

(K. Pachucki et al., PRA 77 (2008) 030501.)

Conversion via interaction with

- H, H^+
- Solid surfaces



Surface-catalyzed op conversion

γ: collision rate

S: sticking probability

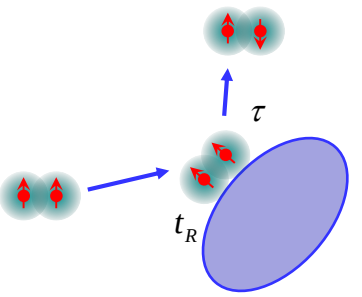
LT ortho to para
conversion probability: P

$$P = S\gamma \frac{\tau^{-1}}{t_R{}^{-1} + \tau^{-1}}$$

$$t_R = t_0 \exp(\frac{E_d}{kT})$$

$$t_0 \approx 10^{-11} - 10^{-13}$$

・・・, but not as simple as thought



t_R: residence time

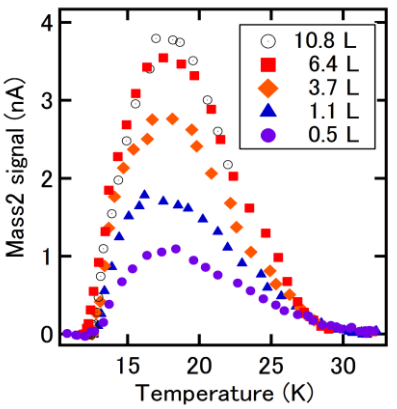
E_d: desorption energy

τ: op conversion time

Prog. Surf. Sci. 88 (2013) 279.

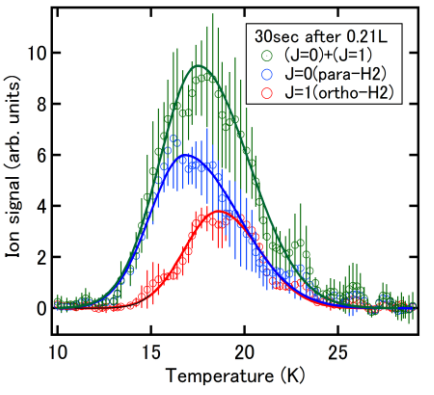
Temperature-Programmed Desorption (TPD)

Ag(111)



T_d~17 K

E_d =28 meV



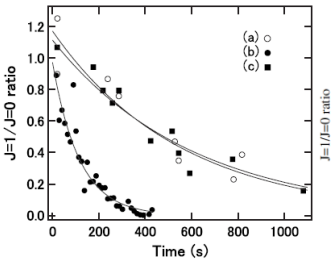
J-selective detection

Time evolution of o/p ratio

T. Sugimoto, KF, PRL 112, 146101 (2014).

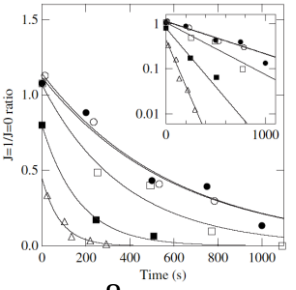
H_2 o-p conversion time: physisorption

Ag: diamag. metal



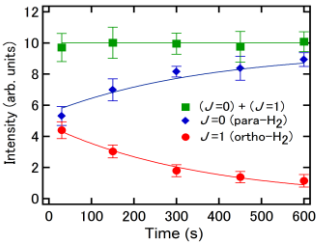
$\tau \approx 700\,\mathrm{s}$

O_2: spin triplet



$\tau \approx 8\,\mathrm{s}$

Amorphous Ice
diamag. insulator



$\tau \approx 400\,\mathrm{s}$

[Mechanism]

Electron exchange (Ilisca model)

Magnetic-field-induced (Wigner model)

Electric-field-induced

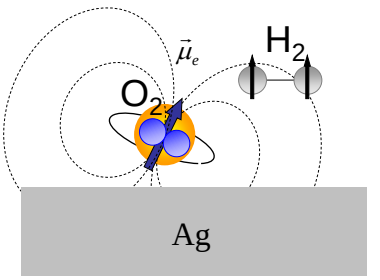
(PRL 90 (2003) 096103; PRB 79 (2009) 085408; Nat. Phys. 7 (2011)307)

H_2 op conversion mechanism

✓ Magnetic-field induced

Inhomogeneous magnetic field

$\tau \approx 10\,\mathrm{s}$

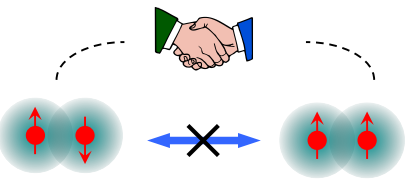


Different torques for the two protons

✓ Electronic mechanism

$\tau \approx 100 - 1000\,\mathrm{s}$

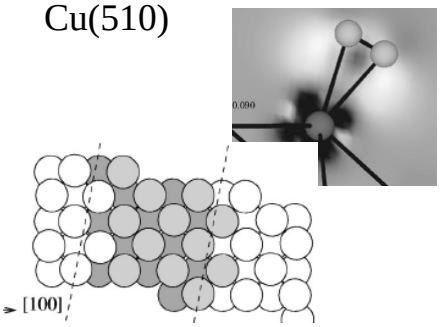
Inter-mixing between ortho and para in the excited states



(E. Ilisca, Prog. Surf. Sci. 41 (1991) 217.)

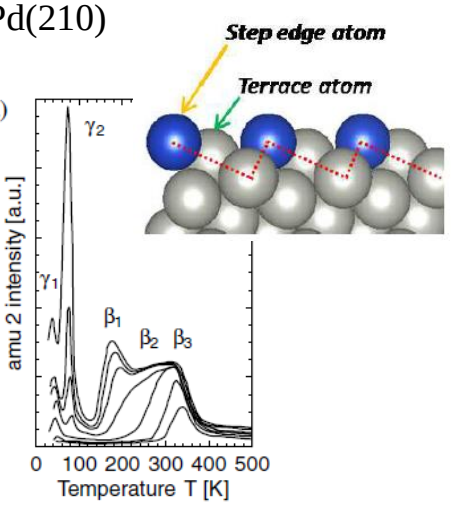
Strongly bound H_2: molecular chemisorption

Cu(510)



L. Bengtsson et al., PRB 61, 16921 (2000)

Pd(210)



P. K. Schmidt et al., PRL 87, 096103 (2001).

✓ Strong binding
- op conversion?
- Rotational state?

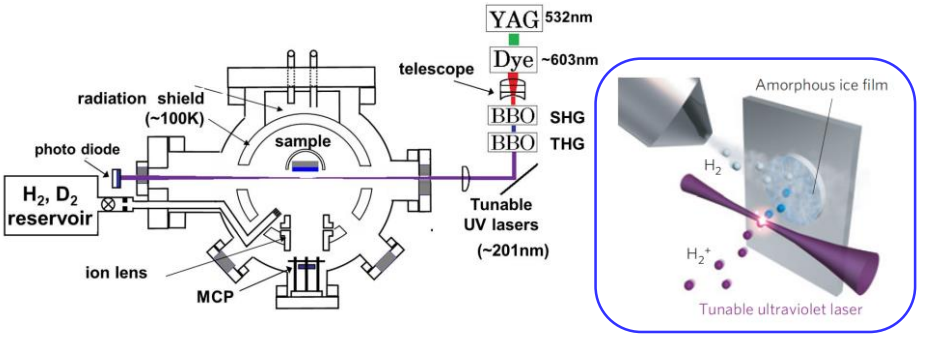
Experiment & theory

1. Sample: Pd(210) in UHV

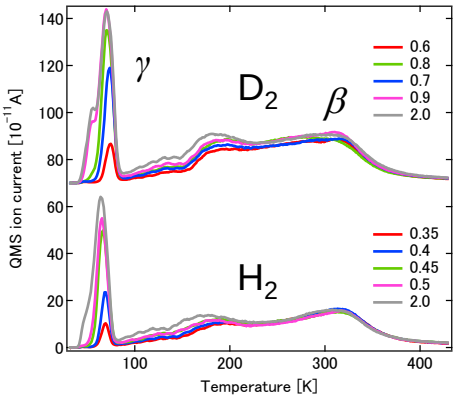
   n-H_2 (o/p=3), p-H_2, o-H_2 (separation with Al_2O_3)

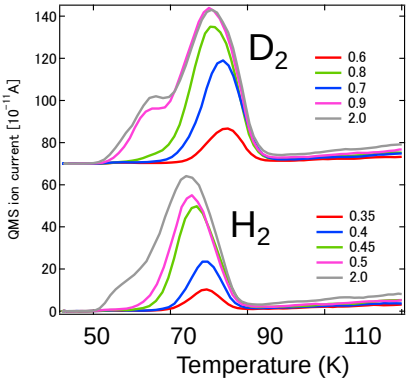
   Detection: REMPI via E,F

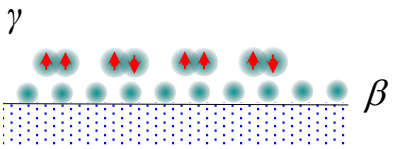
2. DFT & quantum simulation



Pd(210) TPD: isotope dependence





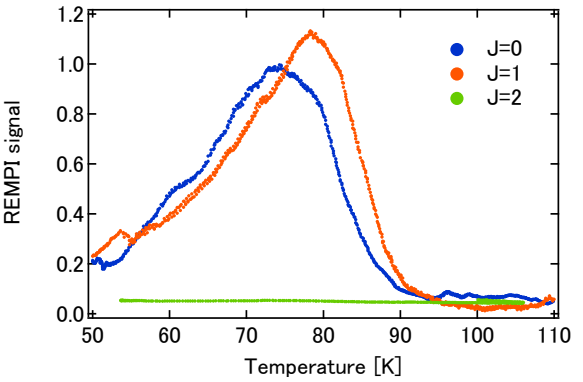


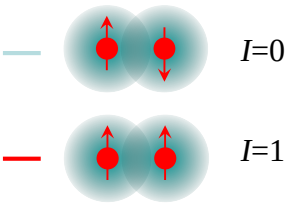
- D_2: 82.6 K
  E_d ~ 213 meV
- H_2: 76.3 K
  E_d ~ 203 meV

due to Zero-point energy

(S. Ohno et al., in prep.)

State-selective TPD: Pd(210)





Redhead's analysis assuming $\nu = 10^{13}$ [s^{-1}]

ΔT_p=5 K

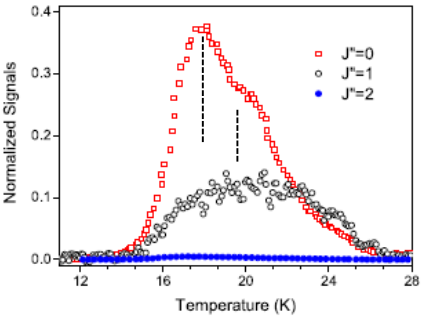
T_p=74K→ ~195meV

T_p=79K→ ~205meV

→ **ΔE=10 meV**

(S. Ohno et al., in prep.)

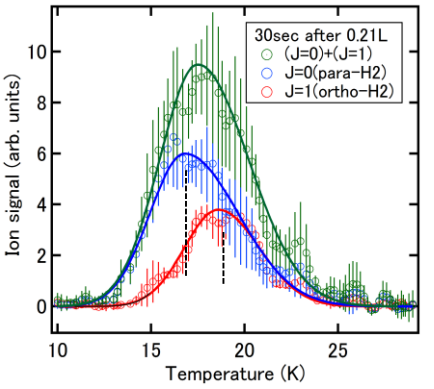
D_2 on amorphous ice



ΔT_p~1.2 K

L. Amiaud et al., PRL 100, 056101 (2008)

H_2 on Ag(111)



ΔT_p~2 K

T. Sugimoto, KF, PRL 112, 146101 (2014).

Potential anisotropy

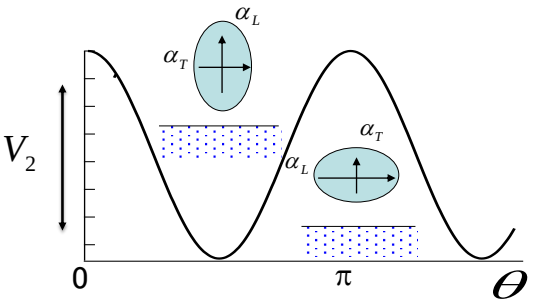
Potential: orientation-dependent

$$V_0(Z,\theta)+V_2(Z,\theta)P_2(\cos\theta)$$

Rotational motion:

$$\frac{J^2}{2I} > V_2$$

quantum rotor

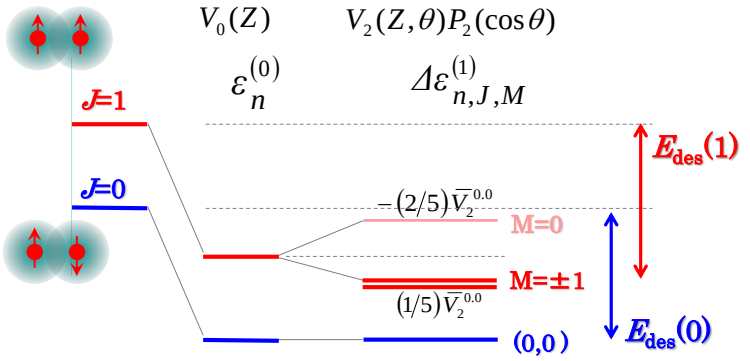


SS 152, 702 (1985); SS 175, L753 (1986)

Effects of the anisotropic potential

- Energy diagram: 1st order perturbation

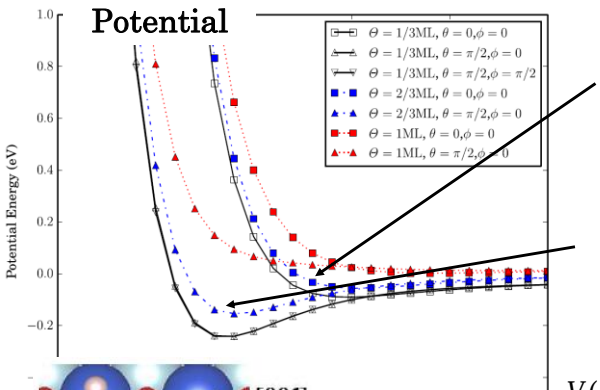
$$V_0(Z,\theta)+V_2(Z,\theta)P_2(\cos\theta)$$



gas adsorbed on surface

SS 152, 702 (1985); PRL 112, 146101 (2014).

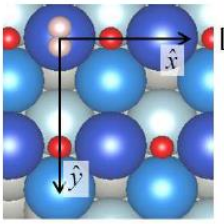
First-principles calculations with DFT



■ :

▲ :

more stable



$V(x,y,z,\ \theta)$

$$H=\frac{p^2}{2M}+\frac{J^2}{2I}+V(x,y,z,\ \theta)$$

→Eigen state

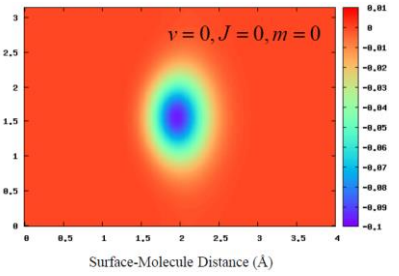
Quantum simulation

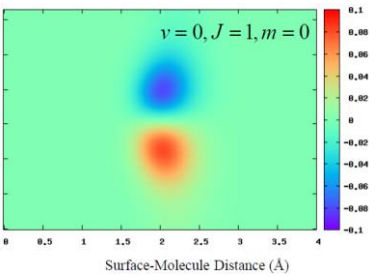
(J, M): E

(J=0, M=0): E=-202.3 meV

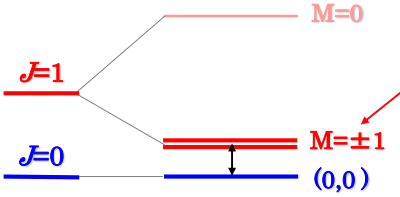
(J=1, M=0): E=-150.0 meV

(J=1, M=±1): E=-197.6 meV





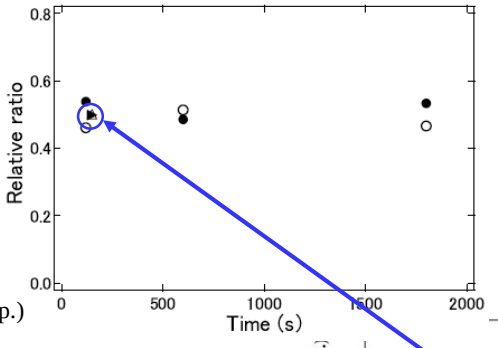
ΔE^g = 14.7 meV



Stabilization →strongly bound

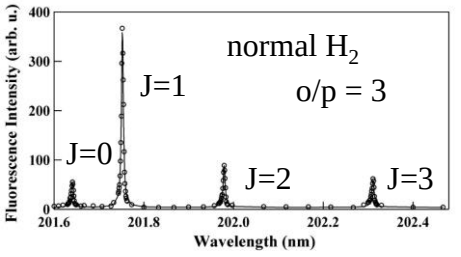
ΔE^a = 4.7 meV

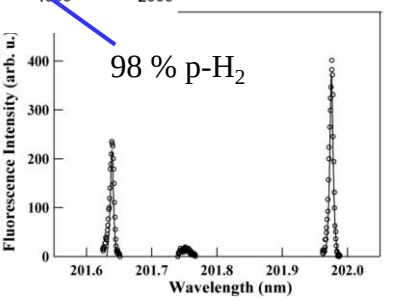
Time evolution of ortho and para



$\tau << 100$ s

(S. Ohno et al., in prep.)





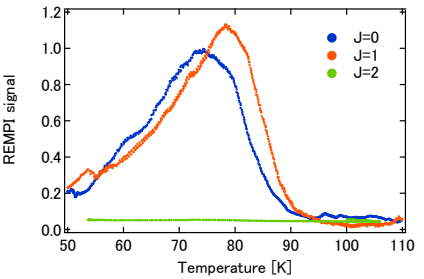
Thermal desorption rate

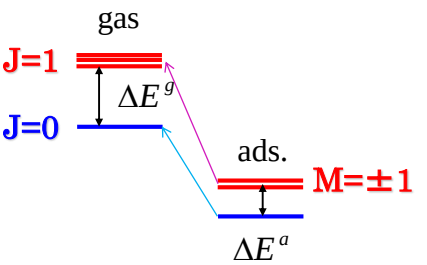
$$I_J \cong \left(\frac{f_R^T}{f_R^A} \nu \right) \exp(-\frac{E_d}{kT})$$

→ Rotational degeneracy ratio at initial and final states

$$\frac{I_{J=1}}{I_{J=0}} = R_a \frac{g^g_{J=1} / g^a_{J=1}}{g^g_{J=0} / g^a_{J=0}} \exp(-\frac{\Delta E^g - \Delta E^a}{kT})$$

R_a : population ratio

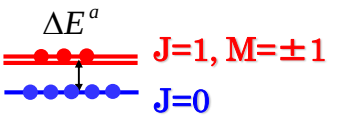




✓ If op conversion is fast,

ortho/para population ratio

$$R_a = \frac{g_{I=1}}{g_{I=0}} \frac{g^a_{J=1}}{g^a_{J=0}} \exp(-\frac{\Delta E^a}{kT})$$



Desorption intensity ratio

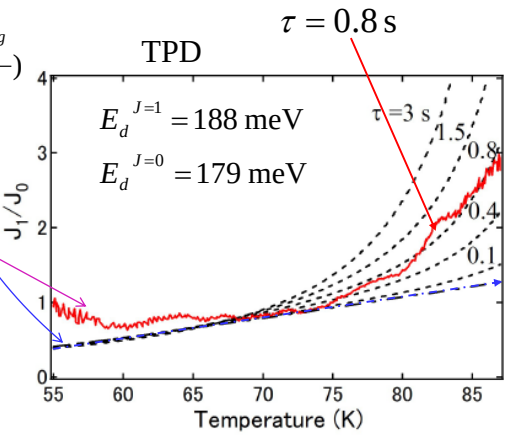
$$\frac{I_{J=1}}{I_{J=0}} = \frac{g_{I=1}}{g_{I=0}} \frac{g^g_{J=1}}{g^g_{J=0}} \exp(-\frac{\Delta E^g}{kT})$$

✓ Simulation with τ

Thermal desorption
of J=1 & J=0

Transition between
of J=1 & J=0 with τ

(S. Ohno et al., in prep.)

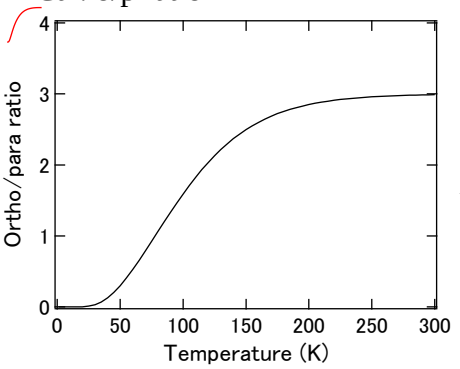


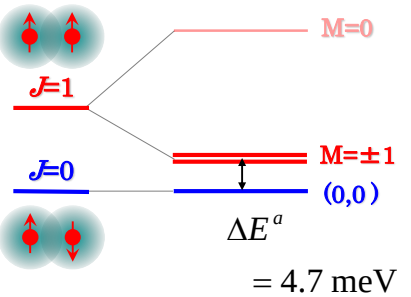
Ortho-para ratio on Pd(210)

$$R_a = \frac{g_{I=1}}{g_{I=0}} \frac{g^a_{J=1}}{g^a_{J=0}} \exp\left(-\frac{\Delta E^a}{kT}\right)$$

3 2

Cal. o/p ratio





= 4.7 meV

With radiation-induced desorption

effective para-ortho conversion

Summary

Rotational state and op conversion of H_2
in molecular chemisorption on Pd(210)

- Potential anisotropy: preference of flat-lying orientation
  → higher desorption temp. of J=1 than J=0
- Fast op conversion: $\tau = 0.8$ s

Cf. physisoption
electronic mechanism: τ ~100-1000 s
magnetic mechanism: τ ~1-10 s

High ortho-para ratio
in the adsorption state on Pd(210)