

物理吸着水素分子の非弾性トンネル分光に観られる 回転励起散乱のメカニズム

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Mechanism of rotational excitation observed in inelastic-electron-tunneling spectroscopy for physisorbed H₂

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A quantum rotor of molecular H₂ retains its rotational motion in a physisorbed state [1-3]. Rotational and vibrational spectroscopy at the single molecule level has been recently succeeded for *para*-H₂ ($J: 0 \rightarrow 2$, Fig. 1) weakly physisorbed on surfaces [4-6]. In spite of the remarkable progress of inelastic-electron-tunneling (IET) spectroscopy technique with scanning-tunneling microscope (STM), mechanism of IET mediated by rotational excitation of H₂ remains to be clarified.

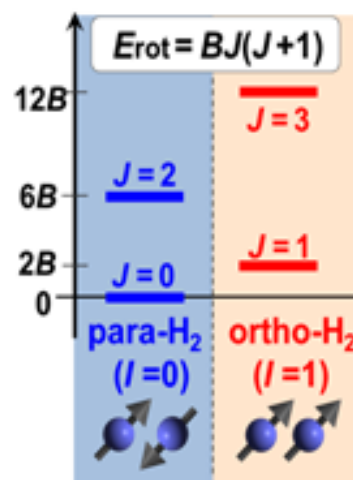


Figure 1. Rotational energy diagram of nuclear spin isomers of *para*-H₂ and *ortho*-H₂ [1-3].

Here we propose a new microscopic IET model based on the resonant coupling [7,8] through rotation-electron interactions between the STM-tip, physisorbed H₂, and a metal surface (Fig. 2). In this model, an electron with σ symmetry in the tip tunnels into the $2p\sigma_u$ or $1s\sigma_g$ state of H₂ through virtual negative (H₂⁻) or positive (H₂⁺) ion

formation, respectively. In this formalism, the anisotropic term of the electron transfer t and U induce the rotational excitation of H_2 , which leads to a rotational selection rule of $\Delta J=+2$, $\Delta J_z=0$.

With this model, we analyzed the observed rotational spectrum in the IET spectra of H_2 physisorbed on Au(110) [4]. Potential anisotropy derived from the peak shift is in good agreement with our DFT calculation showing that rotational symmetry of H_2 in the nanocavity between the STM-tip and Au(110) is significantly broken.

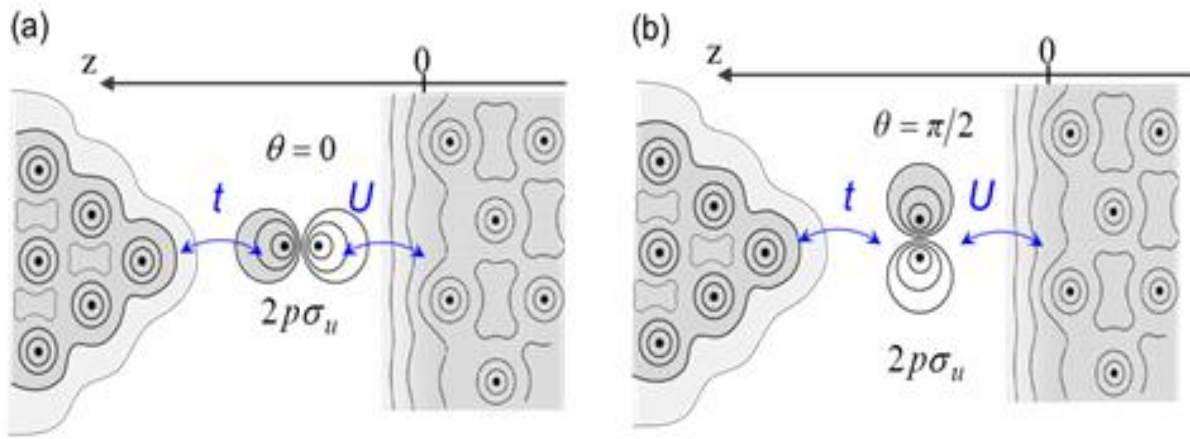


Figure 2. (a) Schematic diagram of molecular-axis angle (θ) dependent transfer matrix elements t between STM-tip and H_2 , and weak hybridization interaction U between H_2 and substrate through the $2p\sigma_u$ orbital of virtual H_2^- state for $\theta=0$ and (b) $\theta=\pi/2$ configuration.

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