Mechanism of rotational excitation observed in inelastic-electron-tunneling spectroscopy for physisorbed H$_2$

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A quantum rotor of molecular H$_2$ 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-H$_2$ (J: 0→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 H$_2$ remains to be clarified.

Here we propose a new microscopic IET model based on the resonant coupling [7,8] through rotation-electron interactions between the STM-tip, physisorbed H$_2$, 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 H$_2$ through virtual negative (H$_2^-$) or positive (H$_2^+$) ion
formation, respectively. In this formalism, the anisotropic term of the electron transfer $t$ and $U$ induce the rotational excitation of $\text{H}_2$, 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 $\text{H}_2$ 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 $\text{H}_2$ in the nanocavity between the STM-tip and Au(110) is significantly broken.

![Figure 2](image)

**Figure 2.** (a) Schematic diagram of molecular-axis angle ($\theta$) dependent transfer matrix elements $t$ between STM-tip and $\text{H}_2$, and weak hybridization interaction $U$ between $\text{H}_2$ and substrate through the $2p\sigma_u$ orbital of virtual $\text{H}_2^-$ state for $\theta=0$ and (b) $\theta=\pi/2$ configuration.