

Two competing mechanisms for photoinduced Cs dynamics on Cu(111)

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Femtosecond pump-probe spectroscopy has clarified the generation mechanism of photoinduced coherent nuclear motions for various systems ranging from isolated molecules to bulk solids. However, the mechanism for adsorbates on metals is less explored and the most fundamental question remains to be answered: What type of electronic transitions is responsible for kicking the adsorbates? In the present paper, we report our experimental and theoretical studies on this question in the photoinduced coherent nuclear motions of Cs adsorbed on Cu(111). Contrary to our previous reports on the other alkalis, where substrate-mediated excitations were inferred exclusively, we show signatures of surface-localized processes whose contribution depends on excitation photon energy. Time-resolved SHG measurement with ultra-high vacuum has been done in the manner previously reported [1]. We have found that the initial phase of the coherent vibration of the Cs-Cu stretching mode shows marked excitation wavelength (λ_{ex}) dependence: the oscillation shows sin-like behavior for $\lambda_{\text{ex}}=800$ nm, while cos-like oscillations were observed for $\lambda_{\text{ex}}<560$ nm. In addition, the power dependence of the initial amplitude shows a strong saturation behavior at $\lambda_{\text{ex}}=800$ nm, which indicates the excitation mechanism depends on the pump photon energy. The adsorbate-metal surface systems generally have a few metastable surface-localized excited states embedded in the metal continuum states. We consider a simplified three-state model [2] consisting of the ground, surface-localized excited, and background continuum states. Under the resonant excitation, the nuclear wavepacket simulation actually gives the sin-like oscillation and the saturation tendency. The experiment with $\lambda_{\text{ex}}=800$ nm is the first experimental realization of the transient-adsorbate mediation mechanism recently proposed in [2]. For $\lambda_{\text{ex}}<560$ nm, the substrate excitation channels open. The substrate-mediated hot electrons scatter on the surface-localized state. The corresponding electronic state gives the cos-like oscillation. We propose that these two mechanisms are fundamental for adsorbates on metals. In both mechanisms, the surface-localized state plays essential roles to displace the adsorbate position.

[1] K. Watanabe, K. Inoue, I. F. Nakai, M. Fuyuki, and Y. Matsumoto, Phys. Rev. B, **80**, 075404 (2009).

[2] T. Yasuike and K. Nobusada, Phys. Rev. B **80**, 035430 (2009).