Excitation mechanism and ultrafast vibrational wavepacket dynamics of alkali-metal atoms on Pt(111)

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Abstract

We have investigated experimentally and theoretically the mechanism for the coherent excitation of stretching vibrational motions of alkali-metal atoms (Cs and K) on a Pt(111) surface and the electronic states involved in this excitation process. The coherent motions were initiated by ultrashort optical pulses and their dephasing processes were monitored by time-resolved second harmonic generation (TR-SHG). TR-SHG traces showed the oscillating modulations of 2.3–2.4 THz for Cs and 4.5–5.2 THz for K-covered surfaces, which are characteristic to the stretching vibrations of the alkali-metal atoms. The first-principles calculations on Cs/Pt(111) based on the density functional theory revealed the strong hybridization between the 6s and 6p orbitals of Cs when Cs is adsorbed on Pt(111). The stretching frequencies estimated from the potential energy curve along this coordinate were in reasonable agreement with the observed ones. Moreover, the calculations on the Pt(111)–(2 × 2)Cs indicate that there is a Cs-induced unoccupied band located in the energy range of 1–2 eV above the Fermi level. The electron density of this band is localized at the vacuum side of Cs and shows the anti-bonding feature with respect to the Cs–Pt bond. Thus, this band is a possible candidate responsible for the coherent excitation of the stretching mode via the impulsive resonant Raman process.
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1. Introduction

Coherent excitation of nuclear motion is the first step toward the coherent control of nuclear dynamics including chemical reactions. There have been extensive studies on the coherent control in the gas [1] and condensed phases [2], but little

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attention has been paid for adsorbates on metal surfaces. Recently, we have investigated the coherent excitation and dephasing of the Cs–Pt stretching vibration on Pt(1 1 1) by time-resolved second harmonic generation (TR-SHG) [3,4]. It has been found that the frequency, initial phase, and modulation depth in the TR-SHG traces depend on many factors including the coverage, surface temperature, and pump fluence [5].

A vibrational wavepacket on the potential energy surface of the electronic ground state can be created by impulsive Raman scattering with an ultrashort optical pulse whose coherent energy width exceeds the energy separation between the adjacent vibrational states. According to the theory of impulsive Raman scattering using the perturbative density matrix formalism [6,7], the initial phase of the created wavepacket motion is sine-like if photon energy is off resonant with the electronic transition of a molecule. When photon energy is close to the resonance energy of the electronic transition, the Raman scattering cross section is strongly enhanced and the initial phase of the wavepacket motion becomes cos-like if the potential minimum of the electronically excited state is displaced from that of the ground state. Therefore, the amplitude and the phase of the nuclear wavepacket motion depend on the energy location and the shape of the potential energy surface of the excited state with respect to the ground state.

The electronic structure and the bonding scheme of alkali-metal atoms on metal surfaces have been extensively studied in the past [8,9]. The work function of a metal decreases significantly by the adsorption of alkali-metal atoms owing to the charge redistribution at the interface between the alkali-metal adlayer and the substrate. The nature of bonding has been controversial, i.e., ionic [10] or covalent [11]. In addition, Bauer et al. [12] have proposed a hybridization model to explain the results of two-photon photoemission spectroscopy on Cs adsorbed on Cu(1 1 1). In this model, a strong hybridization of 6s and 6p orbitals of Cs results in two orbitals, an unoccupied $|6s + 6p_z\rangle$ orbital directed away from the surface and an occupied $|6s - 6p_z\rangle$ orbital located between the Cs ion core and the surface. Carlsson and Hellsing [13] performed the first-principles calculations

of the electronic states of Na on Cu(1 1 1) in the higher coverage regime, showing that the electron charge is accumulated between the Na adlayer and the surface characteristic to covalent bonding. The electrons in the interface region are delocalized laterally to form a quantum well. In spite of those extensive studies on the alkali-metal adsorption on metals, no information is available on the electronic structure specific to the current system, alkali-metals on Pt(1 1 1), particularly the electronic transitions relevant to the coherent excitation of the stretching vibration of alkali-metal atoms.

In this paper, after we describe the experimental findings of the coherent nuclear motions of Cs and K on Pt(1 1 1) investigated by TR-SHG, we discuss the possible mechanism for the coherent excitation based on first-principles calculations.

2. Experimental and computational procedures

The apparatus and procedure for TR-SHG measurements were described in detail elsewhere [4]. Briefly, the experiments were carried out in an ultrahigh vacuum chamber equipped with a cylindrical mirror analyzer for Auger electron spectroscopy. Alkali-metal atoms (K and Cs) from well-degassed alkali dispenser (SAES getters) were deposited on a clean Pt(1 1 1) surface at 110 K. The coverage of alkali atoms was determined by Auger electron spectroscopy and work function measurements. The laser system for TR-SHG was a Ti: sapphire regenerative amplifier (Spectra Physics, Spitfire) with a home-built non-collinear optical parametric amplifier (25 fs, 580 nm). The laser beam was split into two for pump and probe pulses. Second harmonic (SH) signals in p-polarization generated by the probe beam coaxially passed through a band pass filter and were detected by a photomultiplier tube. A chopper was inserted in the optical path of the pump beam for the lock-in detection of pump-induced SH intensity modulations as a function of the pump-probe delay, t. The transient change of the SH intensity, $\Delta SH(t)$, is defined as $\Delta SH(t) = (SH(t) - SH^\circ)/SH^\circ$, where $SH(t)$ and SH° are the SH intensities with and without the pump pulse,