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Review

Electron dynamics of image potential states in weakly bound adsorbate layers: A short review

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Abstract

Image potential states on physisorbate-covered metal surfaces are fascinating model systems for the transition from the quasi-free behavior of electrons at bare metal surfaces towards the molecular electronics in more complex organic overlayers. This article discusses the fundamental properties of these systems and the experimental highlights in the study of rare gas and simple molecular overlayers on noble metal surfaces since the early 90s.

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Keywords: Image potential states; Ultrafast electron dynamics; Dielectric/metal interface; Thin adsorbate layers; Two-photon photoemission; Dielectric continuum model

Contents

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1. Introduction

The study of normally unoccupied electronic surface states on bare and adsorbate-covered metal surfaces is fuelled by many interests. The discrete nature of surface states is often an advantage when investigating fundamental dynamic processes like intraband and interband relaxation [1], which can thus be studied in a situation where they are not obscured by a continuum of simultaneously excited states. Effects that have been studied with the help of surface states include electron–electron and electron–phonon scattering [2,3] and dephasing [1,4,5]. Besides, the spectroscopy and dynamics of surface states are excellent probes of the quality of surface preparation under experimental conditions [6]. The electron dynamics between a metal surface and adsorbed adlayers also has a technological aspect and may well become relevant as electronic devices like light-emitting diodes shrink in size and new technologies like molecular electronics or nanosensor arrays are introduced [7]. Finally, the transient excitation of unoccupied states is an important elementary step in surface photochemistry [8]. In fact, some of the most fascinating discoveries about unoccupied surface or interface states in recent years concern their coupling to atomic or molecular motion [9–14].

Since the early 1990s, the dynamics of unoccupied surface and interface states has been extensively investigated with time-resolved two-photon photoemission (2PPE) spectroscopy [15]. 2PPE is ideally suited for this purpose because of its high temporal and energetic resolution (in the 10 fs and 10 meV range, respectively), and because the number, kinetic energy, and momentum parallel to the surface of the emitted electrons as a function of the delay between the first (pump) and the second (probe) light pulse directly map the lifetime, energy, and momentum of the electrons in the transiently populated intermediate states. The image potential states (IPS) [16–19] which dominate the electron dynamics of bare metal surfaces have been in the focus of these studies from the beginning. Very soon, it was discovered that the existence of these states is not restricted to *bare* surfaces only. Thus in the last 15 years, IPS or states with some IPS character have been investigated with 2PPE in a number of metal–adsorbate systems, which shall be listed here in roughly chronological order: Xe and Kr on Ag(1 1 1) [20–25]; the alkanes *n*-pentane, hexane, *n*-heptane, *n*-octane, neopentane, and cyclohexane on Ag(1 1 1) [9,20,26–29]; Xe, Kr, N_2, and Xe/O_2 and Xe/N_2 heterolayer systems on Cu(1 1 1) [4,11,30–33]; the aromatics benzene, hexafluorobenzene, pyridine, and naphthalene on Cu(1 1 1) [34–43]; benzene, naphthalene, anthracene, and *p*-xylene on Ag(1 1 1) [44–46]; the polar molecules acetonitrile (C_2H_3N), butyronitrile (C_4H_7N), methanol, 1-propanol, 1-butanol, and 1-pentanol on Ag(1 1 1) [12,47]; Xe on Ru(0 0 0 1) [48]; Ar, Kr, and Xe on Cu(0 0 1) [49–52]; *n*-heptane on Au(1 1 1) [53].

The fascinating properties of IPS in these systems, which give an insight into the transition from the quasi-free behavior of electrons at bare metal surfaces towards the