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Nonadiabatic quasiparticle dynamics in time resolved electron spectroscopies of surface bands

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ABSTRACT

Surface localized electronic states constitute electronic environment for a variety of physical and chemical phenomena taking place on surfaces. Various processes of model catalytic reactions may be influenced or mediated by hot electrons and holes excited in quasi-two-dimensional bands occurring on a large number of metal surfaces. Here we discuss several important aspects of nonadiabatic dynamics of these excitations which may affect the measurements of surface electronic properties by ultrafast electron spectroscopies.

1. Introduction

Research in the field of heterogeneous catalysis is truly interdisciplinary and covers many areas of physics, chemistry and materials science. In this short review we shall attempt to elucidate some aspects of ultrafast surface electron dynamics which may play important roles in the various surface phenomena, including the catalytic reactions at gas-solid interfaces.

Catalytic reactions on solid surfaces can be viewed as sequences of chemical bond breakings and makings involving the reactant, transition or intermediate, and product species in interaction with the catalyst surface. These events are characterized by electronic transitions from ground or excited states of the initial molecular configurations of reactants, via the excited states of intermediates, to the final molecular configurations of product species. During these processes substantial amounts of excited electron energies can be transferred to the other dynamical degrees of freedom in the reacting system or dissipated to the heatbath. Various surface science techniques and methods have been developed and employed to study the electronic structure of real and model catalyst surfaces *per se*, and of the reactants and products in interactions with catalyst surfaces. The primary goal of these investigations was to obtain physical and chemical insight into the various stages of studied reactions on well characterized surfaces and thereby assess the corresponding driving potentials and reaction pathways [1–4].

Studies of model catalytic surfaces and their interactions with prototype adsorbates represent a broad research area in which the activities can be traced back to the very beginnings of surface science. Investigations of the electronic properties of clean and adsorbate covered crystal surfaces by various electron spectroscopies constitute an important chapter in this endeavor (for review and exhaustive list of references see contributions to this volume by G.A. Somorjai, C. Campbell, M. Wolf et al., F. Besenbacher, A. Jablonski, and Ref. [5]). This particularly refers to the surfaces of noble and transition metals which have proven as or are deemed to be efficient catalysts in a variety of reactions of practical and scientific interest. Single crystal metal surfaces represent electronic environments for model catalytic reactions whose properties are nowadays accessible by standard and novel surface science techniques. Applications of these techniques can provide spatially-, temporally- and energy-resolved information on the electronic structure and dynamics of participants in the various surface mediated processes [7]. The broad range and high resolution of the acquired data have in many cases enabled to establish microscopic descriptions of the dynamics of electronic and nuclear degrees of freedom during the various stages of surface reactions (see G. Ertl's Nobel Lecture at `http://nobelprize.org/nobel_prizes/chemistry/laureates/2007/ertl-lecture.html`).

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The majority of low index single crystal surfaces of catalytically active noble and transition metals support quasi-two-dimensional (Q2D) surface localized electronic bands. Surface bands around the Fermi and vacuum level arise from a combined action of the attractive image potential and the projection(s) of bulk band gap(s) in the direction perpendicular to the surface [6]. Hence, the electronic environment on a number of catalyst surfaces may be affected by Q2D band structure and concomitant electron dynamics. Of particular importance in the context of surface interactions and reactions is the dynamics of Q2D electronic states on the ultrashort time scale of chemical bond making and bond breaking which is in the range of femtoseconds. The dynamics of surface electrons on this scale is also expected to influence many other surface phenomena such as the electronic and spin response properties of adlayers and nanostructures, the speed and quality of information storage and retrieval needed for the design of future quantum computing devices, etc. Therefore it is of special interest to study the electronic properties and response of paradigmatic model systems of reduced dimensionality such as surface bands in order to gain fundamental understanding of electron dynamics subject to spatial and temporal confinement. A lot of effort has been devoted to develop experimental techniques which would accomplish these goals and recent applications of ultrafast photoelectron spectroscopies have enabled high resolution studies of electron dynamics at surfaces in the real time domain. This provided novel insights into the evolution and decoherence of surface-localized electronic states and opened up new directions in the investigations of surface interactions and reactions on the ultrashort time scale.

Many important aspects of hot charge carrier energetics and dynamics in surface-localized bands have been successfully explored by high resolution one-photon-photoemission (1PPE) spectroscopy [8–12], inverse photoemission (IPE) spectroscopy [13], scanning tunneling microscopy [14,15] (STM), and two-photon-photoemission (2PPE) combining the use of continuous wave (cw) and pulsed pump and probe laser beams with variable delay times [16–30]. Time resolved two-photon-photoemission (TR2PPE) studies of surfaces with ultrashort laser pulses have provided particularly valuable information on quasiparticle dynamics in surface bands which is one of the prerequisites for a better understanding of surface photochemistry. Systematic applications of these methods have resulted in accumulation of the data on characteristic energies and lifetimes of hot electron and hole excitations in Shockley and image potential bands on clean surfaces (hereafter to be referred to as the SS- and IS-bands, respectively), and in the states at surfaces covered with localized defects [31–36] such as adsorbates, cavities, steps, etc. Recent progress in interferometric 2PPE measurements has further enhanced the quality of information on the quasiparticle dynamics at surfaces [24–27].

The majority of theoretical descriptions and interpretations of evolution of quasiparticles created in surface bands during the various stages of spectroscopic measurements have been restricted to the adiabatic or Markovian (quasistationary) picture of hot carrier dynamics. In this approximation the evolution of quasiparticle states is characterized by exponential decay governed by the Fermi golden rule (FGR) type of transition rates [37–39]. Such a description is applicable to steady state evolution of the system during the times that are of the order of or exceed its relaxation and decay times. This regime was tacitly assumed in recent developments of microscopic theories of 2PPE from surface [40–43] and bulk [44] bands. The applicability of phenomenological optical Bloch equations in the simulations of time resolved 2PPE experiments [22,23,30,43,45–47] also rests on this assumption. However, time resolved 2PPE measurements utilizing pump and probe laser pulses of femtosecond duration and short delay times also probe the early non-Markovian evolution of quasiparticles excited in surface bands. Besides the possible direct consequences on the measured time resolved and interferometric 2PPE spectra, this fact may turn out important in the determination of 2PPE correlation traces since in that case the delay times are varied from negative to positive values across zero, in which case the non-Markovian and Markovian evolution of excited quasiparticles may equally contribute to the results of measurements.

In this article we illustrate the main characteristics of nonadiabatic evolution of hot electrons and holes excited in surface bands which are caused by the most common and ubiquitous interactions of quasiparticles with the environment, viz. the interactions with electronic charge density fluctuations in the system and with the impurity defects (adsorbates) present on the surface. Special attention will be paid to the discussion of quasiparticle features that may be used for identification of non-Markovian evolution regimes, namely the decay of survival probability of a quasiparticle and the evolution of its phase in the course of time. Their temporal variations on the ultrashort time scale are expected to leave important signatures in the spectral characteristics of surface bands revealed by ultrafast electron spectroscopies.

2. Amplitudes and intensities of one- and two-photon photoemission from surface bands

To illustrate how ultrafast electron dynamics enters model descriptions of the energy and time resolved one- and two-photon photoemission intensities from surface bands we shall employ time-dependent perturbation theory to describe interactions of electrons with ultrashort laser pulses. In the case of 1PPE from surface bands a laser pulse excites electrons from initially occupied band states below the Fermi energy E_F into final states $|k\rangle$ above the vacuum level $E_V = 0$. The states $|k\rangle$ are outgoing photoemission states in which the electron energy and emission angle can be measured by a suitable electron counter (hereafter to be referred to as the detector). This measurement defines the quantum numbers of the final photoelectron state $|k\rangle$ outside the solid, i.e. the photoelectron total energy E_k and the momentum parallel to the surface. We further assume that the detector plays the role of a projector operator, $\widehat{P}_f$, that in an idealized situation selects photoemitted electrons in the outgoing states $|k\rangle$, viz.

$$\widehat{P}_f = \sum_{k_f} |k\rangle\langle k|. \tag{1}$$

Here the summation over the indices k_f of photoelectron final states is restricted by the angular and energy resolution of the detector. The electron population of the states $|k\rangle$ in this interval at the instant of measurement $t_{\rm obs}$ (hereafter to be referred to as the observation time) is given by:

$$\rho_f(t_{\rm obs}) = \langle\Psi(t_{\rm obs})|\widehat{P}_f|\Psi(t_{\rm obs})\rangle, \tag{2}$$

where $|\Psi(t_{\rm obs})\rangle = U(t_{\rm obs}, -\infty)|\Psi(-\infty)\rangle$ is a many-body wave function of the system obtained by the action of evolution operator $U(t_{obs}, -\infty)$ on the initial ground state of the system $|\Psi(-\infty)\rangle = |0\rangle$ at $t = -\infty$. Here one should observe a difference with respect to the standard definition of photoemission yields based on current–current correlation functions [48–50] which is applicable to steady-state photoemission induced by stationary photon fields.

In the case of one-photon photoemission the operator $U(t_{obs}, -\infty)$ is calculated in first order perturbation theory with respect to the applied electromagnetic field of the laser pulse. This yields $\rho_f(t_{\rm obs})$ corresponding to the population induced by 1PPE process. Both the photoexcited electron in the state $|k\rangle$ and the hole left in the initial electron state may interact with each other and with the dynamical degrees of freedom of the system heatbath. These interactions will give rise to decoherence of primary coherent photoexcited electron-hole pair.