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Laser-induced vibrational excitation and desorption in the Cs/Cu(1 1 1) and Na/Cu(1 1 1) systems

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Abstract

The Cs/Cu(1 1 1) and Na/Cu(1 1 1) systems exhibit a transient excited electronic state localized on the adsorbate. Photo-excitation of this state triggers a motion of the alkali adsorbate away from the surface, leading to vibrational excitation of the adsorbate and possibly to desorption. A theoretical study of these photo-induced processes in the case of an exciting fs laser pulse is reported, based on a time-dependent approach of the adsorbate motion. The mean energy transfer from the laser photon energy to the adsorbate motion is shown to be weak, about 1% of the photon energy. Correspondingly, the vibrational excitation to high lying levels is very weak as well as the desorption process. The initial electronic state of the photo-induced process belongs to a continuum and vibrational excitation and desorption are found to vary rapidly with the energy of the initial electronic state. Initial vibrational excitation of the alkali adsorbate is also found to efficiently favour the desorption process, leading to a drastic variation of the desorption probability with the vibrational temperature of the adsorbate. The present results for the two systems are discussed and compared, in connection with available experimental data on these systems and on similar ones.

Keywords: Desorption induced by photon stimulation; Adatoms; Atomistic dynamics; Copper; Alkali metals

1. Introduction

Many reactive processes at surfaces involve the interaction between electrons and heavy particle motion or more precisely, they involve the formation of an excited electronic state that triggers an evolution in the surface system, leading to a reaction process. For the desorption process, these mechanisms are often referred to as DIET (desorption induced by electronic transitions). A very well-known example of this class of mechanisms is the so-called Menzel–Gomer–Redhead (MGR) mechanism [1,2] for electron-induced and photo-induced desorption of adsorbates. In this mechanism, an adsorbate is initially in its ground electronic and vibrational state in front of the surface. Electron impact or photo-absorption brings the adsorbate up to an excited electronic state, the equilibrium position of which either does not exist, or is not at the same position as that for the ground state. Then, the adsorbate starts to move and if the excited state lifetime is long enough, sufficient energy transfer from electronic variables to heavy particle motion can occur leading to the desorption of the adsorbate. If the energy transfer is too weak for desorption, only vibrational excitation of the adsorbate in its adsorption well occurs. Many DIET processes have thus been discussed in terms of the MGR mechanism, i.e., as involving the transient formation of an excited electronic state (see a recent review on ultra-fast desorption in Ref. [3] and references therein). The success of these mechanisms involving resonant states is linked to the great

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difficulty of transferring energy from electrons to heavy particles, due to the large mass difference; the transient formation of a resonant state significantly increases the interaction time, allowing a weak interaction to become very efficient. A similar phenomena is well known in the field of electron–molecule collisions at low energy: the transient capture of the incident electron to form a resonant negative ion is an efficient doorway to many excitation processes: dissociative attachment, vibrational excitation or electronic excitation (see e.g., [4,5]) The key parameters for the efficiency of this resonant desorption mechanism (DIET) are the transient state lifetime, the desorbing particle mass and the steepness of the excited state potential energy curve. On metal surfaces, lifetimes of excited electronic states are usually short making the desorption probability very low [3].

The present work is devoted to a theoretical study of the energy transfer from an excited electron to the heavy particle motion in the alkali/Cu(111) systems. These systems are very appealing for such a study due to their special characteristics. Indeed, at very low coverage, alkalis are adsorbed as positive ions on Cu surfaces. A very long-lived state has been observed by time-resolved 2-photon photoemission (TR-2PPE) experiments [6–8], corresponding to the capture of an electron by the ionic adsorbate (see a recent review in Ref. [9]); it is noted 'Alk* state' below. Lifetimes up to tens of fs have been reported for the Cs/Cu(111) case. After formation of the resonant state, the adsorbate starts to move out of the surface. A direct observation of the alkali motion induced by electron capture has been performed by Petek et al. [10], who studied the variation of the 2PPE-spectrum as a function of the time delay between the two laser pulses in the Cs/Cu(111) system. This allowed them to determine the change of electronic energy of the Cs* state as a function of time, associated to the Cs* desorption motion. Independently, they could observe the desorption of the Cs adsorbates induced by the laser irradiation of the surface, by looking at the change of the surface work function during the experiment. Though, no direct quantitative link between the TR-2PPE observation and the desorption has been established, and only an upper limit of the photo-desorption cross-section (2.4×10^{-23} cm^2) was reported. This desorption cross-section appears to be very small, in particular much smaller than the photo-desorption cross-section measured by Hellsing et al. [11] in a similar system, K/graphite.

On the theoretical side, a series of studies elucidated the origin of the long lifetime of the Alk* excited state [12–15]. It was shown to be linked to the existence of a surface-projected band gap on the Cu(111) surface. The Alk* state is located inside this surface-projected band gap, leading to a strong decrease of the resonant charge transfer (one-electron energy conserving transition) between the adsorbate and the substrate. Usually, on metal surfaces, the resonant charge transfer is the dominant decay process when it is energetically possible; its quasi-blocking in the Alk/Cu(111) system leads to a considerable increase of the Alk* state lifetime [12]. The variation of the lifetime with the Cu surface index, as well as with the alkali adsorbate, has been discussed [13,14], together with a discussion of the conditions for its occurrence [15,9]. The effect of the Cs motion induced by the Cs electronic excitation was further studied theoretically with the aim of discussing the signature of the Cs motion in the TR-2PPE signal [16,17], in connection with experimental data [18,19]. Both these theoretical studies were devoted to the time evolution of the excited electronic state and its influence on the 2PPE signal. The present work extends these earlier works in that it focuses on the fate of the heavy particle motion, i.e., on the vibrational excitation of the alkali adsorbate in its adsorption well induced by the transient formation of the Alk* state, as well as on its limit, the adsorbate desorption. Two systems are studied and compared: Cs and Na/Cu(111). They correspond to rather different situations: Na is much lighter than Cs, whereas the Na* state is much shorter lived than the Cs* state. These two parameters are expected to influence vibrational excitation and desorption in opposite directions. Section 2 presents the theoretical modelling that is used. Section 3 presents the results on the photo-induced vibrational excitation and desorption processes and Section 4 a concluding discussion.

2. Theoretical framework

We use a theoretical approach based on a wave function representation of the evolving system, similar to the one used in our earlier study of the influence of the Cs motion on the TR-2PPE signals [17]. The quantitative agreement with experiment that was reached in these cases gives confidence in this approach for representing the dynamics of the Alk–Cu system.

2.1. Representation of the system

We consider three electronic states: the initial electronic state corresponding to a substrate electron, noted $\phi_{\mathrm{init},E_\mathrm{i}}$, the resonant Alk* state, noted ϕ_{Alk^*}, and the final substrate state, noted $\phi_{\mathrm{f},E_\mathrm{f}}$. The initial and final electron states belong to a continuum and are indexed by their energy E_i and E_f. The incident photon induces transitions between the initial and Alk* states; the evolution corresponding to each initial state has to be computed independently and the corresponding contributions to the signal summed incoherently. The final states are populated by the decay of the Alk* state which proceeds via one-electron or multi-electron charge transfer transitions (see a discussion in [13,9]), they are in the same energy range as the Alk* state, i.e., far away in energy from the initial states.

The wave function describing the evolution of the system is written as an expansion over these three states with coefficient functions, χ, which depend on both time and Z, the adsorbate–surface distance