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Laser-induced photo-desorption in the Na/Cu(1 1 1) system

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ABSTRACT

Desorption in the Na/Cu(1 1 1) system induced by an electronic excitation is studied using a quantal approach. The system is excited by a laser pulse in the fs range to the Na^* state corresponding to the transient capture of an electron by the alkali adsorbate. The present quantal approach describes on an equal footing the laser-induced vibrational excitation of the adsorbate in the adsorption well and the photo-desorption process. It confirms earlier results using a semi-classical input. It also allows a discussion of the photo-desorption probability with the photon energy: the maximum of the desorption probability per absorbed photon occurs off-resonance in the high-energy wing of the electronic transition. This feature is related to the dynamics of the laser-induced process.

1. Introduction

Shining a laser on a surface covered with adsorbates brings energy to the system that can result in a variety of different processes, among which desorption received a lot of attention. Photo-induced desorption can be a thermal process: if the incident light warms up the substrate, later energy transfer to the adsorbate–substrate vibrational motion can lead to desorption. But desorption can be induced in a more direct way by the incident light via an electronic excitation process, it is then called desorption induced by electronic transition (DIET) (see a recent thorough review of ultra-fast photo-desorption processes in Ref. [1]). In this context, the Menzel–Gomer–Redhead (MGR) mechanism [2,3] is very often invoked, it is schematically pictured in Fig. 1. In this mechanism, the incident photon induces an electronic excitation in the adsorbate (vertical upward red[1] arrow in Fig. 1). In the initial electronic state, the system is at equilibrium at $Z = Z_{eq}$ (Z is the adsorbate–substrate distance) and the equilibrium position is a priori different in the potential energy curve of the excited state. The photo-excitation thus triggers a motion along the Z-coordinate, i.e. induces an energy transfer from the electrons to the heavy particle motion (oblique downward black arrow in Fig. 1); this energy transfer stops when the excited electronic system goes back to the ground state (vertical downward green arrow in Fig. 1). If the energy transfer is large enough, it leads to the desorption of the adsorbate, else it leads to the excitation of the adsorbate vibration in front of the surface. The amount of energy transfer between electrons and heavy particle motion, i.e. the efficiency of the photo-induced process depends in a critical way on the lifetime of the intermediate excited electronic state as well as on the slope of the excited state potential energy curve and on the mass of the desorbing particle.

Among adsorbate systems, alkalis adsorbed at low coverage on (1 1 1) and (1 0 0) surfaces of noble metals have been the subjects of many studies due to the existence of a long-lived excited state localized on the adsorbate and associated to the transient capture of an electron by the alkali adsorbate (see a review in Ref. [4]). This long-lived state was first observed by pump-probe experiments [5–7] in the fs range (time resolved two-photon photoemission, TR-2PPE). The very long lifetime of the Alk^* state (up to tens of fs for Cs^*) has been shown to be due to the existence of a surface-projected band gap on the (1 1 1) and (1 0 0) surfaces of noble metals that partially blocks the resonant electron transfer between the Alk^* state and the metal substrate [4,8–10]. At the adsorption distance, the interaction between the Alk^* state and the substrate is repulsive, so that excitation of the system triggers an outward motion of the adsorbate away from the substrate. The first step of this desorbing motion have been very clearly identified and analyzed in TR-2PPE experiments [11] and it has been also well reproduced in theoretical modeling [12,13]. In addition, the existence of a photo-desorption process induced by the excitation of the Cs^* state has been indirectly evidenced by observing a photo-induced change

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[1] For interpretation of color in Figs. 1–7, the reader is referred to the web version of this article.

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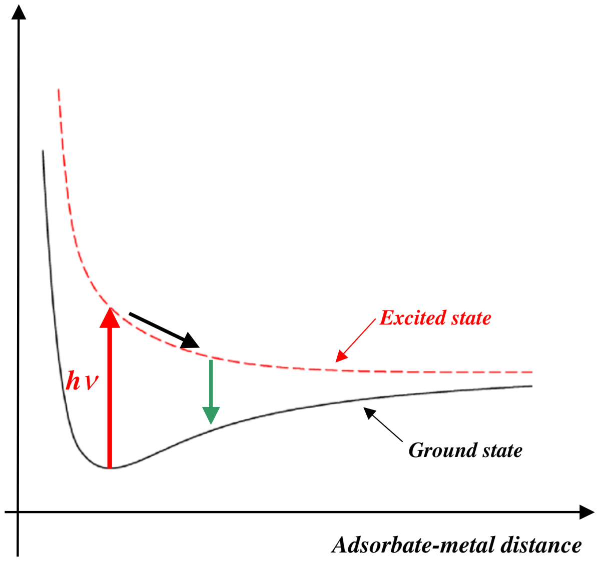

Fig. 1. Schematic picture of a MGR-DIET process (see text for description).

of the surface work function. Though, the desorbing particles could not be directly observed [11] and so, only an upper limit of the photo-desorption cross section ($2.4 \cdot 10^{-23}$ cm^2) could be obtained. This cross section is extremely small [1], in particular compared to that observed in a similar system, K/Graphite [14]. It can be stressed that a priori two different desorption processes can exist in the Cs/Cu(1 1 1) system: if the photo-excited Cs* atom can survive out to infinite atom-surface separation, it will lead to neutral desorption; in contrast, if the Cs* state decays by electron transfer to the substrate and if the energy transferred to the heavy particle motion is large enough, ion desorption will take place.

The present paper is devoted to a theoretical study of the laser-induced desorption of Na adsorbates from a Cu(1 1 1) surface. Recently, laser photo-desorption of alkalis (Cs and Na) from noble metal surfaces involving the transient formation of the long-lived Alk* state has been the subject of several theoretical studies [15–17]. The Cs/Cu(1 1 1) system was studied in two model studies looking at ion desorption [15,17]. They reported a very low desorption probability and a strong dependence of the desorption efficiency on the initial position of the Cs adsorbate in its adsorption well. This points at a very strong enhancement of the desorption probability when the initial state is an excited vibrational level of the Cs–Cu adsorption system. In addition, it was shown that the combined action of a THz pulse and a UV-laser pulse significantly increases the desorption efficiency [17]. The THz field, if strong enough and properly optimized, induces a significant vibrational excitation of the Cs adsorbate in its adsorption well which results in a strongly enhanced desorption probability by the UV-laser pulse. Another work [16], based on earlier studies [8,10,13,18] of the electron dynamics in the Cs/Cu(1 1 1) and Na/Cu(1 1 1) systems, was devoted to laser-induced vibrational excitation of the adsorbate in its adsorption well and to desorption (ions and neutrals) in the two systems. Together with a detailed study of the vibrational excitation, a very low desorption probability was found in both systems, associated to a very fast increase of the desorption probability with the initial vibrational energy of the adsorbate. Ion desorption was found to dominate in Na/Cu(1 1 1) whereas, in Cs/Cu(1 1 1), neutral desorption dominates for low initial vibrational levels and ion desorption for high initial vibrational levels of Cs in its adsorption well. This result is not surprising. In these systems, vibrational excitation to the low lying levels of the adsorbate via laser excitation of the Alk* state is very efficient; however, desorption requires a large energy transfer from the electrons to the heavy particles accounting for the very small desorption probability. In addition, anything that can make easier and/or smaller the required energy transfer, like the choice of an excited vibrational level as the initial state, boosts the desorption efficiency. It is noteworthy that the two theoretical studies of photo-desorption in Cs/Cu(1 1 1) [15,16] lead to very different though both very small desorption probabilities; this was attributed to different modeling (potential energy curves and lifetimes) of the Cs/Cu(1 1 1) system in the two studies.

The present work, devoted to laser-induced ion desorption in Na/Cu(1 1 1), introduces a new approach to compute the photo-desorption probability. It is based on the similarity between laser-induced vibrational excitation and desorption. Two different kinds of states can be defined in the potential energy curve describing the interaction between the Na$^+$ adsorbate and the Cu(1 1 1) surface: bound vibrational levels associated to quantized motion and continuum states corresponding to desorption. In this view, photo-induced ion desorption appears as the continuation of the vibrational excitation process across the desorption energy threshold (the dissociation energy of the adsorption potential energy curve). In Ref. [16], ion desorption has been evaluated using a semi-classical ingredient inside an otherwise quantal treatment. In the present work, we show that quantization of the desorption continuum in a finite box yields an easy and efficient way of computing fully quantal desorption probabilities. The application of this approach to the Na/Cu(1 1 1) system is used to illustrate the dependence of the laser-induced desorption on the laser frequency. More precisely we show how off-resonant laser excitations can be more efficient than resonant excitations in this system.

2. Method

2.1. Dynamics of the laser excitation in Na/Cu

The present work is based on the same wave function representation of the Na/Cu(1 1 1) system as used in Ref. [13,16]. This approach was found to be very efficient in describing the dynamics of the photo-desorption and of the two-photon photoemission, in particular its time dependence [11,19,20]. It involves three electronic states: (i) the initial electronic state corresponding to a substrate electron with energy E_i, noted ϕ_{init,E_i} (following experimental studies, we assumed the initial states to belong to the surface state continuum), (ii) the resonant Na* state, noted ϕ_{Na^*}, and iii) the final substrate state of energy E_f, noted ϕ_{f,E_f}. The contributions from all the possible initial electronic states have to be computed independently and added incoherently. Transitions between the initial states and the Na* state are induced by the laser and the decay of the Na* state via one-electron or multi-electron charge transfer transitions [4,8–10] populates the final states. The total wave function of the system is then written as

$$\left|\psi\right\rangle = \chi_{\mathrm{init},E_i}(t,Z)\left|\phi_{\mathrm{init},E_i}\right\rangle + \chi_{\mathrm{res}}(t,Z)\left|\phi_{\mathrm{Na}^*}\right\rangle + \int \mathrm{d}E_f\, \chi_{E_f}(t,Z)\left|\phi_{f,E_f}\right\rangle \tag{1}$$

where the expansion coefficients are functions of time and of Z, the Na-surface distance.

The Hamiltonian of the total system is given by

$$H(t) = T_Z + H_{\mathrm{el}} + \varepsilon(t) D \cos(\omega_L t) \tag{2}$$

T_Z is the kinetic energy of the heavy particle motion along the *Z-coordinate* and H_{el} is the electronic Hamiltonian in the basis of the three above electronic states. D is the dipolar operator connecting the initial and Na* states. $\varepsilon(t)$ is the envelop of the incident laser pulse and ω_L is the laser frequency. With some approximations