Theoretical study of excited electronic states at surfaces, link with photo-emission and photo-desorption experiments

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Abstract. Excited electronic states at surfaces play a very important role in a variety of surface processes. These excited states have a finite lifetime due to electron-transfer processes and their efficiency as reaction intermediates depends crucially on their lifetime. A review of several physical situations, where an excited electronic state localized on an atom interacting with a metal surface intervenes in a surface process, is presented with an emphasis on the way the metal electronic structure influences the excited state dynamics. Examples are chosen among the alkali/metal systems, stressing how the same transient electronic state can influence different dynamical processes.

1. Introduction

When an atom or molecule is electronically excited near a metal surface, it can evolve into two paths: the excitation can either relax into the metal corresponding to the finite lifetime of the excited state, or trigger an internal evolution of the system opening the way to a variety of processes via electron-heavy particle couplings. The role of excited states as intermediates in surface mechanisms has been invoked in many surface processes: collisional charge transfer, molecular dissociation, desorption and more generally surface reactivity. This important role of excited states prompted many theoretical and experimental studies of excited electronic states at surfaces. Since energy transfer from electronic to heavy particle motion is a slow process, one can expect that the efficiency of a transient state as a reaction intermediate depends crucially on its lifetime. It is thus of paramount importance to
understand the various parameters that govern the lifetime of an excited state on a surface and possibly see how it can be optimised to favour a reaction mechanism.

In this paper, we present a review on the dynamics of excited electronic states at metal surfaces. It is not a comprehensive review, we focus on excited states localized on an atom in front of a surface (an adsorbate or an atom colliding with the surface) as examples of the excitation dynamics at surfaces. Much emphasis is put on the influence of the surface electronic structure on the excitation dynamics and more precisely on the excited state lifetime. Various processes are discussed: charge transfer in atom-surface scattering, long-lived states in Alkali/noble metal systems as they can be probed by Two-Photon Photo-Emission (2PPE) experiments, photo-desorption and atomic manipulation. The examples are taken in Alkali/metal systems (see a recent review in [1]), to emphasize how the same excited electronic state participate in different processes.

2. Relaxation of an electronic excitation on a metal surface

When an excited atom is set in front of a metal surface, various de-excitation paths are possible [2]. First it can decay by a one-electron transition: the excited electron can be transferred into a bulk state of the same energy, it is a resonant, i.e. energy conserving transition, and it is only possible if electron states in the bulk exist in the excited state energy range. Secondly, it can decay by two-electron Auger-like transitions: if an excited atom has a vacancy in an inner orbital, an electron from the surface can fill this vacancy while the excess energy is used to eject another electron. Finally, an inelastic interaction (‘collision’) between the excited electron and a bulk electron can also bring the atom into the ground state. It then leads to the ejection of an electron or to a collective excitation of the surface (a plasmon) [3]. The mono-electronic process, when it is energetically allowed, is in general the most efficient one and it is discussed more in detail below. There are two equivalent ways to look at this one-electron resonant charge transfer (RCT) process. In a first view, the excited atom state is a discrete state localized on the atom, it is degenerate with the continuum of metallic states and coupled with it, so that it acquires a finite lifetime $\tau$ inverse of its decay rate, $\Gamma$, given by the Fermi golden rule. In a second view, the excited electron is bound in a potential well around the atom; there is a potential well inside the metal too and a potential barrier in between. The excited state then decays by electron tunneling through this barrier. In both views, one expects the electron transfer rate to vary rapidly with $Z$, the atom-surface distance, and a simple argument based on overlap between atomic orbitals and metal continuum states predicts an exponential behavior with $Z$ at large distance. One can also expect a very fast electron transfer rate at close distances when basically the potential barrier separating the atom and the surface disappears. Actually, atomic levels that are above the surface Fermi level decay by electron transfer to the metal; for levels below the Fermi level, the argument has to be repeated for holes and a hole on the atom decays by transfer into the metal, i.e. by electron transfer from the metal to the atom.

3. Illustration of the atom-surface charge transfer

3.1 Static case

The electron transfer process between an atom and a surface is illustrated by the results of recent wave-packet propagation (WPP) calculations. This method consists in solving the one-electron time-dependent Schrödinger equation on a grid of points (see [4,5] for details on the WPP method):

$$i \frac{d}{dt} \Psi = \hat{H} \Psi = (\hat{T} + V)\Psi$$

(1)

where $\Psi$ is the electron wave function, $\hat{T}$ is the kinetic energy operator and $V$ the interaction potential between the excited electron and the atom+surface system. Efficient propagation schemes are now available that allow solving equation (1) starting with a well-chosen initial wave function $\Phi_0$. When the atom is at a fixed finite distance from the surface (static situation), the energies and the
lifetimes of the resonant states of the system are extracted from the time dependent wave function $\Psi$ obtained by solving eq.(1). For the resonances associated with excited atomic states interacting with the surface the decay rates thus obtained corresponds to the RCT process [4,5]. The WPP method can also be applied to the RCT in a collisional situation, i.e. to the RCT process when projectile collides with the surface (see below).

One can also extract the wave-function of the resonant state from the solution of equ.(1) and as a typical example, Figure 1 shows the case of a Cs atom interacting with a Cu metal surface. The resonant Cs* state is the lowest lying state localized on the Cs atom, it corresponds to a hybrid of $m = 0$ symmetry, mixture of 6s and 6p orbitals of the free atom ($m$ is the projection of the electron momentum on an atomic axis normal to the surface). In front of a usual metal surface, the binding energy of this state is lower than the surface work function so that this state is an excited state of the Cs-surface system. It decays by transfer of the electron into the metal and the Cs adsorbate at low coverage is positively charged (see a discussion in [1]). Two different cases are considered: a Cs atom at 10 a$_0$ from a free-electron metal and a Cs atom at its adsorption distance on a model Cu(111) surface (the two distances are chosen to roughly correspond to the same decay rate of the Cs* state). Let us first consider the case of the free-electron metal (right part of Fig.1). One recognizes a quasi-circular electronic cloud localized around the atom centre that corresponds to the resonant wave function and that is not much perturbed from the atomic 6s orbital. The electron density inside the metal corresponds to the electron flux leaving the resonance state, i.e. to the resonant charge transfer process. Electron tunnelling through the potential barrier that separates the atom and the metal is favoured along the normal to the surface where this barrier is the thinnest and one can see that the outgoing electron flux corresponding to RCT is concentrated around the surface normal. The RCT rate increases roughly exponentially when the atom approaches the surface and the transfer rate becomes very fast, reaching the eV range at typical adsorption distances (lifetime of a fraction of a fs).

$\begin{align*}
\text{Cs / Cu(111), } Z = 3.5 \text{ a}_0 \\
\text{Cs / Cu 'free electron', } Z = 10 \text{ a}_0
\end{align*}$

Figure 1: Electron density associated to the resonant Cs-localized state in the case of the Cs atom located (a) at 3.5 a$_0$ (adsorption distance) from the image plane of a Cu(111) surface and (b) at 10 a$_0$ from the image plane of a free-electron metal surface. The horizontal black line indicates the position of the image plane of the metal surface and the Cs atom centre is at the origin of coordinates. The logarithm of the electronic density (square modulus of the wave function) is presented in cylindrical coordinates parallel and perpendicular to the surface. $z$, the coordinate perpendicular to the surface, is positive in vacuum. The electron density decreases when going from red to violet. White corresponds to very small electron densities.
The case of the Cu(111) surface (left part of Fig.1) appears completely different. First, one can notice the difference between the electronic clouds around the atom; this is an effect of hybridisation of 6s and 6p orbitals that occurs for short atom-surface distances (the distance is the Cs adsorption distance on Cu(111)). The excited state discussed here is the hybrid polarized away from the surface. Second and most important, the electronic flux going into the metal is much different from the free-electron case. This is a direct consequence of the electronic structure of the Cu(111) surface, compared to that of a free-electron surface (Figure 2).

In the free-electron case, the electronic structure is very simple; the energy of the bands simply follows the parabolic dependence of a free electron as a function of $k_z$, the electron momentum parallel to the surface (Fig.2a). In a real metal, the 3D-periodicities of the crystal result in the existence of certain directions and energy regions in which electron propagation is impossible. In the case of a surface, these are called surface-projected band gaps and one is visible in the schematic picture in Fig.2b: there is not any electronic state in the [-0.7, -5.8] eV energy range with $k_z=0$, i.e. an electron cannot propagate along the surface normal in this energy range. As a consequence, several states can exist in this band gap that are confined to the surface area and that cannot penetrate into the metal (see e.g. in [6]): the surface state (SS in Fig.2b) that is localized close to the surface and the image potential states (IS in Fig.2b) that correspond to an electron bound by its interaction with its own electrical image inside the metal. The difference in the electronic structure between a free-electron metal surface and a surface with a projected band gap has direct consequences on the RCT. On a free-electron metal, we have seen that electron transfer is hugely favoured along the surface normal, where the transparency is the highest. The electron is then preferentially transferred into the $k_z=0$ states of the substrate which are available at the Cs* state energy in the free-electron case (Fig.2a). On a Cu(111) surface, we can see in Fig.2b that there is not any state with $k_z=0$ at the Cs* state energy in which the excited electron could be transferred. An electron can only be transferred into states with a finite $k_z$, either in the surface state continuum or in the 3D-propagating band. The barrier transparency effect is still there and electron transfer occurs mainly as close to the surface normal as possible allowed by the band structure. One can recognize in Fig.1 an outgoing electronic flux going from the Cs adsorbate into the metal, a finite angle away from the surface normal. In the Cs/Cu(111) case, the flux into the surface state continuum is very weak. On the Cu(111) surface, since the states the most efficient for
the RCT are missing, the RCT rate is much smaller than on a free-electron metal surface. At the adsorption distance (3.5 \(a_0\)), the Cs* decay rate amounts to 900 meV on a free-electron metal and it drops to 7 meV on Cu(111) [7]. There is thus a quasi-blocking of the RCT by the surface-projected band gap. Since one-electron transitions are weak, one should consider the contribution from multi-electron interactions. In the Cs* case at the adsorption distance, the multi-electron decay rate amounts to around 20 meV and thus dominates the electron lifetime [8]. One can then conclude on a very efficient RCT process in the case of a free-electron metal and it is much suppressed in the presence of a surface-projected band gap.

In this section we have seen that the RCT process is very efficient in the case of a free-electron metal and it is strongly influenced by the presence of a surface-projected band gap. The quasi-blocking of the RCT by the surface-projected band gap and the drastic reduction of the global electron transfer rate is of paramount importance for a series of physical situations that are underlined below.

3.2 Collisional charge transfer

During an atom-surface collision, when the atom is close to the surface, an electron can jump from/to the projectile. This process is just the one discussed in the previous section in the static case (fixed atom-surface distance). It is then very tempting to assume that the collisional atom moves on a classical trajectory and that at each time along the trajectory the electron transfer rate is the same as in the corresponding static case. Within this adiabatic approximation, the charge state of the atom along the trajectory is given by a rate equation. In the case of transitions between a neutral atom (population \(N_0\) and a positive ion (population \(N_+\)) for example, it is written as:

\[
\frac{dN_0}{dt} = -N_0 \Gamma^0_0 + \Gamma^+_+ N_+ \tag{2}
\]

Depending on the relative energy position of the atomic level and of the Fermi level, the RCT process occurs in one direction or the other. This rate equation approach can be derived from a more general treatment of bound state-continuum transitions, within a set of semi-classical approximations [9]. Correlation effects on the atom (degenerate levels, equivalent electrons) are easily taken into account in this formalism [10], they simply reduce to statistical factors and extra equations. This approach proved to be very successful in a variety of collisional systems, in particular for free-electron metal targets in connection with non-perturbative parameter-free determination of the level energy and of the charge transfer rate [11,12]. In particular, detailed accounts of the cinematically (parallel velocity) assisted resonant collisional electron transfer in grazing collisions could be achieved. In grazing collisions, projectiles are impinging at the surface under very small angles with respect to the surface plane. The motion perpendicular to the surface is slow and the rate equation approach is valid. On the other hand, the motion parallel to the surface is characterized by the large velocity component \(v_z\). The electron has an energy in the target frame different from that it has in the projectile moving frame, and the collision velocity is thus able to assist the electron transfer, modifying the resonance condition between atomic and target states [12].

One expects the effects from the target band structure (reduction of the RCT rate, role of 2D surface continua) to be directly transferred into the dynamical process, via a rate equation approach. And indeed, joint theoretical-experimental studies confirmed the strong effects induced by surface-projected band gaps on collisional charge transfer in grazing angle collisions. The reduction of the charge transfer rates results in an important shift of the effective charge transfer distance toward the surface and most effective, contributions from the 2D-surface state continuum on Cu(111) deeply modify the cinematically assisted resonant electron transfer processes [13,14].

However, recent studies at higher impact angles i.e. at higher collision velocity perpendicular to the surface revealed that the situation is more complex and that the effect of the target electronic structure is not always as obvious as in the above-mentioned systems [15,16].
Figure 3 presents the neutralization probability of Li$^+$ ions colliding on a Ag(100) surface as a function of the projectile energy in the few hundreds eV range [16]. The scattering angle is 135°. Experimental results (circles) are compared with the results of three different theoretical approaches. Ag(100) surface exhibits a surface-projected band gap that strongly affects the energy and width of the Li atom levels interacting with the surface. Two theoretical results were obtained using a rate equation approach (eq.(2)): either with the energy and width corresponding to Ag(100) or with those corresponding to a free-electron metal with the same surface work function. A third set of results (labeled WPP) was obtained by a full dynamical study of electron transfer by wave packet propagation. It consists in solving the time-dependent Schrödinger equation for the active electron in the field of the Ag(100) surface and of the moving atom. The atom is assumed to travel along a classical trajectory and so one has to solve equation (1), in which the potential operator depends parametrically on time via the projectile trajectory. This latter study provides the exact result for the dynamics of the collisional charge transfer (within the choice of potential modeling). In particular all dynamical effects are included. It appears in Fig.3 that the full dynamical WPP result quantitatively accounts for the experimental observations. In addition, the dynamical behavior is very far from the adiabatic rate equation prediction for Ag(100), though very close to the free-electron result. Surprisingly, the Ag(100) surface behaves almost like a free-electron metal and its electronic structure does not seem to influence the outcome of a collision, although it influences the static situation. This is due to the existence of non-adiabatic transitions induced by the projectile motion that are not taken into account by the rate equation approach and that tend to cancel the effect of the target electronic structure. This subtle effect can be understood in the following way. It is linked to the finite time character of a collisional process and has been well illustrated in model calculations on the H--Cu(111) system [5]. When the electron is in an atomic orbital localized on the projectile, it does no ‘know’ about the electronic structure of the surface and of a possible surface-projected band gap. Tunneling from the atom to the metal is thus simply determined by the potential barrier separating atom and target, which is practically the same for a free-electron surface and for a surface with a surface-projected band gap. Later, when the electron wave packet penetrates the metal, it is partially reflected.
by the various atomic planes. These reflections and the corresponding interferences are at the origin of the impossibility of electron propagation in certain energy ranges and more generally of the target electronic band structure. Thus, the electron ‘needs’ a finite time to fully adjust to the target electronic structure; in the mean time, it behaves as in the case of a free-electron metal. This explains the results in Fig.3: for a finite collision time, the system ‘does not know’ of the target band structure and RCT occurs as on a free-electron metal. The typical minimum time required for the band structure to fully develop can be estimated to be of the order of the time needed by the electron to travel between the atomic planes in the crystal.

4. Transient excited states localized on an adsorbate on a metal surface

When an atom is adsorbed on a metal surface, excited electronic states can be localized on it; these states are exactly the same as the transient states that were invoked in the collisional charge transfer process, discussed above. In the adsorbate case, the heavy particle motion associated to thermal vibration of the adsorbate is very slow as compared to the previous section. An adiabatic view is then well adapted to describe the system dynamics, so that the effect of the substrate electronic band structure is expected to play a key role.

The development of fast lasers in the fs range allows the study of excited states at surfaces directly in the time domain [17]. In a 2-photon photo-emission experiment (2PPE), a substrate electron is excited by a first photon to a transient excited state and is photo-emitted in vacuum by the second photon. The spectrum of photo-emitted electrons thus reflects the spectrum of transient excited states. In addition, the time evolution of the population in the intermediate state can be probed in an experiment with two separated laser pulses with a controlled time delay between the two pulses (time–resolved 2-photon photo-emission, TR-2PPE). If the phase relation between the two pulses is well defined, the non-linear character of the 2PPE process also allows to perform an interferometric study, i.e. the second pulse probes both the population and the phase of the excitation produced by the first laser pulse and so it can probe the coherence time of the transient intermediate state [17]. These are the two key parameters for describing an excited state dynamics and its role as an intermediate in a reaction mechanism. The lifetime of the state determines how long it survives and then can induce transitions toward a reaction channel and the coherence time determines the extent to which it can be involved in a quantum control scheme. At this point, one can stress that the reaction induced by an excited electronic state involves an energy transfer from the electrons to the nuclei; due to the large mass ratio, this energy transfer is in general very weak but it is favoured for long-lived transient states for which a weak process can be active for a long time.

Adsorbates are located very close to the surface, so that resonant charge transfer between an excited state and the metal substrate is generally very fast. As an example, on a free-electron metal at adsorption distances, alkali levels have lifetimes of a fraction of a fs. This makes reaction mechanisms at surface a priori weakly efficient. The situation changes drastically if the adsorbate level lies inside a surface projected band gap. As shown from theoretical results in section 3.1, in the case of Cs/Cu(111) the RCT rate is much affected by the surface-projected band gap, which reduces it by two orders of magnitude. Taking into account the multi-electron decay of the Cs*, the theoretical lifetime of the Cs* state is in the 30 fs range. Experimental studies on the Cs*/Cu(111) have shown a Cs* state located a few eV above Fermi level with a lifetime in the few tens of fs range [18,19]. Extracting a precise lifetime from these TR-2PPE experiments is not straightforward due to the Cs motion induced by the Cs* excitation (this point is further discussed below). Coherence time are shorter and have been measured and computed in the 10 fs range [19].

Various alkali/noble metal surface systems exhibit excited states with significant lifetimes. The actual value of the lifetime depends on various parameters such as the position of the level inside the surface-projected band gap or the polarisability of the adsorbate. Up to now, Cs*/Cu(111) is the longest-lived state that has been observed in this context [1].
5. **Atomic motion induced by excitation of a transient adsorbate state**

As an example, let us consider again the case of Cs adsorbates on Cu(111). Figure 4 schematises the 2PPE process in this system and the induced Cs motion. The left part of Fig.4 shows the 2PPE process in which a substrate electron is excited by a first photon (ℏω₁) to the Cs* state and then photo-emitted by a second photon (ℏω₂). The Cs adsorbate is initially at its adsorption equilibrium. In the Cs* intermediate state, the interaction between the adsorbate and the substrate is different from that in the ground state and the adsorption distance is not an equilibrium distance for the excited state. As a result, when the Cs* electronic state is formed, the Cs adsorbate starts to move outward from the surface. This induces a downshift of the Cs* electronic energy. The right part of Fig.4 illustrate this effect: the energy profile (in blue) of the excited state created by the first photon shifts down as the Cs adsorbate moves away from the surface. The spectrum of photo-emitted electrons then depends on the time when the second photon is absorbed: the larger is the time delay between the two photons, the lower is the photo-emitted electron energy. This effect has been very clearly observed experimentally [20]: the spectrum of photo-emitted electrons varies continuously when the Cs-surface distance increases, i.e. when the delay between the two photons is increased. This brings a direct evidence of the photo-induced Cs motion allowing its study directly in real time.

**Figure 4**: Left part: schematic view of the two-photon photo-emission process in the Cs/Cu(111) system: an electron from the substrate is excited to the Cs* state by a first photon and then photo-emitted by a second photon. Right part: schematic view of the evolution of the Cs*/substrate system. After the first photon absorption, the Cs-surface distance increases, leading to a downshift of the Cs* energy visible in the energy spectrum of electrons emitted by the second photon.

Figure 5 presents the energy shift of the maximum of the energy spectrum of the photo-emitted electrons in the Cs/Cu(111) system as a function of the time delay between the two laser pulses. Experimental data [20] and theoretical results [21,22] obtained from a parameter-free modelling of the photo-emission signal are compared. Results provide a direct view at the way the Cs* energy changes with time: one recognizes a quasi-parabolic behaviour corresponding to the accelerated classical motion on the Cs* potential energy curve of the Cs adsorbate initially at rest. One can stress that the energy change is small during the state lifetime (τ ≅ 30fs). Large energy shifts of the Cs* state, i.e. large energy transfers from electrons to heavy particle motion only occur for very late times when the
survival probability in the Cs* state is very small and so these are unlikely. The energy shift varies quadratically with $\tau$, confirming the paramount importance of the state lifetime for the efficiency of the evolution induced by the photo-excitation.

Figures 4 and 5 show that the Cs* energy and thus the energy of the photo-emitted electron change with the time delay between the two laser pulses. This demonstrates well the power of the TR-2PPE method in revealing the dynamics of an adsorbate-substrate system directly in real time. In several systems, it allowed the unveiling of the evolution of the system and the characterisation of the different steps in the rearrangement triggered by the photo-excitation: solvation at surfaces [23], small polaron [24] and 2D-polaron [25] formation. The time evolution of the excited state energy makes the quantitative analysis of TR-2PPE signals non-straightforward. Indeed, looking at the photo-emitted signal at a given energy (to isolate a given transient state) yields a signal that depends both on the state lifetime and on the rate of change of the transient state energy (the studied state moves out of the detection window). As a consequence, direct analysis of the TR-2PPE signal at fixed energy yields effective population decay times that a priori depend on the experimental conditions and in particular on the properties of the exciting laser [22,26]. Another possibility is to define 2PPE signals that follow the transient state change with time, but this requires a precise identification of the various contributions in the spectrum and possibly non-straightforward time-dependent deconvolutions.

![Figure 5: Maximum of the energy spectrum of the two-photon photo-emission from the Cs/Cu(111) system as a function of the time delay between the two photon pulses. Open diamonds and squares: experimental results from [20]; dashed line: theoretical results from [21] and full lines with circles: theoretical results from [22].](image)

6. Desorption induced by electronic excitation

In the previous section, we have seen that the Cs* state excitation in the Cs/Cu(111) system induces an outward motion of the Cs adsorbate from the surface. This corresponds to the beginning of a desorption process and actually, if the energy transfer between the electrons and the nuclei induced by the excitation is large enough the Cs adsorbate will eventually desorb. This is an example of the well-known MGR (Menzel-Gomer-Redhead) [27] mechanism for photo-desorption and many photo-induced or electron-induced desorption processes have been interpreted along this mechanism (see a recent detailed review in [28]). In this mechanism, the excitation of a transient state triggers the desorbing motion of the adsorbate; if the lifetime of the transient state is long, enough energy can be transferred from the electrons to the nuclei to overcome the desorption barrier. In addition, depending on the charge state of the adsorbate at the time the energy transferred becomes large enough, ionic or neutral desorption can occur. If the energy transferred is smaller than needed to overcome the desorption barrier, it results in vibrational excitation of the adsorbate in its adsorption well.
The mean energy transferred from electrons to nuclei in a photo-excitation process is presented in Figure 6 in the case of a laser photo-excitation of the Alk* state in the Alk/Cu(111) system (Alk=Na,Cs) [29]. It has been computed using the description discussed above of the Alk/Cu(111) systems. The adsorbate is initially in one of the vibrational levels in the adsorption potential energy well and the transferred energy is seen to weakly vary with the initial motion of the adsorbate. It appears that the energy transferred is of the same order of magnitude in the two systems. The effect of the Na lifetime, which is much shorter than that of Cs, is roughly balanced by the smaller Na mass and by the steeper Na* potential energy curve. Thus, photo-excitation of the Alk* state results in the vibrational heating of the adsorbate in its adsorption well. For both adsorbates, only a small fraction of the energy brought by the photon (of the order of 3eV) is transferred to the adsorbate motion and most of this energy ends up in exciting bulk electrons. The transferred energy is also much smaller than the desorption barrier which is of the order of 1.9 eV in both systems. As a consequence, one can expect desorption to be a weak process, corresponding to the very high-energy wing of the transferred energy distribution.

Photo-induced desorption following the excitation of the transient Cs* state has been observed indirectly in the Cs/Cu(111) systems: a variation of the surface work-function was recorded following the surface irradiation but no direct measurement of the outgoing Cs flux could be performed and only an upper limit of the desorption cross section was obtained. Figure 7 presents the desorption probability per absorbed photon in the Alk/Cu(111) system as a function of the initial energy of the adsorbate in the adsorption well. The desorption probabilities appear to be extremely small if the adsorbate is initially in its adsorption ground state and this is consistent with the experimental observations.

It also appears in figure 7 that an initial vibrational excitation of the adsorbate in the adsorption well results in a drastic increase of the desorption probability. Two effects are playing a role: first, an initial vibrational excitation of the adsorbate means that less energy is required to desorb and so the process is easier. Second and more important, an initial vibrational excitation means a larger velocity of the adsorbate along its trajectory, so that it travels further away before decaying. This effect is the same as the one met in the resonant dissociative attachment process in electron-molecule collisions. In this process, an electron colliding on a molecule is captured to form a transient negative molecular ion; the capture triggers an energy transfer from the electrons to the heavy particle motion, which, if large enough, leads to dissociation. If the transient state is short lived the process is weakly efficient and is strongly favored by an initial vibrational excitation of the target molecule (see e.g. for the H₂ molecule [30,31]).
Finally, one can mention that excited electronic states localized on adsorbates can also be excited by electrons injected through an STM tip and lead to various reactions or atomic manipulations. As an example, one can mention that recently, such a process has been evidenced in the Li/Ag(100) system similar to the Alk/metal systems discussed at length here. An efficient adsorbate diffusion was found to be induced by electron transfer from the STM tip into an unoccupied state on the Li adsorbate, located around 3.6 eV above Fermi level [32]. A good candidate for this active intermediate is the Li* state similar to the ones studied presently (see a discussion of the various Alkali/Metal systems in [1]). Transferring an electron from the STM tip into this state could excite the adsorbate motion perpendicular to the surface in a way similar to the photo-excitation discussed above. Mode mixing, possibly induced by the STM bias, can then also result in the excitation of the adsorbate motion parallel to the surface, leading to the adsorbate manipulation process observed in [32].

7. Conclusions
Excited electronic states at surfaces are often invoked as reaction intermediates in various surface reaction mechanisms. We have reviewed a series of experimental situations where transient states play a substantial role: collisional charge transfer, photo-excitation of transient states localized on adsorbates, vibrational heating of adsorbates, photo-desorption, atomic manipulation by STM. Examples were chosen in the same class of systems, alkali interacting with a metal. It is remarkable that the same quasi-stationary state, corresponding to the transient capture of an electron by an alkali ion, is the active intermediate in all these reaction processes.

Long excited state lifetimes are of paramount importance for the efficiency of the induced processes. On a free-electron metal surface, resonant electron transfer is usually very fast and this makes excited states very short-lived and so weakly effective as reaction intermediates. In contrast, the presence of a surface-projected band gap strongly alters the resonant electron transfer process leading to the possibility of long-lived states. Alkalis on certain noble metal surfaces present striking examples of these stabilization effects.

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