

Desorption induced by femtosecond laser: nonlinear regime through indirect coupling

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The photodesorption of molecular adsorbates from metallic surfaces has been studied by wave packet propagation of the Schrödinger equation, using a non-conservative three-state phenomenological model. The three-state diabatic model includes the surface band structure, the laser-matter interaction and the interstate coupling. The non-conservative fluctuation/dissipation coupling with the bath is introduced through the third state $|3\rangle$ and its interactions: (i) a delay time (expressed as a phase difference) between $|1\rangle \leftrightarrow |3\rangle$ excitation/de-excitation events related to the fluctuation of the energy with the bath and (ii) a quenching of the electron population of this state $|3\rangle$ related to the dissipation. The desorption yield (Y) is obtained as an average over the desorption probability calculated from a sampling of delays or phase differences. The study of the photodesorption of CO from Cu(111) showed that the model displays: (i) a Gaussian distribution of the desorption probability with the phase difference indicating a random, incoherent character of the coupling between the system and the metal bath; (ii) a nonlinear dependence of the photodesorption yield with the laser fluence governed by a single parameter, the amplitude of the $|1\rangle \leftrightarrow |3\rangle$ transition probability. We obtained a $Y \approx F^{4.9}$ dependence of the desorption yield with the laser fluence, in agreement with the experimental findings.

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1. Introduction

Due to the non-linearity of desorption yield with the laser fluence, the laser induced desorption from metallic surfaces has been intensively studied in the past, both experimentally and theoretically [1-5]. This non-linear behavior seems to be specific for processes at surfaces in the presence of sub-picoseconds lasers and it appears also in other phenomena like SERS [6] and in the photoelectric effect induced by infrared lasers [7].

Many theoretical studies of photodesorption make use of a model of photodesorption at metallic surfaces, originally proposed by Gadzuk *et al.* [8], called Desorption Induced by Electronic Transition (DIET). The actual phenomenological description of this model is as follows: (i) the desorption is initiated by a single, sudden laser excitation of the substrate electrons creating a bath of hot non-equilibrium electrons that will scatter into an unoccupied valence electron resonance of the adsorbate $2\pi^*$ antibonding orbital forming a temporary negative ion; (ii) after the neutralization of this ion, the system returns to the ground state of the adsorbate and an excited state of the metallic substrate; (iii) if the lifetime of the adsorbate resonance is sufficiently long, some energy is transferred to the desorption coordinate leading to desorption if the induced kinetic energy of the nuclei is large enough. An evolution of the original model called Desorption Induced by Multiple Electronic Transitions (DIMET), of pertinence here, considers that to produce desorption, one needs multiple states and/or multiple excitation/de-excitation cycles accumulating the energy in the desorption degree of freedom [9-32]. The reader is referred to the paper of

Guo, Saalfrank and Seideman [5] for an extensive overview of the concepts and theoretical models employed in this domain. A recent paper by one of us [32], gives a panorama of classical and quantum models developed to describe photodesorption process at surfaces, in particular the CO desorption from metallic surfaces.

The published theoretical models of desorption of an adsorbate from a metal are either based on semi-empirical or *ab initio* [13-15] potential energy surfaces (PES). In both approaches, the band structure of a metal is not properly taken into account. Namely, *ab initio* methods use a model cluster approach that reproduces the local surface structure but ignores the surface periodicity. Therefore, one obtains a discrete energy spectrum instead of the band structure of the solid. The projected band structure of the surface can strongly influence the photodesorption results, since, for example, the photodesorption yield is different for CO desorption from Cu (111) [1] or from Cu (100) [4] surfaces. Therefore, the surface projected band structure plays an essential role in the theoretical desorption models.

The photodesorption models suffer from a lack of a microscopic mechanism including the laser interaction with the substrate (bath) electrons. For example, regardless of the way the desorption was treated, the hot electron influence was introduced, generally, through an interaction term that depends on an electronic temperature. This temperature appears to be the only empirical parameter able to induce the non-linearity in the desorption models. However, we already showed [33] that an electronic temperature cannot be defined when the system is submitted to a femtosecond laser because such a laser

drives the electronic population far from the Fermi-Dirac distribution defining the temperature of the electrons. The system returns to equilibrium conditions in a time longer than the desorption time of less than 1 ps. Previously [34] (hereafter abbreviated BRM), we succeeded in obtaining the non-linear behavior of the desorption yield with the laser fluence through an optical potential dependent on the hot electron population. This is one of the possible ways that permits a withdrawal of the assumption of an electronic temperature.

In the present paper we have taken a different route in search of a theoretical model giving rise to the nonlinear behavior of the photodesorption yield with the laser fluence. As in the preceding BRM model, our phenomenological diabatic Hamiltonian is constructed from three *potential energy curves* (PECs) but the interstate interactions are partly different and mainly calculated on a microscopic level. The third PEC, supplementing the usual ground and excited PECs of the DIET model, permits the introduction of: (i) an explicit laser excitation of the adsorbate (called direct) and the substrate (called indirect) included up to now in only a few papers [14-17]; (ii) a particular form of the indirect laser-matter interaction term between states $|1\rangle$ and $|3\rangle$ containing a delay between excitation and de-excitation; this interaction gives rise to a non-conservative character of the system; (iii) a damping of the electrons of the system through a phenomenological quenching of the $|3\rangle$ state, taking the form of a negative imaginary potential. Such an imaginary potential has already been used in papers by other authors for the same purpose of the energy dissipation to the metal [16,26,35,36]. The model is implemented in a time dependent wave packet Schrödinger equation formalism.

We explicitly calculated the dependence of the interaction terms on the desorption coordinate. In the preceding phenomenological models (excluding the *ab initio* approach), many different expressions of the interaction terms, deduced from qualitative arguments, were proposed but, so far, there was no explicit attempt to calculate these dependences. For example, a Lorentzian form [16], a Gaussian form [28,34], an exponential form based on analogy with optical transitions [26], a form derived from a Boltzmann factor [17,24] and finally a decaying exponential form [19] were already proposed and used.

We apply the present phenomenological model to a CO molecule adsorbed on a Cu(111) substrate, a system we have studied before [33] and is rather well characterized both experimentally [1,37] and theoretically [14,15,29,32,34,38-40]. In the calculations presented here we introduce the projected band structure of Cu(111) surface that at the Γ point, materializes as a discrete ground surface state (SS) below the Fermi level.

2. Three-state photodesorption model

Our desorption model is built on three states: the ground state $|1\rangle$ of the system, corresponding to the neutral molecule bonded to the neutral metal, the state $|2\rangle$ corresponding to the excited negative ion resonance of the adsorbate and finally the state $|3\rangle$ corresponding to the neutral CO bonded to the metal having an electron excited by the laser above the Fermi level. Each state is a product of a nuclear and electronic function. As usual in solid state problems, we reduce the multielectronic wave function to the function of one electron.

Let us discuss the physical nature of the electronic states for our present physical system, CO on Cu(111). First, the Cu(111) projected band structure at Γ point ($k_{\parallel}=0$; k_{\parallel} is the wave vector for the electronic motion parallel to the surface) presents a band gap extending between -0.85 and 4.3 eV with a surface state (SS) located in that gap at $E_{SS} = -0.39$ eV [42,43]. So, for $k_{\parallel}=0$ at the Fermi level, there are no available electronic states, the last occupied state being SS. We chose this SS as the ground electronic state of $|1\rangle$. Because this ground state is discrete, no integration over continuum states has to be performed. Secondly, the electronic state of $|2\rangle$ is taken as the $\text{CO-}2\pi^*$ resonance. The two-photon photoemission spectroscopy experiments [44] give the $\text{CO-}2\pi^*$ resonance maximum located at 3.35 eV above the Fermi level with a lifetime estimated between 0.8 and 5 fs. This short experimental lifetime is confirmed by the calculations of one of the present authors [45]. The corresponding resonance width being about 5 eV, the excitation from the ground state can be obtained with a laser of energy between 0.85 and 5.85 eV.

The experiment of Prybyla *et al.* [1] for CO desorption from Cu(111), that we are modeling here, used a laser of 2 eV. Therefore, one positions the electronic state of $|3\rangle$ in the band gap at 2 eV above the ground state. The 2 PPE experiments performed by Ogawa *et al.* [46] and Aeschlimann *et al.* [47] gives evidence for the existence of damped states for any energy of the gap. A transient electronic population may be created by laser excitation for all energies of the gap. The electronic state of $|3\rangle$, positioned at 1.61 eV above the Fermi level in the gap, corresponds to such an electronically damped gap-state of the metal.

In the present model the electronic motion has been integrated out. Each nuclear function is associated to a phenomenological, one-dimensional, diabatic PEC, presented in Fig. 1, or three diabatic channels. The dynamics of the motion of the nuclei occurs on this three PECs and the associated Schrödinger equation in matrix form reads

$$i\hbar \frac{d}{dt} \begin{pmatrix} \varphi_1(z,t) \\ \varphi_2(z,t) \\ \varphi_3(z,t) \end{pmatrix} = \begin{pmatrix} \hat{H}_1 & V_{12}(z,t) + Q_{12}(z) & 0 \\ V_{21}(z,t) + Q_{21}(z) & \hat{H}_2 & V_{23}(z,t) + Q_{23}(z) \\ 0 & V_{32}(z,t) + Q_{32}(z) & \hat{H}_3 - iV_{ee} \end{pmatrix} \begin{pmatrix} \varphi_1(z,t) \\ \varphi_2(z,t) \\ \varphi_3(z,t) \end{pmatrix} \quad (1)$$

The coordinate z is the desorption coordinate and it describes the motion of the CO adsorbate center of mass (CoM) normal to the surface. In this equation the electronic coordinates have been already integrated out.

2.1 The potential curves

The elements on the diagonal of the Hamiltonian matrix are

$$\begin{aligned}\hat{H}_i(z) &= -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial z^2} + V_i(z) \quad i \in (1,3) \\ &= T_i(z) + V_i(z)\end{aligned}\quad (2)$$

corresponding to the kinetic $T_i(z)$ and potential energy $V_i(z)$ operators of the Hamiltonian, for the motion of the nuclei. Because the metal is considered to be of an infinite mass, the reduced mass μ of the system is equal to $\mu = m_c + m_o$. The behavior of the potential energy terms V_i , ($i \in (1,3)$) relative to the desorption coordinate z is displayed in Fig. 1.

The PECs are obtained as in our previous model BRM from a potential proposed by Tully *et al.* [40] using a slab of 768 Cu atoms ($16 \times 16 \times 3$) with a (111) terminal surface and one CO molecule adsorbed on the on-top adsorption site. The curve V_1 , associated to the ground state $|1\rangle$ of the system, has been calculated using the Tully potential [41]. The curve V_2 , associated to the state $|2\rangle$, has been calculated using the Tully potential [41] supplemented by a charge transfer term from the metal to the empty $2\pi^*$ orbital of CO molecule. The third PEC V_3 is associated to state $|3\rangle$. Because of the damping in the gap, the state $|3\rangle$ can be considered short lived and no nuclear relaxation can take place. Therefore we consider V_3 PEC parallel to V_1 PEC.

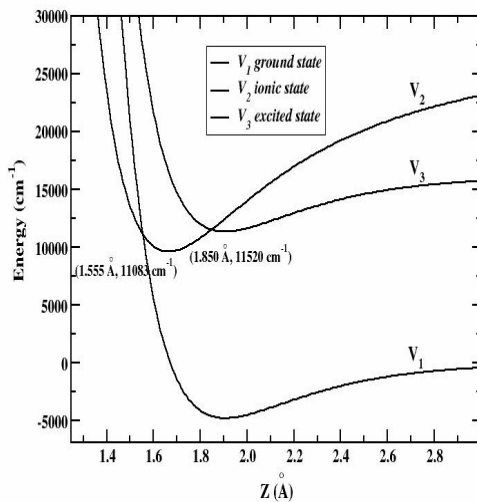


Fig. 1. Potential energy curves for photodesorption of CO from Cu(111) surfaces. The numbers in the parenthesis correspond to the position and energy of the crossing points between potential curves.

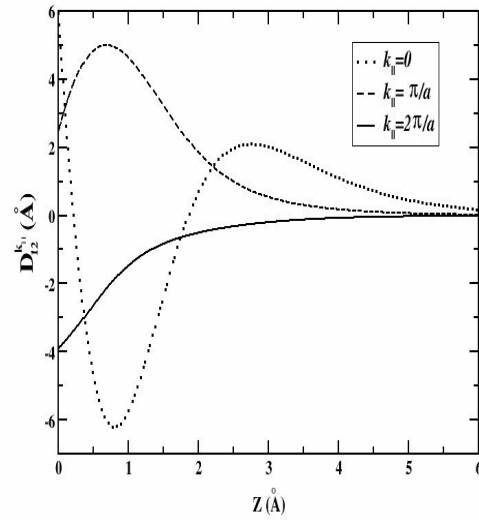


Fig. 2. The transition dipole moment $D_{12}^{k_{ii}}(z)$ as function of z , the CO-surface distance, for different k_{ii} values. The maximum value of the transition moment is arbitrarily set to 1.

The large width of the ion resonance permits the crossing between V_2 and V_3 to be positioned near the ground vibrational level of PEC, V_2 . As in BRM, the zero energy of the adsorbate-substrate model is associated with the desorption asymptote of V_1 PEC.

2.2 Interaction between states

The eq. (1) contains the following interaction terms: (i) the electron transfer V_{ij} between the states $|i\rangle$ and $|j\rangle$ induced by the electromagnetic field of the laser in the dipole approximation; (ii) the diagonal term V_{ee} of the state $|3\rangle$, a phenomenological quenching rate having a dissipative character taking into account implicitly the inelastic coupling to the metal bath of electrons (electron-electron collisions); (iii) the electrostatic interaction Q_{ij} between the diabatic states $|i\rangle$ and $|j\rangle$, that in an adiabatic representation corresponds to a non-adiabatic (non Born-Oppenheimer) coupling of the nuclear derivative operator, a non-radiative electron charge transfer.

The laser-matter interaction from the SS ground state, $|1\rangle$, to the excited CO- $2\pi^*$ resonance, $|2\rangle$, can take place through direct one photon excitation $|1\rangle \rightarrow |2\rangle$ and/or indirect processes $|1\rangle \rightarrow |3\rangle \rightarrow |2\rangle$. In the dipole approximation this laser-matter interaction term can be written as

$$\begin{aligned}V_{ij}(z,t) &= -e \text{Re} \left\{ \langle \phi_j(x', y', z') | x' E_0 \exp[i(kz - \omega t)] | \phi_i(x', y', z') \rangle_{x', y', z'} \right\} \\ &= -e \text{Re} \left\{ D_{ij}^{k_{ij}}(z,t) \exp(i\vartheta_{ij}) E_0 \exp(-i\omega t) g(t) \right\} \\ &= -e \left| D_{ij}^{k_{ij}}(z,t) \right| E_0 \cos(\omega t + \vartheta_{ij}) g(t)\end{aligned}\quad (3)$$

where E_0 is the modulus of the electric field vector, ω is the light angular frequency, $|D_{ij}^{k_{ij}}(z,t)|$ is the electric

dipole moment for the transition between states $|i\rangle$ and $|j\rangle$. As it will be explained in the next section, ϕ_i, ϕ_j are electronic functions dependent on the electronic coordinates x', y', z' . The phase θ_{ij} appears because we consider that the transition moments are not equal (see below) and for convenience we model this difference in the trigonometric function associated with the electric field of the laser. As in the experiment of Prybyla *et al.* [1], we take a laser in a normal incidence configuration with its electric vector parallel to the x' direction (p polarization). The laser pulse temporal shape $g(t)$ is taken to be Gaussian, $g(t) = \exp\left(-\left(t - t_p\right)^2 / t_p^2 \ln 2\right)$ with $2t_p$ the full width at half-maximum (FWHM).

In the present model one uses different approximations for the $|1\rangle \leftrightarrow |2\rangle$ and $|1\rangle \leftrightarrow |3\rangle$ laser-matter interaction terms:

1. for the interaction $|1\rangle \leftrightarrow |2\rangle$ the transition moment is time independent but depends on the desorption coordinate z as the PECs $V_1(z)$ and $V_2(z)$ are not parallel

$$D_{12}^{k_{\parallel}}(z) = D_{21}^{k_{\parallel}}(z), \theta_{12} = \theta_{21} = 0 \quad (4)$$

2. because PECs $V_1(z)$ and $V_3(z)$ are parallel, the transition moments for interaction $|1\rangle \leftrightarrow |3\rangle$ depends on time but not on z

$$|D_{13}^{k_{\parallel}}(t)| \neq |D_{31}^{k_{\parallel}}(t)|, \Delta\theta = \theta_{13} - \theta_{31} \neq 0 \quad (5)$$

As is usually explained in photoabsorption, the momentum of the photon is much smaller than the momentum originating from the solid and therefore momentum conservation requires $\Delta k_{\parallel} = 0$ for any k_{\parallel} . In the CO- $2\pi^*$ resonance state $|2\rangle$, the k_{\parallel} wave number is not a well defined observable because of lack of periodicity. However, one can still impose $\Delta k_{\parallel} = 0$ for any k_{\parallel} , with a maximum of transition probability at $k_{\parallel} = 0$.

In a direct or coherent process where initially, in the metal, $k_{\parallel} = 0$, the laser couples the initial $|1\rangle$ and final $|2\rangle$ states without populating any intermediate state. But in laser induced desorption from metals, direct processes are much less important than the indirect substrate excitation [25]. In indirect or incoherent process, where the initial $k_{\parallel} \neq 0$, the electrons are transferred to the CO- $2\pi^*$ state through an intermediate, damped gap-state $|3\rangle$, followed by multiple phonon scattering that reduces k_{\parallel} to 0 in order to attain state $|2\rangle$, a mechanism advocated by Ogawa *et al.* [46].

In our indirect excitation model we suppose that $|1\rangle \leftrightarrow |3\rangle$ excitation and emission are not equivalent. First, the electron jumps from the ground SS state to the intermediate state $|3\rangle$. There, it can be de-excited directly by a photon emission (interaction V_{31}) to the ground state or, it can interact with the adsorbate state $|2\rangle$ by charge transfer (interaction Q_{32}). In state $|2\rangle$, the electron spends some time, then it can be de-excited to the ground state (coupling Q_{21} or photon emission V_{21}). Or, it can fly back

to the $|3\rangle$ state (interaction Q_{23}) and be de-excited (V_{31} coupling) to the ground SS.

The indirect or incoherent process can also be discussed in terms of collisions. The laser couples the initial and final states through an intermediate state, producing a population of hot-electrons. Then, these electrons can decay by inelastic (single and multiple) electron-electron, quasi-elastic electron-phonon or electron-CO adsorbate scattering [48] and are detected by absorbing a supplementary photon. The processes taking place in the intermediate state give rise to a delay between absorption and emission leading to a loss of coherence between photon excitation and emission [46], **formally** equivalent to a laser pulse having a random phase component [49].

Ballistic and diffusive transport of electrons out of the volume of observation and hot-electron cascade through multiple inelastic collisions with other electrons may also contribute to depopulating $|3\rangle$ (V_{ee} term) [46].

Computationally, the rapid time evolution of this state $|3\rangle$, between laser excitation and de-excitation, shows up in the different moduli $|D_{31}^{k_{\parallel}}(t)|$ and $|D_{13}^{k_{\parallel}}(t)|$ and phases θ_{31} and θ_{13} of the complex time-dependent transition moments (eqs. (3), (5)). The phase difference $\Delta\theta$ is induced by scattering with the electrons and phonons of the bath that changes the k_{\parallel} value of the electron in the state $|3\rangle$, without changing its energy.

To reduce the number of parameters of the model we take $|D_{31}^{k_{\parallel}}(t)| = |D_{13}^{k_{\parallel}}(t)|$ so the entire non-hermiticity of the three-states Hamiltonian matrix corresponding to the open system is cast in the phase difference $\Delta\theta$ (we emphasize that our phase difference can not be related to the dephasing introduced in the density matrix formalism). This phase difference $\Delta\theta$ is at present taken as a random variable, corresponding to a random delay time between absorption and emission. Because only modulo 2π matters in eqs.(3), we restrict its variation to $[0, 2\pi]$. Note that the photodesorption yield we are comparing with the experiment, is an average over phase differences of the photodesorption probability, thus giving a stochastic character to our approach.

The optical potential V_{ee} describes, through a phenomenological quenching rate, the loss of population in the third state $|3\rangle$ due to hot-electron cascade through multiple inelastic collisions with other electrons and ballistic and diffusive transport of electrons out of the volume of observation

$$V_{ee} = \frac{\hbar}{2\tau_{ee}} \quad (6)$$

where \hbar is the Planck's constant and τ_{ee} is the electron-electron collision time in the excited state $|3\rangle$. The two-photon time-resolved photoemission spectroscopy experiment of Ogawa *et al.* [46] gives for the Cu(111) clean surface $\tau_{ee} = 35$ fs, value that we use in our calculations.

In summary, the Hamiltonian of the present model corresponds to an open system introduced at a microscopic level in a DIMET type model: the difference between the transition moments $D_{13}^{k_{ij}}$ and $D_{31}^{k_{ij}}$ corresponds to a system fluctuation and that of the optical potential V_{ee} to a system dissipation to the bath. The reservoir or bath is represented by the substrate electrons and phonons. This terminology is borrowed from the Langevin model of the classical mechanics applied to an open system (see e.g. [50]). Technically, our Hamiltonian is non-hermitian, non-symmetric and non-conservative and it corresponds to an open system. A non-hermitian Hamiltonian containing a dissipative term of interaction with the solid has been used before in the description of the de-excitation process in a DIET "dissipative wave packet model", in a "multiple coupled wave packet approach" [16,51] or in a method we have developed (see BRM). Guo [20] used asymmetric coupling terms that describe electronic transitions where de-excitation is delayed only by a fixed time compared to excitation. The phase difference of our model corresponds to a delay time taken as a statistical observable because the majority of de-excitation processes are random. The present quantum model, where the system is gaining and losing energy from the bath, can be put in parallel with the currently used classical Langevin equations of motion (see e.g. [50] and the discussion in the results section).

2.3 The interaction terms as a function of the desorption coordinate z

In the phenomenological photodesorption models, one usually takes [17,25] the dipole transition moment $D_{12}^{k_{ij}}(z)$ as independent of the desorption coordinate z and this approximation can artificially modify the photodesorption results. In fact the transition dipole moment is proportional to the overlap between the metal and adsorbate electronic wave functions, overlap that tends to zero when the adsorbate-substrate distance increases at desorption.

The transition dipole moment between states $|1\rangle$ and $|2\rangle$, appearing in eqs. (3) and (5), can be approximatively written as the dipole moment between ground SS and $2\pi^*$ excited state

$$D_{12}^{k_{ij}}(z) \equiv D_{SS2\pi^*}^{k_{ij}}(z) = \left\langle \phi_{2\pi^*}^{k_{ij}}(x', y', z'-z) \left| x' \right| \phi_{SS}^{k_{ij}}(x', y', z') \right\rangle_{x', y', z'} \quad (7)$$

where $\phi_{k_{ij}}^{SS}(x', y', z')$ is the SS electronic wave function for a given k_{ij} and $\phi_{2\pi^*}^{k_{ij}}(x', y', z'-z)$ is the $2\pi^*$ electronic wave function. The electronic coordinates x' , y' and z' are integrated out and the result is parametrically dependent on z , the desorption coordinate. To calculate the integral, we have to deal with two electronic coordinate systems: one having the origin at the first surface Cu atom with z' perpendicular to the metal surface and the other one originating at the CO molecule center of mass. As the CO molecule is perpendicular on the copper surface and located on top of a Cu atom, these two coordinate systems

are parallel. In the expression (7) above, the coordinate systems are shifted parallel with respect to each other by z , along the internuclear coordinate. As in the work by Prybyla *et al.* [1] in many experimental set-ups the laser beam is perpendicular to the surface and linearly polarized, the electric vector E_0 pointing in a direction parallel to the surface. Our modeling follows this set-up and, due to the cylindrical symmetry of the two wave functions [52], the results are invariant to the direction of electric vector in the surface plane (here $E_0 \parallel x'$).

The initial ground state wave function $\phi_{k_{ij}}^{SS}(x', y', z')$ is calculated in the nearly free electron approximation ([53,61]). As in our previous work [61], for the electronic wave function of state $|2\rangle$, CO- $2\pi^*$ resonance of $^2\Pi$ symmetry, we took a mixture of two partial waves, namely $p\pi$ and $d\pi$, of the spherical harmonics expansion with the origin at the center of mass of the CO molecule. We used the parameters given in table 1 of our previous work [61].

The dipole matrix element of eq. (7) is calculated by numerical integration and the result is presented in Fig. 2. The integral depends on the exponents of Gaussian functions for the $p\pi/d\pi$ partial waves ratio and is also function of k_{ij} . In order to make a clear comparison of the transition dipole moment for different k_{ij} , in figure 2, the maximum value of the transition moment was set to one. This figure shows that for $z > 1.0 \text{ \AA}$, region covered by our spatial grid used in the propagation, the z -dependence of the transition dipole moment is essentially of exponential form (see eq. (8)) for both $k_{ij}=2\pi/a$ and $k_{ij}=\pi/a$, where $a = 2.08 \text{ \AA}$ is the parameter of the Cu(111) surface. For $k_{ij}=0$ the z -dependence is slightly more complicated.

We assume the same electronic wave function for the states $|1\rangle$ and $|3\rangle$ based on the attenuated behaviour in the metal of both functions. The expression for the interaction terms $Q_{12} = Q_{23}$, both symmetric relative to index inversion, reads

$$Q_{ij}(z) = Q_{ij}^{k_{ij}}(z) = \left\langle \phi_{k_{ij}}^{SS}(x', y', z') \left| \frac{-e^2}{4\pi\epsilon_0 r'} \right| \phi_{2\pi^*}^{k_{ij}}(x', y', z'-z) \right\rangle \quad (8)$$

where e is the electron charge, ϵ_0 the vacuum electric permittivity and $r' = \sqrt{(x'^2 + y'^2 + (z - z')^2)}$ the distance between electron and CO molecule CoM. To calculate this integral, we use a simple approximation due to Gadzuk [55]. Namely the interaction between the initial metal surface $\phi_{k_{ij}}^{SS}$ and the final resonant adsorbate $\phi_{2\pi^*}^{k_{ij}}$ states, corresponding to the resonant charge transfer between two electronic configurations, can be reduced in the end as a single two electron Coulomb interaction. This interaction term can be calculated using the Coulomb potential interaction operator centered on the center of mass of the CO molecule and the appropriate single electron wave functions. Performing such a numerical calculations, with the same parameters as for the dipole moment and present approximate wave functions, one obtains $Q_{ij}(z)=0$ for $k_{ij}=0$. More elaborate calculations, using multi-configuration

wave functions to represent the electronic states, would probably give a non zero result for the zero momentum $k_{||}=0$.

For $k_{||}=2\pi/a$ and $k_{||}=\pi/a$, an exponentially decaying z -dependence of the interactions is obtained. Explicitly the exponential form parameterization, relative to desorption coordinates z , for both $D_{12}^{k_{||}}(z)$ and $Q_{ij}^{k_{||}}$ reads

$$\begin{aligned} D_{12}^{k_{||}}(z) &= d_0 \exp(-\xi z) \\ Q_{ij}^{k_{||}}(z) &= q_0 \exp(-\xi z) \end{aligned} \quad (9)$$

The parameter q_0 is a function of $k_{||}$ and of the exponents of the Gaussian functions for the $d\pi/p\pi$ partial waves. The values of the parameters d_0 , q_0 and ξ , calculated for the wave vector $k_{||}=\pi/a$ i.e. at the boundary of the first Brillouin zone, are: $d_0=0.026$ Å, $q_0=0.052$ eV, $\xi=1.005$ Å⁻¹.

The value of $|D_{13}^{k_{||}}|$ is not calculated here. It is roughly estimated from the atomic transition $4s \rightarrow 4p$ to be about 1 Å. Because the metal transition takes place in the sp band where the electrons are nearly free, we infer that the value of the transition moment in metal will be greater than atomic transition estimation. In calculations we varied its value from 1 Å to 5.5 Å.

2.4 Wave function propagation and the photodesorption yield

Using the Hamiltonian matrix constructed as explained in the preceding subsections, we now solve the time dependent Schrödinger equation (1) by propagating the wave function in space and time. This is done using a third-order split-operator (SO) method [56,57], according to the well known standard scheme

$$\Psi(z, t + \delta t) = e^{-iV\delta t/2\hbar} e^{-iT\delta t/\hbar} e^{-iV\delta t/2\hbar} \Psi(z, t) + O(\delta t^3) \quad (10)$$

Here $\Psi(t)$ is the total nuclear wave function, the column vector of the equation (1) with the elements $\varphi_1(z, t)$, $\varphi_2(z, t)$ and $\varphi_3(z, t)$. \mathbf{V} and \mathbf{T} are the potential and kinetic energy operator matrices appearing in the equations (1) and (2) above. At each time step the wave function is discretized on a one dimensional spatial grid and the kinetic and potential energy operators are applied in a local representation. The kinetic operator contribution is calculated in momentum space using the FFT algorithm. The potential operator is a complex non-Hermitian full matrix. Instead of diagonalizing it, we calculated the contribution of the potential factor by expansion in a power series up to 16-th order. We verified that, for a real \mathbf{V} matrix, the results obtained by the power series and by standard diagonalization are identical.

In the calculations presented in the next section, the total simulation time was 819.2 fs with a time step of $\Delta t=0.1$ fs. The Δt interval was chosen to be small enough

to resolve the variations in the Hamiltonian evolution and the oscillations of the external photon field. The spatial z -grid comprises 2048 equally spaced points at intervals of $\Delta z=0.01$ Å. The values for Δz and Δt are calculated according to the stability conditions of the SO method [56,57]. In order to avoid reflections at the end of the grid, our z -grid extends from $z_{\min}=1.00$ Å, to $z_{\max}=21.47$ Å, so during the propagation time the wave packets never reach the end of the grid and therefore no artificial oscillations occur.

At t_0 we assume that the system is entirely in the state $|1\rangle$ and described by the nuclear function $\varphi_1(z, t)$, the ground vibrational eigen function of the Hamiltonian $\hat{H}_1(z)$ given by eq. (2). This state represents the neutral molecule bonded to the metal with an initial population $p_1(t_0)=\int |\varphi_1(z, t_0)|^2 dz = 1$.

The end of the propagation is reached when the desorption probability $P_{\text{des}}(t)$, defined below, stabilizes at a plateau value. To calculate the desorption probability one writes the total wave function as a sum of two contributions: internal Ψ_I and asymptotic Ψ_A [15,17,26]

$$\Psi(z, t) = h_{z_0}(z) \Psi(z, t) + (1 - h_{z_0}(z)) \Psi(z, t) = \Psi_I(z, t) + \Psi_A(z, t) \quad (11)$$

where $h_{z_0}(z)$ is a smooth cut off function of the Fermi-Dirac type $h_{z_0}(z) = \frac{1}{1 + e^{\sigma(z-z_0)}}$ where $z_0=3$ Å and $\sigma=3$ Å⁻¹ are parameters chosen so that $h_{z_0}(z)$ tends to zero at $z_a=5$ Å, the analysis point. This point also separates the internal and the asymptotic regions and one assumes that, beyond z_a , the CO molecule is desorbed and decoupled from the metal. The desorption probability at a given time t , is calculated as the norm of the asymptotic function

$$P_{\text{des}}(t) = \int_{z_{\min}}^{z_{\max}} |\Psi_A(z, t)|^2 dz \quad (12)$$

which gives simply the probability that the particle is in the region $z \geq z_a$. For a given phase difference $\Delta\theta$, $P_{\text{des}}(t)$ increases with time when the wave function leaves the internal region and then stabilizes at a constant, plateau value $P_{\text{des}}^{as}(\Delta\theta) = \lim_{t \rightarrow \infty} P_{\text{des}}(t)$ taken to be the actual desorption probability.

The desorption yield, related to the experimentally measured yield, is taken as an average value of the desorption probability calculated for a sampling of n phase differences $\Delta\theta_i$

$$Y = \frac{1}{n} \sum_{i=1}^n P_{\text{des}}^{as}(\Delta\theta_i) \quad (13)$$

The results presented in the next section show that the variation of the desorption probability with the phase

difference can be best approximated by a function of a Gaussian shape. For large n , the average of equation (13) tends to the integral

$$Y = \lim_{n \rightarrow \infty} \frac{1}{n} \sum_{i=1}^n P_{des}^{as}(\Delta\theta) = \frac{\int_0^{2\pi} f(\eta) d\eta}{2\pi} \quad (14)$$

where for a continuous variation of $\Delta\theta$, we introduce the notation η . The function $f(\eta)$ is a Gaussian function fitting the numerically calculated points

$$f(\eta) = N \exp \left[-\frac{(\eta - \eta_0)^2}{2\alpha^2} \right] \quad (15)$$

where N is the normalization constant and α is the half width at the half maximum, discussed further later. Good accuracy of the results is obtained by fitting a restricted number of numerical points to eq. (15) and then integrating the second expression of eq. (14).

3. Results and discussion

The phenomenological model developed above has been applied to the study of the photodesorption of CO from Cu(111) surface for a laser of an energy of 2 eV, a pulse duration of 100 fs and a fluence of 44 J/m², conditions corresponding to the experiment of Prybyla *et al.* [1]. In our approach, the Hamiltonian is built from physical quantities: electron transition probabilities V_{ij} , electrostatic interactions Q_{ij} between the diabatic PECs near the crossing points and a quenching rate V_{ee} . The main part of the parameters used in the actual simulation has been calculated in sections 2.2 and 2.3 and some parameters have been taken from the experiment. The two parameters of the system-bath fluctuation/dissipation interaction: i) $\Delta\theta$ is sampled and used in an average procedure to obtain the yield and ii) τ_{ee} is fixed and taken from the experiment. The modulus of the transition moment $|D_{13}^{k_{ij}}|$, connecting the system with the bath and responsible for the yield-fluence dependence, is first roughly estimated from the atomic transition $4s \rightarrow 4p$ then this is **the single parameter** adjusted to fit the experiment. The results presented in Figs. 3 and 4 are obtained using $|D_{13}^{k_{ij}}| = 4 \text{ \AA}$.

The measured experimental photodesorption yield was $\sim 0.05 \text{ ML}$ [1] corresponding to a quantum efficiency of 10^{-3} molecules for a photon. In Fig. 3, we present the results of the calculated photodesorption yield (eq. (14)), at $k_{ij} = \pi/a$, as function of the laser fluence between 30 J/m² and 60 J/m². The obtained yield for a CO adsorbed molecule, between 10^{-3} and 10^{-2} molecules for a photon at a fluence of 44 J/m², agrees well with the experimental yield [1].

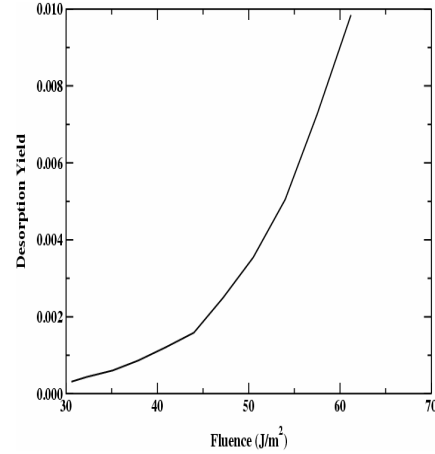


Fig. 3. The desorption yield as a function of the laser fluence.

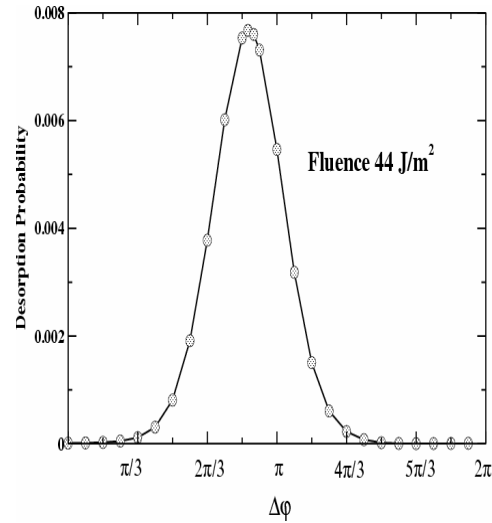


Fig. 4. The desorption probability as a function of the phase difference $\Delta\theta$ at a laser fluence of 44 J/m². The numerical values of the parameters are given in table 2. The circles correspond to the 26 calculated values of the yield. The results fit a Gaussian distribution given in eq. (15).

At a given laser fluence, the desorption yield has been obtained as an average of desorption probability over a sampling of phase difference $\Delta\theta$. Namely, the desorption probability at a given phase difference is calculated from the population in the asymptotic region. Then the calculation is repeated for a sampling of 26 phase differences. The resulting curve is displayed in figure 4 for a fluence of 44 J/m². Desorption takes place even for zero or 2π phase difference but the desorption probability is 10^{-3} smaller. The obtained shape can be best fitted to a Gaussian function $f(\eta)$ for all fluences used in the experiment. Finally, the desorption yield Y is obtained, using eq. (14), as an analytic integral of the Gaussian desorption probability $f(\eta)$.

The parameters of the fitting are given in Table 1. One sees that, except for the normalization constant N of the

Gaussian function, the parameters of the fit by a Gaussian function do not strongly vary with the laser fluency. First, the width α of this Gaussian in eq. (15) corresponds to a quadratic fluctuation of the desorption probability given by the relation $\alpha^2 = \frac{1}{n} \sum_n (\eta - \eta_0)^2$. This quadratic fluctuation diminishes by about 25% and the position of the Gaussian maximum η_0 rises by 5% when the fluence is doubled. Therefore rising the fluence diminish the spread of the phase difference with a minor modification of the most probable phase difference. With increasing fluence, the system follows more closely the external laser field. Now the normalization constant N is given in the statistical Gaussian distributions by $\frac{1}{\sqrt{2\pi\sigma^2}}$. The

normalization constant N calculated from this expression varies only slightly with the laser fluence. Actually, the normalization factor N obtained from the present model varies sharply with the laser fluence: at a fluence of 61.2 J/m² it is 39 times higher than at 30.6 J/m². This situation reflects the enhancement of desorption probability with the laser fluence.

Let us comment on the Gaussian dependence of the desorption probability with the phase difference. Such a form is well known in statistical analysis of data, for example when studying the behavior of a thermodynamic observable relative to a weakly fluctuating parameter about a mean value. A Gaussian distribution is also found when connecting, through incoherent processes, a quantum mechanical harmonic oscillator with a bath (see e.g. Messiah [59]). Therefore one deduced that the phase difference $\Delta\theta$ behaves like a fluctuating parameter.

The present formulation can also be compared to the classical Langevin formalism (see e.g. Head-Gordon and Tully [50]). There, the interaction with the bath in the Newton equations of motion of the nuclei contains a random fluctuating force (energy gain) and a friction/dissipation (energy loss) terms. As discussed in this paper, in our model the random/fluctuating term is the phase difference $\Delta\theta$ and the dissipation/loss term is the quenching V_{ee} but of course our method is based on quantum mechanics.

Table 1. Parameters fitting the desorption probability to a Gaussian shape.

Fluence (J/m ²)	N	η_0	α	Yield
30.6	0.0013	148.5	34.3	0.00031
32.3	0.0018	150.2	34.7	0.00043
35.1	0.0026	151.1	33.8	0.00060
37.9	0.0037	153.3	33.5	0.00086
40.9	0.0053	154.7	33.0	0.00120
44.0	0.0076	155.5	30.	0.00158
47.2	0.0110	156.0	31.1	0.00249
50.5	0.0160	159.2	31.5	0.00354
54.0	0.0230	160.1	30.5	0.00504
57.5	0.0341	160.0	30.5	0.00726
61.2	0.0508	160.2	27.5	0.00984

We obtained a power law $Y \sim F^{4.9}$, value situated between the experimental values of 3.7 and 8, the first obtained for CO/Cu(111) by Prybyla *et al.* [1] and the second for CO/Cu(100) by Struck *et al.* [4]. The deduced power law of $Y \sim F^{4.9}$ is better than the power law $Y \sim F^{2.7}$ obtained recently by Micha *et al.* [15] for CO on Cu(001), using a density matrix treatment dependent on an electronic temperature.

One would like to know how the conclusions of the model will change if one allows the variation of the parameters of the model. First, the above results have been obtained at $k_{ij} = \pi/a$. If one performs calculations with the z -dependence of the transition moment corresponding to $k_{ij} = 0$, the corresponding transition moment first oscillates before decaying exponentially (see Fig. 2). With this transition moment we obtained a slightly lower desorption yield, due to the compensation of the positive and negative lobes of the oscillatory part of the transition moment, but the same yield-fluence dependence.

Further, we have tested the stability/robustness of our model against other parameters: i) d_0 , the amplitude of the exponential form of $D_{12}^{k_{ij}}(z)$ (eqn. (9)); ii) q_0 the amplitude of the exponential form of Q_{ij} . As a general trend, the modification of d_0 and q_0 amplitudes influences only the yield value and do not modify the yield-fluence dependence. However, if q_0 of Q_{ij} is greater than 0.52 eV (10 times greater than the actual value of 0.052 eV calculated for $k_{ij} = \pi/a$) the yield diminishes when rising the fluence. The uses of a Gaussian instead of exponential dependence in Q_{ij} or a z -independent form of $D_{12}^{k_{ij}}(z)$ influence again only the value of the yield.

In conclusion, modifying all the parameters of our model, but the amplitude $|D_{13}^{k_{ij}}|$ of the system-bath interaction, will modify the desorption yield itself having only a minor impact on the yield-fluence dependence. Therefore, the modulus is **the single parameter** responsible for the nonlinearity. Changing this amplitude immediately changes the yield-fluence dependence. For example, calculations performed with $|D_{13}^{k_{ij}}| = 0$, i.e. no indirect process allowed, show lower yield values and a yield fluence dependence of maximum $Y \sim F^2$. This result indicates that, even if desorption may be produced by direct excitation of the negative ion resonance, this is not the main process and that the interaction between the adsorbate and the bath included in the indirect process contributes substantially to the desorption dynamics. A similar conclusion was reached also by Saalfrank [25] in the past but from a different point of view. Further, between 1 Å and 3 Å the dependence is close to $\sim F^3$, from 3.5 Å to 4.5 Å it is close to $\sim F^5$ and at 5.5 Å it is $\sim F^7$. For this last value of $|D_{13}^{k_{ij}}|$ the yield becomes almost 1 and saturates. We conclude that our model is robust and agrees with a mechanism of desorption mediated by the substrate.

4. Conclusions

In this paper we presented a quantum mechanical phenomenological, three-state, desorption model including the interaction with the substrate bath, able to take into account direct and indirect excitation processes relative to the adsorbate. This model was designed to explain qualitatively and semi-quantitatively the femto second laser induced desorption and we advocate that the present model gives a new physical insight into this process.

The direct excitation occurs by electronically exciting the adsorbate. The dominant indirect process is introduced naturally using a third electronic state $|3\rangle$ representing the excited substrate. The interpretation of the experimental results favors indirect desorption dynamics with an initial excitation of the substrate (electrons and phonons). In our theoretical model the interaction with the bath is realized through: i) a fluctuation corresponding to the phase difference, $\Delta\theta$, appearing because the absorption and emission transition moments are not equivalent (see eqs. (3,5)); ii) a dissipation corresponding to the electron-electron collisions, V_{ee} . The excited electrons of the substrate bath interact with the adsorbate and the energy is converted to the desorption degree of freedom. If this energy is higher than the asymptotic energy, desorption occurs. The functional dependence of the desorption probability is Gaussian demonstrating the random and incoherent character of the system-bath coupling. The desorption yield is obtained as an average of the desorption probability by sampling the phase differences.

The model was able to reproduce the nonlinear behavior of the desorption yield Y with the laser fluence $Y \sim F^{4.9}$. This result is situated between the experimental values of 3.7 and 8, the first obtained for CO/Cu(111) by Prybyla [1], the second for CO/Cu(100) by Struck [4]. The nonlinear yield-fluence relation depends on a single parameter, namely the modulus $|D_{13}^{k_{ij}}|$ coupling the system with the substrate. Changing this value between 1 and 5.5 Å, changes the exponent of the fluence in the yield expression between 3 and 7. Higher values of the moment modulus produce a saturation in the yield up to one.

The present model replaces the temperature of the electrons, a phenomenological parameter usually introduced in the quantum mechanical models [5,14,32], by fluctuation and dissipation terms that parallel the classical dynamics Langevin equation used to describe the interaction of a system with a bath. In our model, the desorption yield function of laser fluence also depends on a single parameter, the modulus of the transition moment $|D_{13}^{k_{ij}}|$ coupling the system with the substrate, but this parameter is microscopic and is directly connected to the proposed mechanism of photodesorption.

The present model can be applied to photodesorption of other adsorbate-metallic substrate systems. Also, the calculation of the electronic parameters can be done to a higher degree of accuracy or one can include other states in the model as, for example, the first image state of the

Cu(111) surface. In the experiments of two-photon photoemission on CO/Cu(111) [37] it has been shown that a strong coupling occurs between the CO negative ion resonance and the first image state of the metal and we think that such a coupling could play an important role in the desorption process. We also intend to introduce a less phenomenological approach of the energy exchanges in the system, for example by explicitly calculating some of these contributions, notably the electron-phonon interaction term. The extension of the model along these lines is now under development.

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