



Laser Field Characteristics Investigation in the Chemisorption Process for the System Na/W(111)

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Abstract: Detailed theoretical treatment and model calculations for describing the interaction between species and solid surface, in the presence of a monochromatic electromagnetic field (laser field) throughout the chemisorption process, have been developed. Our previous work for the scattering process in the presence of laser field and the well known Anderson model for atomic chemisorption are the basis in deriving our theoretical treatment. The derived occupation number and the chemisorption energy are presented as a function of laser parameters and normal distance from the surface as the adatom approaches to the surface. The model calculation is applied to the Na/W(111) system for its experimental and academic importance. Many important features are explained concerning the adatom charge state and the bonding type. One can conclude that the laser field is a controlling tool of ionization and bonding type, which is experimentally the truth.

Keywords: chemisorption process; monochromatic electromagnetic field; occupation number; chemisorption energy;

I. Introduction

Surface chemical reactions, in which at least one of the reaching species is adsorbed on solid surface, are important for chemical industry. It is hence of interest to investigate laser-stimulated surface processes [1] which include surface excitation [2-4], desorption [5,6], dissociation [7,8] and catalysis [9]. Laser-stimulated surface processes have been investigated during the past several years, due to both their academic interest and industrial potential. Recent progress in the experimental and theoretical studies and applications of laser-stimulated surface processes have been reported [10]. Laser excitation or desorption of adspecies have been investigated theoretically by a variety of techniques including Morse potential models [11] and master equation approaches [12]. Since the charge transfer is the essence of chemistry, surface catalysis would be greatly affected by this phenomenon. With laser, chemists have begun to control chemical reaction dynamics in gas-phase reactions and the reactions occurring at the gas-solid interface [13]. In this paper, the chemisorption of atoms on solid surfaces in the presence of laser field is studied. The theoretical treatment in our previous works [14-16] and the well-known Anderson model [17,18] for atomic chemisorption are our basis in deriving the occupation numbers and the binding energy formulas in the static case of u (atomic velocity) $\rightarrow 0$.

In order to develop a "basis treatment", many complications must be avoided such as,

1. The variation of the screening length with laser field parameters is not taken into account.
2. The dependence of the intra-atomic Coulomb interaction on laser field parameters is not considered as well as the correlation effect on the surface site.
3. The electronic excitations in the adatom-surface orbitals are neglected.
4. The effect of surface temperature is not considered since by including it, one must establish the heating of the system due to laser field.

Each of these remarks may have a wide-range of researching both theoretically and experimentally, which may be considered as future work.

II. Derivation of the Adatom Occupation Numbers

To derive a formula for the occupation number n_A of the adatom level, we get use of the following equation that is derived in our previous paper [15](eq. (20)),

$$\dot{C}_{A\mu'}(t) = -\frac{i}{\hbar} \varepsilon_{im}(t) C_{A\mu'}(t) - \frac{i}{\hbar} \left[\tilde{V}_{A\mu'}(t) + \tilde{W}_{A\mu'}(t) \right] - \frac{1}{\hbar^2} \sum_{\mu} \left[\tilde{V}_{A\mu'}(t) + \tilde{W}_{A\mu'}(t) \right] \int_{t_0}^t \left[\tilde{V}_{\mu A}(t') + \tilde{W}_{\mu A}(t') \right] C_{A\mu'}(t') dt' \quad (1)$$

which is treated firstly as the velocity of the atom goes to zero. This means, that the occupation number and all the related chemisorption functions are calculated as a function of the normal distance Z from the surface. By using the following definitions,

$$C_{A\mu'}(t) = \bar{C}_{A\mu'}(t) e^{-i \int_{t_0}^t \epsilon_{im}(t') dt'}, \quad \tilde{V}_{A\mu'}(t) = V_{A\mu'}(t) e^{-i(E_{\mu'} - E_A^\infty)t}$$

$$\tilde{W}_{A\mu'}(t) = W_{A\mu'}(t) e^{-i(E_{\mu'} - E_A^\infty)t} \left(e^{i\delta} e^{i\omega_L t} + e^{-i\delta} e^{-i\omega_L t} \right) \quad (2)$$

However, $|C_{A\mu'}(t)|^2 = |\bar{C}_{A\mu'}(t)|^2$. Then we get from eq.(1),

$$\bar{C}_{A\mu'}(t) = -i e^{-iE_A^\infty t - \int_0^t G(t') dt'} \int_0^t \left[V_{A\mu'}(t') + W_{A\mu'}(t') (e^{i\delta} e^{i\omega_L t'} + e^{-i\delta} e^{-i\omega_L t'}) \right] \\ \times e^{-i(E_{\mu'} - E_A(Z))t' + \int_0^{t'} G(t'') dt''} dt' \quad (3)$$

where the function $G(t)$ at certain Z is given by,

$$G(t) = \pi \sum_{\mu} \left\{ |V_{A\mu}(t)|^2 + 2V_{A\mu}(t)W_{A\mu}(t) (e^{i\delta + i\omega_L t} + e^{-i\delta - i\omega_L t}) \right. \\ \left. + |W_{A\mu}(t)|^2 (2 + e^{2i\delta + 2i\omega_L t} + e^{-2i\delta - 2i\omega_L t}) \right\} \quad (4)$$

The first term of eq. (4) includes the adatom energy level broadening due to coupling interaction with the surface band levels while the third one includes the adatom level broadening due to laser field coupling interaction. The second one includes the interference between the two over mentioned coupling interactions. Then by using the definition of the atomic level broadening [19], we can write

$$\Delta_C(Z) = \pi \sum_{\mu} |V_{A\mu}(Z)|^2 \delta(E - E_{\mu})$$

$$\Delta_L(Z) = \pi \sum_{\mu} |W_{A\mu}(Z)|^2 \delta(E - E_{\mu}) \quad (5)$$

$$\Delta_{int}(Z) = \pi \sum_{\mu} V_{A\mu}(Z) W_{A\mu}(Z) \delta(E - E_{\mu})$$

As our derivation works in the limit $u \rightarrow 0$, the atomic level broadenings are written as a function of the normal distance. So eq. (4) can be written in the wide band approximation limit as,

$$G(t) = \Delta_C + 2\Delta_{int} (e^{i\delta + i\omega_L t} + e^{-i\delta - i\omega_L t}) + \Delta_L (2 + e^{2i\delta + 2i\omega_L t} + e^{-2i\delta - 2i\omega_L t}) \quad (6)$$

with,

$$\Delta_C = \pi \bar{\rho} |V(Z)|^2, \quad \Delta_L = \pi \bar{\rho} |W(Z)|^2, \quad (7)$$

$$\Delta_{int} = \pi \bar{\rho} V(Z) W(Z), \quad \bar{\rho} = 1/\text{band width}$$

Then by integrating eq. (6), we get

$$\int G(t') dt' \\ = (\Delta_C + 2\Delta_L)t + \frac{2\Delta_{int}}{i\omega_L} (e^{i\delta + i\omega_L t} - e^{-i\delta - i\omega_L t}) + \frac{\Delta_L}{i2\omega_L} (e^{2i\delta + 2i\omega_L t} - e^{-2i\delta - 2i\omega_L t}) \\ = (\Delta_C + 2\Delta_L)t - \frac{2i\Delta_{int}}{\omega_L} (e^{i\delta + i\omega_L t} - e^{-i\delta - i\omega_L t}) - \frac{i\Delta_L}{2\omega_L} (e^{2i\delta + 2i\omega_L t} - e^{-2i\delta - 2i\omega_L t}) \quad (8)$$

And by getting use of the definition of exponential function [20], we write,

$$e^{\int G(t') dt' - i(E_{\mu} - E_A(Z))t} \\ = e^{-i(E_{\mu} - E_A(Z))t} e^{(\Delta_C + 2\Delta_L)t} \sum_{nmlk} \left(\frac{-2i\Delta_{int}}{\omega_L} \right)^n \left(\frac{2i\Delta_{int}}{\omega_L} \right)^m \left(\frac{-i\Delta_L}{2\omega_L} \right)^l \left(\frac{i\Delta_L}{2\omega_L} \right)^k \\ e^{n(i\delta + i\omega_L t)} e^{m(-i\delta - i\omega_L t)} e^{l(2i\delta + 2i\omega_L t)} e^{k(-2i\delta - 2i\omega_L t)} \quad (9)$$

By substituting eq. (9) in eq. (3) we get,

$$\begin{aligned} \bar{C}_{A\mu'}(t) = & -i e^{-iE_A^\infty t - \int_0^t G(t') dt'} \sum_{nmlk} (-1)^{n+l} \left(\frac{2i\Delta_{int}}{\omega_L} \right)^{n+m} \left(\frac{i\Delta_L}{2\omega_L} \right)^{l+k} \\ & e^{i\delta(n-m+2l-2k)} \left\{ \frac{V_{A\mu} e^{-i[E_\mu - E_A(Z) + i(\Delta_C + 2\Delta_L) + \omega_L(n-m+2l-2k)]t}}{E_\mu - E_A(Z) + \omega_L(n-m+2l-2k) + i(\Delta_C + 2\Delta_L)} \right. \\ & + \frac{W_{A\mu} e^{i\delta} e^{-i[E_\mu - E_A(Z) + \omega_L(-1+n-m+2l-2k) + i(\Delta_C + 2\Delta_L)]t}}{E_\mu - E_A(Z) + \omega_L(-1+n-m+2l-2k) + i(\Delta_C + 2\Delta_L)} \\ & \left. + \frac{W_{A\mu} e^{-i\delta} e^{-i[E_\mu - E_A(Z) + \omega_L(1+n-m+2l-2k) + i(\Delta_C + 2\Delta_L)]t}}{E_\mu - E_A(Z) + \omega_L(1+n-m+2l-2k) + i(\Delta_C + 2\Delta_L)} \right\} \end{aligned} \quad (10)$$

However, if the perturbation is time dependent harmonic one, then the system levels generated from $E_A(Z)$ will be $E_A(Z) + n\omega_L$, with $\omega_L \equiv \hbar\omega_L$ and $n = 0, \pm 1, \pm 2, \dots$. Some of these levels are thrown above Fermi level and the others below the conduction band bottom position. So they may do not effectively take parts in the resonance charge exchange process. Accordingly, all the terms in eq. (10) are neglected except for $n = m = l = k = 1$, so eq. (10) can be written as,

$$\begin{aligned} \bar{C}_{A\mu}(t) = & e^{-i(E_\mu - E_A^\infty(Z))t} \left\{ \frac{V_{A\mu}}{E_\mu - E_A(Z) + i(\Delta_C + 2\Delta_L)} \right. \\ & + \frac{W_{A\mu} e^{i\delta + i\omega_L t}}{(E_\mu - E_A(Z) - \omega_L) + i(\Delta_C + 2\Delta_L)} + \frac{W_{A\mu} e^{-i\delta - i\omega_L t}}{(E_\mu - E_A(Z) + \omega_L) + i(\Delta_C + 2\Delta_L)} \left. \right\} \end{aligned} \quad (11)$$

The adatom's occupation level can be given by [21],

$$n_A = \frac{1}{\pi} \int \sum_{\mu} |\bar{C}_{A\mu}|^2 \delta(E - E_\mu) dE \quad (12)$$

Substituting eq. (11) in eq. (12), we get the following expression,

$$\begin{aligned} n_A = & \frac{1}{\pi} \int \frac{\Delta_C dE}{(E - E_A(Z))^2 + (\Delta_C + 2\Delta_L)^2} + \frac{1}{\pi} \int \frac{\Delta_L dE}{(E - E_A(Z) - \omega_L)^2 + (\Delta_C + 2\Delta_L)^2} \\ & + \frac{1}{\pi} \int \frac{\Delta_L dE}{(E - E_A(Z) + \omega_L)^2 + (\Delta_C + 2\Delta_L)^2} \\ & + \frac{1}{\pi} \int \frac{\Delta_{int} e^{-i\delta - i\omega_L t} dE}{[(E - E_A(Z)) + i(\Delta_C + 2\Delta_L)][(E - E_A(Z) - \omega_L) - i(\Delta_C + 2\Delta_L)]} \\ & + \frac{1}{\pi} \int \frac{\Delta_{int} e^{i\delta + i\omega_L t} dE}{[(E - E_A(Z)) - i(\Delta_C + 2\Delta_L)][(E - E_A(Z) - \omega_L) + i(\Delta_C + 2\Delta_L)]} \\ & + \frac{1}{\pi} \int \frac{\Delta_{int} e^{-i\delta - i\omega_L t} dE}{[(E - E_A(Z)) - i(\Delta_C + 2\Delta_L)][(E - E_A(Z) + \omega_L) + i(\Delta_C + 2\Delta_L)]} \\ & + \frac{1}{\pi} \int \frac{\Delta_{int} e^{i\delta + i\omega_L t} dE}{[(E - E_A(Z)) + i(\Delta_C + 2\Delta_L)][(E - E_A(Z) + \omega_L) - i(\Delta_C + 2\Delta_L)]} \\ & + \frac{1}{\pi} \int \frac{\Delta_L e^{2i\delta + 2i\omega_L t} dE}{[(E - E_A(Z) + \omega_L) - i(\Delta_C + 2\Delta_L)][(E - E_A(Z) - \omega_L) + i(\Delta_C + 2\Delta_L)]} \\ & + \frac{1}{\pi} \int \frac{\Delta_L e^{-2i\delta - 2i\omega_L t} dE}{[(E - E_A(Z) + \omega_L) + i(\Delta_C + 2\Delta_L)][(E - E_A(Z) - \omega_L) - i(\Delta_C + 2\Delta_L)]} \end{aligned} \quad (13)$$

There are nine terms, the first three terms do not include the time-dependent exponential term while the others six terms include it. These six terms turn to be zero due to averaging over the phase, with n is an integer

$$\frac{1}{2\pi} \int_0^{2\pi} e^{\pm i n \delta} d\delta = 0$$

That leaves the occupation number time-independent term.

III. The Model Calculation

Eq. (13) is employed to calculate the occupation number of the atomic energy level which can be written as,

$$\begin{aligned} n_A = & \frac{1}{\pi} \frac{\Delta_C}{\Delta_C + 2\Delta_L} \int_{u_0}^{E_F} \frac{\Delta_C + 2\Delta_L}{(E - E_A(Z))^2 + (\Delta_C + 2\Delta_L)^2} dE \\ & + \frac{1}{\pi} \frac{\Delta_L}{\Delta_C + 2\Delta_L} \int_{u_0}^{E_F} \frac{\Delta_C + 2\Delta_L}{(E - E_A(Z) - \omega_L)^2 + (\Delta_C + 2\Delta_L)^2} dE \\ & + \frac{1}{\pi} \frac{\Delta_L}{\Delta_C + 2\Delta_L} \int_{u_0}^{E_F} \frac{\Delta_C + 2\Delta_L}{(E - E_A(Z) + \omega_L)^2 + (\Delta_C + 2\Delta_L)^2} dE \end{aligned} \quad (14)$$

with u_0 and E_F are the bottom of the band and Fermi energy respectively. Accordingly, eq. (14) can also be written as [21],

$$n_A = \sum_n g_n \int_{u_0}^{E_F} \rho_n(E) dE \quad (15)$$

with,

$$\rho_n(E) = \frac{1}{\pi} \frac{\Delta_C + 2\Delta_L}{(E - E_A(Z) + n\omega_L)^2 + (\Delta_C + 2\Delta_L)^2} \quad (16)$$

$$g_0 = \frac{\Delta_C}{\Delta_C + 2\Delta_L}, \quad g_1 = g_{-1} = \frac{\Delta_L}{\Delta_C + 2\Delta_L} \quad (17)$$

Since $\sum_n \rho_n$ is the local density of states on the adatom in the presence of laser field. The spin dependence of

$n_A \Rightarrow n_A^\sigma$ and $\rho_n \Rightarrow \rho_n^\sigma$ is considered throughout the adatom energy level $E_A(Z)$ as well as the chemisorption function, i.e. the broadening one. Note that, $E_A(Z)$ is written as $E_A^{\pm\sigma}(Z)$, $+\sigma$ for spin up and $-\sigma$ for spin down atomic levels. By incorporating the repulsive electron-electron Coulomb interaction U [22,23] on the adatom, the $E_A^\sigma(Z)$ takes the following expression,

$$E_A^{\pm\sigma}(Z) = E_A^\infty + U n_A^{\mp\sigma}(Z) \quad ; \quad E_A^\infty = \phi - V_i \quad (18)$$

ϕ and V_i are the metal work function and the ionization energy of the adsorbed atom respectively.

$E_A^{+\sigma}$ and $E_A^{-\sigma}$ differ by U whose value may be taken as $V_i - V_A$, with V_i and V_A are the ionization and the affinity energies respectively. As the atom is far away from the surface then $n_A^{+\sigma} = 1$ and $E_A^{+\sigma} = \phi - V_i$ while $n_A^{-\sigma} = 0$ and $E_A^{-\sigma} = (\phi - V_i) + U$. Now as the atom approaches the surface, U decreases due to the screening out of the electron-electron interaction and its effective value can be given by [24,25],

$$U = V_i - V_A - 2\varepsilon_{im}(Z) \quad (19)$$

where $\varepsilon_{im}(Z)$ is the image shift [26], $\varepsilon_{im}(Z) = \frac{e^2}{4(Z + Z_0)}$ with Z_0 is the screening length.

In chemisorption theory calculation, the broadening function as well as the intra-atomic electron-electron interaction, both make the theoretical treatments achieve higher a priori accuracy in calculations of charge

fractions (i.e. $n_A^{\pm\sigma}$). In the limit of wide band approximation, Δ_C^σ and Δ_L are calculated from the following formalisms [27],

$$\Delta_C^\sigma(Z) = \Delta_{C_0} e^{-2\alpha_C^\sigma Z} \quad ; \quad \Delta_L(Z) = \Delta_{L_0} e^{-2\alpha_L Z} \quad (20)$$

With, $\alpha_L = \sqrt{2|V_i|}$ and α_C^σ will be defined later. Δ_{C_0} and Δ_{L_0} represent the broadening at $Z = 0$ with Δ_{L_0} equal to $\pi\bar{\rho}W_o^2$, W_o is the coupling strength due to laser field. $\bar{\rho} = 1/4\beta$, 4β is the energy band width.

In order to calculate the occupation numbers and all the related functions, we firstly solved eq. (14) analytically,

$$\begin{aligned} n_A^\sigma = & \frac{1}{\pi} \frac{\Delta_C^\sigma}{\Delta_C^\sigma + 2\Delta_L} \left(\tan^{-1} \frac{E_F - E_A^\sigma}{\Delta_C^\sigma + 2\Delta_L} - \tan^{-1} \frac{u_o - E_A^\sigma}{\Delta_C^\sigma + 2\Delta_L} \right) \\ & + \frac{1}{\pi} \frac{\Delta_L}{\Delta_C^\sigma + 2\Delta_L} \left(\tan^{-1} \frac{E_F - E_A^\sigma - \omega_L}{\Delta_C^\sigma + 2\Delta_L} - \tan^{-1} \frac{u_o - E_A^\sigma - \omega_L}{\Delta_C^\sigma + 2\Delta_L} \right) \\ & + \frac{1}{\pi} \frac{\Delta_L}{\Delta_C^\sigma + 2\Delta_L} \left(\tan^{-1} \frac{E_F - E_A^\sigma + \omega_L}{\Delta_C^\sigma + 2\Delta_L} - \tan^{-1} \frac{u_o - E_A^\sigma + \omega_L}{\Delta_C^\sigma + 2\Delta_L} \right) \end{aligned} \quad (21)$$

Then eqs. (21) and (18) must be solved self-consistently using the following initial conditions as the species is far away from the surface (i.e. at $Z = 10 \text{ nm}$), $n_A^{+\sigma} = 1$ and $n_A^{-\sigma} = 0$.

IV. The Chemisorption Energy

The chemisorption energy, E_{che} , in general, is defined as being the difference between the final and the initial energies of the system. According to Anderson model, the chemisorption energy is the change in the initial ground state energy on switching on the coupling. In general, the chemisorption energy is divided into two parts. These are the metallic part and the ionic part [28].

The metallic part of the bond energy, results from allowing the valance electron of the adatom to spread throughout the metal and the metal electrons to spread a bit into the region of the adatom. This part is given by [29],

$$E_M(Z) = \sum_{\sigma} \int_{-\infty}^0 E \rho_A^\sigma(E) dE - U n_A^{+\sigma} n_A^{-\sigma} \quad (22)$$

Then, by substituting the formula of local density of states on the adatom in the presence of laser field eq.(12) in eq. (22), we get

$$E_M(Z) = \sum_{\sigma} \sum_{n=0,\pm 1} g_n \int_{u_o}^{E_F} E \rho_n^\sigma(E) dE - U n_A^{+\sigma} n_A^{-\sigma} \quad (23)$$

$$\begin{aligned} E_M(Z) = & \frac{1}{\pi} \sum_{\sigma} \left[E_A^\sigma \frac{\Delta_C^\sigma}{\Delta_C^\sigma + 2\Delta_L} \left\{ \tan^{-1} \frac{E_F - E_A^\sigma}{\Delta_C^\sigma + 2\Delta_L} - \tan^{-1} \frac{-2\beta - E_A^\sigma}{\Delta_C^\sigma + 2\Delta_L} \right\} \right. \\ & + (E_A^\sigma - \omega_L) \frac{\Delta_L}{\Delta_C^\sigma + 2\Delta_L} \left\{ \tan^{-1} \frac{E_F - (E_A^\sigma - \omega_L)}{\Delta_C^\sigma + 2\Delta_L} - \tan^{-1} \frac{-2\beta - (E_A^\sigma - \omega_L)}{\Delta_C^\sigma + 2\Delta_L} \right\} \\ & + (E_A^\sigma + \omega_L) \frac{\Delta_L}{\Delta_C^\sigma + 2\Delta_L} \left\{ \tan^{-1} \frac{E_F - (E_A^\sigma + \omega_L)}{\Delta_C^\sigma + 2\Delta_L} - \tan^{-1} \frac{-2\beta - (E_A^\sigma + \omega_L)}{\Delta_C^\sigma + 2\Delta_L} \right\} \\ & + \frac{\Delta_C^\sigma}{2} \ln \left\{ \frac{(E_F - E_A^\sigma)^2 + (\Delta_C^\sigma + 2\Delta_L)^2}{(-2\beta - E_A^\sigma)^2 + (\Delta_C^\sigma + 2\Delta_L)^2} \right\} + \frac{\Delta_L}{2} \ln \left\{ \frac{(E_F - E_A^\sigma + \omega_L)^2 + (\Delta_C^\sigma + 2\Delta_L)^2}{(-2\beta - E_A^\sigma + \omega_L)^2 + (\Delta_C^\sigma + 2\Delta_L)^2} \right\} \\ & \left. + \frac{\Delta_L}{2} \ln \left\{ \frac{(E_F - E_A^\sigma - \omega_L)^2 + (\Delta_C^\sigma + 2\Delta_L)^2}{(-2\beta - E_A^\sigma - \omega_L)^2 + (\Delta_C^\sigma + 2\Delta_L)^2} \right\} \right] - U n_A^{+\sigma} n_A^{-\sigma} \end{aligned} \quad (24)$$

Note that in eq. (24), the laser field frequency is added explicitly to the atomic energy levels positions and the broadening due to laser field is also add to the broadening function due to coupling interaction. The ionic energy is the energy associated with bringing a unit of charge infinitely far removed from the metal up to a distance Z from the surface. However as the atom is brought to the surface, its sharp state broadens and overlaps a bit with the metal conduction band such that the effective net charge on the ion is now a function of distance [29],

$$Z_{\text{eff}}(Z) = 1 - n_A^{\sigma} - n_A^{-\sigma} \quad (25)$$

Now, the work or the change in energy to bring the charge from $Z' = \infty$ to $Z' = Z$ is given by,

$$E_I(Z) = - \int_Z^{\infty} \frac{Z_{\text{eff}}^2(Z') dZ'}{4(Z' + Z_o)^2} \quad (26)$$

Finally, eq. (26) is calculated numerically to get the total chemisorption energy,

$$E_{\text{che}}(Z) = E_M(Z) + E_I(Z) \quad (27)$$

The dominant energy contribution depends on

- 1- Whether the adatom is one of electronegative nature or electropositive one.
- 2- The surface electronic structure, i.e. whether the surface is clean or not.
- 3- The laser field parameters.

V. Results and Discussion

We apply our theoretical treatment to real systems in order to extract some physical useful conclusions about the effects of laser field throughout the chemisorption process. The model calculation is applied to the system of Na on W(111). The chemisorption dynamics of Na-atom ($V_i = 5.14$ eV) and ($V_A = 0.54$ eV) [30] as it approaches the surface of W(111) ($\phi = 4.4$ eV) [31] is investigated. This system is of the type $\phi < V_i$. The screening length is fixed on $Z_o = 0.11635\text{nm}$, this value gives the experimental atomic chemisorption energy which is equal to 2.35 eV [32] in the absence of laser field. The parameter β is fixed on 3 eV which works in the wide band approximation limit.

The adatom energy level broadening function that is used for this system is given by [33],

$$\Delta_C^{\pm\sigma}(Z) = \frac{(q_A^{\pm\sigma})^2}{16V(Z+r_i)} \sqrt{2V - q_A^{\pm\sigma 2}} \left(1 + \frac{1}{2(Z+r_i)q_A^{\pm\sigma}} \right) e^{-2(Z+r_i)q_A^{\pm\sigma}} \quad (28)$$

where, $q_A^{\pm\sigma} = \sqrt{2|E_A^{\pm\sigma}|}$, $V = 2\beta + \phi$ and r_i is the atomic radius of the adatom. The Δ_C^{σ} -laser field parameters dependence is being throughout E_A^{σ} . This formula is usually used for the alkali adatoms adsorption on transition metal surface because it gives the general physical features for their chemisorption dynamics, while Δ_L is given by eq. (20).

To calculate the occupation numbers $n_A^{\pm\sigma}$ and all the related chemisorption functions, eqs. (21) and (18) are solved self-consistently to determine the adatom charge state as it approaches to the surface. So the initial conditions at large distance from the surface are,

$$n_A^{\sigma}(\infty) = 1, \quad n_A^{-\sigma}(\infty) = 0 \quad (29)$$

The occupation numbers and the related chemisorption functions are considered as an "input-data" to calculate the chemisorption energy and its contributions. This energy is calculated as a function of normal distance to the surface, i.e. the potential energy surfaces. This step is an important one in the chemisorption theory calculation. Since, the potential energy surfaces give the type of bonding at every normal distance from surface, which is what one needs for comparison with the experimental findings.

Figs.(1) shows our results for the chemisorption energy as a function of the normal distance Z and the laser coupling strength W_o at the laser field frequency $\omega_L = 0.17\text{a.u.}$. It is clear that the "adsorption potential well" minimum for $W_o \geq 0.4$ a.u. at certain value of Z may considered as equilibrium distance or "the adsorption position", Z_{ad} . The distance Z_{ad} can be considered as a variation in screening length ΔZ_{oL} due to laser field effect. So the total screening length will be $Z_o + \Delta Z_{\text{oL}}$ for $W_o \geq 0.4$ a.u.. The distance Z_{ad} , at which the adsorption well is noticed [14], is of the most interesting one. This distance is used to extract a non-linear relationship between the screening length ΔZ_{oL} and the laser coupling strength W_o and the laser field

frequency ω_L as in fig.(2), which shows that the value Z_{ad} increases with W_o and ω_L . The relationship between ΔZ_{oL} and ω_L for different values of W_o ($W_o \geq 0.4$ a.u.) is estimated by using best fitting from fig.(2), it takes the following non-linear expression,

$$\Delta Z_{oL} = 0.040967 - 0.474458\omega_L + 3.47495\omega_L^2 \quad \text{for } W_o = 0.4(\text{a.u.})$$

$$\Delta Z_{oL} = 0.285885 - 0.472888\omega_L + 3.46112\omega_L^2 \quad \text{for } W_o = 0.7(\text{a.u.})$$

$$\Delta Z_{oL} = 0.440347 - 0.462996\omega_L + 3.42910\omega_L^2 \quad \text{for } W_o = 1(\text{a.u.})$$

The coefficients in the linear terms are varied due to laser coupling variation. Fig. (3) shows the occupation numbers as a function of ω_L for different values of laser coupling strength W_o ($W_o \geq 0.4$ a.u.) at ($Z = Z_{ad}$). It is clear that the values of $n_A^{+\sigma} (= n_A^{-\sigma})$ increase with W_o and ω_L . The solutions are non-magnetic ($n_A^{\sigma} = n_A^{-\sigma}$) where there is no net spin on the adatom at relatively small distance. The calculated $\Delta_C^{\pm\sigma}$ and Δ_L are also presented in fig.(4) and fig.(5) as a function of ω_L for different values of W_o ($W_o \geq 0.4$ a.u.) at ($Z = Z_{ad}$). The values of $\Delta_C^{\pm\sigma}$ and Δ_L decrease with W_o and ω_L . In fig. (6), the chemisorption energy and its contributions parts (the ionic and metallic parts) are presented as a function of ω_L for different values of W_o ($W_o \geq 0.4$ a.u.) at ($Z = Z_{ad}$), where the metallic part is nearly equal to the chemisorption energy and the ionic part has relatively very small contribution. It is well known that the Na atom adsorbed at W surface as positive ion with ionic bond [22] but by using laser field the Na atom also adsorbed as positive ion but with metallic bond. From this, one can conclude that the type of bond on the surface can be controlled by laser field. This is not contracted with the experimental role of using laser field for the desorption of atoms or ions from solid surfaces. Finally, to know more about laser effect, $E_{che}(=E_{ad})$, where E_{ad} the chemisorption energy at $Z = Z_{ad}$ is presented as a function of W_o and ω_L in fig.(7). It is clear that the values of $|E_{ad}|$ increase with W_o and ω_L .

VI. Conclusions

1. Our theoretical treatment and the model calculation describe and explain precisely the dynamics of the chemisorption process in the presence of laser field throughout potential surfaces calculations.
2. One of the most interesting features in our treatment is introducing the level broadening due to the interference between the electronic coupling and the laser field coupling interactions.
3. The laser field is a tool for controlling the charge states on the adatom and the type of bonding with solid surface.
4. Our theoretical treatment for the chemisorption process illustrates all the reaction dynamics for the adsorption process, which we consider as a "basis treatment" for other related surface processes such as adatom desorption from solid surface.

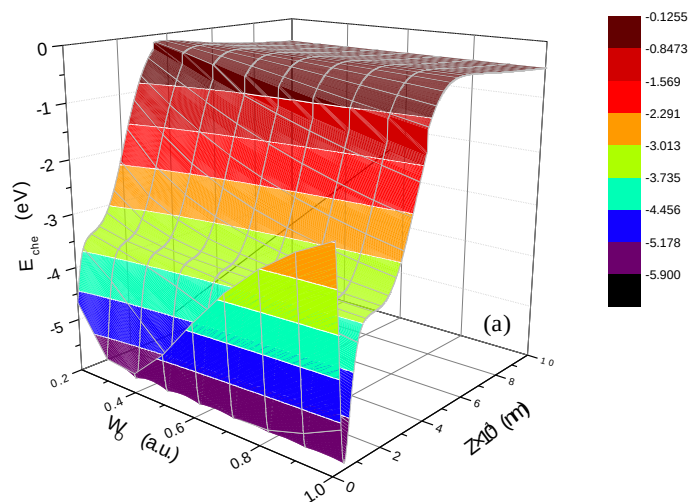


Fig. (1): a. The chemisorption energy as a function of W_o and Z at $\omega_L = 0.17\text{a.u.}$

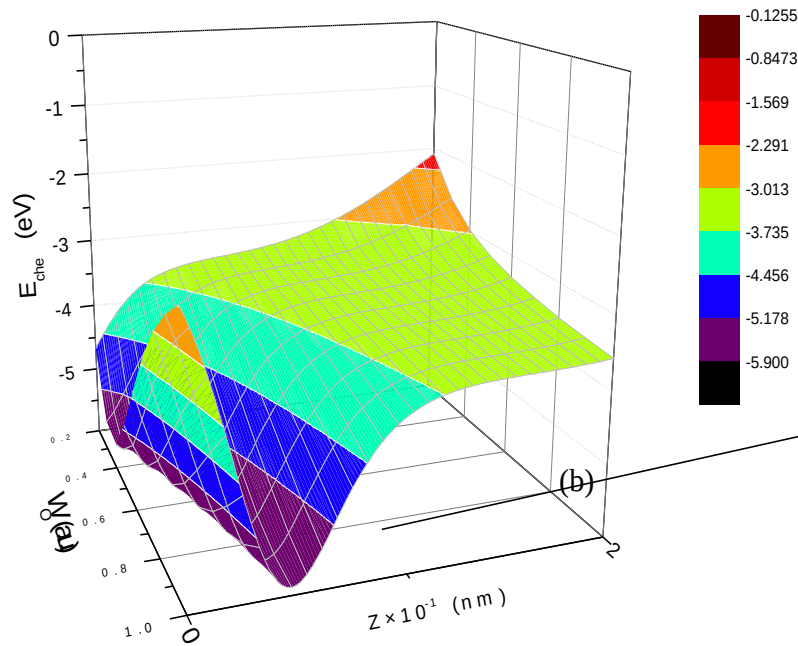


Fig. (1): b. The figure illustrates the variation with distance at closest approach where $Z = 0 \rightarrow 0.2\text{nm}$.

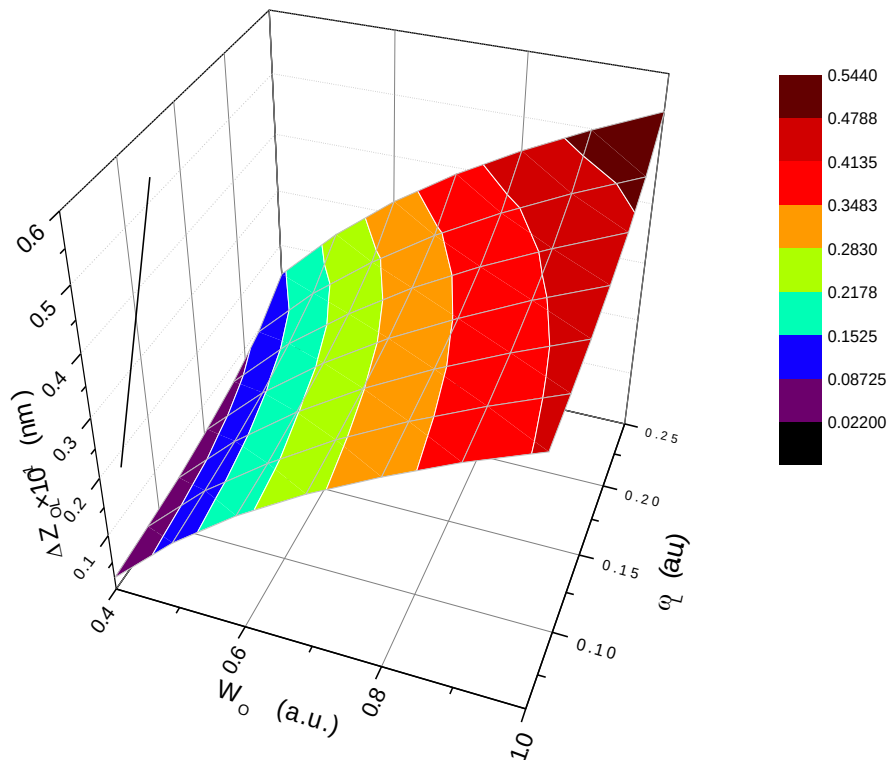


Fig. (2): The relationship between ΔZ_{oL} , ω_L and W_o ($W_o \geq 0.4$ a.u.).

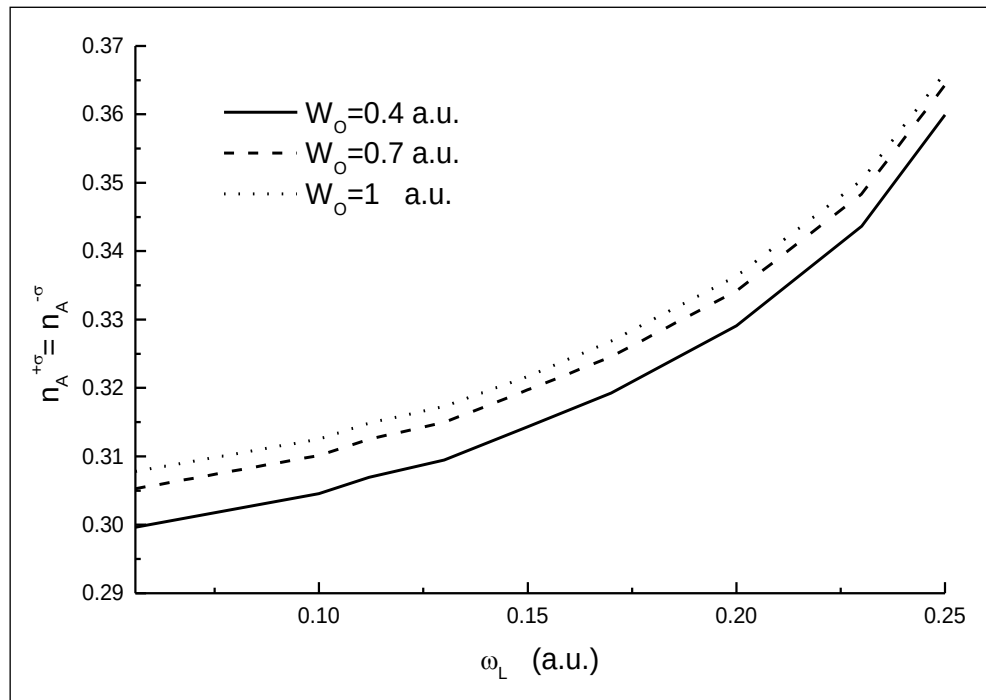


Fig. (3): The values of $n_A^{+\sigma}$ as a function of ω_L for different values of W_o ($W_o \geq 0.4$ a.u.) at $(Z = Z_{ad})$.

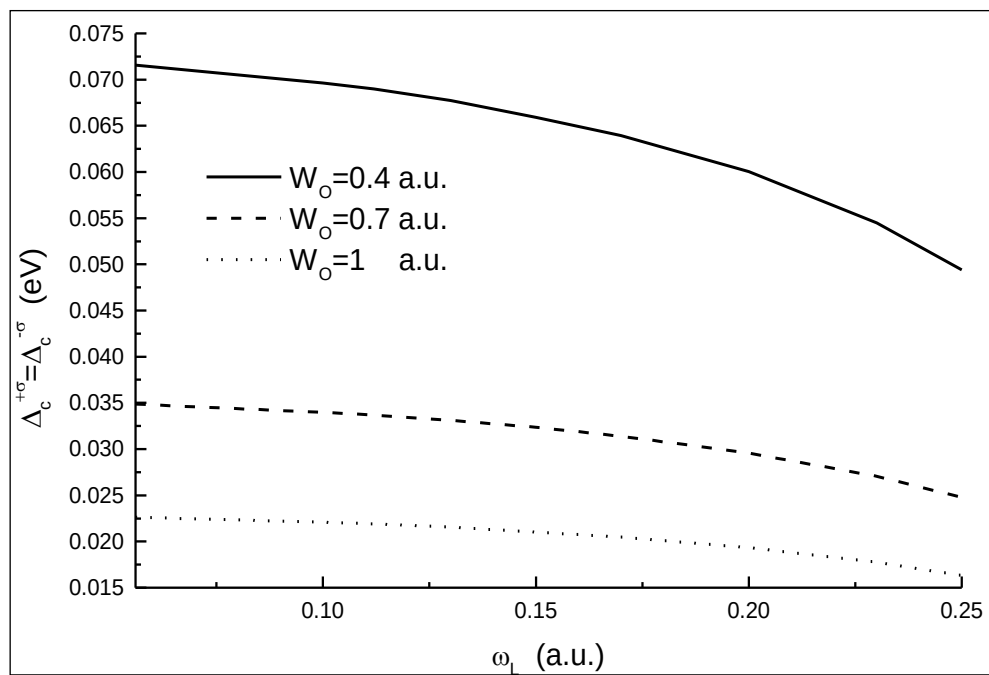


Fig. (4): The values of $\Delta_C^{+\sigma}$ as a function of ω_L for different values of W_o ($W_o \geq 0.4$ a.u.) at $(Z = Z_{ad})$.

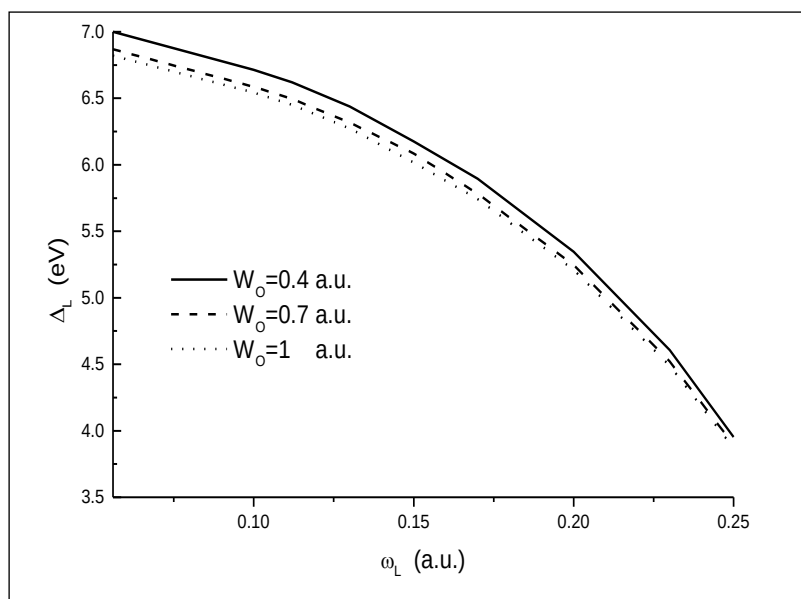


Fig. (5): The values of Δ_L as a function of ω_L for different values of W_0 ($W_0 \geq 0.4$ a.u.) at ($Z = Z_{ad}$).

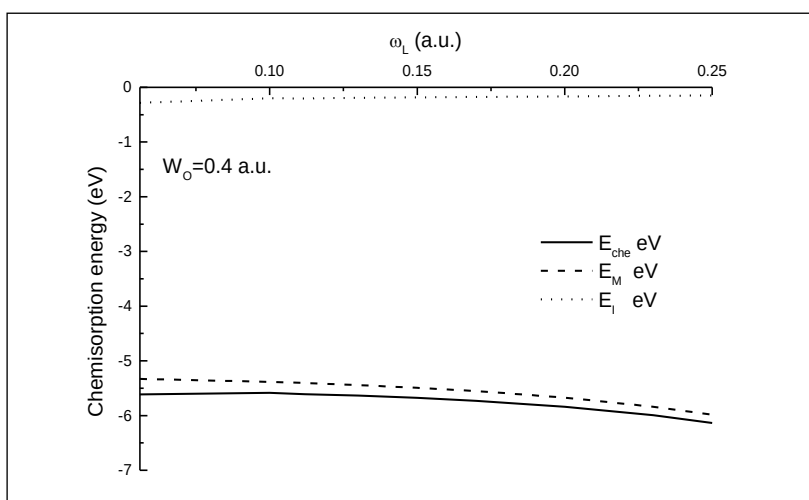


Fig. (6): a

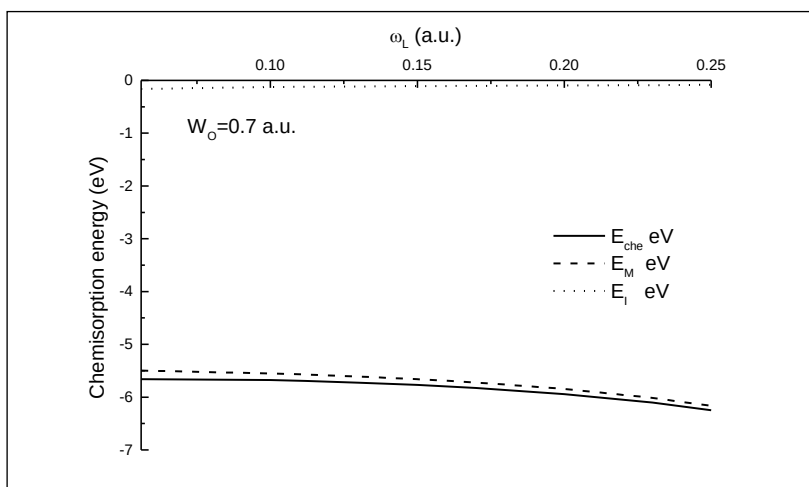


Fig. (6): b

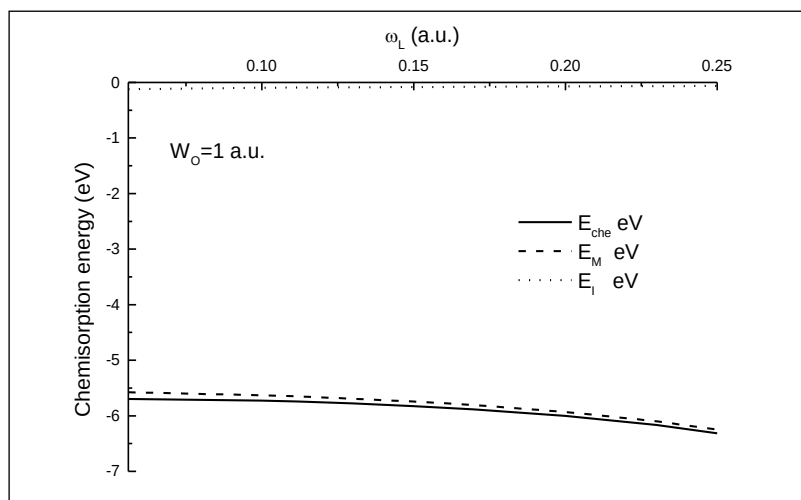


Fig. (6): c. The chemisorption energy and its contributions (the ionic and metallic parts) as a function of ω_L for different values of W_o ($W_o \geq 0.4$ a.u.) at ($Z = Z_{ad}$).

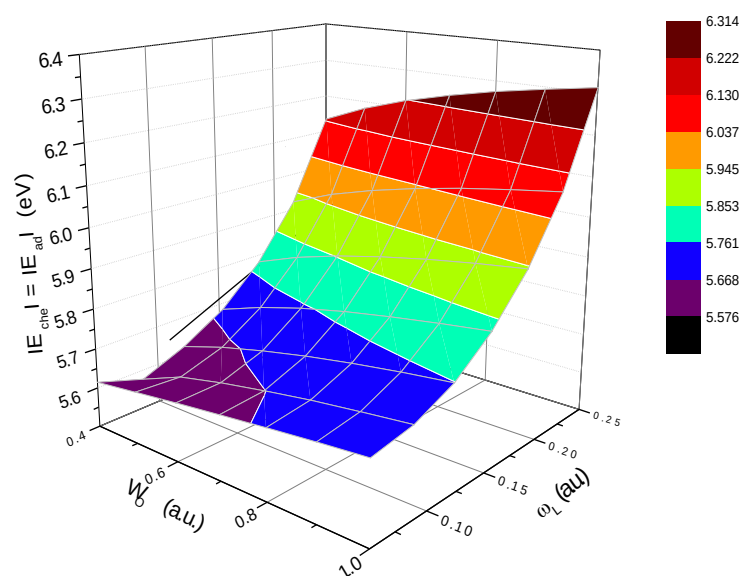


Fig. (7): The chemisorption energy at ($Z = Z_{ad}$) as a function of ω_L and W_o ($W_o \geq 0.4$ a.u.).

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