Quantum-size effects on chemisorption properties: CO on Cu ultrathin films

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Abstract

We address, by means of ab-initio calculations, the origin of the correlation that has been observed experimentally between the chemisorption energy of CO on nanoscale Cu(001) supported films and quantum-size effects. The calculated chemisorption energy shows systematic oscillations, as a function of film thickness, with a periodicity corresponding to that of quantum-well states at \( \bar{\Gamma} \) crossing the Fermi energy. We explain this trend based on the oscillations, with film thickness, of the decay length on the vacuum side of the quantum-well states at the Fermi energy. Contrary to previous suggestions, we find that the actual oscillations with film thickness of the density of states per atom of the film at the Fermi energy cannot account for the observed trend in the chemisorption energy.

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I. INTRODUCTION

Understanding and controlling the structure-size dependence of the chemical activity in materials with reduced dimensionality is a longstanding target of surface science, whose practical significance stems from potential applications in catalysis, gas sensing, and anti-corrosion. A recent exciting development in this area is the observation, in metal films a few atomic layers thick, of a correlation between quantum-size effects and properties such as chemisorption\(^1\) and surface oxidation\(^2-5\).

Danese et al.\(^1\) in particular, have observed experimentally systematic oscillations in the desorption temperature of CO adsorbates on ultrathin epitaxial Cu(001) films on fcc-Fe(001), as a function of film thickness. Such Fe-supported films give rise experimentally to well resolved series of quantum-well states (QWS’s)\(^1,6\) The largest CO desorption temperatures were found to coincide with Cu film thicknesses at which a QWS crosses the Fermi energy, \(E_F\), in inverse photo-emission (IPE) spectra taken at normal incidence\(^1\).

Typically, modifications in chemisorption properties of metal surfaces are achieved by monolayer or submonolayer deposition of a second metal, forming a surface alloy, and exploiting related local surface mechanisms such as site blocking or charge exchanges.\(^7,8\) Using thin-film QWS’s instead is an interesting new approach to tailor surface chemisorption properties. In spite of its interest, however, the precise mechanism and key parameter behind the QWS-related modifications of the chemisorption properties are not yet fully understood.

Very recently, quantum-size effects have also been reported in the initial oxidation rate of ultrathin Mg, Al, and Pb supported films\(^2-5\). The effect was initially suggested to be due to periodic oscillations, with film thickness, in the magnitude of the density of states (DOS) of the films at the Fermi energy\(^2,4,5,9\). The DOS per atom of the film is a parameter which is often invoked in model reactivity theories\(^10\) and which may account for the observed reactivity trends of the Pb films\(^4,5\) — although other parameters have also been invoked\(^11,12\).

In the case of the Mg films, however, it was observed later on that the actual variation in the DOS per atom of the film at \(E_F\) could not simply account for the order-of-magnitude change in the initial oxidation rate of the films.\(^13\) Moreover, for the Al films, significant differences were observed between the DOS and reactivity trends as a function of film thickness\(^3\).

In the cases of the Mg and Al films, for which the precursor adsorption mode of the \(O_2\) molecule on the surface should be physisorption, the key parameter responsible for the
changes in the initial oxidation rate was then proposed to be the decay length in vacuum, \( \lambda \), of the electronic local density of states of the film at the Fermi energy.\textsuperscript{13,14} Modifications in \( \lambda \) can be expected to have a direct exponential influence on the electron transfer rate by resonant tunneling, which is believed to control the initial sticking of the \( \text{O}_2 \) molecules on such surfaces.\textsuperscript{15} The same argument, however, based on tunneling processes, does not hold in the case of \( \text{CO} \) on \( \text{Cu}(001) \), where the molecule is clearly chemisorbed and the modulated value is the chemisorption energy. In this case, the key factor responsible for the observed changes is still an open issue.

In this work, we investigate by means of \textit{ab initio} calculations, the correlation between the chemisorption energy of \( \text{CO} \) molecules on \( \text{Cu}(001) \) films and quantum-size effects. The observed systematic oscillations in the chemisorption energy can be understood in terms of periodic modifications, with film thickness, in the decay length of the QWS’s at the Fermi level. The paper is organized as follows. In Section II we briefly present the calculation method and parameters used. In Section III A we examine the electronic spectra of free-stranding and fcc-Fe-supported \( \text{Cu}(001) \) films with thicknesses in the range 3-12 monolayers (ML). In Section III B we examine the \( \text{CO} \) chemisorption energy on the corresponding films. The trends and microscopic origin of the correlation between electron quantum-size effects and chemisorption energies are analyzed in Section III C. Our conclusions are summarized in Section IV.

II. COMPUTATIONAL DETAILS

The calculations were carried out within the generalized gradient approximation (GGA) to density-functional theory (DFT), using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.\textsuperscript{16} We employed the pseudopotential-plane-wave method, as implemented in the PWscf code of the QUANTUM-ESPRESSO distribution.\textsuperscript{17} For carbon, oxygen, iron, and copper, we used the Rabe-Rappe-Kaxiras-Joannopoulos ultrasoft pseudopotentials of the PWscf library. The semicore \( \text{Cu} \) 3d states were treated as valence states. The nonlinear core correction\textsuperscript{7} to the exchange-correlation potential was used for \( \text{Cu} \) and \( \text{Fe} \).

In the experimental study by Danese \textit{et al.},\textsuperscript{7} the Cu films were grown on a closely latticed matched template formed by 5-ML of fcc Fe(001) deposited on a \( \text{Cu}(001) \) substrate. In our study, we considered both free-standing and fcc-Fe-supported \( \text{Cu}(001) \) films, with/without
the CO adsorbates. All calculations involving the Cu films on Fe were spin-polarized calculations. The systems were modeled using slab geometries in supercells. The length of the supercell was set to 85 Å in all cases. A kinetic-energy cutoff of 30 Ry was used for the plane-wave expansion of the Kohn-Sham orbitals.

For the supported Cu films, we considered slabs containing 5 Fe(001) ML plus 3 to 12 Cu(001) ML deposited on one side. The Cu theoretical lattice constant of 3.68 Å was used to construct the slabs (the experimental value is 3.61 Å); we neglected the effect of the small lattice mismatch between fcc-Fe and Cu. To evaluate the work functions of the Cu(001) supported films, we employed larger, symmetric slabs of \( n \)-ML Cu/5-ML Fe/\( n \)-ML Cu (3 \( \leq n \leq 12 \)). The smallest vacuum region used was 31 Å, corresponding to a 29-ML slab. For the CO covered films, we used asymmetric slabs with CO adsorbed on one side of the slab. We considered the cases of the Cu(001)-(1 x 1)-CO and Cu(001)-c(2 x 2)-CO surfaces, corresponding to CO coverages \( \Theta = 1 \) ML and \( \Theta = 0.5 \) ML, respectively. Experimentally, the desorption measurements in Ref. [1] were performed for the Cu(001)-c(2 x 2)-CO surface.

The adsorption site of the CO molecule is known from experiment to be the on-top site. This is in agreement with our PBE-GGA calculations, and consistent with the results of previous GGA calculations using the same type of pseudopotentials. We note, however, that although our GGA calculations yield the correct adsorption site for CO on Cu(001), this is not so in general within GGA for other transition metal surfaces - where the underestimation of the CO gap gives rise to a different site preference with respect to experiment. We therefore also checked that changing the CO gap (with a GGA + U scheme, and \( U_{CO} = 0.75 \) eV, as in Ref. [22]) does not affect (within 0.1 meV) the calculated variations of the chemisorption energy with film thickness.

The CO molecule is vertical on Cu(001), the experimental Cu-CO bonding distance is \( d(Cu-C) = 1.92 \) Å and the C-O distance is \( d(C-O) = 1.13 \) Å. From calculations for the Cu(001)-c(2 x 2)-CO surface, using a 12-ML thick Cu film, we find \( d(Cu-C) = 1.9 \) Å and \( d(C-O) = 1.15 \) Å, in good agreement with the experimental values and with previous GGA results for thinner Cu films. We kept these distances fixed in the remaining part of our study. We also elected to use the same frozen Cu (Cu/Fe) slab geometry for the CO covered and uncovered Cu films, as our main purpose here is to understand the correlation between the CO-Cu(001) chemisorption energy and quantum-size effects, which are of electronic origin.
We evaluated the CO chemisorption energy as:

\[ E_{ch}(CO) = -(E_{slab+CO} - E_{slab} - E_{CO}) \]  

where \( E_{slab} \) and \( E_{slab+CO} \) are the total energies of the slab without and with the adsorbed carbon monoxide, respectively, and \( E_{CO} \) is the total energy of the CO molecule in the gas phase. For the calculation of the isolated carbon monoxide molecule, we have used a cubic cell with a parameter of \( a = 15 \, \text{Å} \). The corresponding equilibrium C-O distance was found to be \( d(C-O) = 1.14 \, \text{Å} \).

In the self-consistent calculations for the \((1 \times 1) \, [c(2 \times 2)]\) surfaces, the integrations over the Brillouin zone were performed using a \( 24 \times 24 \times 1 \, [18 \times 18 \times 1] \) k-point grid centered at \( \Gamma \). A Gaussian smearing of the electronic levels of 0.01 Ry was used to determine the Fermi energy. The relative values of the chemisorption energy were found to be converged to within \( \sim 1 \, \text{meV} \) with respect to the kinetic-energy cutoff, k-point grid, and vacuum size. For the calculations of the DOS of the film at the Fermi energy, we increased the k-point grid to \((40 \times 40 \times 1)\), in order to ensure a numerical accuracy of 0.0004 eV\(^{-1}\) on the DOS value per atom and spin. To calculate the local density of states at \( E_F \), used to evaluate the decay length \( \lambda \), we employed a \((48 \times 48 \times 1)\) k-point grid and a Gaussian smearing of 0.005 Ry. We determined \( \lambda \) from a fit, assuming an exponential decay of the local density of states at distances beyond \( \sim 2.4 \, \text{Å} \) from the outermost atomic plane. The numerical accuracy on \( \lambda \) was estimated as 0.002 Å.

III. RESULTS AND DISCUSSION

A. Quantum-well states of the free-standing and supported Cu(001) films

In Fig.1(a), we show the calculated energy levels of the QWS’s with wavevector \( k_{||} = 0 \) for the free-standing Cu(001) films, as a function of film thickness. The unoccupied levels at \( \bar{\Gamma} \) are the states probed in normal-incidence IPE experiments. In Fig.1(b), we also show the energy bands of the Cu bulk states with wavevectors perpendicular to the films, i.e., along the \( \Gamma - X \) line (\( \Delta \) direction) of the bulk Brillouin zone. The QWS’s of the films at \( \bar{\Gamma} \) originate from these bulk states.

The QWS’s of interest near the Fermi level, in Fig.1(a), with energies in the range \([E_F - 1.5 \, \text{eV}, E_F + 1.5 \, \text{eV}]\), derive from the upper part of the bulk Cu 4sp band, in Fig.1(b), which
FIG. 1: (a) Calculated energies of the quantum-well states at $\bar{\Gamma}$ in the free-standing Cu(001) films as a function of film thickness. (b) Dispersion of the Cu bulk bands along the [001] direction (i.e., the $\Gamma - X$ direction of the bulk Brillouin zone), perpendicular to the surface of the films. The zero of energy corresponds to the Fermi level.

crosses the Fermi energy and has its maximum at the X point. The spectrum in the energy range $[E_F - 5 \text{ eV}, E_F - 1.5 \text{ eV}]$ is dominated by the more localized Cu $3d$-band states. The lower part of the bulk Cu $4sp$ band (below $E_F - 5 \text{ eV}$) produces another series of QWS’s, in Fig.1(a), located in the energy range $[E_F - 9 \text{ eV}, E_F - 5 \text{ eV}]$.

In Fig. 2 we display the band structures of the 6-ML and 10-ML free-standing Cu(001) films along the high-symmetry lines of the surface Brillouin zone. The low-dispersion $3d$ bands can be easily recognized in the energy range $[E_F - 5 \text{ eV}, E_F - 1.5 \text{ eV}]$. We also note that the two series of quantum-well levels at $\bar{\Gamma}$, originating from the top and bottom part of bulk Cu $4sp$ band along the $\Delta$ direction, give rise to two characteristic series of parabolic-like subbands, in Fig. 2 near the surface Brillouin-zone center.

In Fig.1(a), one can observe that the energies, near $E_F$, of the QWS’s of the film at $\bar{\Gamma}$ increase with increasing film thickness and cross the Fermi energy at 5 ML and at 11 ML. This is in good agreement with the IPE measurements, where the crossing occurs at 5 ML and at 10-11 ML. The trend of increasing energy with increasing film thickness of the $\bar{\Gamma}$
FIG. 2: Band structure of the 6-ML (left panel) and 10-ML (right panel) free-standing Cu(001) films along the high-symmetry lines of the surface Brillouin zone. The zero of energy corresponds to the Fermi level.

QWS’s (which is opposite to the trend of the QWS’s near $E_F$ in the Mg(0001), Al(111), and Pb(111) films\textsuperscript{2–4}) results from the negative effective mass of the 4\textit{sp} band of bulk Cu, at the X point, in the $\Delta$-direction. The top of the Cu 4\textit{sp} bulk band, at about 1.5 eV above $E_F$ in Fig.1(b), corresponds to the bottom of the “inverted” 1-D quantum well which determines the energies, near $E_F$, of the QWS’s of the film at $\bar{\Gamma}$. With increasing film thickness, the quantum-well levels become increasingly closer to the bottom of the inverted quantum well at $\sim 1.5$ eV above $E_F$.

The periodicity of the crossing of $E_F$ by $\bar{\Gamma}$ QWS’s can be derived from the Bohr-Sommerfeld rule\textsuperscript{25} considering the parabolic-like part of the bulk Cu 4\textit{sp} band in Fig.1(b) and its intersection with $E_F$. The empty section of the Cu 4\textit{sp} bulk band runs over 17 \% of the Brillouin-zone X – $\Gamma$ line, and therefore every $1/0.17 = 5.8$ ML a quantum-well level of the film at $\bar{\Gamma}$ should cross the Fermi energy, according to the Bohr-Sommerfeld rule.\textsuperscript{25} This is in good agreement with the crossing periodicity of 6 ML we find in Fig.1(a), and consistent with the 5-6 ML crossing periodicity observed in the IPE spectra.\textsuperscript{1} Our results are also in good agreement with previous DFT calculations for the $\bar{\Gamma}$-state spectra of the free-standing Cu(001) films and their analysis\textsuperscript{26,27}

As the experimental Cu films in Ref.\textsuperscript{1} were grown on fcc Fe(001), we also investigated the effect of the Fe substrate on the QWS spectra. In Fig. 3, we show the calculated partial
density of states at $\Gamma$ of the Cu(001) films on the fcc-Fe(001) substrate, as a function of film thickness. The partial density of states of the film was obtained by summing the spin-up and spin-down atomic-projected density of states at $\bar{\Gamma}$ of the Cu atoms in the film. The results in Fig. 3 show that the sequence of thicknesses at which the QWS peak maxima cross $E_F$ remains exactly the same as for the free-standing films, namely 5 and 11 ML.

![Graph of DOS at $\bar{\Gamma}$](image)

FIG. 3: Partial densities of states of the Cu(001) films at $\bar{\Gamma}$, for the Fe-supported Cu films. The film thickness increases from 3 to 12 atomic layers (bottom to top curve).

**B. Quantum-size effects on the CO chemisorption energy**

The calculated CO chemisorption energies of the free-standing and Fe-supported Cu(001) films are shown in Fig. 4 for the two CO coverages $\Theta = 1$ ML and $\Theta = 0.5$ ML. The behavior as a function of film thickness is rather similar for the two CO coverages. For the free-standing films (and for both $\Theta = 1$ ML and $\Theta = 0.5$ ML), the chemisorption energy is largest at 3 ML, and displays a local minimum at 7 ML and a local maximum at 10 ML; for $\Theta = 1$ ML, in addition, a local minimum (maximum) is present at 4 (5) ML. In the case of the Fe-supported films, both $\Theta$ coverages give rise to the same trends: local maxima are found in the chemisorption energy at 4 and 10 ML, and a local minimum is present at 6 ML.
FIG. 4: Calculated chemisorption energy of the CO molecule for the free-standing (upper panels) and Fe-supported (lower panels) Cu(001) films, as a function of film thickness. Left panels show the results for the Cu(001)-(1x1)-CO surface and right panels for the Cu(001)-c(2x2)-CO surface, corresponding to CO coverages of 1 ML and 0.5 ML, respectively.

The presence of the Fe substrate modifies thus the trends of the chemisorption energy at low film thickness (below 8 ML), giving rise to a pronounced maximum at 4 ML and also shifting the local minimum from 7 ML (in the free-standing case) to 6 ML (for the supported films). At larger film thicknesses, instead, a local maximum is found at 10 ML in all cases. The presence of the substrate gives rise to a systematic oscillatory behavior in the chemisorption energy, which improves the agreement with the experimental trend. Experimentally, the local maxima in the chemisorption energy occur at 5 and 10-11 ML, and a local minimum is observed at 6 ML.

For the supported films, the oscillatory behavior of the chemisorption energy shows a correlation with the periodic crossing of $E_F$ by a QWS at $\bar{\Gamma}$. In fact, the theoretical maxima in the chemisorption [at 4 and 10 ML, in Fig. 4(c) and (d)] are found to occur systematically 1 ML before the crossing of $E_F$ by a QWS (at 5 and 11 ML, in Fig. 3). It may appear
surprising, at first sight, that the presence of the substrate restores a trend which one would expect to be intrinsically related to the properties of the film. It should not be forgotten, however, that effects other than those induced by the QWS near $E_F$ can be expected to have a major influence on the chemisorption energy for free-standing films only a few monolayers thick. Indeed, the presence of a free Cu surface with broken bounds a few Cu ML away from the CO covered surface may be expected to strongly modify (enhance) the strength of the CO-Cu bound.

We find that the chemisorption energy for $\Theta = 0.5$ ML is considerably larger than that for $\Theta = 1$ ML (by $\sim 0.56$ eV, at large film thickness). This is consistent with the experimental trend, and an increased CO-CO repulsion at coverages larger than 0.5 ML.$^{29-31}$ The chemisorption energy for the Cu(001)-c(2×2) surface ($\sim 0.74$ eV) is consistent with previous GGA values,$^{21}$ and somewhat larger than the experimental value (0.57 eV).$^{29}$

C. Discussion and microscopic interpretation

In order to better understand the mechanism and identify the key parameter responsible for the oscillations in the chemisorption energy, we have investigated the behavior with film thickness of (i) the DOS per atom of the films at the Fermi energy, (ii) the work function of the films, and (iii) the decay length in vacuum ($\lambda$) of the electronic local density of states of the films at $E_F$. Both the DOS and $\lambda$ have been invoked as possible key factor responsible for the oscillations in the oxidation rate of ultrathin metal films, while the work function is a parameter, known to exhibit quantum-size effects,$^{32,33}$ which has also been shown to be important when discussing reactivity, e.g., in relation with catalytic promotion.$^{34}$

In Fig. 5, we display the calculated DOS per atom at $E_F$ of the free-standing Cu(001) films, as a function of film thickness. The DOS clearly displays short-period (2 to 3 ML) oscillations, which neither follow the periodic crossing between the QWS at $\bar{\Gamma}$ and $E_F$ (in Fig. 3) nor show a correlation with the oscillations in the chemisorption energy of the supported films (in Fig. 4). We note that the results in Fig. 5 are consistent with the calculated DOS($E_F$) behavior reported for free-standing films with thicknesses larger than 7 ML in Ref. 26. The short-period oscillations of the DOS($E_F$) can be related to a beating effect due to a supersposition of short and long Fermi-wavelength oscillations.$^{26}$

In Fig. 6 we show the theoretical dependence of the work function on film thickness, for
FIG. 5: Calculated density of states per atom at the Fermi energy for the free-standing Cu(001) films, as a function of film thickness.

the free-standing and Fe-supported Cu(001) films. The work-function dependence on film thickness is similar for the supported and unsupported films$^{35}$ although the amplitude of the oscillations is slightly reduced in the supported case. One can notice periodic cusps, corresponding to local minima in the work function at 5 ML and 11 ML, which coincide with the thicknesses of the crossing of $E_F$ by a QWS at $\bar{\Gamma}$. These periodic cusps in the work function, when a QWS at $\bar{\Gamma}$ crosses $E_F$, are consistent with the jellium-model predictions by Schulte.$^{32}$ We also observe that the work function, in Fig. 6, is largest at 3 ML and shows a local maximum at 8 ML. The calculated value at the largest Cu thickness (4.43 eV at 12 ML) is close to the experimental work-function value of the Cu(001) surface (4.59 eV)$^{36}$.

An increase/decrease in the work function may be expected to shift the Cu 3$d$ states to lower/higher energy with respect to the vacuum level and possibly also with respect to the CO electronic levels. Therefore one could expect that maxima/minima in the work function may lead to a decreased/increased interaction (hybridization) between the occupied Cu 3$d$ states of the surface and the empty CO $2\pi^*$ states of the isolated molecule, and hence may correspond to minima/maxima in the chemisorption energy.$^{37,38}$ However, comparing the oscillations of the work function (Fig. 6) and of the chemisorption energy of the supported films (Fig. 4), one observes that the local maxima in the chemisorption energy (at 4 and
FIG. 6: Calculated work function of the free-standing (left panel) and Fe-supported (right panel) Cu(001) films, as a function of film thickness.

10 ML) are shifted by -1 ML with respect to the minima in the work function (at 5 and 11 ML), and that the local minimum of the chemisorption energy (at 6 ML) also does not correspond to the local maximum of the work function (at 8 ML). Furthermore, normal-emission photoelectron spectra of Cu(001) films indicate a monotonic shift of the Cu 3d-levels as a function of film thickness. The 3d centroid moves slightly away from $E_F$ with increasing thickness, which would tend to monotonically decrease the Cu(3d)-CO(2π*) interaction and monotonically weaken the Cu-CO bond. Hence, for CO on Cu films, a shift in the 3d-band energy does not appear to be the dominant factor in determining the trend with film thickness of the CO chemisorption energy.

In Fig. 7 we present the calculated decay length, $\lambda$, as a function of Cu film thickness, with and without the Fe substrate. The trends are identical in the two cases. The decay length exhibits pronounced oscillations, with a first maximum at 5 ML followed by a minimum at 6 ML, a gradual increase to a second maximum at 10 ML, and a subsequently gradual decrease for thicknesses up to 12 ML. We note that this behavior exactly coincide with the experimental trends of the desorption temperature in Ref. 1. Apart from the local maximum at 4 ML, instead of 5 ML, the behavior of the calculated chemisorption energy of
the supported films, in Fig. 4, also follows the trends of \( \lambda \) in the range 5-12 ML (with a local minimum at 6 ML and a local maximum at 10 ML). In Fig. 7, we also reported (see inset) the calculated CO chemisorption energy obtained for 1 ML (upper panel) and 0.5 ML (lower panel) of CO on the Fe-supported Cu(001) films, as a function of the decay length \( \lambda \) of the supported films. Except for the cases of 3 and 4 ML — which are the films for which the chemisorption energy critically depends on the substrate (see Fig. 4), there is a rather clear correlation (linear relation) between the calculated chemisorption energy and decay length. One may note that the variation in the chemisorption energy is rather small (12 meV) in the range 5-12 ML. However, this is consistent with the small variation in the desorption temperature reported in Ref. 1.

The oscillations in \( \lambda \) are found to be virtually in phase with the periodic crossing of \( E_F \) by a QWS at \( \bar{\Gamma} \). This is consistent with the predictions for \( \lambda \) of a particle-in-a-box model.\textsuperscript{13,14} The model predicts that all states \( \psi_{n,k\parallel} \) of a given subband \( n \) have the same decay length \( \lambda_n \sim 1/\sqrt{-E_n} \), where \( E_n \) is the energy of the subband state \( n \) at \( k\parallel = 0 \), measured relative to the vacuum level.\textsuperscript{13,14} Hence \( \lambda \) is dominated by the decay length of the states at \( E_F \) belonging to the subband whose energy at \( \bar{\Gamma} \) is closest to the Fermi level.\textsuperscript{40} With increasing width \( L \) of the film, the energy of the highest-occupied QWS at \( \bar{\Gamma} \) (of the inverted quantum well) increases with respect to \( E_F \). Therefore, \( \lambda \) first increases as \( \lambda_n \sim 1/\sqrt{-E_n} \), until the QWS \( n \) at \( \bar{\Gamma} \) crosses \( E_F \), at which point \( \lambda \) decreases to the next value \( \lambda_{n+1} \sim 1/\sqrt{-E_{n+1}} \) of the highest-occupied QWS at \( \bar{\Gamma} \); \( \lambda \) then increases again with increasing \( L \), displaying systematic oscillations with film thickness \( L \), as observed in Fig. 7.

The effect of \( \lambda \) on the chemisorption energy may be understood in terms of an increased/decreased overlap, with increased/decreased \( \lambda \), between the most extended QWS’s of the film (on the vacuum side) at \( E_F \) and the frontier orbitals of the molecule,\textsuperscript{28} namely the CO 5\( \sigma \) highest-occupied molecular orbitals (HOMO) and 2\( \pi^* \) lowest-unoccupied molecular orbitals (LUMO). The enhanced/reduced hybridization (a) between the unoccupied QWS’s just above \( E_F \) and the CO 5\( \sigma \) HOMO and (b) between the occupied QWS’s of the film at or just below \( E_F \) and the CO 2\( \pi^* \) LUMO are both expected to strengthen/weaken the CO bonding to the Cu surface.\textsuperscript{41} The former interaction is associated with an electronic charge transfer from the 5\( \sigma \) orbitals of the molecule to the surface (donation), whereas the latter leads to an electronic charge transfer from the metal surface to the CO 2\( \pi^* \) orbitals (back donation). The latter interaction is expected to be the dominant one.\textsuperscript{37,38,41}
FIG. 7: Calculated decay length in vacuum $\lambda$ of the electronic local density of states at the Fermi energy for the free-standing (left panel) and Fe-supported (right panel) Cu(001) films, as a function of film thickness. The inset shows the calculated CO chemisorption energy obtained for 1 ML (upper panel) and 0.5 ML (lower panel) of CO on the Fe-supported Cu(001) films as a function of the decay length $\lambda$ of the corresponding Fe-supported Cu film.

Hence, for Cu thicknesses larger than 4 ML, the trends we obtain in the chemisorption energy can be understood in terms of systematic changes in the decay length of the QWS’s at $E_F$, which influence the interaction between filled/empty QWS’s of the film at $E_F^{(+/-)}$ and the LUMO/HOMO of the molecule. We note that the calculated and experimental chemisorption energy display the same trend as a function of film thickness in the range 5-12 ML. The main differences occurs at 4 ML: while the experimental chemisorption energy decreases with decreasing thickness from 5 to 3 ML, the calculated value has a maximum
at 4 ML. Such a difference, however, can be expected for the thinnest films considered, namely 3 and 4 ML, as the behavior of their chemisorption energy sensitively depends on the substrate (see Fig. 4). One may therefore also expect the details of the experimental interface (e.g., atomic intermixing at the interface) to affect the chemisorption energy of these films.

We note that in our calculations the maximum in the chemisorption energy does not occur exactly when a QWS at $\Gamma$ crosses $E_F$, but 1 ML before. We believe this is related to the fact that, in the calculations, the quantum-well subband with energy closest to $E_F$ at $\Gamma$ (see Fig. 2) barely touches the Fermi level at 5 ML (and 11 ML). In this situation, although the unoccupied QWS’s just above $E_F$ may interact with the 5$\sigma$ of the molecule, the occupied QWS at $\Gamma$ cannot interact, by symmetry, with the CO 2$\pi^*$ states. In fact, based on projections on the atomic states, we find that the QWS’s near $E_F$ at $\Gamma$ are composed mainly of Cu 4$s$ states, with a small component of Cu 3$d_{\sigma}$ states (about 10 % for the $\Gamma$ QWS’s within 0.2 eV of the Fermi level). In the region near the Brillouin-zone center, a 3$d_{\pi}$ component, which can mix with the CO(2$\pi^*$) orbitals, appears in the QWS’s, near $E_F$, when going outside $\Gamma$, e.g., along the $\Gamma - M$ direction. The 3$d_{\pi}$ component increases linearly with $k_{||}$ (reaching, e.g., $\sim$ 10 % at 1/5 of the $\Gamma - M$ distance for the 10 ML QWS with subband energy at $k_{||} = 0$ closest to $E_F$ in Fig. 2). In order thus for the QWS’s with the largest possible decay length at $E_F$ to mix with the 2$\pi^*$ states, a small, but non-vanishing fraction of the corresponding quantum-well subband should be occupied. This corresponds to an optimal situation in which the highest occupied QWS at $\Gamma$ is closest to, but not yet crossing $E_F$. In our calculations, this situation corresponds to the 4- and 10- ML cases, which in fact yield maxima in the calculated chemisorption energy.

IV. SUMMARY AND CONCLUSIONS

We have performed first-principles calculations, based on DFT, to study the modulations with film thickness in the chemisorption energy of CO molecules on Cu(001) films. We have examined Fe-supported and free-standing Cu(001) films with thicknesses in the range 3-12 ML. The presence of the substrate has an important influence on the chemisorption energy for thicknesses of 4 ML and below. The calculated CO chemisorption energy of the supported films displays systematic oscillations, as a function of film thickness, with a periodicity cor-
responding to that of quantum-well states at $\Gamma$ crossing the Fermi energy. These oscillations in the chemisorption energy are understood in terms of periodic modulations of the decay length in vacuum of the quantum-well states at the Fermi energy. These modulations of the decay length are expected to influence the interaction of the quantum-well states with the frontier orbitals of the molecule. Contrary to previous suggestions, we find that the actual oscillations with film thickness of the density of states per atom of the films at the Fermi energy cannot account for the observed modulations of the chemisorption properties.

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