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# Effect of $c(2\times2)$-CO overlayer on the phonons of Cu(001): A first-principles study

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We have examined the effect of a $c(2\times2)$-CO overlayer on the surface phonons of the Cu(001) substrate by applying density-functional perturbation theory with both the local density approximation and generalized-gradient approximation (GGA) embodied in the Hedin-Lundqvist and the Perdew-Burke-Ernzerhof functionals, respectively. Our GGA results trace the Rayleigh wave softening detected by helium atom scattering (HAS) experiments to changes in the force constants between Cu surface atoms brought about by CO chemisorption and not merely to the effect of CO mass load on half of the surface atoms. The calculated surface phonon-dispersion curves reveal changes in the polarization of some modes, the most consequential of which is for those originally along the $\bar{Y}$ direction of the clean surface Brillouin zone (SBZ) that are backfolded along the $\bar{\Delta}$ direction of the chemisorbed SBZ. The $S_1$ mode along the $\bar{Y}$ direction of the $1\times1$ SBZ—where it has mixed vertical and shear-horizontal polarization—, for example, is backfolded as a longitudinal-vertical mode, thereby indicating that $S_1$—predicted a long time back along $\bar{\Delta}$ for the clean surface—may be indirectly assessed in the vicinity of $\bar{X}$ upon CO adsorption by standard planar scattering techniques. These findings further suggest that some of the energy losses detected by HAS along $\bar{\Delta}$—originally interpreted as multiphonon excitations of the adlayer frustrated translation mode—may actually correspond to backfolded substrate surface modes.

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## I. INTRODUCTION

Although it is understandable that a large proportion of theoretical investigations in catalytic surface science is dedicated toward understanding the surface electronic and geometric structure as well as the energetics of such processes as chemisorption and thermal activation as a function of catalyst element and surface geometry, two decisive aspects are often overlooked: attestation of the dynamical stability of the model system[1] and understanding of the vibrational dynamics of the reactant-catalyst complex. Analyses in catalysis that ignore the vibrational dynamics of the system under consideration disregard that the reaction path and the so-called *attempt frequency* (rate pre-exponential factors) pertaining to each process are themselves determined by the displacement patterns and frequencies of the phonons of the system, respectively. Moreover, according to harmonic transition-state theory, the entire spectrum of phonons (at the equilibrium and transition states) of the composite system is required in order to determine the attempt frequency of any given process and not just those vibrational modes in which reactants are primarily involved. Still, it is frequently assumed that the changes in free energy governing the rates of adsorbate reactions (or dynamical processes) involve little contribution from the substrate because of relatively low chemisorption energies, as in the case of carbon-monoxide (CO) adsorbed on noble-metal surfaces. The CO binding energy on Cu(001), for example, is only 0.57 eV (Ref. 2)—20 times smaller than the carbon-oxygen binding energy and about three times smaller than the chemisorption energy of CO on Ni(111).[3,4] Nevertheless, ultraviolet and x-ray photoelectron spectra indicate a significant interaction between the molecular and the Cu orbitals.[5–10] Specifically, the valence levels of CO molecules adsorbed on Cu are rearranged, broadened, and shifted with respect to those of molecules in the gas phase, in a fashion similar to that observed for Ni(001)—albeit, of course, to a lesser degree. In each of the above cases, molecular adsorption also impacts the substrate phonons. Another example is the case of the hydrogen overlayer on Pt(111),[11,12] in which the frequency of the substrate Rayleigh wave (RW) at the zone boundaries is modified substantially from its value on clean Pt(111). Furthermore, even in the case of Cu self-diffusion, in which the substrate may be expected to play a less important role on the grounds of the short-range interaction among coinage metal atoms, it has been shown that the contribution of the substrate to free energy changes in the course of adatom hopping is non-negligible.[13] Should the Cu-CO interaction have a range comparable to or longer than the Cu-Cu interaction, for instance, grasping the microscopic details of CO-related reactions facilitated by metallic surfaces will demand taking into consideration all interatomic couplings within the system.

We have recently applied[14] density-functional perturbation theory[15,16] (DFPT) to examine the vibrational modes of

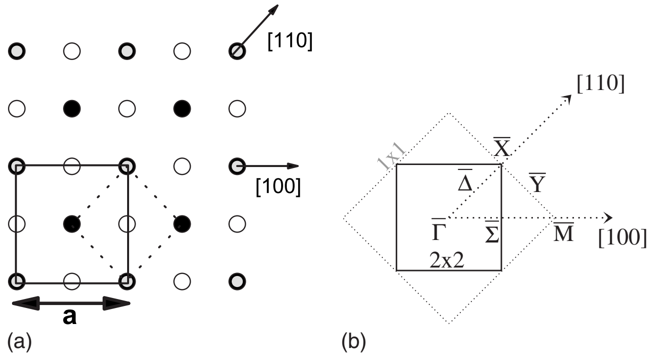

FIG. 1. (a) The top view of the surface shows CO (gray circles) and first (filled circles) and second (open circles) layer atoms of Cu(100). The $1\times1$ (dashed line) and the $c(2\times2)$ (solid line) surface unit cells are underlined. (b) The corresponding $(1\times1)$ (dotted line) and $c(2\times2)$ surface Brillouin zones (solid line) showing the $\bar{\Gamma}$, $\bar{X}$, and $\bar{M}$ points and the $\bar{\Delta}$, $\bar{\Sigma}$, and $\bar{Y}$ directions.

a $c(2\times2)$-CO adlayer on the Cu(001) surface. Since all pertinent interatomic interactions were automatically included in our approach, we were able to calculate the phonon frequencies at arbitrary propagation directions, i.e., in the entire surface Brillouin zone (SBZ). Analysis of the displacement vectors showed that the CO modes are influenced by molecule-substrate and molecule-molecule interactions. Interactions among neighboring CO molecules, separated by ~3.6 Å, were such as to disperse and/or split the C-O stretch, the frustrated rotation (FR), and the frustrated translation (FT) modes. More importantly, our calculations showed that omission of the dynamics of the substrate lowers the frequency of the Cu-CO stretch mode by ~17% (from 47 to 39 meV).[14] The frequencies of two adlayer modes, the Cu-CO stretch and the FT modes, were found to depend strongly on whether the local density approximation (LDA)—via the Hedin-Lundqvist functional—or the generalized gradient approximation (GGA)—via the Perdew-Burke-Ernzerhof (PBE) functional—was used. In fact, contrary to experimental assessments,[5,17] LDA not only renders the top adsorption site a shallow local minimum,[3] it also forces the FT mode of the adsorbed CO molecules to be unstable almost everywhere along the $\bar{\Delta}$ and $\bar{\Sigma}$ directions of the $c(2\times2)$ SBZ [Fig. 1(b)]. Such dynamical instabilities are indicators of the inability of LDA to describe the Cu-CO interaction, which consequently leads to a wrong result for the preferred adsorption site of CO on the surface. The problem, in turn, originates from the expression for the exchange-correlation energy, which is inherently approximate in the Kohn-Sham formulation and thus leads to non-exact cancellation of the Coulomb self-interaction.[18] On the other hand, GGA-PBE, though not systematically free of self-interaction, introduces an enlargement of the energy gap between the highest occupied molecular orbital (HOMO) ($5\sigma$) and the lowest unoccupied molecular orbital (LUMO) ($2\pi^*$) of CO, thus reducing the hybridization between the latter and the metallic *d* states,[19,20] removing the discrepancy between theory and experiment regarding the preferred adsorption site of CO on Cu(001),[3] and accurately reproducing the dispersion of the FT mode as measured by helium atom scattering (HAS) experiments.[14,17]

In the present work, we turn again to real-space force constants and phonon dispersion of $c(2\times2)$-CO/Cu(001) to analyze the effect of CO molecules on the dynamics of the Cu(001) substrate. First of all, the different scenarios exhibited by GGA-PBE and LDA regarding the C-Cu interaction call for revisiting the effect of the CO adlayer on Cu(001). Ellis *et al.*[17] observed via HAS measurements that the RW of Cu(001) softens upon CO adsorption in comparison with that of the clean surface. The later effect was only partially explained by the mass overloading of the CO-*covered* Cu atoms since the softening obtained by simply increasing the mass of such atoms while keeping intact the force constants of the clean surface underestimates the observed softening. Lewis and Rappe[21] later on obtained the frequencies of the Cu(001) surface and CO overlayer modes by using LDA DFT calculations and the “frozen-phonon” method. Since their calculated frequency of the *backfolded* RW at $\bar{\Gamma}$ is in reasonable agreement with the corresponding HAS measurement and no significant changes in the calculated force constants of the Cu substrate were obtained, they concluded that mass overloading is the main reason for the RW softening. As we shall see, it is not straightforward to attribute the softening to either factor. On the one hand, while only one of the two Cu surface atoms in the unit cell adsorbs and carries CO, the RW refers to vibrations of both atoms in the surface unit cell. On the other hand, *covered* and *bare* atoms relax in opposite directions upon CO chemisorption. That is, covered atoms not only support a CO molecule but also relax outward with respect to the interlayer spacing of bulk Cu, whereas bare atoms relax inward [more markedly than surface atoms of clean Cu(001) according to GGA-PBE]. Developing a rationale for the softening of the RW becomes even more complex given that, despite the disagreement between LDA and GGA-PBE in the prediction of both structural features and changes in the force constants of the substrate,[22] both reproduce reasonably well the HAS measurements of the RW at the zone center.

In this work we also focus on the substrate modes which exist along the $\bar{Y}$ direction of the clean SBZ and are now backfolded along the $\bar{\Delta}$ direction of the chemisorbed SBZ with changed polarization. Our calculations, in fact, suggest that some of the energy losses detected by HAS in this direction—and ascribed[17] to multiphonon excitations of the adlayer FT mode—may actually correspond to surface backfolded modes. Such backfoldings and polarization changes may be the key for the experimental detection of modes that are otherwise inaccessible to planar scattering techniques. Of particular relevance is the $S_1$ mode whose shear horizontal (SH—parallel to the surface and perpendicular to the propagation direction) polarization along $\bar{\Delta}$ ($\bar{\Gamma}$-$\bar{X}$ direction) on the clean surface has made it inaccessible to such scattering techniques. Note that this mode has mixed vertical (V—perpendicular to the surface) and SH polarization along $\bar{Y}$ on the clean surface. As $\bar{Y}$ is backfolded to coincide with $\bar{\Delta}$ in the presence of the $c(2\times2)$ overlayer, the polarization of $S_1$ switches to mixed longitudinal (L—parallel to the surface and to the propagation direction) and V polarization. In the vicinity of $\bar{X}$, however, it is L polarized and at $\bar{X}$ it is degenerate with the original SH polarized $S_1$.

The rest of this work is organized as follows. Section II contains the computational details. Section III summarizes results concerning the structure of bulk Cu, the clean Cu(001) surface, and the $c(2\times2)$-CO/Cu(100) chemisorbed surface. Section IV presents our results and discussion of the dynamics of all three systems. Section V lays out the central conclusions of this study.

## II. COMPUTATIONAL DETAILS

Periodic supercell calculations are performed on the basis of the DFT formalism and the norm-conserving pseudopotential (PP) approach.[15] The present results are derived from the mixed basis (MB) technique.[23] Results using both LDA and GGA are obtained. The former is applied through the Hedin-Lundqvist[24] parametrization of the exchange-correlation functional, whereas GGA is introduced via the PBE expression.[25]

The clean and the CO-chemisorbed Cu(001) surfaces are simulated with symmetric slabs inside a tetragonal unit cell containing either nine (for LDA) or seven (for GGA-PBE) layers of Cu. On the chemisorbed surface, CO molecules are symmetrically located on each side of the slab. Periodically repeated slabs are separated by a distance equivalent to 11 and 9 vacuum layers, correspondingly. Integrations inside the Brillouin zone are performed by sampling it with special $k$ points of discrete $8\times8\times8$, $8\times8\times1$ and $6\times6\times1$ meshes for bulk Cu, Cu(001), and CO-$c(2\times2)$-Cu(001), respectively.

The calculation of the lattice-dynamical matrices at specific $q$ points of the SBZ is based on the linear-response theory embodied within DFPT,[15,16] as implemented in the MB scheme in Ref. 26. The dynamical matrices for bulk Cu, Cu(001), and $c(2\times2)$-CO/Cu(001) are calculated at points of $4\times4\times4$, $4\times4\times1$, and $2\times2\times1$ $q$-point meshes, respectively. The real-space force constants in these systems are obtained by the standard Fourier transform of the corresponding dynamical matrices.[27] The force constants of both surfaces are then matched with those of bulk Cu to model a clean and a chemisorbed asymmetric slab of 50 layers and used to obtain the frequencies at arbitrary $q$ points. Surface modes on the clean surface have been identified as those whose amplitude weight in the two outermost layers is larger than 20%. We identify as surface modes those whose amplitude weight in the six outermost atoms (including C and O) are larger than 20%, and characterize as resonances those whose amplitude weight is larger than 5%. For further details of the computational methods, we refer the reader to Ref. 22.

## III. STRUCTURAL PROPERTIES: RESULTS AND DISCUSSION

Our results for the bulk Cu lattice parameter [3.57 Å (LDA) and 3.68 Å (GGA-PBE)] are in good agreement with all-electron[28] (AE) and pseudopotential[3,21] calculations. However, our calculated bulk modulus, $B$ [170 GPa (LDA) and 128 GPa (GGA-PBE)], falls below that provided by AE calculations.[28] Discrepancies in this respect are, in fact, expected since $B$ involves the second derivative of the energy with respect to the volume, being thus more susceptible to the differences between AE and PP calculations than the lattice parameter. As for agreement with experiment,[29–31] LDA underestimates the lattice constant and yields larger bulk modulus. GGA-PBE, as expected, overcorrects LDA, though it reproduces better the experimental bulk modulus than LDA does. Further details and comparisons can be found in Ref. 22.

TABLE I. Percentage change in the interlayer spacing of the outermost layers of Cu(100) compared to the bulk situation.

| | Theor.[a] | | Expt. | |
|---|---|---|---|---|
| | LDA | GGA-PBE | SPLEED[b] | MEIS[c] |
| $\Delta d_{12}$ | −2.57 | −2.82 | −1.2 | −2.4 |
| $\Delta d_{23}$ | +0.55 | +0.58 | +0.9 | +1.0 |
| $\Delta d_{34}$ | +0.30 | Fixed | | |

[a] This work.
[b] Reference 45.
[c] Reference 34.

A schematic top view of the structure of Cu(001) and the $c(2\times2)$-CO adlayer on Cu(001) is shown in Fig. 1(a). The relaxation of the interlayer distances normal to the surface of the clean Cu(001) has been extensively studied theoretically.[3,15,21,32,33] Nevertheless, before conducting our study on the CO-chemisorbed surface, it is essential to test the applied methodology on the well characterized clean Cu(001) surface, which will also serve as a reference to appraise the extent to which CO chemisorption affects it. Notice in Table I that both LDA and GGA-PBE produce an inward relaxation of the surface layer of ~3%. These results are in agreement with earlier pseudopotential calculations[3,15,21,32,33] and with surface structure measurements via the medium ion energy scattering (MEIS) technique (see Table I).[34]

As illustrated in Fig. 1(a), the primitive supercell of the CO-covered surface contains two Cu atoms per layer, which are nonequivalent in odd numbered layers since CO sits directly above only one of them. Accordingly, atoms in the first layer are referred either as covered or bare atoms. To our knowledge, there is no experimental characterization of the substrate geometry after CO adsorption. Nevertheless, in agreement with previous calculations,[3,21] our results[14,22] indicate that the first and third layers rumple, while the second layer atoms do not. Quantitative differences, however, arise between LDA and the GGA-PBE results regarding the interlayer relaxations of the Cu(001) surface upon CO adsorption. We refer the reader to Table I in Ref. 14 for the details of the structure of $c(2\times2)$-CO/Cu(001) and their comparison with available experimental data and other calculations.[3,21] Here, we only stress that, although both LDA and GGA agree on the fact that CO raises the original inward contraction of covered atoms and even makes them relax slightly outward with respect to the bulk situation, such outward relaxation is two times larger within the GGA-PBE than what is within the LDA. In addition, according to LDA, the inward relaxation of bare atoms is slightly decreased by CO, whereas GGA-PBE predicts that bare atoms undergo an inward relax-

TABLE II. Frequencies (in meV) of the surface modes of Cu(100) at the high-symmetry points $\bar{X}$ and $\bar{M}$ [see Fig. 1(b)]. The main polarization (SH, L, or V) is denoted in parenthesis and the superscript indicates the layer showing largest amplitude weight.

| | | Theor. | | | Expt. | |
|---|---|---|---|---|---|---|
| | | LDA | | GGA-PBE | EELS | EELS |
| | | This work | Ref. 15 | This work | Ref. 39 | Ref. 40 |
| $\bar{X}$ | $S_1$(SH$^1$) | 9.7 | 9.9 | 9.1 | | |
| | $S_4$(V$^1$) | 14.6 | 14.0 | 13.5 | 13.2 | |
| | $S_5$(SH$^2$) | 15.6 | 15.0 | 14.3 | | |
| | $S_6$(L$^1$) | 27.0 | 26.1 | 24.1 | | 25.2 |
| $\bar{M}$ | $S_1$(V$^1$) | 18.7 | 17.9 | 16.9 | 17.0 | |
| | $S_2$(V$^2$) | 22.3 | | 20.0 | | 20.3 |
| | (SH$^{1,2}$) | 22.3 | 21.1–21.7 | 20.1 | | |
| | $L_1$(L$^{1,2}$) | 22.3 | | 20.1 | | 20.4 |

ation which is even larger (∼−4.0%) than that of the topmost atoms of the clean surface. Note in passing that for the Cu-C and C-O bond lengths, for which experimental data are available,[35] GGA-PBE gives slightly better agreement to the experimental results than LDA does.[14,22] Likewise, our GGA-PBE calculation produces a chemisorption energy of 0.68 eV at $\theta=0.5$ ML, to be compared to the experimental value[2] of 0.57 eV. LDA, on the other hand, gives a much higher value of 4.00 eV.

## IV. LATTICE DYNAMICS: RESULTS AND DISCUSSION

For completeness and consistency, we have calculated the dispersion of the phonons for bulk Cu and for the Cu(001) surface before doing the same for the chemisorbed surface. As for bulk Cu, we need only to mention that our[22] calculated phonon dispersion is in reasonable agreement with neutron inelastic-scattering (NIS) measurements.[36,37] In the case of the dispersion of the surface phonons of Cu(001), we find it appropriate to present a comparison of our results with those[15,38] obtained recently by DFPT methods using both LDA and GGA-PBE and with those from experiments[39,40] in Table II. The notation for the surface phonons is in accordance with that introduced by Allen *et al.*[41] The $(1\times1)$ and $c(2\times2)$ SBZs corresponding to the clean and the chemisorbed surfaces, respectively, are shown in Fig. 1(b). We reiterate that the $(1\times1)$ SBZ is defined so that its zone boundaries along the [100] and [110] directions correspond to the $\bar{M}$ and $\bar{X}$ points, respectively. In addition, the $\bar{\Gamma}$-$\bar{M}$, $\bar{\Gamma}$-$\bar{X}$, and $\bar{X}$-$\bar{M}$ segments are denoted as the $\bar{\Sigma}$, $\bar{\Delta}$, and $\bar{Y}$ directions, respectively. It is also important to note that the $q$ space of $(1\times1)$ SBZ which is outside the $c(2\times2)$ SBZ is *backfolded* within the $c(2\times2)$ SBZ.

We now turn briefly to the highlights of the results in Table II which summarizes the Cu(001) phonon frequencies at high-symmetry $q$ points ($\bar{X}$ and $\bar{M}$). Full details of our results can be found in Ref. 22. Note that although a number of surface modes and resonances are found—especially along $\bar{Y}$ (Ref. 41)—we describe only those modes which are of interest in the discussion of the chemisorbed surface (see Figs. 2 and 3). We should point out that the sharp longitudinal resonance detected in HAS measurements[42] is not reproduced in DFPT calculations. An explanation as to why theory and experiment differ on this particular issue remains an open question that deserves further investigation. Nevertheless, for the purpose of this work, we shall not pursue the origin and/or modifications of such longitudinal resonances since they completely vanish after CO chemisorption.[17] Notice that the issue of the longitudinal resonance persists for several metal surfaces.[15] Chis *et al.* recently addressed the case of Al(001) (Ref. 43) and Cu(111).[44]

With regard to the $c(2\times2)$-CO/Cu(001) system, LDA indicates that the chemisorption of CO has a negligible impact on the force constants mediating the interaction between bare atoms and their first nearest neighbor (NN) in the second layer, whereas those mediating the interaction between covered atoms and their first NN in the second layer, $YY$, $YZ$,

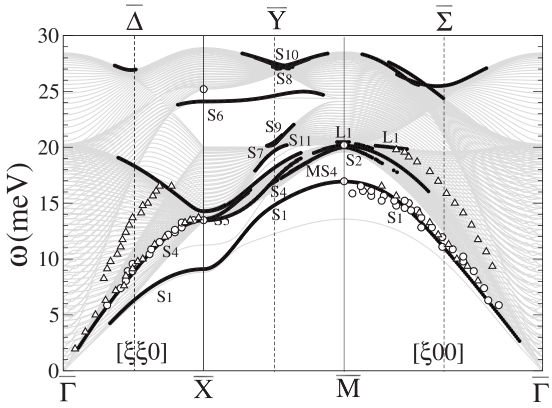

FIG. 2. GGA-PBE phonon dispersion of Cu(100), modeled by a 50-layer slab. Theoretical surface modes (filled circles) are compared with HAS (open triangles) and electron-energy-loss spectroscopy (EELS) (open circles) measurements taken from Refs. 39, 40, 42, and 46.

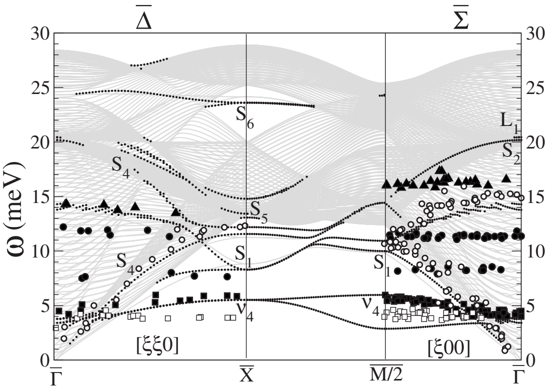

FIG. 3. GGA-PBE phonon dispersion of $c(2\times 2)$-CO/Cu(100), modeled by a Cu 50-layer slab. Note that the dispersion curves of the high-lying modes, which correspond to the C-O stretch and the Cu-CO stretch modes, are omitted in this figure since the emphasis here is on the modes of the substrate. Filled circles denote theoretical surface modes. Experimental data are taken from Ref. 17: filled circles and triangles were associated with multiphonon processes. Open circles correspond to the substrate Rayleigh wave. Squares were associated with the FT mode of CO on the perfect $c(2\times 2)$ structure (filled) and on defects in the adlayer at lower coverage (open).

*ZY*, and *ZZ*, are mildly softened by 12%, 12%, 24%, and 6%, respectively, as compared to the clean surface.[22] GGA-PBE, in contrast, finds that CO chemisorption modifies considerably the force constants of not only covered atoms but also of bare ones. Not surprisingly, though, the major effect occurs on covered atoms, whose corresponding force constants are softened by 40%, 20%, 38%, and 14%, respectively, while those of bare atoms are stiffened by 14%, 14%, 14%, and 9%, respectively. Unlike the *interlayer* force constants, intralayer force constants between bare atoms and their first NN covered atoms are barely altered by CO chemisorption, independently of the exchange-correlation approximation. Namely, they are ∼5% (GGA-PBE) or ∼8% (LDA) stiffer than would be if CO were not present. Tables III and IV summarize the frequencies obtained at $\bar{\Gamma}$ and $\bar{X}$, respectively, and compare them with those obtained in experiments—when available—and former theoretical studies. Sections IV A and IV B below deal in detail with the characterization of the vibrational modes of the Cu(001) substrate shown in Fig. 3. Note, however, that because of the failures of LDA outlined in Sec. I and for the sake of clarity, our discussion will be focused on the results obtained via GGA-PBE. LDA results are mentioned only for cases of substantial discrepancy with GGA-PBE.

TABLE III. Frequencies (in meV) at $\bar{\Gamma}$ of the surface vibrational modes of $c(2\times 2)$-CO/Cu(001).

| | Theor. | | | Expt. |
|---|---|---|---|---|
| | LDA | | GGA | HAS |
| | This work[a] | Ref. 21[b] | This work[a] | Ref. 17 |
| $S_1$ | 15.8 | 16.0 | 14.2 | 15.2 |
| $L_1$ | 22.6 | | 20.2 | |
| $S_2$ | 23.1 | 23.2 | 20.4 | |

[a] DFPT.

[b] DFT-FD.

TABLE IV. Frequencies (in meV) at $\bar{X}$ of the surface vibrational modes of $c(2\times 2)$-CO/Cu(001).

| | Theor. | | Expt. |
|---|---|---|---|
| | LDA | GGA | HAS |
| | This work | This work | Ref. 17 |
| $S_1$ | 9.3 | 8.3 | |
| $S_4$ | 13.1 | 11.6 | 12.3 |
| | 13.3 | 12.2 | |
| $S_5$ | 15.2 | 13.1 | |
| | 15.6 | 14.8 | |
| $S_6$ | 27.1 | 23.6 | |

### A. Substrate modes along $\bar{\Sigma}$

In the following analysis, one must bear in mind that modes proper to the clean Cu(001) surface [i.e., within the $(1\times 1)$ SBZ] in the $\bar{\Sigma}$ direction which appear along the second half segment from the $\bar{\Gamma}$ point to the $\bar{M}$ point become accessible in the first half segment upon CO chemisorption. The reason is that modes along the second half segment are backfolded onto the first one, that is, inside the $c(2\times 2)$ SBZ (see Fig. 1).

(a) *The* $S_1$ mode. The Rayleigh wave, known as $S_1$,[41] is the surface mode with the lowest frequency along $\bar{\Sigma}$ direction. On the clean surface, at $\bar{M}$, its polarization is mainly vertical (V) and localized in the first layer. It acquires an additional L polarization as it approaches the $\bar{\Gamma}$ point. On the chemisorbed surface, $S_1$ increases its frequency along $\bar{\Sigma}$ until it reaches the zone boundary. There, except for a 1 meV gap, it matches the backfolded $S_1$, which increases its frequency on the way back to the SBZ center and reaches its maximum at $\bar{\Gamma}$. Regarding the gap between the RW branches at the zone boundary, we find that the higher (lower) branch corresponds to a mode whose amplitude weight is primarily vertical in bare atoms (covered atoms dragging the molecule to some extent), involving also a small contribution from the L-polarized vibration of covered (bare) atoms. The frequency of the higher branch, in fact, equals that of the RW on the clean surface at the zone boundary, which perhaps suggests that bare atoms are not affected by the presence of CO. As we shall see, this is not always the case. At $\bar{\Gamma}$, where the softening with respect to the clean surface is maximal, the backfolded $S_1$ mode corresponds to an *out-of-phase* vibration between covered and bare atoms. In this case, the contribution of bare atoms is 50% larger than that of covered atoms and CO molecules are dragged parallel to the latter. Close to $\bar{\Gamma}$, $S_1$ is broadened and appears as a finite-width resonance whose maximum amplitude weight can be as low as 6% in the first two layers. It softens by ~16% at $\bar{\Gamma}$, overestimating, in fact, HAS measurements (~10%). We observe that although LDA and GGA-PBE predict different effects of CO chemisorption on the force constants of the first layer, in both cases $S_1$ softens by the same percentage.

(b) *The* $S_2$ mode. This mode is mostly V polarized and localized in the second layer at the zone boundary. On the clean surface, this mode soon forms part of a band of bulk resonances along $\bar{\Sigma}$ whose maximum amplitude weight comes from either the second and first layers (with mixed V and L polarization) when close to the SBZ boundary or first layer (with mixed V-L polarization) when close to $\bar{\Gamma}$. GGA-PBE and LDA yield slightly different results as to its prevalence along $\bar{\Sigma}$ and its degree of localization (see Ref. 22).

On the chemisorbed surface, however, $S_2$ only appears backfolded from $\bar{M}$ to $\bar{\Gamma}$. It disappears sharply as soon as it immerses into the bulk band. At $\bar{\Gamma}$, $S_2$ is well inside the bulk band, even though no coupling to bulk modes is observed. On the contrary, it is more localized on the chemisorbed surface than on the clean surface (at $\bar{M}$). $S_2$, in addition, stiffens by ~3 meV on the chemisorbed surface.

(c) *The* $L_1$ mode and the corresponding SH branch. $L_1$ refers to a L-polarized mode mostly localized in the first layer of the clean surface at the zone boundary of the SBZ. It rapidly becomes a resonance as it approaches $\bar{\Gamma}$. As a consequence, on the CO-covered surface, it appears mainly as a backfolded mode. At $\bar{\Gamma}$, the backfolded $L_1$ and its degenerate SH pair stiffen very slightly (~1%) on CO chemisorption. Neither $L_1$ nor its degenerate SH pair are totally localized in the first or second layers (as in the clean surface) but exhibit a significant contribution of ~60% to the amplitude weight from deeper layers. Outside $\bar{\Gamma}$, the backfolded $L_1$ rapidly disappears, while the backfolded SH mode disperses and becomes more localized toward the zone boundary, where it matches the branch that originally appears on the clean surface but vanishes rapidly back to $\bar{\Gamma}$.

### B. Substrate modes along $\bar{\Delta}$

Here, one should notice that, like the *backfolding* along Σ, modes proper to the clean surface along $\bar{Y}$ are backfolded to $\bar{\Delta}$ in the $c(2\times2)$ SBZ [see Fig. 1(b)]:

(a) $S_1$ and the corresponding $L$ branch. $S_1$ is the mode of lowest energy of Cu(001) and is totally localized in the first layer at the $\bar{X}$ point. It cannot be detected by standard planar scattering techniques on the clean surface since its polarization is SH all along $\bar{\Delta}$. $S_1$ changes rapidly to V polarization along $Y$ but, to our knowledge, no experimental data along $\bar{Y}$ are yet available.

On the chemisorbed surface, $S_1$ is localized totally in the first layer and the CO overlayer. The latter vibrates *in phase* with the covered Cu atoms but with much smaller amplitude. $S_1$ softens at $\bar{X}$ by ~8% (see Tables II and IV). Interestingly, the calculations reveal a L-polarized mode that is degenerate with $S_1$ at $\bar{X}$, albeit the degeneracy is broken outside $\bar{X}$. Such a mode corresponds to the part of $S_1$ which is SH along $\bar{Y}$ in the SBZ of the clean surface and which is backfolded along $\bar{\Delta}$ on the chemisorbed SBZ. Note that since $\bar{\Delta}$ and $\bar{Y}$ are perpendicular, SH modes along $Y$ are necessarily L modes with respect to $\bar{\Delta}$. The backfolded $S_1$ remains L polarized as it goes across $\bar{\Delta}$ toward $\bar{\Gamma}$ up to the crossing point with the RW, where it becomes V polarized. It is slightly softened around the zone boundary, just as much as $S_1$ at $\bar{X}$. The softening becomes stronger—similar to that of the RW—right after crossing the RW and the transitioning to V polarization. Note that Ellis *et al.*[17] observed some HAS peaks precisely at the region where backfolded $S_1$ is V polarized. Those peaks were at the time said to be associated with multiphonon excitation bands. The excellent fit of their measured dispersion to our backfolded $S_1$ ($\bar{Y}$ is backfolded onto $\bar{\Delta}$), however, suggests that it is the latter mode that is observed rather than multiphonon excitation bands.

(b) *The* $S_4$ mode. This is the RW along $\bar{\Delta}$. On the clean surface, it is essentially V polarized, although a L contribution is also present. Although its amplitude weight is greatest at the first layer, it decays slowly as a function of the layer depth. On the chemisorbed surface, it is also mostly localized (~60%–70%) in the first layer and, to lesser degree, in the molecule. $S_4$ also displays a small splitting at $\bar{X}$ (see Table IV), yet in this case both branches are softened with respect to that of the clean surface by 9.6% and 15.0% at $\bar{X}$, while HAS measurements[17] find a softening of ~8.2%. From the first layer, only the covered (bare) atoms contribute to the mode with lower (higher) energy. The backfolded $S_4$, on the other hand, originally arises along $\bar{Y}$ on the clean surface and has V polarization at the zone boundary and a predominantly SH character as it crosses $\bar{Y}$. On the chemisorbed surface, this mode is also V polarized close to the zone boundary. In GGA-PBE, it broadens and becomes a resonance as soon as it immerses into the bulk band, reappearing as a surface mode close to $\bar{\Gamma}$ with mixed L and SH polarization. In LDA, however, $S_4$ remains highly localized on the surface and changes smoothly to L polarization.[22]

(c) *The* $S_5$ mode. The polarization of this mode is SH and it is predominantly localized in the second layer on the clean surface. On the chemisorbed surface, it is also strongly localized in the second layer but with mixed SH and L polarization. It rapidly becomes a resonance along $\bar{\Delta}$ toward $\bar{\Gamma}$. At $\bar{X}$, $S_5$ splits (see Table IV). In GGA-PBE both branches are totally localized in the second layer. One of these softens by 8.4% and the other stiffens by 3.5%. LDA shows that the lower branch softens while the other—bearing ~25% contribution from deeper layers—does not change at all.

(d) *The* $S_6$ *mode*. This mode develops inside the spectrum gap, close to the zone boundary with a frequency of 23.6 meV (see Table IV). On the clean surface, it has a predominant L polarization in the first layer. On the chemisorbed surface, however, it is found to be degenerate with a SH pair at $\bar{X}$. Note in Fig. 3 that the degeneracy is broken inside the SBZ. Our calculations find that $S_6$ and the SH branch remain nearly dispersionless and involve an additional V polarized second layer vibration, as found on the clean surface. These modes are, incidentally, more localized in the first layer of the chemisorbed surface than in that of clean Cu(001). At the right end of the bulk band gap (see Fig. 3), $S_6$ softens slightly and becomes a resonance as it penetrates the bulk band. The SH branch, in contrast, extends well inside the bulk band and becomes more localized at the top two layers. According to GGA-PBE, $S_6$ softens at $\bar{X}$ by 2.0%, while LDA predicts no softening (see Table IV).

## V. SUMMARY AND CONCLUDING REMARKS

We have carried out a first-principles study of the dynamics of a $c(2\times2)$ CO overlayer chemisorbed on Cu(100). Our calculations show that LDA displays a mild effect of CO chemisorption on the relaxations and force constants of the surface. Although the adsorption site that LDA predicts is not in agreement with experimental results, it is able to give good agreement with the HAS data for the frequency at the zone center of the backfolded RW. This feature is rather unexpected in consideration of the poor ability of LDA to describe the Cu-CO interaction and its less successful description of the acoustic modes of bulk Cu and the RW in Cu(001).[22] GGA-PBE, on the other hand, finds that CO chemisorption significantly perturbs the structure and the first NN force constants of the surface layer atoms. Softening of the RW is well reproduced, only slightly overestimated by $\sim$1 meV at $\bar{\Gamma}$. It is surprising that, while LDA and GGA-PBE differ considerably in the response of the substrate to CO chemisorption, the actual percentage softening of the backfolded RW with respect to the clean surface is comparable. We find that softening of the RW along $\bar{\Sigma}$ and $\bar{\Delta}$ is not necessarily connected with the vibration of the covered atoms, which indicates that mass overloading alone cannot account for it. If that were the case, all surface modes involving the first-layer atoms would be softer. On the contrary, $L_1$, for example, does not soften, notwithstanding the leading involvement of first-layer atoms. In fact, it slightly stiffens, consistently with the hardening of intralayer force constants of the first layer. Yet, the correspondence between changes in Cu force constants and the softening and/or stiffening of the various modes cannot be disentangled by categorizing the modes in conformity with the atomic layers involved, propagation direction, and polarization characteristics. For example, $S_2$, the V mode in the second layer, stiffens. In turn, while the $S_1$ mode (along $\bar{\Delta}$) softens slightly in the region where it is L polarized and totally localized in the first layer, it undergoes a stronger softening in the region where it is V polarized and involves contributions from deeper layers. Softening of the RW thus seems to result not only from the effect of the mass of CO but also from interactions of surface atoms with atoms beyond their first NN. These interactions subdue differences in the local bonding of the surface atoms and result in an overall softening of the RW, regardless of whether covered or bare atoms are primarily involved.

Our results call attention to the importance of the folding of $\bar{Y}$ (of the $1\times1$ SBZ) onto $\bar{\Delta}$ [of the $c(2\times2)$ SBZ], which displays backfolded modes along the latter. For example, backfolded $S_1$ and backfolded $S_4$ are found along $\bar{\Delta}$ with changed polarization that may make them observable by standard scattering techniques. In particular, $S_1$ acquires V polarization close to $\bar{\Gamma}$ and L polarization close to $\bar{X}$. The close correspondence between HAS data[17] associated to CO multiphonon excitation bands and our calculated dispersion of the backfolded $S_1$ mode hints that the measured peaks rather arise from this surface mode and not from the frustrated translation of the overlayer. Perhaps even more importantly, backfolded $S_1$ becomes as well discernible to planar scattering spectroscopy techniques close to the zone boundary since its polarization changes from SH [along $\bar{Y}$ of the $(1\times1)$ SBZ] to L polarization [along $\bar{\Delta}$ of the $c(2\times2)$ SBZ] in that region. The above thus implies that the frequency of $S_1$ [SH-polarized in Cu(001)] can indirectly be measured in the vicinity of $\bar{X}$ via backfolded $S_1$. We believe, in fact, that some of the peaks observed and assigned to 2 T *overtones* by Ellis *et al.*[17] along $\bar{\Delta}$ may instead correspond to the L-polarized region of backfolded $S_1$. Our results here thus call for reinterpretation of the HAS data.

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