

Adsorbate induced changes in surface stress and phonon dispersion curves of chemisorbed systems

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 224005

(<http://iopscience.iop.org/0953-8984/20/22/224005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 12:28

Please note that [terms and conditions apply](#).

Adsorbate induced changes in surface stress and phonon dispersion curves of chemisorbed systems

Sampyo Hong and Talat S Rahman

Department of Physics, University of Central Florida, Orlando, FL 32816-2385, USA

Received 8 November 2007, in final form 15 January 2008

Published 13 May 2008

Online at stacks.iop.org/JPhysCM/20/224005

Abstract

We present a summary of theoretical results documenting changes in surface stress and surface phonon frequencies for selected light gas adsorbates on Ni(001) and Cu(001) which, when compared with experimental data, provide critical information on surface geometry and electronic structure. Our calculations of the surface electronic structure are based on density functional theory, using the pseudopotential method, while the evaluation of surface dynamics relies on the density functional perturbation theory. A $c(2 \times 2)$ overlayer of C on Ni(001) and of N on Cu(001), causes a large change in the surface stress ($\approx 5 \text{ N m}^{-1}$) turning it from tensile to compressive in both cases. We find that while adsorbate induced surface stress change depends on the height at which the adsorbate sits on the surface, it is not a direct measure of the propensity of the substrate to reconstruct. We also consider examples of changes in surface electronic structure, and surface force fields and hence the characteristics of surface phonon dispersion curves, brought about by chemisorption, and compare them with experimental data where available.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

For several decades experimental and theoretical studies of surface phonon dispersion curves have provided much needed insight into the nature of the bonding between atoms and molecules chemisorbed on surfaces. Similar has been the case for adsorbate induced changes in surface stress, particularly since questions have been raised about its link to the propensity of a surface to undergo reconstruction. Recent focus on atomistic techniques, such as scanning tunnelling microscopy (STM), appear to have overshadowed the vantage point of such tools to uncover changes in surface electronic structure and geometry in the presence of adsorbates. There is no question that the advent of the STM has opened many new doors of scientific discovery. In fact, the entire effort in nanoscale science owes a good deal to techniques such as STM which being based on coordinate space are sensitive to the local environment, and do not require long range order in the system, unlike most spectroscopic methods. The tremendous flurry of STM activity and accompanying revelations of novel phenomena remind one of the early days of surface science when the need to understand nanoscale

phenomena led to rapid discovery and advancement of a number of experimental and theoretical techniques. Low energy electron diffraction (LEED), electron energy loss spectroscopy (EELS), helium atom surface scattering (HAS), and surface extended x-ray absorption fine structure (SEXAFS) are among some of the early leading techniques, which were also accompanied by advances in theoretical methods used for their interpretation. Independent theoretical techniques such as those based on *ab initio* electronic structure calculations or model interaction potential were also developed to get further insights in surface geometry, structure, and dynamics. Given these advances, the power of STM, and more recent efforts to complement STM with spectroscopic techniques, we have perhaps arrived at the long sought goal of unravelling surface structure and dynamics accurately, and uniquely, using a set of complementary techniques. In this regard, the conference on vibrations at surfaces offers avenues to focus on some essential microscopic information provided by surface dynamical studies which are difficult to obtain from other techniques. We thus expect there to be a resurgence in the application of experimental and theoretical techniques to obtain information on surface geometry, structure, and

dynamics as probes for understanding surface electronic structural changes brought about on chemisorption.

The fact that we continue to learn from examinations of surface phonons and their dispersion for chemisorbed systems is understandable. Phonon frequency being the second derivative of the total free energy of the system with respect to atomic coordinates is a direct measure of surface force fields and dynamical stability of surfaces. Surface vibrational studies are thus unique in the sense that they provide structural, dynamical and thermodynamical information at the same time. This is particularly true for lattice dynamical calculations because they can be performed even for statically stable, but dynamically unstable structures, to obtain insights into microscopic processes controlling structural changes (relaxation, reconstruction, etc). At the same time microscopic investigations of surface stress may also reveal local atomistic information and their global impact. With regard to surface reconstruction, attention has usually turned to surface stress and the logical tendency has been to assign the latter's relief as the driving force for the former [1–5]. Characteristics of surface phonon dispersion curves have also been traced to adsorbate induced surface stress [6, 7]. Although, as we shall see, the connection may not be so direct, trends in surface stress changes on chemisorption provide information on the delicate balance between surface geometry and nature of the bonding between surface atoms that eventually conspire either to stabilize the surface or to let it reconstruct [8, 9]. In this paper, we have chosen to present summary of theoretical results that we have obtained on specific systems which collectively help us decipher the relationship, if any, between adsorbate induced surface stress and reconstruction, and their manifestation in surface phonon dispersion curves. We have chosen to focus on the chemisorption of a few light gases on Ni(001) and Cu(001) since these systems continue to be the subject of a large number of investigations as some questions still remain. In particular, to address the question of the role of surface stress in determining surface structure and dynamics, we consider the cases of $c(2 \times 2)$ overlayers of C and O on Ni(001) and of N on Cu(001), the last of which also serves as an illustrative example of the richness of information available from surface phonon dispersion curves, when compared with experimental data. The next section contains few details of the theoretical techniques employed. This is followed by a summary of our results for adsorbate induced changes in surface stress on Ni(001) and Cu(001) in section 3, and on their surface phonons in section 4. Section 5 contains concluding remarks.

2. Some details of theoretical methods

Our electronic structure calculations are based on density functional theory and the plane-wave pseudopotential method. Theoretical models and computational setups used for C/Ni(001) systems were reported elsewhere [8, 9] with a recipe for calculations of surface stress. For the Cu(001) surface with overlayers we have carried out non-spin-polarized calculations based on plane-wave basis set [10] and the ultrasoft pseudopotential scheme [11]. The computer code

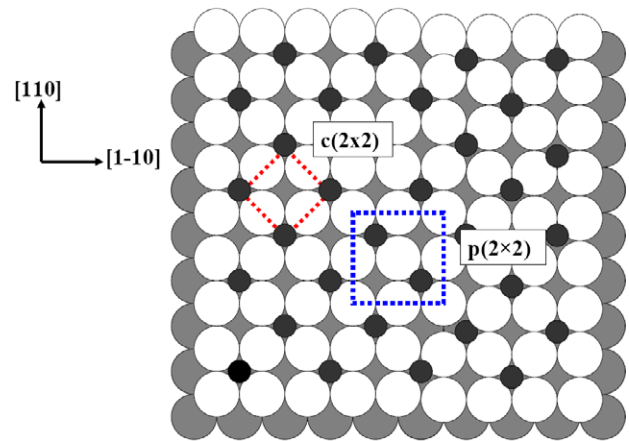


Figure 1. $c(2 \times 2)$ and $p(2 \times 2)$ surface unitcell on Cu(001) surface. White and grey circles are first and second Cu layers while dark circles are N atoms.

used was Quantum-Espresso [12]. Ultrasoft pseudopotentials were employed for all elements. For the exchange–correlation energy, the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof functional was implemented [13]. A kinetic energy cutoff of 544 eV for the plane-wave basis set was found to yield convergent results. To simulate the $c(2 \times 2)$ N overlayer on unreconstructed and rumpled Cu(001), we used the unit cell (shown in figure 1). In addition, a $p(2 \times 2)$ surface unit cell (figure 1) was used for calculations of surface stress for a hypothetical clock reconstructed Cu(001) surface. In each case the supercell consisted of a slab of nine Cu layers separated by 15 Å of vacuum. The slab was symmetric about the centre layer with overlayers on both sides. The Monkhorst–Pack scheme [14] was used for $(9 \times 9 \times 1)$ and $(6 \times 6 \times 1)$ k -point sampling of the Brillouin zone for the $c(2 \times 2)$ and $p(2 \times 2)$ structures, respectively. A Fermi level smearing of 0.27 eV was applied [15]. For the unreconstructed Cu(001), all atoms were relaxed until forces acting on them became less than $2.3 \times 10^{-2} \text{ eV \AA}^{-1}$. For the rumpled and the clock reconstructed surfaces, Cu atoms in the first layer were held fixed at specific positions since these are hypothetical and not stable structures, while other atoms were relaxed to relieve unwanted stress that could exist in other layers until forces on these atoms became less than $1.8 \times 10^{-2} \text{ eV \AA}^{-1}$. Note that forces on the fixed atoms were found to be less than 0.5 eV \AA^{-1} . Note also that aim in this work is to obtain qualitative and quantitative understanding of phenomena.

For calculations of the frequencies and eigenvectors of surface phonon modes for the unreconstructed $c(2 \times 2)$ N/Cu(001), we have carried out density functional perturbation theory calculations based on the linear response theory and the harmonic approximation [16]. Phonon dispersion curves were obtained by standard Fourier interpolation method using a (2×2) q -point mesh. Surface force constants were merged with bulk force constants and an asymmetric bulk slab of 45 layers was added to obtain projected bulk phonon modes using standard lattice dynamical methods. Vibrational modes were labelled as surface modes when the eigenvectors contained

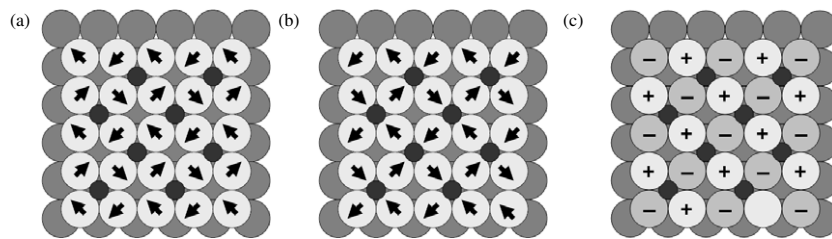


Figure 2. Clock, diamond and rumpling reconstruction patterns.

contributions larger than 30% from atoms in the top two Cu layers.

3. Adsorbate induced stress on Ni(001) and Cu(001)

According to experimental observations for $c(2 \times 2)$ overlayers of C and O on Ni(001), the adsorbate atoms sit in the four-fold hollow site: C sitting almost coplanar with the Ni surface layer atoms [17], and O at a height of about 0.9 Å above the Ni layer [18]. Both adsorbates cause the top layer Ni atoms to relax outward by about 10% as compared to the clean Ni surface [1]. The effect of the C layer is more dramatic as it reconstructs Ni(001) to produce a surface, with $p4g$ symmetry and a glide plane, which may be modelled by either the ‘clock’ or the ‘diamond’ structures (see figure 2) [17, 19–25]. Notably, the reconstruction initiates at a coverage of 0.34 ML of C. In contrast, one-half monolayer of O on Ni(001) results in $c(2 \times 2)$ structure with no reconstruction [18, 26].

Experimental measurements of adsorbate induced stress on Ni(001) have found a correlation between the restructuring of the substrate and the coverage dependence of surface stress since for the case of the C overlayer the measured stress assumes a constant value at 0.34 ML coverage [2], coinciding with the onset of surface reconstruction. In each case the stress change is found to be compressive, while the stress on clean Ni(001) is reported to be tensile. It has been argued that both compressive and tensile stresses lead to observed anomalies and the larger the surface stress, the more likely it is that the surface would reconstruct [6].

The implications of surface stress also have been discussed in the literature [4, 5, 27] for the related case of a $c(2 \times 2)$ N overlayer on Cu(001). These studies have found that N atoms adsorb in four-fold hollow sites, almost coplanar with first layer Cu atoms, and form square patches of dimension of about $50 \text{ \AA} \times 50 \text{ \AA}$, which possess the $c(2 \times 2)$ symmetry locally, and are surrounded by Cu strips (clean surface area). The N overlayer is predicted to induce large stress on the Cu(001) surface, whose relief is said to lead to the formation of the patches [4, 5]. Recently Hoefft and co-workers [4, 5] proposed another model which may provide additional stress relief within the patches. In this model, the first layer Cu atoms produce a large rumpling of the surface as one-half of them move upwards and the other half move downwards on N adsorption, elongating the bond between Cu atoms and, thereby, relieving compressive stress on the surface. This model is interesting as the large rumpling in the first layer had not been proposed earlier. The model, however, relies on

the interpretation of STM images and photoelectron diffraction (PhD) data: the bright spots in the STM images must be from Cu not N atoms, otherwise it will contradict the PhD data. Thus, the lingering issue of this system has been the structure of the first layer Cu atoms and the interpretation of its STM images. While it was proposed that the bright spots in the STM images may be just distortions, not the image of Cu atoms that can be caused by the STM tip with an asymmetric apex [28], recently simulated STM images showed that the bright spots were N atoms. As interpretation of STM measurements may not be unique, calculations of surface stress and surface phonon dispersion provide alternate ways of verifying these conclusions. Surface modes with displacement vectors along the surface normal would be particularly sensitive to the proposed surface rumpling and should display anomalous features.

The proposed formation of islands of locally reconstructed metal surfaces on light gas adsorption is not particular to the case of N on Cu(001). Similar effect is known to exist for 0.5 ML local coverage of C on Ni(001)—a system for which also questions have been raised about the relationship between stress and surface reconstruction. At the same time surface phonon dispersion curves for these very systems have not validated the relationship conclusively. In the case of the C overlayer, however, it is well established that it induces a clock type of reconstruction on Ni(001) at coverage beyond 0.34 ML [2]. For the N overlayer on Cu(001), several experimental and theoretical studies find no reconstruction [27, 29, 30], while others have proposed both the clock type [31] and the rumpling reconstruction [4, 5] in the first Cu layer resulting from stress relief reconstructions. On the other hand, a $c(2 \times 2)$ O overlayer on Ni(001) induces no reconstruction. These three systems thus offer good opportunities for comparative microscopic studies of adsorbate induced surface stress and its relationship to surface reconstruction.

The calculated surface stress for these systems are shown in table 1. Results for the Ni(001) systems are taken from [12, 13]. Just as in the case of clean Ni(001), surface stress is found to be tensile for clean Cu(001) (1.2 N m^{-1}). On Ni(001), the $c(2 \times 2)$ O overlayer reduces the tensile stress to 1.5 N m^{-1} . On the other hand, the C overlayer which reconstructs Ni(001), changes the tensile stress into a compressive one of 1.8 N m^{-1} . Thus in the case of C adsorption, the change in the surface stress is large (4.9 N m^{-1}). This change in stress is accompanied with the C overlayer sitting much closer to the Ni surface (0.2 \AA) and giving rise to a remarkable expansion of first and second Ni

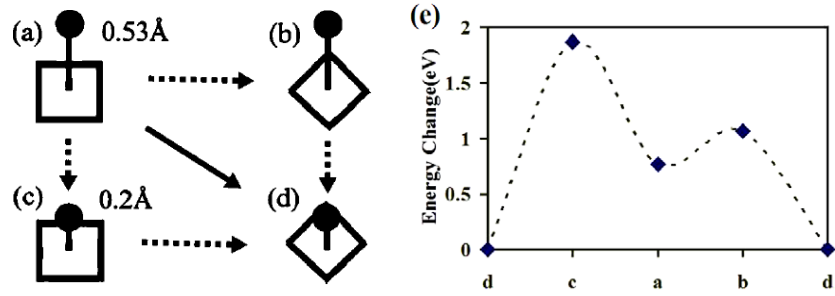


Figure 3. The four surface geometries considered for examining the correlation between adsorbate height, the ensuing stress, and the propensity of the substrate to reconstruction with the adsorbate lying high and/or low in the four-fold hollow site on (a) and (c) unreconstructed Ni(001) or (b) and (d) $p4g$ reconstructed Ni(001). (e) The differences in the total energy for the C/Ni(100) systems for structures (a)–(d). The dashed line is a guide to the eye.

Table 1. Calculated surface stress (in N m^{-1}) for clean and adsorbate covered Ni(001) and C/Ni(001).

System	Surface stress (N m^{-1})
Ni(001)	+3.1
O/Ni(001)	+1.5
C/Ni(001) reconstructed	−1.8
Cu(001)	+1.2
N/Cu(001)	−4.1

layers separation (10% of bulk spacing). In contrast, the O overlayer on the unreconstructed Ni(001), sits further away from the Ni surface (about 0.8 \AA) and the Ni top layer spacing undergoes an expansion of about 5%. For the N overlayer on the unreconstructed Cu(001), stress changes are more similar to those of the C overlayer on Ni(001) rather than those of the O overlayer on the unreconstructed Ni(001). For instance, while surface stress of clean Cu(001) is tensile of 1.2 N m^{-1} , the N overlayer induces a compressive stress of 4.1 N m^{-1} . The related change of the surface stress of 5.3 N m^{-1} is comparable to that induced by the C overlayer on Ni(001). In fact, not only the surface stress but also the adsorption height is similar in these two cases. We find that the N overlayer sits 0.17 \AA above the Cu surface, which compares well with 0.2 \AA height that we find for the C overlayer on the reconstructed Ni(001). Experiments also observed similar trends: 0.1 \AA for the C overlayer on Ni(001) [17] and $0.07\text{--}0.4 \text{ \AA}$ for the N overlayer on Cu(001) [4, 5, 29, 31].

In a recent publication [8] the possibility of a correlation between the adsorbate height, the ensuing stress and the propensity of the substrate to reconstruct in the presence of the electronegative adsorbates was examined for the case of the C/O overlayer on Ni(001), by setting up four (some hypothetical) structures that we reproduce here in figure 3. The structure in figure 3(a) is a hypothetical $c(2 \times 2)$ C overlayer on unreconstructed Ni(001). We are assuming here that if in experiments the metastable structure (3(a)) is initially formed, slight perturbation of atomic displacement would collapse it to the stable structure (3(d)). This transformation involves both reduction of the adsorbate height and reconstruction of the surface. Structures 3(b) and (c) provide, respectively, the scenarios in which the surface either first reconstructs, or pulls the adsorbate closer to itself. The calculated surface

Table 2. Surface stress (in N m^{-1}) calculated analytically for configurations (a)–(d) of the C/Ni(001) system in figure 3. The values in parenthesis are for the O overlayer.

Configuration	Surface stress (N m^{-1})
a	−3.0 (−1.7)
b	+1.6 (+2.0)
c	−10.6 (−7.7)
d	−1.8 (−1.7)

stress for these four C/Ni structures are summarized in table 2, and their total energy difference is represented in figure 3(e). For structures (a) and (d), the difference in their total energy is found to be 0.769 eV per equivalent supercell, while the difference in their surface stress is 1.2 N m^{-1} . Note that this reduction in surface stress arises from both reconstruction of the surface, as well as, the descent of the adsorbate. The descent of the adsorbate (3(a)–(c)) enhances the compressive stress from -3.0 N m^{-1} to -10.6 N m^{-1} , while the clock reconstruction alone (3(a) and (b)) reverses the stress to tensile and lowers it to $+1.6 \text{ N m}^{-1}$. At the same time, the clock reconstruction (step 3(c) and (d)) also introduces a reduction of stress by $+8.8 \text{ N m}^{-1}$. In either scenario, clock reconstruction relieves surface stress by a considerable magnitude. The descent of the C atoms to the low lying position on Ni(001) without reconstruction, for example, would have the surface under high compressive stress of -10.6 N m^{-1} , as seen from table 2. Such an increase in compressive stress on lowering of the adsorbate is, however, not limited to C overlayers. The calculated changes in the stress induced by the O overlayer at heights of 0.78 \AA , 0.53 \AA and 0.2 \AA in table 2 show remarkable similarity in the values for the O and C overlayers further illustrating that adsorbate induced surface stress depends strongly, and quite understandably, on how far the adsorbate is from the surface.

The above statement is also true for the N overlayer on Cu(001). As we discussed earlier, the N overlayer sits nearly coplanar with the surface and induces a compressive stress change of 5.3 N m^{-1} . In the calculations, when we applied the clock reconstruction to Cu(001) in the presence of $c(2 \times 2)$ N overlayer, it reduced the surface stress from -4.1 to -2.9 N m^{-1} , although the effect is not as strong as in the case of C on Ni(001). However, we would argue that

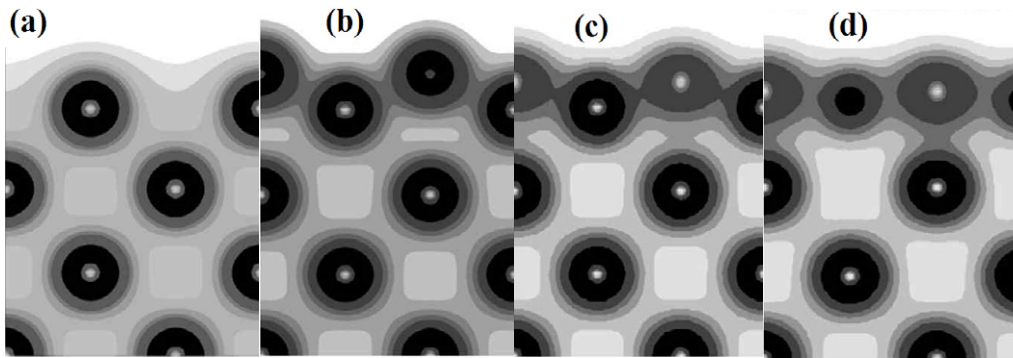


Figure 4. Charge density plot (side-view) of (a) clean Ni(001), (b) O/Ni(001), (c) unreconstructed C/Ni(001), and (d) reconstructed C/Ni(001).

the clock reconstruction is not favoured energetically since we find the total energy of the reconstructed N/Cu(001) system is higher than that of the unreconstructed one. For the structure in which we introduce a rumpling of 0.34 \AA in the first layer to unreconstructed Cu(001) such that one-half of the top most Cu atom is 0.07 \AA above the N atom, according to the proposed model [4, 5], the rumpling reconstruction is found to increase surface stress from 4.1 to 5 N m^{-1} . (We need to emphasize that since this rumpled structure is not the ground state of the system, substantial stress remained along the vertical axis, although the in-plane forces were reduced to zero due to the perfect $c(2 \times 2)$ symmetry of the surface.) The rumpling reconstruction thus appears in our calculations to be not favourable either in terms of the reduction of the stress or of the total energy. We also note that with regard to the correlation of surface stress change and reconstruction, the N overlayer on Cu(001) appears to be more akin to the O overlayer on Ni(001), despite sitting so close to the surface layer.

As we have seen above, an adsorbate sitting very close to the surface layer may induce stress-reducing reconstruction provided such an arrangement also lowers the total energy of the system. This lowering of total energy happens in the case of the C overlayer on Ni(001), and not for the O overlayer on Ni(001) or the N overlayer on Cu(001), pointing to the importance of considerations of the nature of the bonding between the adsorbate and the surface atoms in developing an understanding of surface geometry. To illustrate this point we turn again to the cases of O and C overlayers on Ni(001) as discussed previously in [8] and from where we reproduce figure 4 showing the charge density distributions for the four cases relevant to the discussion here. In the case of O/Ni(001) (4(b)) hardly any covalent bonding appears with the Ni atoms directly below them. On the other hand, some overlap of charge densities is already apparent for the C atoms on unreconstructed Ni(001) (4(c)) and this bonding becomes even stronger as the Ni surface reconstructs (4(d)). The formation of the covalent bond between C and the second layer Ni atom is found to be crucial for the stability of C/Ni(001) surface structure. Also, apart from formation of the C–Ni covalent bond, the clock reconstruction in C/Ni(001) is accompanied by a dramatic reduction of the local electronic charge on the adsorbed carbon, which is liable to decrease the

electron–electron repulsion on C site [9]. Thus, as we have seen [9], criterion for surface reconstruction need to be based on considerations beyond that of simple stress-reduction and require consideration of electronic structural changes induced by the adsorbates such as the extent of covalent bonding with the substrate atoms.

4. Adsorbate induced effects on surface phonons of Ni(001) and Cu(001)

As we have seen earlier, while C and O overlayers are responsible for substantial changes in the electronic structure of the Ni(001) surface, they also make remarkable changes in the phonon spectrum of the surface. The reader is referred to the original papers for illustration of the experimentally observed surface phonon dispersion curves for clean Ni(001) [32], $c(2 \times 2)$ O/Ni(001) [30], and $c(2 \times 2)$ - $p4g$ C/Ni(001) [33]. It is interesting to see the large softening of the Ni Rayleigh mode upon O adsorption (S_4 mode) by 6.8 meV at the X point of the surface Brillouin zone (figure 5). However, the same mode did not undergo a softening in the case of C overlayer on Ni(001) before and after the reconstruction occurred (see figures 3 and 9 in [33]). The softening of this mode for O/Ni(001) was at that time attributed to the O overlayer induced compressive stress, which resulted in a nonzero first derivative of the pair potential between the surface Ni atoms [6]. Although the correlation of stress to the softening of atomic force constants is appealing, it does not apply to the case of C overlayer on Ni(001), which induces on the surface a higher compressive stress than the O overlayer but the Rayleigh mode is not softened! [33]. In fact, as we saw earlier, the calculated absolute stress on Ni(001) upon O adsorption was still tensile. Thus, it is not simple to correlate phonon frequency change to stress change because while the former is the second derivative of the total energy with respect to atomic coordinates, the latter is the first derivative of the total energy with respect to volume. On the other hand, lattice dynamical studies showed without assuming the presence of surface stress that the clock reconstruction pattern can happen on any surface when the force constant between the first and the second layer Cu atoms become softened [25].

Now let us turn to the surface phonon dispersion curves of the unreconstructed $c(2 \times 2)$ N/Cu(001). Our calculated surface

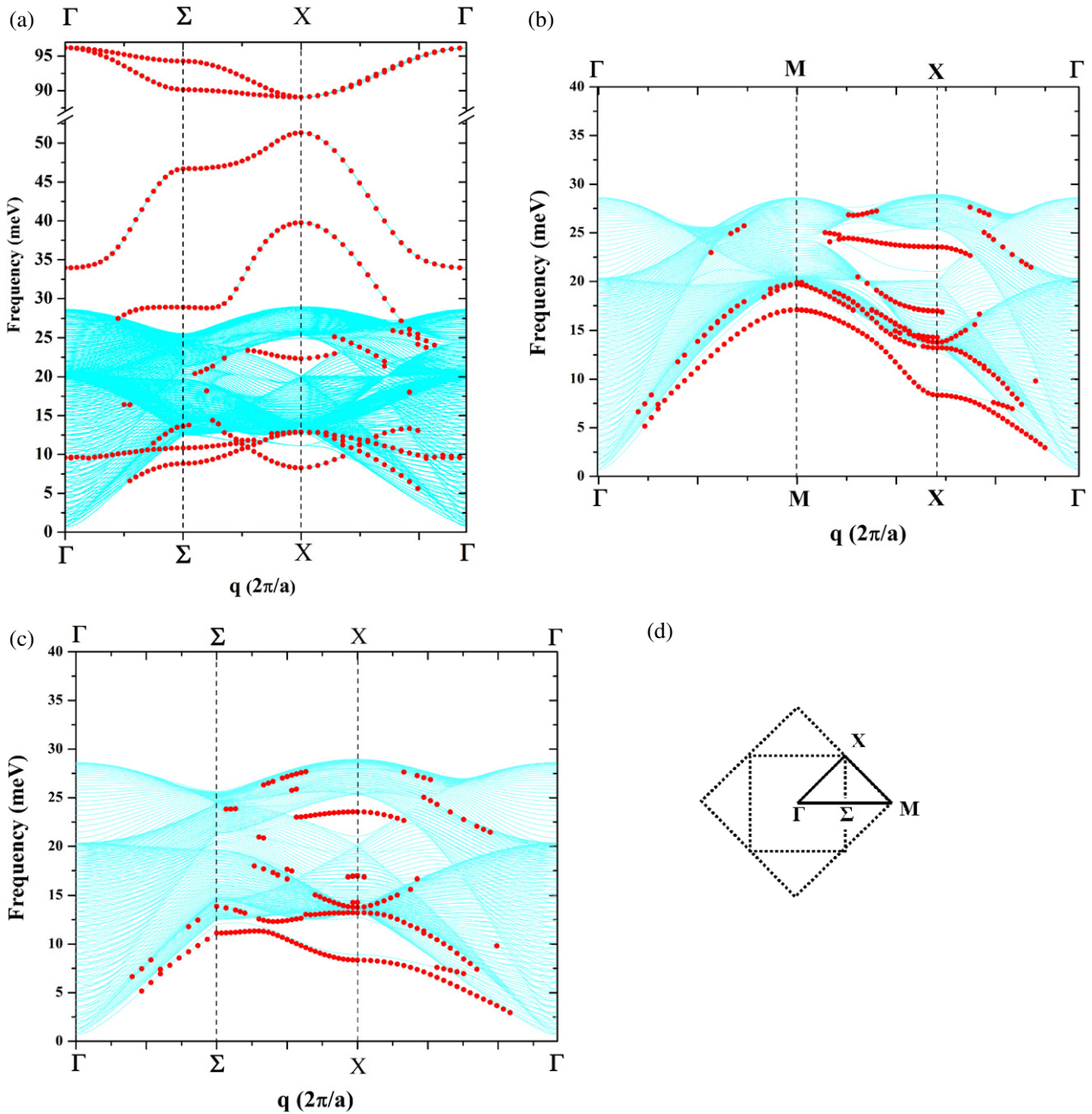


Figure 5. Calculated surface phonon dispersion curves (a) for unreconstructed $c(2 \times 2)$ N/Cu(001), (b) and (c) for clean Cu(001) along different directions: in (b) along Γ MX direction and in (c) along Γ Σ X direction.

phonon dispersion curves for the unreconstructed $c(2 \times 2)$ N/Cu(001) is presented in figure 5(a) together with those for clean $p(1 \times 1)$ Cu(001) in figures 5(b) and (c) along two different paths in the surface Brillouin zone which is presented in figure 5(d), respectively. The solid lines correspond to bulk-projected modes, the filled-circles in the lower part are the Cu substrate surface modes and the ones in the upper part are the vibrations of N atoms. In general our calculated surface modes for the unreconstructed $c(2 \times 2)$ -N/Cu(001) surface are in good agreement with data from He atom scattering (HAS) measurements [30]. It is remarkable that the flat optical mode stretching from left to right in figure 5(a) is in good agreement with experiment. From figure 5, we note that the

surface modes of Cu(001) undergo remarkable changes in the presence of the N overlayer. First of all, the mode at Γ with energy of 9.5 meV, which is the backfold from the mode at M (17.1 meV), underwent a considerable softening (6.6 meV). This mode corresponds to displacements of the first layer Cu atoms along the surface normal. Modes at Σ with energy of 8.8 meV and 10.8 meV also underwent slight softening (about 1 or 2 meV). Both modes display vertical displacements of the first layer Cu atoms coupled to displacements (both vertical and longitudinal) of the second layer Cu atoms with more weight from the top layer atoms. On the other hand, some modes underwent significant stiffening. The mode on top of the bulk backgrounds with a large dispersion is one

Table 3. Averaged in-plane force-constant coupling (in dyne cm^{-1}).

Layer	N/Cu(001)	Cu(001)	Bulk Cu
1	21 007	13 308	
2	14 684	14 831	15 126
3	15 026	14 793	
4	15 050	14 843	

such mode. It has vibrational energy of 28.8 meV at Γ and 39.7 meV at X and consists of longitudinal displacements of the first layer Cu atoms. The mode at 8.2 meV at X also shows a large dispersion. It has almost same frequency as its Cu(001) counterpart (8.3 meV) and its polarization changed from shear horizontal to in-plane. The displacement patterns of these two modes are of particular importance as shown in figures 2(a) and (b), respectively. Both the clock and diamond type displacement patterns were once proposed as the pattern of the reconstructed C/Ni(001) although the clock type is now preferred. Also the clock displacement pattern has been discussed as a possible reconstruction for the reconstructed $c(2 \times 2)$ N/Cu(001) surface [31]. However, as this displacements do not induce any significant reduction in the mode frequencies, we think the clock reconstruction does not occur on the Cu(001) surface. It is interesting to know what causes the diamond mode to show such a large dispersion. In fact, it can be easily understood from the fact that in the diamond displacement pattern the Cu atoms directly move towards the N atoms. As the N–Cu bond is very strong, its bond length change will cause very large restoring force on Cu atoms, and as a result this mode will vibrate with very high frequency. This is confirmed by the analysis of force-constant matrices. For the N–Cu interaction, the largest component of the N–Cu force constant is $2 \times 10^5 \text{ dyn cm}^{-1}$, which is almost an order of magnitude larger than even the largest force constant for the Cu–Cu interactions ($2.4 \times 10^4 \text{ dyn cm}^{-1}$). This force constant has a large impact on the diamond mode (39.7 meV), but not on the clock mode (8.3 meV) because of the displacement patterns associated with these modes.

To fully appreciate the changes in the strength of coupling between any two atoms we need to take into account all components in the force-constant matrix $\Phi_{\alpha\beta}$ connecting the two. For this purpose, the convenient concept of an average coupling strength $\langle I \rangle$ for a bond length σ is introduced [34]. It is defined as

$$\langle I \rangle \equiv \sqrt{\frac{1}{3} \sum_{\alpha\beta} \Phi_{\alpha\beta}^2(\sigma; i, j)} \quad (1)$$

where α and β are Cartesian coordinates, and σ is the bond length connecting atoms i and j . Calculated coupling strength $\langle I \rangle$ of the in-plane and the interlayer Cu–Cu force-constant matrices are presented in table 3 and 4 for the unreconstructed $c(2 \times 2)$ -N/Cu(001) and clean Cu(001), respectively. Upon N adsorption the average strength of the first layer *in-plane* Cu–Cu force constants increase 58%, while the *interlayer* Cu–Cu coupling strength between the first layer and the second layer decreases 39%, with respect to those of Cu(001). The large softening of the interlayer bonds agrees well with the large expansion of the first and second interlayer distance

Table 4. Averaged interlayer force-constant coupling (in dyne cm^{-1}).

Layers	N/Cu(001)	Cu(001)	Bulk Cu
1, 2	10 543	17 270	
2, 3	14 370	14 552	15 126
3, 4	14 761	14 872	
4, 5	15 175	14 956	

(8%). These changes may be associated with a charge transfer model. In other word, the large softening of the interlayer coupling and the large stiffening of the in-plane Cu–Cu force constants may suggest that the charges depleted from the interlayer bonds move to the in-plane Cu–Cu bonds, as well as, the newly formed N–Cu bonds upon N adsorption. On the other hand, upon creation of the clean surface, the in-plane coupling surprisingly reduced by 12% and the interlayer coupling increased by 14% with respect to the bulk Cu–Cu coupling. This suggests that not only some charges depleted from the dangling bonds but also ones from the in-plane Cu–Cu bonds seem to transfer mostly to the interlayer bonds. However, it is not possible to associate these changes in the in-plane force constants to the sign of the induced surface stresses. For example, upon N adsorption, we expect a large tensile stress on Cu(001) as a result of the stiffening of the in-plane force constants. But this is not what we find in our calculations. Rather, *our calculated stress values correlate with the changes in the interlayer force constants*, suggesting that most significant contribution to surface stress comes from the interlayer bonds between the first layer and the second layer. If the interlayer bonds become weak, a compressive stress results on the surface. In other words, in the case of a large expansion between the first and second substrate layer atoms upon adsorption, we suggest that the surface undergoes a large compressive stress.

We now comment on the phonon dispersion curves in view of the proposed rumpling model as a stress relief mechanism. The mode at Γ (mode energy of 9.5 meV) has vertical displacements (within the first Cu layer) which are equivalent to that of Hoefl's rumpling model (figure 1(c)). The softening of the mode (about 7 meV) might be a sign of reduced surface stress and of enhanced vibrational amplitudes of the surface atoms, providing support to the interpretation of the data. However, our calculated surface stress for the mode is never reduced and the softening is also not dramatic enough to produce a negative frequency, of the mode. The unrumpled structure is thus stable dynamically as well as statically. This confirms the validity of the traditional model of $c(2 \times 2)$ N overlayer on Cu(001).

5. Conclusion

Our calculations of the surface electronic structure are based on density functional theory and the pseudopotential method, while the evaluation of surface dynamics relies on the density functional perturbation theory. For the related cases of $c(2 \times 2)$ overlayers of N on Cu(001) and C and O on Ni(001), our recently calculated dispersion curves for surface phonons,

when combined with insights from calculated surface stress and surface electronic charge densities, provide rationale for when the substrate may undergo surface reconstruction. In regard to the recently proposed rumpling model for $c(2 \times 2)$ N/Cu(001) structure, we find no rumpling of the top Cu layers and N atoms always site above Cu atoms. Although our calculated surface phonon dispersion curves show a substantial softening of the mode connected to the rumpling in the first layer Cu, still the unrumped structure is stable dynamically as well as statically. We find no anomaly in regard to the clock displacement mode in our surface phonon dispersion curves.

Acknowledgments

We would like to thank Marisol Alcantara for having performed the calculations of the dispersion of N/Cu(001). We would like to thank Jane Hinch for sharing with data from He-atom-surface scattering prior to publication and for engaging discussions. We have also gained from many discussions and exchanges with Klaus Peter Bohnen, Rolf Heid, Sergey Stolbov, and Abdelkader Kara. This work was supported in part by grant CHE-0741423 from the National Science Foundation.

References

- [1] Ibach H, Müller J E and Rahman T S 1986 *Phil. Trans. R. Soc. A* **318** 163
- [2] Sander D, Linke U and Ibach H 1992 *Surf. Sci.* **272** 318
- [3] Ibach H 1997 *Surf. Sci. Rep.* **29** 193
- [4] Hoelt J T, Polcik M, Kittel M, Terborg R, Toomes R L, Kang J-H and Woodruff D P 2001 *Surf. Sci.* **492** 1
- [5] Driver S M, Hoelt J-T, Polcik M, Kittel M, Terborg R, Toomes R L, Kang J-H and Woodruff D P 2001 *J. Phys.: Condens. Matter* **13** L601
- [6] Driver S M and Woodruff D P 2001 *Surf. Sci.* **492** 11
- [7] Müller J E, Wuttig M and Ibach H 1986 *Phys. Rev. Lett.* **56** 1583
- [8] Rahman T S, Rocca M, Lehwald S and Ibach H 1986 *J. Electron Spectrosc. Relat. Phenom.* **38** 45
- [9] Hong S, Kara A, Rahman T S, Heid R and Bohnen K P 2004 *Phys. Rev. B* **69** 195403
- [10] Stolbov S, Hong S, Kara A and Rahman T S 2005 *Phys. Rev. B* **72** 155423
- [11] Ihm J, Zunger A and Cohen M L 1979 *J. Phys. C: Solid State Phys.* **12** 4409–22
- [12] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
- [13] Baroni S, Dal Corso A, de Gironcoli S and Giannozzi P 2006 <http://www.pwscf.org>.
- [14] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [15] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [16] Methfessel M and Paxton A 1989 *Phys. Rev. B* **40** 3616
- [17] Baroni S, Giannozzi P and Testa A 1987 *Phys. Rev. Lett.* **58** 1861
- [18] Giannozzi P, de Gironcoli S, Pavone P and Baroni S 1991 *Phys. Rev. B* **43** 7231
- [19] Kilcoyne A L D, Woodruff D P, Robinson A W, Lindner T, Somers J S and Bradshaw A M 1991 *Surf. Sci.* **253** 107
- [20] Frenken J W M, van der Veen J F and Allan G 1983 *Phys. Rev. Lett.* **51** 1876
- [21] Onuferko H, Woodruff D P and Holland B W 1979 *Surf. Sci.* **87** 357
- [22] Daum W, Lehwald S and Ibach H 1986 *Surf. Sci.* **178** 528
- [23] Rieder K H and Wilsch H 1983 *Surf. Sci.* **131** 245
- [24] Schmid M, Biedermann A and Varga P 1993 *Surf. Sci.* **294** L952
- [25] Klink C, Olesen L, Besenbacher F, Stensgaard I and Laegsgaard E 1993 *Phys. Rev. Lett.* **71** 4350
- [26] Bader M, Ocal C, Hillert B, Haase J and Bradshaw A M 1987 *Phys. Rev. B* **35** 5900
- [27] Rahman T S and Ibach H 1985 *Phys. Rev. Lett.* **54** 1933
- [28] Szeftel J M, Lehwald S, Ibach H, Rahman T S, Black J E and Mills D L 1983 *Phys. Rev. Lett.* **51** 268
- [29] Yoshimote Y and Tsuneyuki S 2003 *Surf. Sci.* **514** 200
- [30] Wofford T E, York S M and Leibsle F M 2003 *Surf. Sci.* **522** 47
- [31] Lederer T, Arvanitis D, Tischer M, Comelli G, Troeger L and Baberschke K 1993 *Phys. Rev. B* **48** 11277
- [32] Ciftlikli E Z, Shuttleworth I G, Goncharova L V, Hinch B J, Alcántra M O, Hong S and Rahman T S 2008 at press
- [33] Zeng H C and Mitchell K A R 1989 *Langmuir* **5** 829
- [34] Zeng H C, Sodhi R N S and Mitchell K A R 1987 *Surf. Sci.* **188** 599
- [35] Lehwald S, Szeftel J M, Ibach H, Rahman T S and Mills D L 1983 *Phys. Lett.* **50** 518
- [36] Rocca M, Lehwald S, Ibach H and Rahman T S 1987 *Phys. Rev. B* **35** 9510
- [37] Heid R and Bohnen K P 2003 *Phys. Rep.* **387** 151