Adsorbate-induced Surface Stiffening: Surface Lattice Dynamics of Ru(001)-(1×1)-O

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Abstract

The dynamical properties of the high-density Ru(001)-(1×1)-O phase has been investigated by a combined high-resolution electron energy loss spectroscopy and density functional theory study. Due to a strong static outward relaxation of the first Ru layer a soft Rayleigh phonon mode is expected. However, a Rayleigh mode stiffening together with a new high energy in-plane phonon mode above the bulk bands is found which is related to a strong adsorbate-induced intralayer force constant stiffening which counteracts an interlayer softening. This structurally rather simple system with one surface atom per (1×1) unit cell demonstrates the limited applicability of previously adopted models.

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The dissociative chemisorption of oxygen on nickel, platinum and ruthenium surfaces has been often treated as a model system for reactive adsorbates on transition metal surfaces. Besides their structural and electronic properties the *dynamical* properties of oxygen adlayers have been the focus of several studies, e.g. on Ni(100) [1, 2], Pt(111) [3], and Ru(001) [4, 5, 6]. Within the various oxygen model systems, the (1×1)-O high-coverage phases play an important role due to their strong influence on the properties of the first substrate layers, their possible catalytic importance, and their unchanged adsorbate overlayer periodicity [3, 7]. Although they are barely accessible under ultrahigh vacuum (UHV) conditions using molecular oxygen, these dense adlayers have often been claimed to bridge the gap in catalysis between studies under UHV and ambient pressure/real conditions [8].

For the Ru(001)-(1×1)-O surface just recently a strong oxygen-induced outward relaxation of 3.7 % for the first Ru layer was found based on a density functional theory (DFT) and low energy electron diffraction (LEED) study [7]. The (1×1)-O induced outward relaxation is in fact the strongest relaxation known on Ru(001) [8]. Such static structural changes which are driven by a charge redistribution within the first layers will also modify the dynamical properties of the surface. E.g., it is commonly accepted that an outward relaxation of the first layer will soften the Rayleigh wave [1, 2, 4, 10]. Indeed, for the Ru(001)-(1×1)-O surface a peculiar soft vibrational mode has been found and explained as a soft phonon mode due to the first layer relaxation [4]. However, it could not be confirmed in a subsequent high resolution electron energy loss spectroscopy (HREELS) study [9] questioning this interpretation.

On the theoretical side the calculation of dynamical properties of an adsorbate covered surface is rather demanding, because it requires an accurate description of the adsorbate induced changes of structural *and* electronic properties. Often, theoretical descriptions of surface phonon spectra were based on empirical force-constant models whose parameters were fitted to experimental dispersion curves [2, 11, 12]. Recently, it has been found that bulk Ru exhibits pronounced phonon anomalies due to strong electron-phonon coupling [13], indicating the need for a large parameter set to accurately describe its phonon spectrum. Previous models of the dynamics of clean and adsorbate covered Ru(001) surfaces had used only a small number of force constants [12, 14] and are, therefore, inadequate for a modeling of substrate dynamics. DFT based ab initio methods provide an unbiased and often very accurate description of vibrational properties. Early applications to surfaces using frozen-
phonon techniques were limited to phonons at high-symmetry points of the surface Brillouin zone (SBZ) \[15\] or to rough estimates of the interatomic coupling \[16\]. The way to a more complete calculation of surface vibrations was opened by the development of numerically efficient linear-response schemes in connection with pseudopotential plane-wave techniques \[17, 18\]. However, due to their localized \(d\) electrons, transition metal surfaces have been almost prohibitive to be dealt with by this standard approach using a plane-wave basis only. These numerical limitations have been overcome by a recent implementation of the linear-response formalism in the framework of a mixed-basis pseudopotential method \[19\], where in addition to plane waves also local functions are employed to better represent the more localized parts of the valence states. This theoretical technique which recently explained successfully the anomalous lattice dynamics of bulk Ru \[13\], is here applied to a single crystal surface for the first time.

Clearly, the Ru(001)-(1×1)-O surface is a benchmark for our understanding of adsorbate-induced changes of the dynamical surface properties. We present in this letter a combined, theoretical DFT and experimental HREELS, study on the surface phonon dispersion of the Ru(001)-(1×1)-O surface. It will be shown that the presence of an adsorbate layer induces a large stiffening of the coupling within the first Ru layer, which gives rise to a new substrate phonon appearing \(above\) the bulk spectrum. This is in contrast to the Rayleigh mode which exhibits only small changes due to a balancing of this intralayer stiffening by interlayer softening.

For the preparation of a well-ordered high-density O-(1x1) layer dissociative adsorption of \(\text{NO}_2\) at a surface temperature of 600 K has been used \[7\]. Preparation of this phase with high exposures of molecular oxygen is also possible but leads to less ordered and incomplete (1×1)-O layers due to the necessity of vacant sites for the dissociative adsorption \[5\]. HREELS data for the Ru(001)-(1×1)-O layer in off-specular scattering geometry are shown in Fig. 1 for an electron energy of 121 eV and a constant total scattering angle of 120°. From bottom to top the off-specular angle increases with the corresponding parallel momentum transfer \(k_\parallel\) along the \(\Gamma\text{KM}\) direction in reciprocal space as indicated on the right side of Fig. 1. Details of the experimental setup as well as a discussion of the adsorbate modes above 500 cm\(^{-1}\) have been presented elsewhere \[5\]; here we focus on the substrate phonons. In Fig. 1 three prominent phonon modes can be easily identified. At a momentum transfer of 0.3 Å\(^{-1}\) an energy loss peak at 62 cm\(^{-1}\) dominates which is accompanied by a corresponding energy
gain peak at -62 cm\(^{-1}\). This phonon mode shifts up in energy to 101 and 130 cm\(^{-1}\) at 0.61 and 0.91 Å\(^{-1}\). At higher momentum transfer this mode is difficult to identify at the electron energy of 121 eV. In the momentum range from 1.3 to 1.79 Å\(^{-1}\) a new high energy mode around 280 cm\(^{-1}\) is discernible. It initially shifts up in energy and then, for momenta above 1.60 Å\(^{-1}\), down again. Additionally a strong phonon loss at 230 cm\(^{-1}\) is visible at 0.91 Å\(^{-1}\).

The experimental phonon frequencies extracted using various electron energies in the range of 16 to 256 eV and various k\(\parallel\) are summarized by open symbols in Fig. 2. The (1×1) SBZ is shown schematically in the inset. The dashed lines and the solid circles in Fig. 2 indicate the phonon dispersion curves for the surface projected bulk and the surface phonons, respectively, as determined by first principles linear-response calculations. The theoretical results correspond to an asymmetric 50 layer slab with an adlayer covered surface on one side and a bulk truncated surface on the opposite side of the slab. Ab initio force constants for Ru bulk taken from Ref. [13] have been combined with surface force constants, which were extracted from mixed-basis linear-response calculations [32] for a symmetric slab consisting of 6 Ru layers and one O layer added on each side. All but the two innermost layers have been relaxed. The local-density approximation using the Hedin-Lundqvist form of the exchange-correlation functional has been applied [33].

In the calculations several modes (marked with solid circles) show strong localization at the surface, i.e. exhibit high amplitude weights within the first Ru layers. The most striking feature is the high energy split-off surface phonon (\(S_{SO}\)) which is peeled off from the bulk bands around the \(\overline{K}\) point and which is located at approximately 280 cm\(^{-1}\) (35 meV) there. At the \(\overline{K}\) point it is located 19 cm\(^{-1}\) higher than any bulk phonon mode. It is important to note that calculations based on the force constants of bulk Ru and the geometrical structure of the truncated crystal do not show any surface phonon located above the bulk bands. Similarly previous theoretical studies of the hcp (001) or fcc (111) surface phonons did not find such a mode [20, 21]. Therefore this split-off phonon indicates significantly changed dynamical properties of the (1×1)-O surface in comparison to the Ru bulk.

The second feature which is experimentally clearly visible is attributed to the Rayleigh wave (RW). The experimentally observed phonon dispersion for k\(\parallel\) > 0.2 Å\(^{-1}\) agrees within 10 cm\(^{-1}\) with the calculated dispersion curve. The comparison with the bulk phonon bands shows that it is located well below the bulk bands as observed for many other surfaces [14]. Note however that the dispersion of the RW is shifted upwards in energy (for k\(\parallel\) > 0.7 Å\(^{-1}\)
as compared to the results for the truncated bulk in the absence of oxygen (lowest dashed line). Besides these two modes which are visible within a wider part of the SBZ, modes at 170 and 200 cm$^{-1}$ (21 and 25 meV) are experimentally discernible around the K point which can also be found in the calculated surface phonon dispersion curves.

For the RW phonon and the $S_{SO}$ mode, the symmetry- and layer-resolved vibrational amplitudes are displayed in Fig. 3. From its dominantly vertical character in the first Ru layer throughout the whole SBZ the Rayleigh mode (left side of Fig. 3) has been identified. It corresponds to the prominent $S_1$ mode which has been described for fcc(111) and hcp(001) surfaces [20, 22, 23]. Along ΓK, admixtures of longitudinal and shear horizontal character can be seen which are small for the first layer but substantially for the second layer Ru atoms. This mixing is possible because the ΓK direction is a low symmetry ($C_1$) direction. On the other hand, along the ΓM direction the Rayleigh mode involves only atomic motions within the sagital plane (vertical-longitudinal) because this direction lies within a surface mirror plane (has $C_S$ symmetry). At the K point which exhibits $C_3V$ symmetry, the movement of the O and Ru atoms in each layer are either purely vertical or purely in plane. For the Rayleigh mode we find vertical movements of the first layer Ru atoms and in-plane movements for the O and the second layer Ru atoms. It is strongly localized within the first and second Ru layers here. The mode which is visible around the K point at 170 cm$^{-1}$ (just below the bulk bands) corresponds to the $S_5$ mode of Ref. [20] and has a similar displacement pattern; but here the first layer Ru atoms move in plane and the O and second layer Ru atoms move vertically. As for the RW the $S_5$ phonon is shifted upwards in energy as compared to the truncated bulk calculations (dashed lines in Fig. 2).

For the high energy mode at the K point (right side of Fig. 3), the movements of the O and Ru atoms are completely in plane circular for all layers. When the O atom moves counter clockwise, the first layer Ru atoms move clockwise, or vice versa. For the deeper Ru layers the pattern repeats. The movement is mainly located in the first Ru layer with only minor contributions from second or deeper layers. However it has also appreciable amplitude on the O atoms despite the large Ru to O mass mismatch. This indicates some hybridization with the Ru-O bending modes although the adsorbate modes are a factor of two higher in frequency (520 to 565 cm$^{-1}$). Close to the M point the phonon mode exhibits some vertical movement of the O atoms and a dominantly shear horizontal movement of the first layer Ru atoms which renders the experimental identification of this mode difficult close to the
M point. Because of the pure in-plane movement of this mode its high energy at K points to a significant stiffening of the intralayer force constants due to the oxygen overlayer. This is indeed confirmed by the detailed theoretical analysis of the interatomic force constants. They exhibit a large increase of the nearest neighbor coupling within the first Ru layer by a factor of 2.5 compared to the bulk.

The adsorbate-induced changes of the surface dynamical properties can be related at least partly to its changed geometrical and electronic structure: For the Ru(001)-(1×1)-O surface we find a large outward relaxation (3.83 %) of the first-to-second Ru layer spacing, \( d_{12} \), with respect to the bulk layer spacing which is accompanied by a contraction of the second-to-third layer spacing of -0.47 %. This finding is in perfect agreement with a previous DFT-GGA calculation and recent LEED studies which found values of 2.7 and 3.7 % for \( d_{12} \) and -0.9 and -0.5 % for \( d_{23} \), respectively \cite{7, 8}. It has been shown that the large expansion of the first Ru interlayer spacing is the result of a weakening of the attraction between the top and second substrate layers due to an oxygen-induced charge removal from the Ru \( d \) states \cite{7}. Consistent with this picture, we find from the theoretical analysis that the outward relaxation indeed weakens the interlayer force constants between the first and second Ru layers which alone would imply a RW softening. Such a softening has been found for several examples, e.g. for oxygen on Ni(100), Cu(100), and Pd(100) \cite{2, 11, 24, 25}. However we find here – against this generally assumed rule \cite{10} – a Rayleigh phonon stiffening in the presence of a strong outward relaxation. The explanation is closely related to the observation of the new \( S_{SO} \) mode. The intralayer stiffening which at the K point peels off the \( S_{SO} \) mode from the bulk bands counteracts the softening of the RW. It even leads to an over-compensation near the SBZ boundary where the intralayer couplings are more effective than in the limit of long wavelengths. Thus the unexpected stiffening of the RW phonon and the \( S_{SO} \) mode around the K point are both consequences of the adsorbate-induced intralayer stiffening. Part of this stiffening might be of electrostatic origin. It is known from theoretical studies of O adsorbates on Rh \cite{20, 21}, Pt \cite{28, 29}, and Ru surfaces \cite{30} that due to the large electronegativity of oxygen the O-metal bond is slightly ionic, i.e. there exists a small charge transfer from the metal surface to the O layer. For example, a charge transfer of 0.3 electrons per surface atom has been proposed for Pt(111)-(1×1)-O \cite{29}. Consequently, the substrate is somewhat positively charged leading to an enhanced Coulomb interaction. Indeed, we find that for the nearest neighbor bond of the first Ru layer, the
changes in the diagonal components of the force constant matrix (longitudinal and transverse force constants) with respect to the bulk have the form of a Coulomb mediated coupling. However, this explanation would require effective charges of more than one electron per Ru site, which seems to be unreasonably large. In addition, we also find significant changes in the off-diagonal (tensorial) components of the force constant matrix. Thus, the adsorbate induced modifications of the binding properties are rather complex and involve many-body interactions as well.

To summarize, the different behaviour of intra- and interlayer force constants for the Ru(001)-(1×1)-O surface shows clearly that an adsorbate covered surface – even in the simplest case of unchanged symmetry and only a single atom per layer in the unit cell – cannot be described with force constants which are scaled from the respective bulk values. Here the dense adlayer introduces a strong intralayer force constant stiffening in combination with an interlayer softening. It has been demonstrated that the former leads to a new high energy in-plane phonon mode above the bulk bands. For the RW mode the intralayer stiffening counteracts the phonon softening which might be expected otherwise on the simple basis of first-layer relaxation.

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[1] S. Lehwald, J. M. Szeftel, H. Ibach, T. S. Rahman, and D. L. Mills, Phys. Rev. Lett. 50, 518 (1983).
[2] J. Szeftel and S. Lehwald, Surf. Sci. 143, 11 (1984).
[3] D. Neuhaus, F. Joo, and B. Feuerbacher, Phys. Rev. Lett. 58, 694 (1987).
[4] P. He and K. Jacobi, Phys. Rev. B 55, 4751 (1997).
[5] T. Moritz, D. Menzel, and W. Widdra, Surf. Sci. 427-428, 6468 (1999).
[6] K. L. Kostov, M. Gsell, P. Jakob, T. Moritz, W. Widdra, and D. Menzel, Surf. Sci. Lett. 394, L138 (1997).
[7] C. Stampfl, S. Schwegmann, H. Over, M. Scheffler, and G. Ertl, Phys. Rev. Lett. 77, 3371 (1996).
[8] D. Menzel, Surf. Rev. Lett. 6(5), 835 (1999).
[9] R. Berndt, J. P. Toennies, and C. Wöll, Surf. Sci. 244(3), 305 (1991).
[10] M. Rocca, Landolt-Börnstein, vol. III/42 (2001), and references therein.
[11] T. S. Rahman and H. Ibach, Phys. Rev. Lett. 54, 1933 (1985).
[12] J. Braun, K. L. Kostov, G. Witte, L. Surnev, J. G. Skofronick, S. A. Safron, and C. Wöll, Surf. Sci. 372(1-3), 132 (1997).
[13] R. Heid, L. Pintschovius, W. Reichardt, and K.-P. Bohnen, Phys. Rev. B 61(18), 12059 (2000).
[14] T. S. Rahman, A. B. Anton, N. R. Avery, and W. H. Weinberg, Phys. Rev. Lett. 51, 1979 (1983).
[15] K. M. Ho and K.-P. Bohnen, Phys. Rev. B 32, 3446 (1985).
[16] J. E. Müller, M. Wuttig, and H. Ibach, Phys. Rev. Lett. 56, 1583 (1986).
[17] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. 58, 1861 (1987).
[18] P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B 43, 7231 (1991).
[19] R. Heid and K.-P. Bohnen, Phys. Rev. B 60, R3709 (1999).
[20] R. E. Allen, G. P. Alldredge, and F. W. de Wette, Phys. Rev. B 6, 632 (1972).
[21] R. E. Allen, G. P. Alldredge, and F. W. de Wette, Phys. Rev. B 4(6), 1682 (1971).
[22] R. E. Allen, G. P. Alldredge, and F. W. de Wette, Phys. Rev. B 4(6), 1661 (1971).
[23] J. E. Black, F. C. Shanes, and R. F. Willis, Surf. Sci. 133, 199 (1983).
[24] Y. Chen, S. Y. Tong, J.-S. Kim, L. L. Kesmodel, T. Rodach, K.-P. Bohnen, and K. M. Ho,
Phys. Rev. B 44, 11394 (1991).

[25] L. Chen and L. L. Kesmodel, Surf. Sci. 320, 105 (1994).

[26] K. Stokbro and S. Baroni, Surf. Sci. 370, 166 (1997).

[27] M. V. Ganduglia-Pirovano and M. Scheffler, Phys. Rev. B 59, 15533 (1999).

[28] P. J. Feibelman, Phys. Rev. B 56, 10532 (1997).

[29] A. Kokalj, A. Lesar, M. Hodoscek, and M. Causa, J. Phys. Chem. B 103, 7222 (1999).

[30] P. J. Feibelman, Phys. Rev. B 59, 2327 (1997).

[31] R. Heid, D. Strauch, and K.-P. Bohnen, Phys. Rev. B 61, 8625 (2000).

[32] The linear-response implementation from [19] is based on the “Fortran90 Program for Mixed-Basis Pseudopotential Calculations for Crystals” by B. Meyer, C. Elsässer, and M. Fähnle, Max-Planck-Institut für Metallforschung, Stuttgart (unpublished).

[33] Details of the norm-conserving pseudopotentials and local functions have been described in previous works [13, 31]. A cutoff of 22 Ry has been employed for the plane-wave basis, and the SBZ sampling was performed on a 18x18 hexagonal $k$-point mesh corresponding to 37 $k$ points in the irreducible wedge.
FIG. 1: HREEL spectra in the off-specular scattering geometry for Ru(001)-(1×1)-O at the indicated momentum transfer along $\Gamma K M$ direction ([10\bar{1}0] direction). The electron energy is 121 eV with a total scattering angle of 120°.
FIG. 2: Phonon dispersion curves for the Ru(001)-(1×1)-O surface. Open symbols indicate the experimental data; theoretical dispersion curves for an asymmetric 50 layer slab are indicated by dashed lines, while filled circles represent surface modes (identified by a weight larger than 20 % in the first three layers). In the inset the hexagonal SBZ is sketched.
FIG. 3: Relative layer-resolved vibrational weights for the Rayleigh (left panel) and the high energy split-off mode (right panel) along ΓK, KM, and ΓM. Shown are the total sum (full lines) and the weights of the vertical, longitudinal and shear horizontal components (dotted, dashed, and dash-dotted lines, respectively).