



Water adsorbate influence on the Cu(110) surface optical response

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ABSTRACT

Surface reflectance anisotropy may be utilized for characterizing surfaces, interfaces, and adsorption structures. Here, the reflectance anisotropy and surface dielectric functions of the thermodynamically most favored water adsorbate structures on the Cu(110) surface (i.e. hexagonal bilayers, pentagonal chains, and partially dissociated water structures) are calculated from density-functional theory and compared with recent experimental data. It is shown that the water overlayer structures modify in a geometry-specific way the optical anisotropy of the bare surface which can be exploited for in situ determination of the adsorption structures. For hexagonal bilayer overlayer geometries, strong features in the vacuum ultraviolet region are predicted. The theoretical analysis shows a noticeable influence of intraband transitions also for higher photon energies and rather slight influences of the van der Waals interaction on the spectral signatures. Water induced strain effects on the surface optical response are found to be negligible.

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Reflectance anisotropy spectroscopy (RAS) is a comparatively simple and powerful tool for studying surfaces and interfaces [1–4]. Thereby the relative difference of the normal incidence reflectance along two different polarization directions is measured. Thus information on the surface dielectric function anisotropy and, indirectly, on the related optical transitions between surface states and thus the surface structural properties is obtained. It is a non-destructive surface probe that – in contrast to many other surface analysis techniques – does not require ultrahigh vacuum conditions. Being optical, it can be used, e.g., in the reactive, relatively high-pressure sample ambients of organometallic chemical vapor deposition or to access liquid–solid interfaces. Even complicated adstructures such as the adenine adsorption configuration at the Au(110)–electrolyte interface can thus be explored by RAS [5]. In many instances, however, the full potential of RAS can only be exploited when the measured data are compared with microscopic calculations of the surface optical response. Optical spectra of semiconductor and metal surfaces can nowadays be simulated with true predictive power based on density-functional theory (DFT) and/or many-body perturbation theory [4,6].

While the optical response of the bare Cu(110) surface has been intensively investigated by both experiment and theory [7–11,6], relatively little is known on the influence of water on the Cu(110) optical

properties. Water is ubiquitous and single adsorbed water molecules or even thin water films can be expected on the Cu(110) surface at ambient conditions. The influence of water on the metal surface optical response is also interesting in the context of adsorbate structures investigated at liquid–solid interfaces [5]. Very recently Denk et al. [12] investigated experimentally the influence of water on the Cu(110) optical anisotropy in the energy range from 1.5 to 9.3 eV. They concluded that the water overlayer modifies the optical anisotropies characteristic for the clean Cu surface, but no distinct spectral features associated with the H₂O molecules were detected in the energy range probed.

Here we use density-functional theory in order to predict and rationalize the optical anisotropy of the energetically most favored water adsorbate structures on Cu(110). In particular we are interested in the origin of the measured features, and to what extent they can be used to discriminate between structurally different water configurations. The measurements are compared with recent experimental data [12], which are complemented with additional RAS measurements performed for partially dissociated water structures.

The DFT calculations are performed using the Vienna *Ab initio* Simulation Package (VASP) [13]. The electron–ion interaction is described by the projector augmented wave scheme [14]. We use the PW91 functional [15] to describe the electron exchange and correlation energy within the generalized gradient approximation. The dielectric function is calculated within the independent particle approximation [16,17,4]. Its intraband contribution is obtained from the plasma frequency tensor following the approach of Ref. [6]. The calculations employ a plane-

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wave basis with an energy cutoff of 400 eV and a Brillouin zone (BZ) sampling using Monkhorst-Pack points with a density corresponding to $25 \times 35 \times 1$ $\mathbf{k}$ points per (1×1) surface unit cell. Thereby a Gaussian smearing with an energy broadening of 0.2 eV is used.

The reflectance anisotropy spectra for the surface of cubic Cu substrate with a lattice constant of 3.63 Å are calculated from the surface dielectric anisotropy (SDA) approximated here by the difference of the in-plane components of the slab polarizability, $\Delta\epsilon_s = \epsilon_s^{[1\bar{1}0]} - \epsilon_s^{[001]}$, obtained for a symmetric 21 layer Cu slab plus adsorbates. A vacuum region of 13 Å separates neighboring slabs along the surface normal. This supercell setup is found to lead to numerically converged RAS spectra. Following Aspnes and Del Sole et al. [18–20], the RAS spectra are given by

$$\frac{\Delta r}{r} = \frac{2\omega d}{ic} \frac{\Delta\epsilon_s}{\epsilon_b - 1}, \quad (1)$$

where ϵ_b is the Cu bulk dielectric function, ω the light frequency, d is the half-slab thickness and c is the speed of light. The RAS calculations are performed for the clean Cu(110) surface as well as for the thermodynamically stable water adsorbate structures determined earlier by some of the present authors [21].

The experiments reported in this work are performed under ultra high vacuum conditions with a base pressure of 1×10^{-10} mbar. The chamber is equipped with a beetle-type variable-temperature scanning tunneling microscope designed to work in the temperature range of 14 to 500 K [22]. A photoelastic modulator based reflectance anisotropy spectrometer of the Aspnes type [23] is attached to it. The light beam is directed to the sample at close-to-normal-incidence through a strain-free magnesium fluoride window. The Cu–CuO stripe phase was prepared as described earlier [24], by exposing the Cu(110) surface to 0.5 L ($1 \text{ L} = 10^{-6}$ Torr s) oxygen and annealing to 600 K.

The adsorption structure of water on Cu(110) has been subject to many experimental as well as theoretical investigations. Thereby three major configurations, hexagonal bilayers, pentagonal chains and partially dissociated water structures were identified as most stable and relevant [25–28,21]. According to the surface phase diagram calculated in Ref. [21], partially dissociated water structures, hexagonal bilayers, parallel pentagon chains (cf. Fig. 1) and the bare surface represent the thermodynamic ground state with decreasing water partial pressure or increasing temperature, respectively. In dependence on the orientation of the uppermost water molecules' protons pointing either away or towards the substrate, the hexagonal bilayer occurs as H-up or H-down geometry, respectively.

Experimentally, RAS spectra were measured in two energy ranges, 1.5–5.0 eV and 5.0–8.0 eV at the surface temperature of 125 (130) K [12]. The adstructures formed at 0.3 (0.3) Langmuir, 1.1 L, 1.5 (1.6) L and 2.1 (5) L water on the Cu(110) surface are attributed to parallel pentagon chains, hexagonal bilayer islands, homogeneous hexagonal bilayer and 3D growth, respectively [12].

Fig. 2 shows the calculated RAS and SDA spectra of the clean Cu(110) and the hexagonal bilayer (H-down and H-up) covered substrate along with the corresponding experimental data [12]. The clean surface is characterized by a strong optical anisotropy P_a at around 2 eV (cf. black line in Fig. 2) that arises mainly from transitions between surface states at the $\bar{Y}$ point of the (110) surface Brillouin zone (SBZ), see Fig. 3, and from $\Delta_5 \rightarrow \Delta_1$ transitions near the X point of the fcc BZ [7,29,30], see Fig. 4. The present calculations (red line) well reproduce the experimental data, albeit at slightly lower energies, due to the DFT band-gap problem. Upon absorption of a hexagonal water bilayer, the measured intensity of the P_a and P_c peaks is strongly reduced (magenta). This corresponds well to the calculated spectra that both for the H-down (blue) and H-up (cyan) models of the bilayer adsorption predict a strong reduction of the P_a feature and a somewhat reduced P_c intensity. However, there are clear differences between the calculated RAS signatures

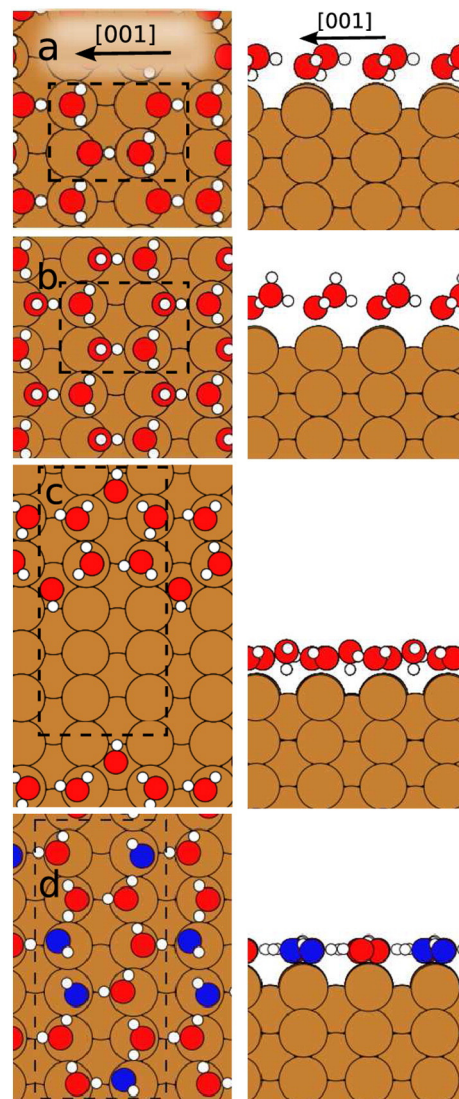


Fig. 1. (left) Top and (right) side view of the atomic structure of (a) H-down, (b) H-up, (c) pentagonal chain, and (d) partially dissociated water. Brown, red, and white circles represent copper, oxygen, and hydrogen atoms. Oxygen atoms in hydroxyl are colored in blue. The supercell of each structure is marked with a dashed rectangle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the H-down and H-up geometries: In addition to reducing the P_a intensity, the H-up model also leads to slight redshift of this feature. A corresponding redshift, but of smaller magnitude is also observed in the measured data. The measured RAS data in conjunction with the present simulations thus suggest that the hexagonal bilayer contains both H-down and the H-up structures, in support of earlier work by Pettersson, Nilsson and co-workers [25]. Pronounced differences between the H-down and the H-up RAS signal are also observed at higher energies, above 10 eV.

After having essentially reproduced the experimental findings for the hexagon bilayer structure, it is interesting to understand the mechanisms that lead to the water-induced changes of the Cu(110) optical anisotropy. The quenching of the surface states and/or water-related relief of surface strain could be obvious reasons for a reduction of anisotropy signals. In order to probe the latter effect, calculations were performed for the clean Cu(110) surface using the atomic structure of the water-adsorbed substrate. It turns out, however, that the corresponding RAS signal is nearly indistinguishable from the original RAS data of bare surface. This excludes any substantial strain contribution. Furthermore,

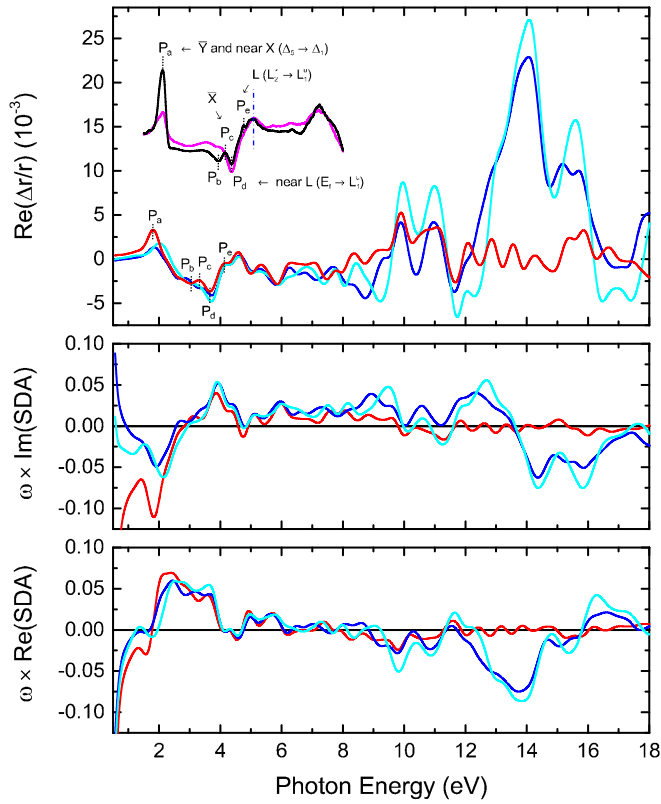


Fig. 2. Calculated RAS (upper panel) and frequency scaled SDA spectra (imaginary and real part shown in middle and lower panel) for the clean Cu(110) surface (red) as well as for the H-down (blue) and H-up (cyan) models for adsorbed hexagonal water bilayer structures are compared with the corresponding RAS measurements for clean (black) and bi-layer water covered surfaces (magenta) [12]. The experiments were performed in two different energy ranges (separated by the blue vertical dashed-dotted line). The experimental curve is shifted upwards for easier comparison with calculation. Relevant features P_a to P_e are labeled, and partially related to electronic transitions in the band structure, cf. Refs. [7,29–32,10]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the detailed inspection of the calculated band structure indicates no significant changes of the Cu surface state energies. In fact, it is observed that the bare copper surface states that contribute substantially to P_a , i.e., a mixed p_y and p_z valence state 0.5 eV below the Fermi level (b_1 in Fig. 3 and blue line in Fig. 5) and a conduction state of mixed s , p_z and d_{yz} orbital character at around 1.5 eV above the Fermi level (b_2 in Fig. 3 and red line in Fig. 5) survive the water absorption essentially unchanged. At the same time, however, we find a strong modification of

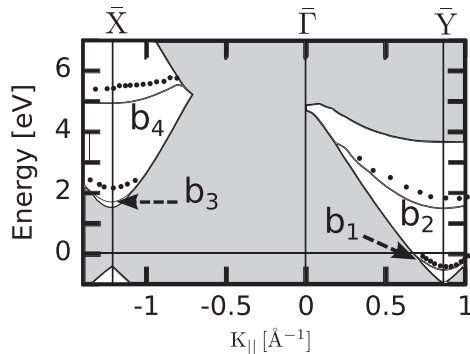


Fig. 3. The calculated Cu(110) surface band structure with prominent surface states labeled as b_1 to b_4 . The projected bulk bands are shown in gray. The calculated bound surface states are compared with experimental data [33,31] indicated by dots. The transition at $\bar{Y}$ from b_1 to b_2 and at $\bar{X}$ from a surface resonance to b_3 are partially responsible for P_a and P_c , respectively.

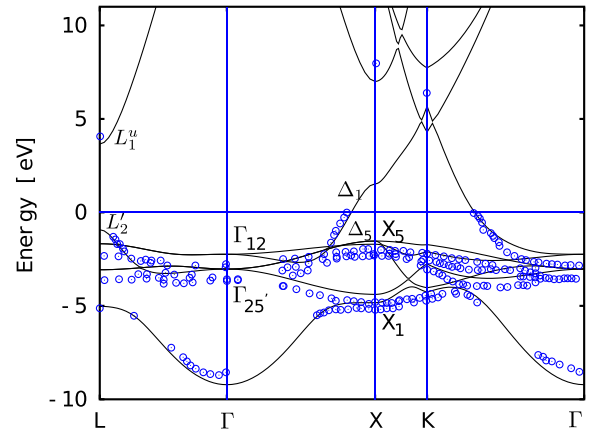


Fig. 4. The calculated Cu bulk bands (black) in comparison to experimental data (blue symbols) [34]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the surface modified bulk states that contribute to P_a : Anisotropic contributions to the bare surface signal arise from $\Delta_5 \rightarrow \Delta_1$ transition near the high symmetry X point of the BZ (cf. Fig. 4). The orbital character and spatial orientation of both the initial (substantially d -like) and final (mainly p -like) states are clearly affected by the water adsorption and thus lead to a modification of P_a .

The onset of the optical absorption of bulk water and one-dimensional water structures occurs for photon energies larger than 7 and 4 eV, respectively [35,36]. Here we find the appearance of additional optical anisotropies due to water adsorption to be limited to the vacuum ultraviolet region, beyond the energy window experimentally probed. We calculate strong RAS features at around 14 eV (Fig. 2), corresponding to a broad positive SDA⁽²⁾ signal at around 12 eV and a negative SDA⁽²⁾ feature around 14 eV. The positive SDA signal arises substantially from the anisotropy of two transitions: (i) between d states at around -4 eV and s and p_z -like states above 8 eV, and (ii) between copper d states at -3.5 eV and states at around 9 eV. In both cases the initial and/or the final-state wave functions spread into the adsorbed water layer. This can be nicely seen in Fig. 6, where the electronic density of states has been spatially resolved. Obviously, electronic states far below and above the Fermi energy are noticeable in the water layer. Therefore the presence of the broad positive anisotropy in the dielectric function in this energy region can be directly traced back to the adsorption of water on the surface. Similarly, the negative SDA⁽²⁾ feature at around 14 eV arises from transitions between: (i) copper d states at

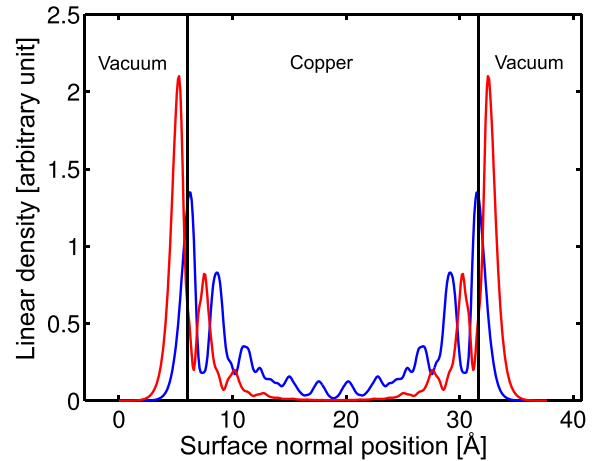


Fig. 5. Localization of the b_1 (blue) and b_2 (red) Cu(110) surface state along the surface normal for k points near $\bar{Y}$, cf. Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

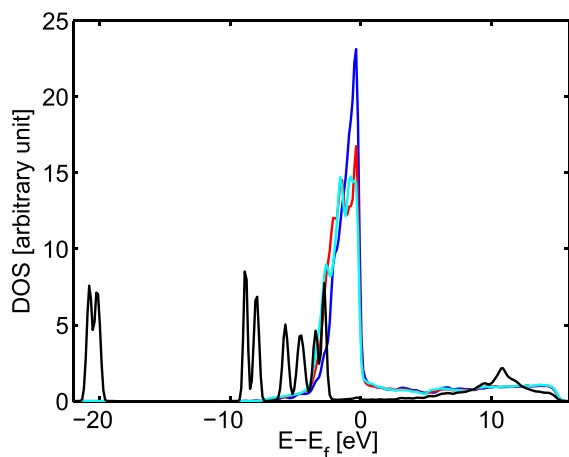


Fig. 6. The layer resolved density of states calculated here for the hexagonal H-down overlayer structure. Blue, red, and cyan represent first, second, and bulk like copper layers and black represents water layer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

–3.5 eV and *s* and *p* metal states at 11 eV, and (ii) *d* states at –1.7 eV and substrate *p* states at 13 eV.

An earlier theoretical study by some of the present authors [21] finds that dispersion forces tend to favor the hexagonal water overlayer structure more than the partially dissociated and pentagonal chain adsorbate model. However, the overall influence of dispersion forces on the water adsorption geometry was found to be minor. This is in line with the present DFT-D calculations, where the addition of a semiempirical London-type interaction term [37,38] using the D2 parameter set suggested by Grimme [39] results for the hexagonal H-down structure in O–O distances that are shortened by about 2%, and a reduction of the substrate-adsorbate distance by about 4%. The effect of these structural changes on the calculated RAS data is shown in Fig. 7. We find the structural changes to result mainly in a blueshift of the RAS spectrum, with only minor modifications of the line shape. Therefore we do not expect the inclusion of dispersion forces to modify substantially the surface optical response calculated here.

This does not hold for the inclusion of intraband transitions in the calculated spectrum. In Fig. 8 we show the RAS spectrum of the hexagonal H-down structure calculated by including the intraband contributions of both bulk and surface layer (blue), bulk only (red), and by completely ignoring intraband transitions (green). It is clear from

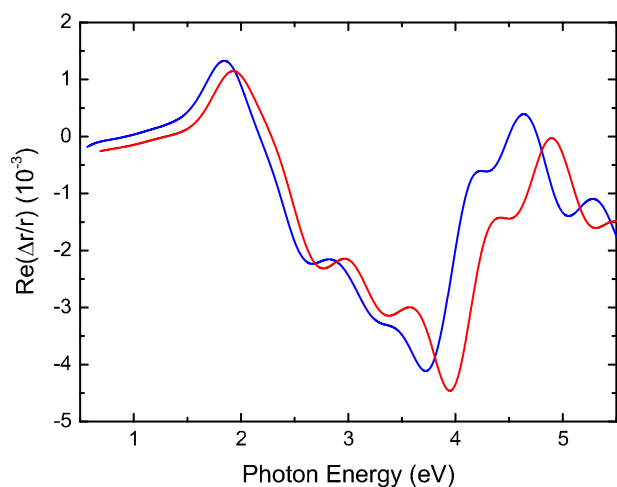


Fig. 7. The RAS calculated for the hexagonal H-down overlayer structure without (blue) and with (red) consideration of van der Waals interaction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

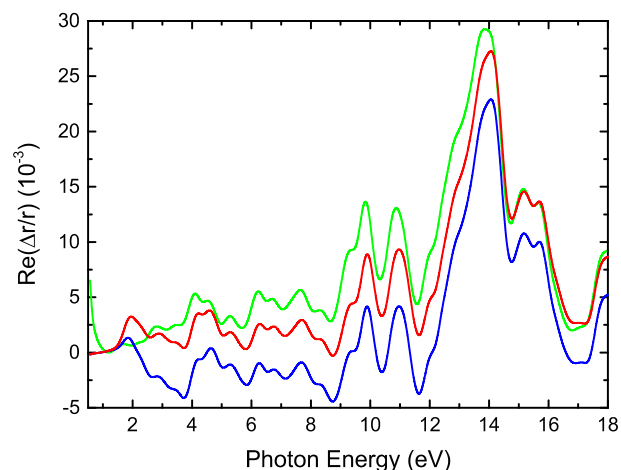


Fig. 8. The RAS calculated for the hexagonal H-down overlayer structure by including the intraband transition contributions from both bulk and surface (blue), from bulk only (red), and by completely ignoring intraband transitions (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the figure that qualitative spectral signatures due to intraband transitions arise only for low photon energies, but that they cause a shift of the RAS data that is noticeable for the complete spectral range: The calculated plasma frequency of the bulk, $\hbar\omega_{\text{intraband}} = 8.9$ eV, contributes in the denominator of the RAS (cf. Eq. (1)) as $\omega_{\text{intraband}}^2/\omega^2$, and the surface plasma frequencies $\hbar\omega_{\text{intraband}}^{[1\bar{1}0]} = 6.9$ eV and $\hbar\omega_{\text{intraband}}^{[001]} = 7.4$ eV as $((\omega_{\text{intraband}}^{[1\bar{1}0]})^2 - (\omega_{\text{intraband}}^{[001]})^2)/\omega^2$. Thus, while the contribution of the intraband transitions to the dielectric function in the denominator of Eq. (1) decreases with $1/\omega^2$, also the amplitude of the components caused by interband transitions decreases and both contributions become comparable in size. Moreover, due to the ω scaling of the numerator, the anisotropy of the intraband surface dielectric function drops weaker than $1/\omega^2$.

The results up to now have shown that for photon energies in the visible range the water adsorption modifies the Cu(110) surface optical response rather than to give rise to novel water-water transition related features. Therefore it is not clear to what extent RAS can be used to discriminate reliably between different water overlayer structures. To explore this question, we investigate in the following the RAS features of further thermodynamically stable structures, i.e., layers of partially dissociated water molecules and water molecules arranged in pentagon chains. The description of the latter requires a 2×6 translational symmetry, i.e., large surface unit cells. For computational reasons the plane-wave energy cutoff had to be limited to 300 eV and the number of conduction bands was reduced in this case. Test calculations for the H-down structure show that up to photon energies of 10 eV the RAS calculated with an energy cutoff of 300 eV is indistinguishable from the calculation performed with an energy cutoff of 400 eV, and even for higher energies up to 18 eV there are only negligible differences. The calculated spectra for photon energies below 5 eV discussed below can therefore be considered to be numerically reliable.

The RAS and SDA spectra of the water chain geometry are shown in Fig. 9 lhs, along with the corresponding measurements [12]. In very good agreement with the experimental data, the simulations show a reduction of the P_a peak and the increase of the P_c peak due to formation of water chains on Cu(110). While the reduced P_a intensity occurs for the monolayer adsorption as well, P_c was weakened rather than enhanced upon formation of water bilayers. This demonstrates that RAS is able to discriminate between different overlayer structures.

Fig. 9 rhs shows calculated RAS and SDA data for the partially dissociated water structure in comparison with the predictions for the clean surface. As can be seen, the P_a feature is nearly completely quenched, but there are enhanced optical anisotropies for photon energies

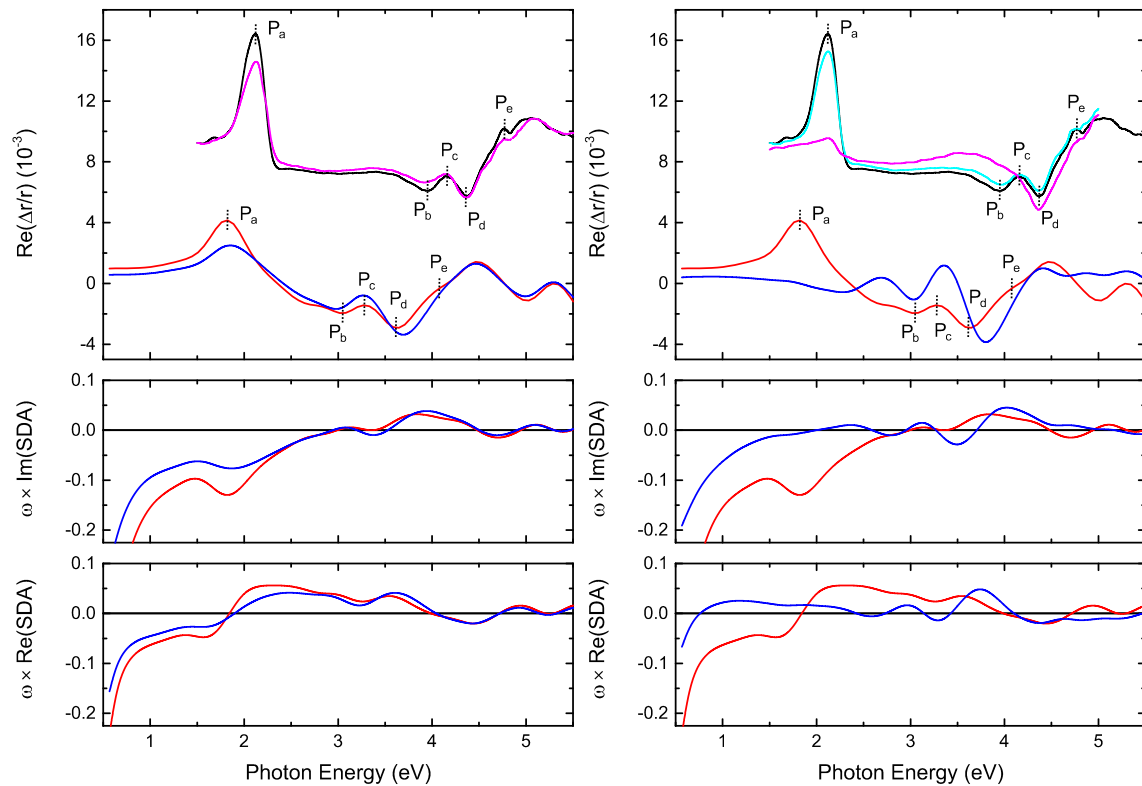


Fig. 9. Calculated RAS (upper panels) and frequency scaled SDA spectra (imaginary and real part shown in middle and lower panels) for the clean Cu(110) surface (red) as well as for the pentagon chain structure (blue—left) and the partially dissociated water overlayer (blue—right) are compared with the corresponding RAS measurements [12] for clean (black) and pentagon chain structure (magenta—left). The experiments were performed in two different energy ranges (separated by the blue vertical dashed-dotted line). The experimental data on the right hand side are present measurements for bare surface (black), the Cu(110)-CuO stripe phase (cyan), and water adsorbed on the Cu(110)-CuO stripe phase (magenta). To compensate for numerical inaccuracies, the RAS of the clean surface is recalculated with bigger supercell of the same size of the supercell of pentagon chain structure and the partially dissociated water overlayer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

between 2.5 and 4.5 eV. In order to compare these calculations with experimental data, we exploit the fact that on oxygen preadsorbed Cu(110) surfaces a dissociation of the water molecules occurs [40,28]. Therefore first oxygen is adsorbed on Cu(110) surface, creating self-organized CuO stripes [24] with a coverage of $\theta = 0.1$. Fig. 9 rhs (upper panel, cyan) shows that the effect of oxygen adsorption on the Cu(110) optical anisotropy is negligible. Adsorption of water on this surface (magenta) essentially quenches P_a , enhances P_d peak, and gives rise to a broad positive feature between about 3 and 4 eV. This is in rough agreement with the RAS spectrum calculated for the partially dissociated water structure. The remaining discrepancies between measured and calculated optical response of the partially dissociated water structure might be related to structural differences due to the preadsorption of oxygen. Turning to the reason for the disappearance of the P_a peak, our band-structure analysis shows that the Cu(110) surface states partially responsible for this feature are removed upon water absorption. This is different from the case of the hexagonal bilayer adsorption discussed above, where the reduction of the P_a peak occurs due to surface modified bulk states.

In conclusion, density-functional theory has been used to calculate the optical response of water-adsorbed Cu(110) surfaces from *first principles*. Thereby thermodynamically stable hexagonal overlayers (H-down and H-up), pentagon chains and partially dissociated water structures were considered. The calculated data are in good agreement with recent measurements and show that RAS is sensitive to the structural details of the water overlayer and can thus be used as a diagnostic tool to characterize Cu(110) in the presence of water: The RAS data of the H-down and the H-up hexagon models, e.g., can be distinguished from each other by the shift of the P_a peak. The RAS of the pentagon chains is unique among the structures considered here due to an enhanced P_c feature. Partially dissociated water overlayers, on the other

hand, completely quench the P_a signal and enhance as well as blueshift the P_d feature. The structure-dependent modification of the Cu(110) optical response is mainly related to changes of the substrate electronic properties, i.e., changes of the surface-modified bulk states upon formation of hexagonal overlayers and the quenching of surface states due to partially dissociated overlayer structures. Strain effects are of minor importance. Electronic transitions that directly involve water related states modify the surface optical anisotropy in the vacuum ultraviolet region only. The effect of dispersion forces on the calculated RAS data, studied here exemplarily for the H-down overlayer structure, is minor. We mainly observe a slight non-uniform blue shift due to reduction of the inter-atomic distances. The intraband transitions, in contrast, play a significant role for the calculated RAS, especially for photon energies below 5 eV.

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