Vibrational Anisotropy of a CO Monolayer on Ni(110).

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Abstract. − We have determined the structure of CO/Ni(110) with high accuracy using surface X-ray diffraction. CO molecules are bound in short-bridge sites, tilted alternately to form a lattice with *p2mg* symmetry. The atomic positions agree well with previous LEED results, but the increased sensitivity permits accurate anisotropic vibrational parameters to be determined as well. We find vibrations which are substantially larger parallel to the surface plane than perpendicular, implying the existence of a low-frequency vibrational mode not seen in an earlier EELS study.

X-ray diffraction is a well-established technique for the study of surface structures [1]. The technique is most effective for the study of heavier elements because the signal increases as the square of the atomic number. The start of operations of new «third generation» undulator sources of X-rays, such as the European Synchrotron Radiation Facility (ESRF) in Grenoble, will begin to allow the systematic investigation of surfaces of light elements as well, including adsorbates from the first row of the periodic table. This opens the extremely important field of adsorbed gases on substrates, which are model catalytic systems. Many X-ray diffraction studies of adsorbate-induced reconstruction have been reported previously [2, 3], but in these examples the greatest part of the diffraction signal comes from the reconstructed substrate, not the adsorbate. Since our experiment was partly motivated to demonstrate that such experiments are possible, we chose a system in which substrate reconstruction is *disallowed by symmetry*, so all of the signal in the fractional-order peaks would arise from the adsorbed layer. With the powerful ESRF source we found this was in excess of 1000 counts per second.

Mechanical excitations of adsorbed layers are observed routinely in surface science by means of inelastic-scattering methods, such as thermal-energy He atom scattering (TEAS) or electron energy loss spectroscopy (EELS). The knowledge of the phonon dispersion curves obtained in this way should permit a prediction of the overall amplitude of thermal vibrations as a function of temperature, and this should be directly comparable with the

Debye-Waller factor measured in a diffraction experiment. Indeed there has recently been renewed interest in the interpretation of vibration amplitudes obtained in this way for CO/Ru(0001) [4].

In the case of CO/Ni(110), the C-O and C-Ni chemical bonds are both oriented fairly close to the surface normal direction. Since these bonds are largely covalent in nature, they have large force constants in the perpendicular direction, but are relatively free to «wag» in the parallel direction. This gives rise to characteristic low-frequency phonon modes which are referred to as «frustrated translation» and «frustrated rotation». Thus a large anisotropy of the resulting vibrations is expected. The experiment we describe here sought to measure that anisotropy for direct comparison with the phonon dispersion curves measured by Voigtländer et al. [5]. In addition there are accurate measurements of the angular part of the vibration amplitude from X-ray Photoelectron Diffraction (XPD) [6, 7] available for comparison.

At saturation coverage on Ni(110), CO forms a 2×1 structure with the symmetry of plane group $p2mg$, as evidenced by systematically absent reflections along the (10) axis. The structure, shown in fig. 1, was determined by low-energy electron diffraction (LEED) [8,9]. It has two CO molecules per unit cell, one in every short-bridge site, but alternately displaced to one side and the other of the (10) direction, thus providing the glide-plane symmetry of $p2mg$. This structure has been confirmed by EXAFS [10], TEAS [11] and photo-emission-extended fine-structure methods (PEFS) [12]. The structure is slightly controversial, since the EELS study [5] found better agreement with the vibration mode assignment if the molecule were adsorbed on top sites, bonded to one substrate atom, not two. The structure can be prepared at 100 K by simply dosing [5-12], but also exists at higher temperatures in equilibrium with an ambient pressure of CO, with a critical pressure of $6 \cdot 10^{-8}$ Torr at 300 K [13].

Our experiment was carried out at the ID3 beamline of the ESRF, which is a new facility dedicated to surface X-ray diffraction [14]. The CO monolayer was prepared by dosing the sputter-annealed Ni(110) substrate with $5 \cdot 10^{-6}$ Torr at 300 K while monitoring the diffraction signal at $(1/2, 1, 0.2)_{surface}$ until saturation. The pressure could then be reduced to
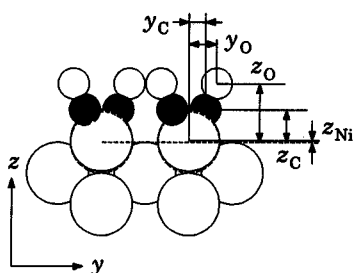

Fig. 1.   Fig. 2.

Fig. 1. – Side and top views of the CO/Ni(110) 2×1 $p2mg$ structure. The unit cell is indicated by a dashed line. There is a glide plane symmetry along the x-axis relating the two CO molecules in the unit cell.
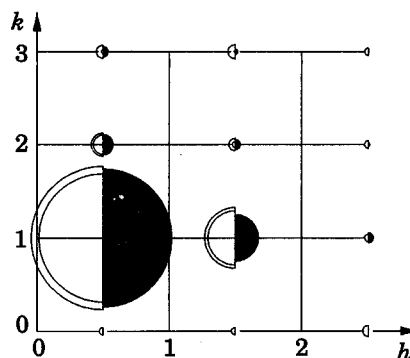
Fig. 2. – In-plane half-order structure factors measured for CO/Ni(110) at $L = 0.2$. The radius of the left semicircle is the observed value, with its error bar indicated; the radius of the right semicircle (shaded) is calculated using the model of fig. 1 and the best fit parameters from model I in table I.
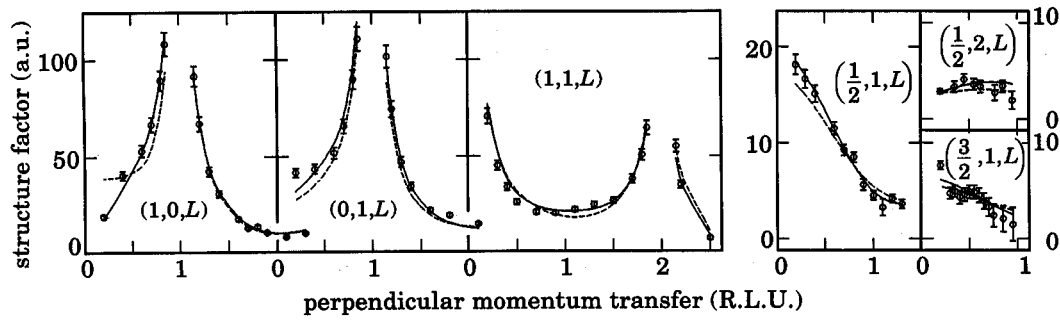
structure factor (a.u.)

perpendicular momentum transfer (R.L.U.)

$(1,0,L)$ $(0,1,L)$ $(1,1,L)$ $\left(\frac{1}{2},1,L\right)$ $\left(\frac{1}{2},2,L\right)$ $\left(\frac{3}{2},1,L\right)$

Fig. 3. – Comparison of the L-dependence of observed and calculated structure factors for CO/Ni(110) for three superstructure reflections and three crystal truncation rods. The full curve is the best-fitting model with CO in short-bridge sites of the Ni(110) substrate, while the dashed curve has CO in top sites.

$1 \cdot 10^{-7}$ Torr without change, but when the CO pressure was removed altogether, the signal disappeared in about 15 minutes. A total of 163 structure factor data were collected as ω-scans at an X-ray wavelength of 0.77 Å and an incidence angle of 3°, representing 85 independent points of reciprocal space. The integrated measurements were corrected for Lorentz factor, polarization and active sample area. The agreement among stronger ($F > 2\sigma$) symmetry equivalents was 5.6%, which is a measure of the systematic error in the data [15]. Representative in-plane data are shown in fig. 2, and out-of-plane ones (as a function of L) in

TABLE I. – *Refined structural parameters for* CO/Ni(110). *Model* I *is isotropic; model* II *is anisotropic. Distance parameters are defined in fig.* 1. B *is a Debye-Waller thermal parameter defined in eq.* (1). *Errors in the last significant digit are given in parentheses.*

Parameter		LEED (ref. [8])	LEED (ref. [9])	Model I, $\chi^2 = 2.2$	Model II, $\chi^2 = 1.7$
y_C	(Å)	0.68(7)	0.47(8)	0.67(4)	0.60(6)
y_O	(Å)	1.01(9)	0.86(9)	1.08(2)	1.05(2)
z_C	(Å)	1.33(5)	1.30(4)	1.33(5)	1.30(3)
z_O	(Å)	2.40(7)	2.38(7)	2.39(4)	2.40(3)
z_{Ni}		0.02(2)	—	0.035(4)	0.045(4)
B_{bulk}	(Å^2)	—	—	1.32(2)	1.3
$B_{Ni}(xy)$	(Å^2)	—	—	2.0(2)	2.4(3)
$B_{Ni}(z)$	(Å^2)	—	—	—	1.7(1)
$B_C(xy)$	(Å^2)	—	—	10.8(9)	16(2)
$B_C(z)$	(Å^2)	—	—	—	0
$B_O(xy)$	(Å^2)	—	—	5.8(3)	5.4(4)
$B_O(z)$	(Å^2)	—	—	—	3.7(10)
CNi bond	(Å)	1.95(5)	1.85(4)	1.92(5)	1.87(3)
CO bond	(Å)	1.12(5)	1.85(7)	1.13(5)	1.20(4)
C angle	(°)	27(3)	20(4)	27(2)	26(3)
CO angle	(°)	17(3)	20(4)	21(3)	26(4)

fig. 3. The systematic absences are consistent with the plane group $p2mg$.

Because the structure was known[8,9], it was not necessary to attempt structure determination *ab initio*. We used the structure model of fig. 1 to calculate a structure factor, varying the parameters indicated in table I in a χ^2 minimization[1], and immediately obtained a good fit with a χ^2 of 2.2. The comparison between calculated and observed structure factors is shown in fig. 2 and 3. Also shown as a dashed line in fig. 3 is a fit to the CO on-top model[5]. While the fit to the fractional orders is almost indistinguishable, there are serious discrepancies in the CTRs which are sensitive to the registry of the CO layer with respect to the substrate. The χ^2 here was 9.1, so we could disregard the on-top model. In table I we compare our fit parameters («model I») with those obtained by LEED[8,9]. Excellent agreement is found for the five displacement parameters, and both the C-O and C-Ni bondlengths agree well within their error bars. We find a significant *outward* substrate relaxation of 2.5% of a layer spacing, compared with a 12% contraction reported for the clean Ni(110) surface[16]. This is understood to be due to participation of Ni valence electrons in the bonding to C. The agreement with the structural data obtained with other techniques is reasonable, but not perfect. The O edge EXAFS study[10] obtained a value of y_O of only 0.83(8) Å, whereas their value for the O-Ni distance of 2.84(5) Å is in excellent agreement with our value of 2.87(4) Å. The PEFS method[12] obtained the same value of z_{Ni} of 0.02(4) Å with the same (outward) sign and a C-Ni distance of 1.94(2) Å in good agreement with our value of 1.92(5) Å, but obtained $y_C = 0.41$(5) Å and deduced $y_O = 0.79(9)$ Å, both rather far from our values. We are in good agreement with the tilt angle of the CO molecule observed directly in XPD[6] to be 21(1)°.

Now we turn to the new information obtained in our experiment, which concerns the remaining four parameters needed in the fit. The Debye-Waller parameters are related to the magnitude of vibrations in the structure, $B = 8\pi^2 \langle u^2 \rangle$, where u represents the displacement of a given atom from its ideal site in the crystal lattice, and $\langle \rangle$ represents a time or ensemble average. There is a small enhancement of vibration of the topmost Ni layer, well within the expected range[17]. The more dramatic figures are those for the C and O atoms, representing root-mean-square amplitudes of 0.37 Å and 0.27 Å, respectively. These unusually large amplitudes are a significant fraction of the displacements of these atoms from the (10) axis themselves. The large vibration is the explanation of the rapid decay of intensity with diffraction order which can be seen in fig. 2.

Since the minimum χ^2 of 2.2 has not yet reached the value of 1.0, where all of the discrepancy between observation and calculation is accounted for by the experimental errors, this means there is some remaining information in the data. We, therefore, tried fitting *anisotropic* Debye-Waller factors for the surface atoms. When separate in-plane (xy) and vertical (z) parameters were varied, a significant improvement was found with the values indicated in the «model II» column of table I, and a final χ^2 of 1.7. The direction of this anisotropy is as expected, because the covalent bonds are oriented mainly vertical in the structure; such bonds are much stiffer with respect to stretching than to bending. When the x- and y-components of B were allowed to vary independently we obtained values of $B_C(x) =$ = 13(3) Å^2 and $B_C(y) = 18(3)$ Å^2, but no further improvement in χ^2 was found. This observation of the in-plane/out-of-plane anisotropy of the Debye-Waller factors in CO/Ni(110) is the main new result of this paper.

The most detailed prior experiment concerning vibration amplitudes was by XPD[6]. The subsequent analysis of the details of the electronic forward scattering of the C 1s photoelectron by the O atom[7] retrieved angular r.m.s. vibration amplitudes of 12° along x and 17° along y. If we assume these vibrations to be of an O atom pivoting about a stationary C atom or *vice versa*, this would predict Debye-Waller factors of 4.5 Å^2 along x and 7.6 Å^2 along y. The anisotropy between the two in-plane values is in the expected direction (and

consistent with the x-y anisotropy measurement), with a slightly greater amplitude along (01), corresponding to motion across the bridge between the two Ni neighbours.

The data of table I show a clearly larger vibration amplitude on the C atom than on the O atom, yet it is the C that is bonded to the Ni substrate. To explain this apparent anomaly, we note that the intermolecular «contacts» between the CO molecules must be mainly between the O atoms. As noted by several authors [9,10], this high-coverage CO monolayer has the O's spaced equidistant from each other, forming an approximately close-packed layer: this argues that the CO tilting originates from intermolecular contacts along the [1$\bar{1}$0] direction. If this is correct, then the vibrations of the O's would arise from phonons within this layer, but the C's would have *additional* vibration due to pivoting about the O's. We would then estimate (assuming independent modes) the effective B to be the *sum* of the oxygen's B and that due to the pivoting, i.e. $B_C(x) = 5.4 + 4.5 = 9.9$ Å^2 and $B_C(y) = 5.4 + 7.6 = 13.0$ Å^2, not far short of our observed values (perhaps because of the lower temperature). We can exclude a second possible explanation, that the C atoms were statically disordered, randomly occupying two different sites; extensive searching with this model yielded only $\chi^2 = 2.1$ with isotropic B's.

Next we examine the 2D phonon spectrum that has been carefully measured for CO/Ni(110) by EELS [5]. Several bands were mapped out over the whole 2D Brillouin zone, and show very different frequencies, allowing an easy identification of the well-known C-O stretching modes near 2000 cm^{-1} and the Ni-CO stretch at 400 cm^{-1}. The two modes below 150 cm^{-1} were assigned as frustrated translation of the CO. The last modes show considerable dispersion with one mode appearing to be acoustic. It is widely accepted that each mode in the phonon spectrum will have an occupation given by the Planck distribution, and hence that the total vibration amplitude can be calculated at a given temperature. The standard expression for this is [18]

$$B = \frac{h}{2mN} \sum_j \frac{\cos^2(q, e_j)}{\nu_j} \left(\frac{1}{\exp[h\nu_j/k_B T] - 1} + \frac{1}{2} \right), \tag{1}$$

where the summation is over all modes and N k-vectors in the Brillouin zone and (q, e_j) is the angle between the momentum transfer and the polarization vector of the mode. We calculated a theoretical B_T by direct evaluation of eq. (1), taking $m = 28m_P$, $T = 300$ K and smoothly interpolating the dispersion surface between the given x ([1$\bar{1}$0]) and y ([001]) directions [5]. Since the expression in eq. (2) is dominated by the lowest frequencies, the contributions from the 400 cm^{-1} and 1900 cm^{-1} modes are unimportant in B_T. The 150 cm^{-1} modes give $B_T(x) = 0.80$ Å^2 and $B_T(y) = 0.98$ Å^2, which shows the observed direction of the x-y anisotropy, but still falls far short of the observed magnitudes. We must conclude that the 150 cm^{-1} modes are not the lowest, and that there exist additional softer modes, and the mode assignment of Voigtländer et al. [5] is unlikely to be correct. A series of TEAS studies of CO on other metal surfaces [19,20] have indeed reported frequencies of frustrated translation to be only of the order of 30–40 cm^{-1}, with a value of 34 cm^{-1} for bridge-bonded CO on Ni(100) [20]. If we assume the same value for CO in the same site on Ni(110) in our study, we find the appropriate magnitude for the in-plane vibrational amplitude.

In summary, we have determined the structure of CO/Ni(110) with unprecedented accuracy using the new undulator surface X-ray diffraction facility at ESRF. The positional parameters agree well with previous LEED experiments, but the increased sensitivity permits accurate anisotropic vibrational parameters to be determined as well. We find vibrations which are substantially larger parallel to the surface plane than perpendicular. The large in-plane amplitude is explained by the low frequency of the frustrated translation of the CO molecules.

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