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The electronic structure of NO on metal surfaces

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Abstract. We report electronic structure calculations for NO overlayers on Ni{111} and Ag{111}, and interpret recent ARUPS data for these systems.

A variety of experimental techniques [1–3] have shown that below 300 K nitric oxide adsorbs molecularly, and probably in a perpendicular orientation, on a Ni{111} surface. At around half-monolayer coverage a well ordered c(4 × 2) LEED pattern is observed. Recent ARUPS data [3] for this surface showed a strong $\simeq$1.5 eV splitting of the $1\tilde{\pi}$ adsorbate orbitals at normal emission; two possible explanations were put forward—the splitting could be caused either by the local twofold symmetry of the adsorption site or by lateral interactions between adsorbed NO molecules. We report here the results of electronic structure calculations to discriminate between these mechanisms.

The calculations were performed using an atomic-orbital basis for a periodic slab geometry [4]; with just three layers of metal atoms and two adsorbed molecules per unit cell the matrix dimension is an easily manageable 120. Our assumed geometry, having NO in two inequivalent surface bridge sites and assumed Ni–N and N–O nearest-neighbour distances of 2.1 and 1.15 Å respectively, is shown in figure 1. The results for this system gave zone-centre binding energies for the adsorbate-induced bands centred at 14.9 eV ($4\tilde{\sigma}$), 9.4 eV ($5\tilde{\sigma}$), and $\simeq$9.3 eV ($1\tilde{\pi}$), in good correspondence with the experimental peak positions. Calculated band maxima and minima associated with σ-states all occur at the zone centre, where the splittings are about 1 eV; for the $1\tilde{\pi}$ states the calculated zone-centre splitting is 1.6 eV, and the total band width is 2.1 eV. The broad π-splitting is shown to arise almost entirely from direct NO–NO lateral interactions, although of course it is only the interaction of these orbitals with the surface that allows the band edges to be folded back to the zone centre and so revealed in normal-angle photoemission.

Another system where the NO molecule is believed to stand perpendicular to the surface is NO/Ag{111}. Here also our calculated adsorbate orbital energies (see figure 2(*a*)) match closely with the NO-induced peaks observed at normal emission (at 2.5, 3.3, and 8.4 eV, with the Ag 4d band at 4–7 eV) in synchrotron radiation photoemission studies [5]. On this surface the maximum coverage seen experimentally is much lower, and we modelled the system by a 0.25 ML coverage, with no direct lateral interaction between chemisorbed species. Because the interaction between NO and the silver substrate is so weak, the calculated peak positions show little variation between on-top, bridge, and threefold adsorption sites (for an estimated N–Ag distance of 2.3 Å). The

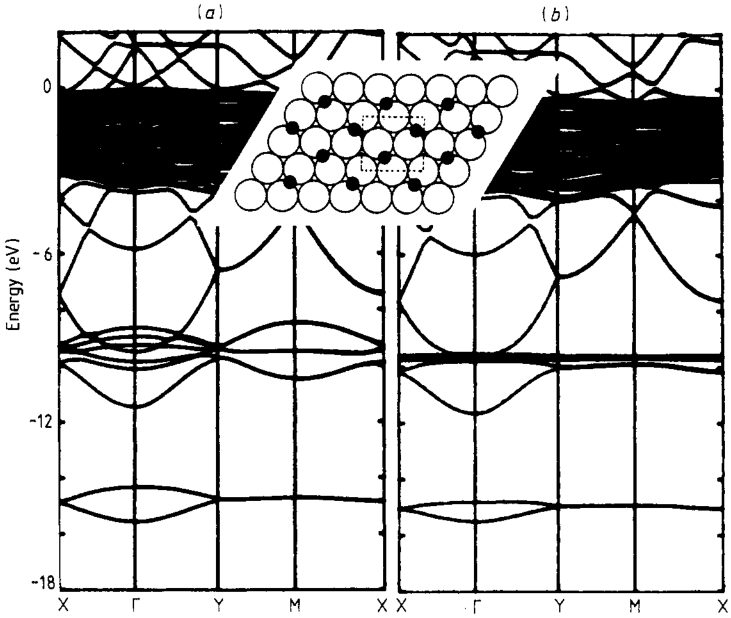

Figure 1. The geometry (inset) and bands for NO on Ni(111) (*a*) with and (*b*) without direct NO–NO interaction.

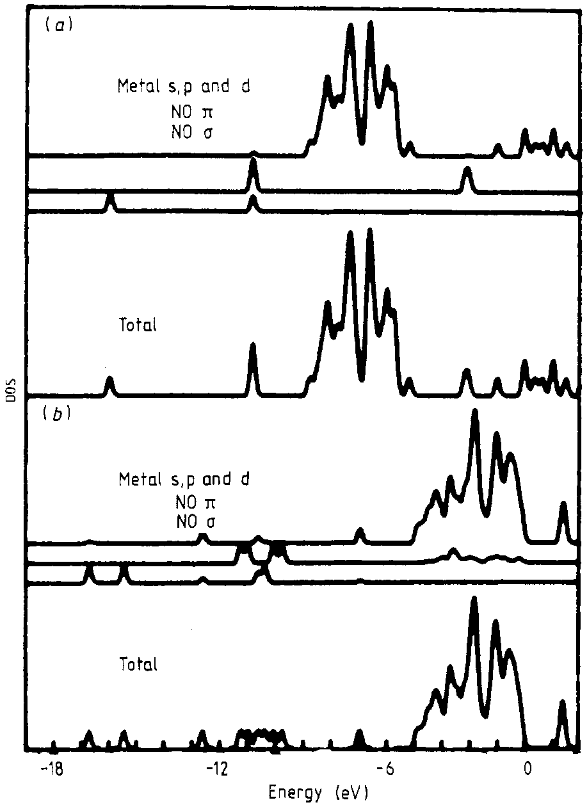

Figure 2. Calculated zone-centre states and their orbital decomposition for NO on (*a*) Ag(111) and (*b*) Ni(111).

main difference between the adsorption on the two metals is that on Ag the occupied $2\bar{\pi}^*$ NO orbitals are easily identifiable, whereas on Ni the contribution from these molecular orbitals is masked within the d band.

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