

Vibrational Spectra of N₂ on Ni(110)

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High-resolution electron-energy-loss spectra of N₂ adsorbed on Ni(110) give evidence of only a single species at all coverages.

N₂ chemisorption on Ni(110) at low temperatures (< 130 K) occurs in two stages.^{1,2} The first, characterized by an almost constant adsorption enthalpy and a positive surface potential, culminates (at thermal equilibrium) in the formation of a p(2 × 1) structure in which all the adsorbed molecules are equivalent.² Further adsorption induces falls in the adsorption enthalpy and the surface potential, and low-energy electron diffraction (LEED) shows a range of compression structures with more than one type of adsorption site occupied. CO adsorption on a variety of metals displays similar features, and in many of these instances vibrational spectroscopy can distinguish molecules adsorbed at different sites, discriminating especially between 'linear' molecules bound to a single surface atom and bridged species. Linearly bonded N₂ has been detected on Ni(110) by i.r. spectroscopy,¹ but instrumental limitations precluded a search for bridged N₂, and

similarly prevented study of the metal-nitrogen bond. We report here a high-resolution electron-energy-loss study which overcomes these restrictions.

The ultra-high vacuum apparatus used, the specimen preparation procedure, and the operating conditions of the Leybold-Heraeus ELS22 spectrometer were identical with those of our investigation of CO adsorption on Ni(110).³

Figure 1 shows the growth with coverage of the ¹⁴N₂ vibrational spectrum in the specularly reflected beam: $\nu_{\text{Ni-N}}$ and $\nu_{\text{N-N}}$ bands occur at 42 mV (339 cm⁻¹) and 272 mV (2194 cm⁻¹) respectively at all coverages. [The $\nu_{\text{N-N}}$ value agrees with the earlier i.r. results. ¹⁵N₂ gives $\nu_{\text{Ni-N}} = 40$ mV (323 cm⁻¹) and $\nu_{\text{N-N}} = 263$ mV (2122 cm⁻¹)]. The $\nu_{\text{Ni-N}}$ band intensity is similar to that of $\nu_{\text{Ni-C}}$ in the CO/Ni(110) system, whereas the $\nu_{\text{N-N}}$ intensity is much weaker than the corresponding $\nu_{\text{C-O}}$ one.

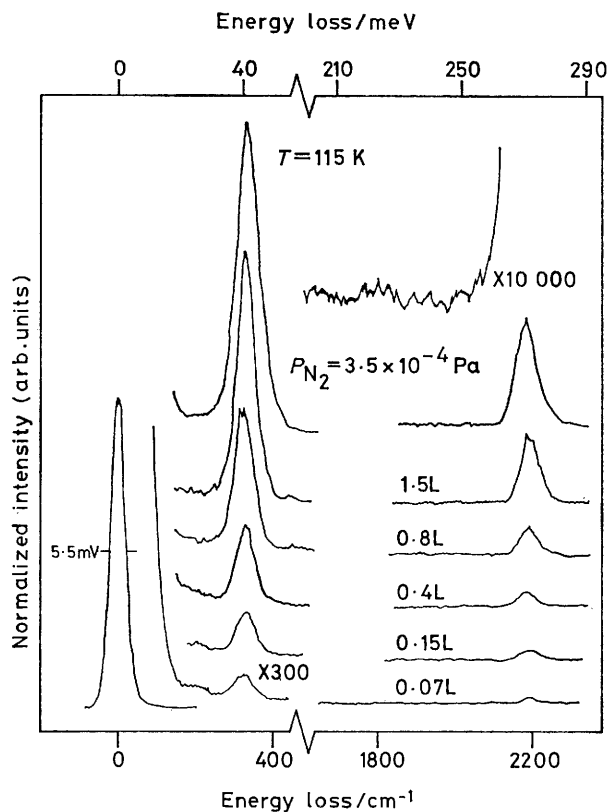


Figure 1. $^{14}\text{N}_2$ vibrational spectra of N_2 on Ni(110). (1 L \equiv 1.33×10^{-4} Pa s)

As one moves away from the specular direction both band intensities fall rapidly, showing that a dipolar scattering mechanism operates, although the rate of fall does indicate substantial intermolecular dipole coupling within the monolayer, a phenomenon also seen with CO on Cu(100).⁴ No additional bands were observed in the off-specular experiments.

The absence of any band corresponding to a bridged species established another similarity between the $\text{N}_2/\text{Ni}(110)$ and CO/Cu adsorption systems. As the top spectrum in Figure 1 shows, even at saturation there is no feature above noise level in the relevant frequency region, although a band having only 1% of the intensity of the 272 mV one would be readily detectable. LEED observations indicate that under the conditions of this spectrum the N_2 molecules are packed along the rows of the (110) surface at a separation of 1.5 lattice spacings, so the true density of bridge molecules must be high. As with CO/Cu there are two possible explanations for this discrepancy: either the frequency difference between linear and bridge molecules is very small, or else intermolecular interactions in the adlayer are so strong that the presence of a bridged species is masked by intensity transfer.⁵ The existence of large dipole coupling effects in both systems lends some support to the second hypothesis.

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