Summary Abstract: Nitric oxide adsorption on Ru(001) at 78 and 120 K: Temperature dependence on the bonding geometry

Udo Schwalke[a] and W. H. Weinberg
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

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The influence of surface temperature on NO adsorption on Ru(001) between 78 and 120 K has been investigated by high-resolution electron energy-loss spectroscopy (EELS) and thermal desorption mass spectrometry. Metastable NO adsorption states were isolated at 78 K and were identified by EELS. In all cases, heating of the NO overlayer from 78 to 120 K resulted in an *irreversible* conversion between adsites. All the measurements were performed in an UHV system that has been described in detail previously.[1] Experimental techniques were employed that have also been documented thoroughly.[1,2]

At low surface coverages ($\theta_{NO} < 0.3\,\theta_{sat}$), the population of NO adsorbed either in bridge-bonded or in on-top sites was found to be strongly temperature dependent, as shown in Fig. 1. In Fig. 1(a) the surface temperature was held at 120 K during an exposure of 0.4 L of NO, and the EEL spectrum was recorded after recooling to 78 K. The dominant loss feature is centered at 1400 cm^{-1} and is attributed to the ν(NO) band of bridge-bonded molecular NO. The ν(NO) frequency of 1400 cm^{-1} is consistent with NO adsorbed either in twofold or in threefold sites.[2,3] The two low-frequency bands at 360 and 680 cm^{-1} were found to be correlated with the intense ν(NO) band at 1400 cm^{-1}. The loss feature at 360 cm^{-1} is assigned to the ν(Ru–NO) vibration of this bridge-bonded NO. The mode at 680 cm^{-1}, however, indicates that the symmetry of the admolecule is reduced to C_s, suggesting either an inclined or a bent bridge-bonded NO.[4] This mode is then due either to a frustrated translation [antisymmetric ν(Ru–NO)] or a hindered rotation. The presence of a second molecular NO binding state is evident from the nitrogen–oxygen stretching band at 1140 cm^{-1}.[5] This value of ν(NO) is unusually low in frequency, indicating a strong reduction of the intramolecular force constant. Such a weakening of the nitrogen–oxygen bond may be caused, for example, by rehybridization of a side-on bonded NO molecule.[6] The EEL spectrum shown in Fig. 1(a) is in excellent agreement with those reported previously under similar conditions.[2,3,5] However, if the adsorption of NO is carried out at 78 K, an additional, intense ν(NO) stretching vibration appears in the EEL spectrum at 1780 cm^{-1}, as may be seen in Fig. 1(b). This indicates the presence of terminally bonded NO. The corresponding ν(Ru–NO) stretch at 560 cm^{-1} is consistent with NO adsorbed in on-top sites. Annealing the NO adlayer from 78 to 120 K results in a complete and irreversible conversion of the terminally bonded NO to bridge-bonded NO. There is neither desorption nor dissociation of any NO during this site conversion. This suggests that the NO adlayer is "frozen" into a metastable configuration at 78 K. If the NO overlayer is heated, the terminally bonded NO converts at a measurable rate to the energetically more favorable bridge-bonded adsite. Since at low coverages the integrated EEL intensity was found to be proportional to the NO coverage,[7] the rate of conversion (i.e., intensity as a function of time) could be measured at a number of temperatures between approximately 95 and 120 K. An analysis of these data indicates that the activation energy for this transition, probably single-particle hopping of terminal NO to an adjacent bridging site, is approximately 5.9 kcal/mol with a preexponential factor of 2×10^{10} s^{-1} for the rate coefficient. If the "transmission coefficient" is assumed to be unity, this preexponential factor corresponds to a frequency of approximately 0.7 cm^{-1} for the vibration parallel to the surface. Since the actual value of this frustrated translational frequency is expected to be one to two orders of magnitude greater than this, the transmission coefficient is evidently equal to approximately 10^{-1}–10^{-2}.

Trapping of NO into metastable binding states at 78 K as well as interconversion between adsorption states of NO

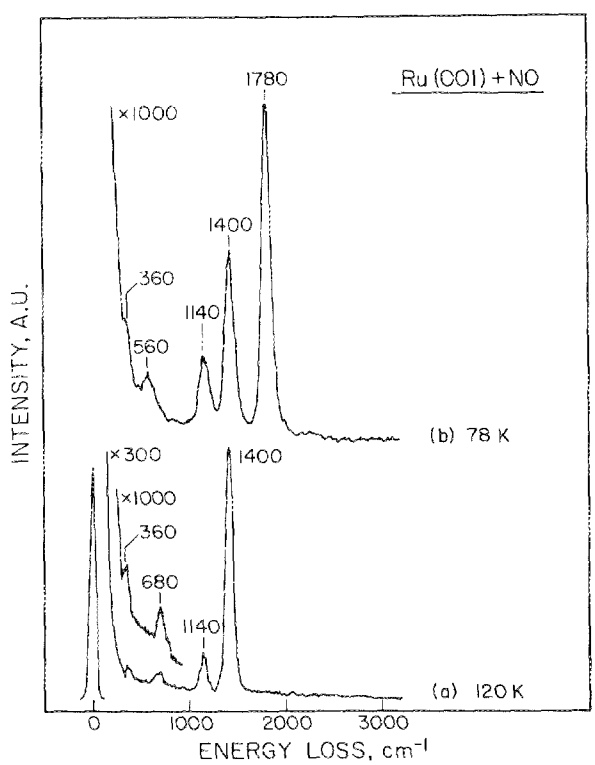

FIG. 1. Electron energy-loss spectra recorded after exposing 0.4 L (1 L = 10^{-6} Torr s) of NO to the clean Ru(001) surface at (a) 120 and (b) 78 K. The probability of adsorption is the same at 78 and 120 K, and the coverages are identical in the two spectra.

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