

The importance of the β'_2 adstate, and that its presence is due to the "stepped" nature of the reconstructed surface, has been confirmed further by studies of propane, cyclopropane, and propylene on the Ir(111) surface. For the species which do not contain π bonds, very little reactivity is observed. An approximate estimate (assuming that the saturation coverage for hydrogen corresponds to one hydrogen atom per iridium surface atom) suggests that less than 2×10^{13} molecules cm^{-2} adsorb irreversibly. This would imply that the number of hydrogen adsorption sites involved is approximately $1.5 \times 10^{14} \text{ cm}^{-2}$, which could be accounted for as sites occurring on the crystal edge and at surface defects. Propylene, however, has been found to be approximately as reactive on this surface as on the Ir(110)-(1 \times 2) surface, with a saturation coverage of the irreversibly absorbed overlayer of $(2 \pm 0.5) \times 10^{14}$ molecules cm^{-2} . Apparently, no particular adsite dominates the Ir(111) surface chemistry, in con-

trast to the importance of the β'_2 adsite on the Ir(110)-(1 \times 2) surface (especially insofar as the adsorption of paraffins is concerned).

^{a)}Supported by the National Science Foundation under Grant No. CHE-82-06487.

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Summary Abstract: The adsorption and decomposition of N₂O on Ru(001)^{a)}

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(Received 27 September 1982; accepted 12 October 1982)

PACS numbers: 68.45.Da, 82.65.My

Several studies of the linear triatomic N₂O as a ligand in the inorganic chemistry of Ru have appeared in the literature.¹ One question addressed in these studies concerns the mode of bonding: Ru-N-N-O or Ru-O-N-N? In the present work, we have used high resolution electron energy loss spectroscopy (EELS) and thermal desorption mass spectroscopy (TDMS) to investigate the adsorption of N₂O on the Ru(001) surface; the results are compared with the inorganic chemistry of Ru-N₂O complexes. We find evidence that N₂O binds to Ru(001) at 75 K via the N atom in both vertical and inclined configurations, and that chemisorbed N₂O both desorbs molecularly and decomposes to N₂(g) and O(ads) when the surface is heated.

Figure 1 shows a series of EEL spectra recorded for the adsorption of N₂O on Ru(001) at 75 K. For low exposures [~ 0.8 langmuir (L)], the spectra are dominated by dipolar features at 2290 cm^{-1} (N-N stretch), 1290 cm^{-1} (N-O stretch) and 230 cm^{-1} (Ru-N₂O vibration). The additional feature at 470 cm^{-1} is assigned to the N-N-O bending mode of the adsorbed species, and its weak intensity indicates, via the surface dipole selection rule, that N₂O is terminally bonded in a nearly vertical configuration. The absence of features at 280 and 2200 cm^{-1} due to adsorbed N₂² and at 500–550 cm^{-1} due to adsorbed oxygen³ indicates that decomposition is not detectable for adsorption at 75 K. For N₂O exposures > 2 L, the NNO bending mode appears at

540 to 560 cm^{-1} , and its intensity grows more rapidly with increasing exposure than the intensities of the modes at 1290 and 2290 cm^{-1} . This suggests that an inclined linear configuration is dominant at high surface coverages, as has been observed at all coverages for N₂O on Pt(111).⁴ Also visible in the spectra for exposures > 2 L is a band at 2570 cm^{-1} . This feature is assigned to the first overtone of the NO stretch, appearing with enhanced intensity due to Fermi resonance with the fundamental band at 2290 cm^{-1} .⁵ The N₂O monolayer in contact with the substrate is filled at an exposure of 10 L, and the coverage is approximately twice that at 3 L.

The EELS bands at 2290, 1290, and 540–560 cm^{-1} can be compared with the corresponding gas phase vibrations at 2224, 1286, and 588 cm^{-1} , respectively.⁵ The appearance of a "blue shift" of the N-N stretch from 2224 to 2290 cm^{-1} upon adsorption, while the NO stretch is unchanged, suggests that N₂O bonds via the N end of the molecule. A similar conclusion was reached by Umbach and Menzel⁶ who deduced from ultraviolet photoemission spectroscopy that bonding to Ru(001) at low coverages occurs via the 7 σ orbital, localized on the N end of N₂O. This assignment is also consistent with the most probable bonding of N₂O in Ru complexes,¹ and of N₂O on Pt(111).⁴

When the surface is heated to 115 K following a low exposure (0.8 L N₂O at 75 K), a new EELS feature grows at 490–500 cm^{-1} as the other peaks decrease in intensity. This fea-

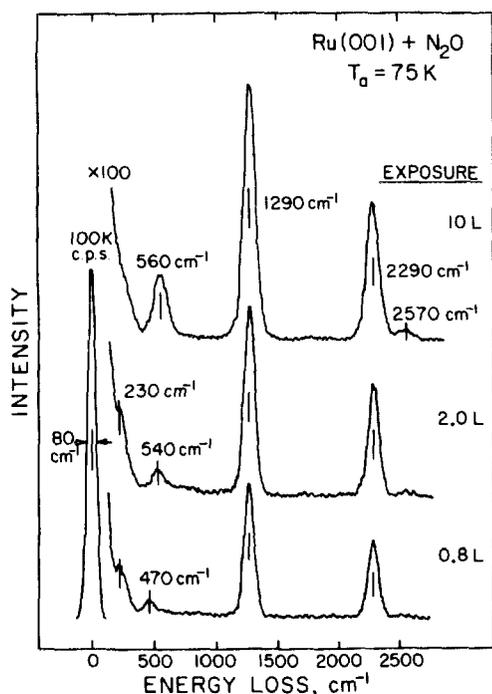


FIG. 1. High resolution electron energy loss spectra for the adsorption of N₂O on Ru(001) at 75 K.

ture is attributed to the Ru–O stretch³ of adsorbed oxygen from the decomposition of N₂O and is the only extra peak seen in EELS for $T \gtrsim 140$ K. Thus, heating appears to cause both molecular desorption and decomposition of N₂O, leaving residual oxygen but no adsorbed N or N₂.

The TDMS data complement the EELS results. For exposures $\lesssim 1$ L, the only desorption product is N₂, which desorbs between 100 and 120 K. As the coverage increases, desorption of N₂O is seen, with peaks appearing at 107 and 118 K. For exposures > 7 L, these features saturate and two new N₂O peaks grow at 87 and 95 K. Surprisingly, the higher T feature at 95 K grows without apparent saturation for exposures above 10 L, indicating that it is associated with multilayer formation.

Identity of the four N₂O states seen in the TDMS experiments is complicated by the fact that molecular decomposition and desorption occur simultaneously. Based on a combination of EELS and TDMS, however, including studies of N₂O coadsorbed with oxygen, we identify the TDMS states as follows. The peak at 118 K is due to N₂O which has had its binding energy modified by interaction with oxygen from decomposition. The peak at 107 K is due to inclined N₂O, and the state desorbing at 87 K (which populates *before* the 95 K multilayer state) may be required sterically to fill the monolayer.

Finally, we note that Umbach and Menzel⁶ reported adsorption of a state of N₂O lying parallel to the surface at high coverages, in the presence of partially dissociated N₂O at 85 K. The appearance of an intense NNO bending mode at 540–560 cm⁻¹ at high surface coverages indicates that the adsorbed N₂O molecules are indeed inclined away from the surface normal. However, the absence of strong perturbations to the N–N and N–O stretching frequencies, as would be expected for a linear species bonded flat to the surface, indicates that N₂O does not bond in a state strictly parallel to the Ru(001) surface at 75 K.

¹Supported by the National Science Foundation under Grant No. CHE82-06487.

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