necessary that they be examined in detail. To be convincing, the theory would have to deal with realistic models of heterogeneity, involving wide ranges of magnitudes and scale lengths to model the variety of substrates used in the cited experiments.

An alternative explanation is that superfluid onset is not strictly a uniform-film phenomenon. If the films undergo phase condensation before superfluid onset and if superfluidity involved a collective state of the two-phase system then a critical-temperature gap would not necessarily appear. Such a state is quite different from that discussed by Nelson and Kosterlitz.[1] It is, however, consistent with the theory of clustering and percolation,[20,21] which has been proposed to explain results obtained on more uniform surfaces.[22,23]

I wish to thank Eytan Domany, John Rehr, and Michael Schick for several very useful discussions. This work was supported by the National Science Foundation Grant No. DMR-72-03003-A04.

---

[1] D. R. Nelson and J. M. Kosterlitz, Phys. Rev. Lett. 39, 1201 (1977). See also J. M. Kosterlitz and D. J. Thouless, J. Phys. C 6, 1181 (1973).

[2] D. J. Bishop and J. D. Reppy, Phys. Rev. Lett. 40, 1727 (1978).

[3] I. Rudnick, Phys. Rev. Lett. 40, 1454 (1978).

[4] J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).

[5] M. Bretz *et al.*, Phys. Rev. A 8, 1589 (1973).

[6] R. L. Elgin and D. L. Goodstein, Phys. Rev. A 9, 2657 (1974).

[7] R. J. Rollefson, Phys. Rev. Lett. 29, 410 (1972); B. P. Cowan *et al.*, Phys. Rev. Lett. 38, 165 (1977).

[8] S. V. Hering, S. W. Van Sciver, and O. E. Vilches, J. Low Temp. Phys. 25, 793 (1976).

[9] S. B. Crary and O. E. Vilches, Phys. Rev. Lett. 38, 973 (1977); S. B. Crary, O. Ferreira, and O. E. Vilches, unpublished.

[10] K. Carneiro, W. D. Ellenson, L. Passell, J. P. McTague, and H. Taub, Phys. Rev. Lett. 37, 1695 (1976).

[11] M. Bretz, Phys. Rev. Lett. 38, 501 (1977).

[12] S. E. Polanco and M. Bretz, Phys. Rev. B 17, 151 (1978).

[13] C. E. Campbell and M. Schick, Phys. Rev. A 3, 691 (1971).

[14] M. D. Miller and C. W. Woo, Phys. Rev. A 7, 1322 (1973).

[15] R. L. Siddon and M. Schick, Phys. Rev. A 9, 907 (1974).

[16] L. M. Sander, M. Bretz, and M. W. Cole, Phys. Rev. B 14, 61 (1976).

[17] A. D. Novaco, Phys. Rev. B 13, 3194 (1976).

[18] M. Schick, J. Walker, and M. Wortis, Phys. Rev. B 16, 2205 (1977).

[19] J. H. Scholz, E. O. McLean, and I. Rudnick, Phys. Rev. Lett. 32, 147 (1974).

[20] J. G. Dash, Phys. Rev. B 15, 3136 (1977).

[21] B. A. Huberman and J. G. Dash, Phys. Rev. B 17, 398 (1978).

[22] J. A. Herb and J. G. Dash, Phys. Rev. Lett. 29, 846 (1972).

[23] M. Bretz, Phys. Rev. Lett. 31, 1447 (1973).

Adsorption and Dissociation of Nitric Oxide on the Ru(001) Surface

G. E. Thomas and W. H. Weinberg
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

(Received 11 September 1978)

The adsorption of nitric oxide and its dissociation on the Ru(001) surface have been studied through the vibrational energies of the adsorbed layer. The inelastic electron scattering measurements show that two distinct states of molecular NO are adsorbed at 130 K. The dissociation of a bridged NO is complete at 316 K, whereas a linear form remains on the surface until 500 K. This is explained by a difference in activation energies for dissociation of NO and by the blocking of sites by nitrogen and oxygen adatoms.

The adsorption and reaction of NO on metal surfaces is a subject of obvious interest in surface chemistry. In addition to the industrial importance of the catalytic reduction of NO, the wide variety of NO complexes in metal nitrosyls suggests that the surface chemistry of NO will be a fertile area of research.[1] In this work, we report the first vibrational measurements of NO on the Ru(001) surface and direct evidence of two forms of adsorbed NO with differing activation energies for dissociation.

Previous studies have been made of NO chemisorbed on the Ru(101) and Ru(100) surfaces as well as on a Ru field-emission tip.[2-6] The photoemission measurements of NO adsorbed on the Ru(100) surface by Bonzel and Fischer were carried out well above room temperature and indicated molecular adsorption only at the highest coverages.[2] Reed *et al.* present chemical evidence that NO is primarily adsorbed associatively on Ru(101) at 300 K and suggest that the dissociation reaction may be sensitive to the surface crystallography.[4] Madey has reported measurements of the angular distribution of the ion beams desorbed by electron bombardment [ESDIAD (electron-stimulated desorption ion angular distribution)] of NO adsorbed on the Ru(001) surface at 90 K.[7] The results indicate that NO is bound molecularly and is perpendicular to the surface.

The inelastic electron scattering measurements presented here show the molecular adsorption and dissociation of NO on the basal plane of Ru as a function of surface temperature. The electron spectrometer employed in the electron energy-loss spectra has been described in detail elsewhere.[8] The Ru sample was cut and polished within 1° of the [001] direction using standard techniques. It was mounted on a manipulator equipped with liquid-nitrogen cooling and cleaned with oxidation and reduction cycles *in situ*.[9] The cleaning procedure has been found to yield both a sharp 1 × 1 LEED (low-energy electron diffraction) pattern and the characteristic Auger spectrum of a clean surface.[10] Depending on the history of the sample, prolonged annealing above 1600 K was occasionally necessary to remove the surface oxygen, as measured by the vibrational-energy loss feature at 530 cm^{-1}.[11] The crystal was exposed to NO through a gas doser, and the coverages were established relative to saturation using the integrated peaks of thermal desorption spectra.[12]

The intensity of the elastically scattered electron beam varied by a factor of 10 depending on the NO exposure and treatment, indicating that order-disorder phenomena were affecting the angular spread of the specular beam. In order to assure a good signal-to-noise ratio throughout, the electron spectrometer was tuned so that 2×10^6 cps appeared in the elastic channel of the beam reflected specularly from the clean surface. The full width at half maximum of the elastic peak was approximately 18 meV during these measurements to attain this counting rate. The primary energy of the electron beam was 4 eV. Due to the large variation in the elastic intensity in the spectra presented here, the intensities relative to the elastic intensity cannot be compared directly from spectrum to spectrum. The role of ordering phenomena in the inelastic scattering intensity has been discussed by Ibach.[13]

The vibrational spectra of chemisorbed NO are shown as a function of coverage in Fig. 1. The temperature of exposure was between 120 and 150 K. Two nitrogen-oxygen stretching frequencies are observed, in the ranges 1411–1508 cm^{-1}, where both frequencies increase with increasing surface coverage. The higher frequency, which is characteristic of a linear NO in metal nitrosyls, appears only at fractional coverages above 0.35. In addition, a very weak feature at approximately 1145 cm^{-1} appeared in some spectra and disappeared within a few minutes even below 140 K. This peak may be due to other oxides of nitrogen present in the NO supply or to a temporary complex formed in adsorption. It could not be characterized further in these measurements. A third vibrational loss between 532 and 548 cm^{-1} is found at higher coverages. This is in the range of the vibrational mode of atomic oxygen on the Ru(001) surface studied previously[14] and shows that some dissociation of NO occurs at 130 K. The Ru-NO vibration of a variety of metal nitrosyls has been found to vary between 572 and 638

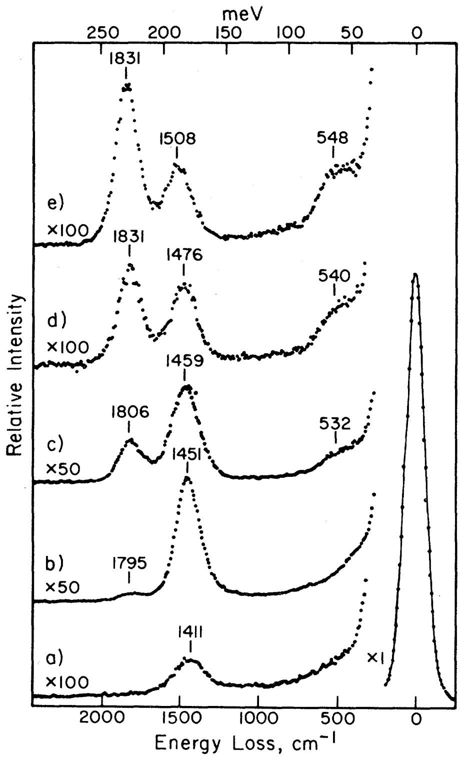

FIG. 1. Vibrational spectrum of NO adsorbed on the Ru(001) surface below 150 K as a function of coverage. The coverages relative to saturation are (a) 0.12, (b) 0.35, (c) 0.55, (d) 0.67, and (e) 0.82.

cm^{-1} depending on the other substituents of the complex.[15] Neither this mode nor a Ru-N stretching mode of dissociated NO could be resolved from the single low-frequency peak which is attributed to the metal-oxygen vibration. This is presumably due to a small dynamic effective charge associated with these vibrational modes.

The chemistry of metal nitrosyls has been reviewed by Eisenberg and Mayer.[16] In general, a nitrogen-oxygen stretching frequency ($\nu_{\rm NO}$) above 1800 cm^{-1} is associated with a linear NO. Frequencies in the range between 1620 and 1750 cm^{-1} are due to bent nitrosyls with M-N-O bond angles between 124° and 177°. This correlation is not exact, since electronic effects due to other ligands are quite important in the N-O bond of metal nitrosyls.[17] However, the $\nu_{\rm NO}$ peak which appears at 1831 cm^{-1} at high coverages is interpreted most reasonably as a linear NO bound to the surface through the nigrogen atom.

The first adsorption state on this surface exhibits a stretching frequency too low to be due either to a linear or to a bent nitrosyl complex. Bridging nitrosyls, however, exhibit lower stretching frequencies. The nitrosyls in $Ru_3(CO)_{10}(NO)_2$ are bonded to two Ru atoms and have stretching frequencies of 1517 and 1500 cm^{-1} (Ref. 17); in the compound $(C_5H_5)_3Co_3(NO)_2$, the nitrosyls are both bonded to the three cobalt atoms, and the most intense N-O stretching band appears at 1405 cm^{-1} (Ref. 18). The lower-frequency vibration, indicated in Fig. 1, then, is due to a more highly coordinated nitrosyl. The Ru(001) surface is threefold symmetric, and the analogy with the μ_3-nitrosyl tricobalt structure suggests that the first adsorption state of NO at 130 K is in a threefold site. The increase in both N-O stretching frequencies with coverage may result from direct interactions or from changes in the chemisorptive bond. The same phenomenon is seen frequently in the CO stretching frequency as a function of CO coverage and has been the subject of recent discussion.[19] The analogy with the metal nitrosyl complexes suggests that NO is perpendicular to the surface in both adsorption states.

In order to illustrate the steps involved in the dissociation of NO, a series of experiments was performed in which the surface prepared with molecularly adsorbed NO was heated briefly at approximately 5°/sec and allowed to cool. The maximum temperature was maintained for approximately one second. The surface cooled below 140 K during the recording of the vibrational spectrum, so that only irreversible changes in the adsorbed layer could be observed. The vibrational spectrum is shown as a function of temperature treatment in Figs. 2 and 3 for surfaces prepared with NO coverages (relative to saturation) of 0.35 and 0.8, respectively.

In Figs. 2(b) and 2(c), spectra are shown which illustrate the irreversible change in the adsorbed layer as the surface is heated to room temperature. The low-frequency N-O stretching mode disappears well before complete dissociation occurs, although the appearance of the peak at 538 cm^{-1} indicates that some dissociation has taken place. After this surface is heated to 407 K, dissociation is complete. The intermediate state of the surface [Fig. 2(c)] is characterized by a single N-O stretching frequency at approximately 1782 cm^{-1} and a low-frequency mode at 538 cm^{-1}, depending upon coverage.

One explanation for the change in the vibrational spectrum is that the bridged NO begins to dissoci-

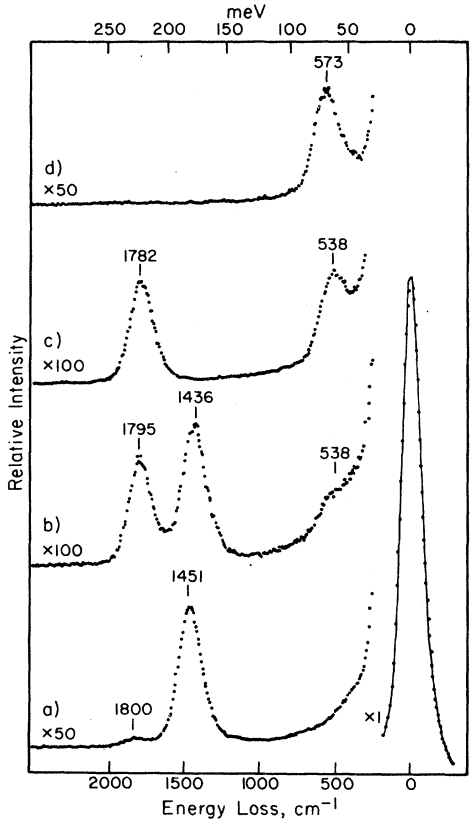

FIG. 2. Effect of heating the surface with an NO coverage of 0.35. (a) After exposure at 147 K. (b) After heating to 290 K. (c) After heating to 316 K. (c) After heating to 407 K.

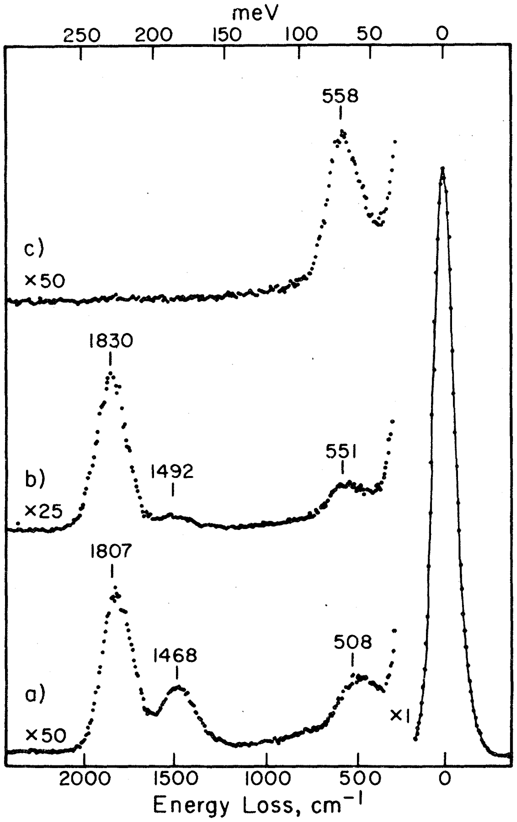

FIG. 3. Effect of heating the surface with an NO coverage of 0.8. (a) After exposure at 158 K. (b) After heating to 406 K. (c) After heating to 500 K.

ate near room temperature, and that the N and O atoms displace the remaining NO from the threefold or bridged sites. The linear form of NO is less reactive and does not dissociate until higher temperatures are reached. The metal-oxygen stretching frequency is consistent with its occupying a threefold or bridge site.[14]

The mechanism of site blocking also explains results obtained for an NO coverage of 0.8 (Fig. 3). Here the disappearance of the more highly coordinated NO is nearly complete only at 406 K, after complete dissociation would have occurred for an NO coverage of 0.35; and the linear NO is not removed until 500 K. The final transformation of the saturated surface is accompanied by the rapid evolution of NO and the beginning of N_2 desorption. The dissociation of the linear NO is prevented at high coverage by the lack of sites for the reaction products. The transformations observed in these experiments are most likely limited kinetically in the brief heating cycles. The temperatures of reaction and corresponding vibrational spectra given here characterize the activation energies for dissociation qualitatively.

Thus a relatively simple scheme is proposed in which the two forms of NO adsorbed on the Ru(001) surface have different activation energies for dissociation. The dissociative reaction is poisoned by the reaction products below their temperature of desorption.

We thank Patricia Thiel and Dr. John Yates for their assistance and helpful suggestions in this work. We have benefitted also from useful discussions with Professor John Bercaw and Professor Robert Grubbs.

This work was supported in part by the National Science Foundation under Grant No. CHE77-16314. One of us (G.E.T.) acknowledges receipt of an IBM Predoctoral Fellowship. One of us (W.H.W.) acknowledges receipt of an Alfred P. Sloan Foundation Fellowship and a Camille and Henry Dreyfus Foundation Teacher-Scholar Fellowship.

---

[1] R. L. Klimisch and J. G. Larson, in *Catalytic Chemistry of Nitrogen Oxides* (Plenum, New York, 1975).

[2] H. P. Bonzel and T. E. Fischer, Surf. Sci. 51, 213 (1975).

[3] R. Ku, N. A. Gjostein, and H. P. Bonzel, Surf. Sci. 64, 465 (1977).

[4] P. D. Reed, C. M. Comrie, and R. M. Lambert, Surf. Sci. 72, 423 (1978).

[5] T. W. Orient and R. S. Hansen, Surf. Sci. 67, 325 (1977).

[6] R. Klein and A. Shih, Surf. Sci. 69, 403 (1977).

[7] T. E. Madey, to be published.

[8] G. E. Thomas and W. H. Weinberg, to be published.

[9] T. E. Madey and D. Menzel, J. Appl. Phys. Jpn., Suppl. 2, Pt. 2, 229 (1974).

[10] E. D. Williams and W. H. Weinberg, to be published.

[11] G. E. Thomas and W. H. Weinberg, to be published.

[12] P. A. Thiel, G. E. Thomas, W. H. Weinberg, and J. T. Yates, Jr., to be published.

[13] H. Ibach, Surf. Sci. 66, 56 (1977).

[14] G. E. Thomas and W. H. Weinberg, J. Chem. Phys. (to be published).

[15] E. E. Mercer, W. A. McAllister, and J. R. Durig, Inorg. Chem. 5, 1881 (1966).

[16] R. Eisenberg and C. D. Meyer, Acc. Chem. Res. 8, 26 (1975).

[17] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1978), 3rd ed.

[18] J. Müller and S. Schmitt, J. Organomet. Chem. 97, C54 (1975).

[19] G. D. Mahan and A. A. Lucas, J. Chem. Phys. 68, 1344 (1978).