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Infrared Spectra of NO Adlayers on Pt; Their Interpretation in Terms of a Vibrational-Coupling Model

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Infrared spectra of NO adsorbed on single-crystal Pt (111) and polycrystalline Pt foil have been measured over a temperature range 100 to 473 K and at adsorbant pressures from 5×10^{-10} to 1 Torr. Relatively intense absorption bands have been found over the wavenumber range 1450–1780 cm^{-1}, the wavenumber depending on the temperature, coverage and, apparently, the presence of impurities. A model based on an assumed interaction force constant coupling NO molecules adsorbed on adjacent sites accounts quantitatively for most of the spectroscopic observations.

INTRODUCTION

In previous papers (*1*, *2*) we have reported the infrared reflection–absorption spectrum (IRRAS) of NO adsorbed on a polycrystalline Pt substrate in the presence of NO gas at pressures in the range 0.001 to 1 Torr. The observed wavenumber shifts of the NO stretching mode with temperature and pressure were ascribed to the formation of linear arrays of NO adsorbed on adjacent sites and were explained in terms of a model in which we admitted a coupling force constant between nearest-neighbor NO molecules. These earlier spectroscopic observations were made with the polycrystalline Pt substrate mounted in a metal vacuum system through which the gas-phase adsorbant was flowing under stirred-tank conditions. The substrate was cleaned by heating first in O_2 and then in H_2 and the NO adsorbate was established by heating the reduced substrate briefly in the flowing NO.

We have now assembled a new all-metal apparatus which can be operated both at high pressures (10^{-3}–10^{3} Torr) and under uhv (5×10^{-10} Torr) and with this apparatus we have studied the IRRAS spectrum of NO adsorbates on single-crystal Pt (111) and on a polycrystalline Pt foil which we believe to have a reconstructed (110) surface. The results of these studies corroborate and extend our previous findings.

EXPERIMENTAL METHOD

The IRRAS spectrometer used for these measurements has been described in complete detail (*3*). The vacuum system was built from standard UHV components and has a volume of about 1.2 liters. For most of the measurements reported here, it was pumped by a liquid-nitrogen trapped single-stage mercury diffusion pump or a 30 liter/sec triode ion pump. The vacuum system could be isolated from either of these pumps by metal-sealed valves. Later a Ti sublimation pump was added to increase the pumping speed of the system. The infrared transmitting windows of calcium fluoride were sealed to conflat flanges with silver chloride (*4*). Pressures between 10^{-3} and 10^{+3} Torr were measured with a wide range Pirani gauge; pressures lower than 10^{-3} Torr were measured with a nude Bayard–Alpert gauge. Since we wished to keep the volume of the system small, The Bayard–Alpert gauge was mounted inside a $1\frac{1}{2}''$ nipple which became fairly hot when the gauge was on. Because of degassing from the walls of this nipple, the actual pressure

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at the sample was probably somewhat lower than that indicated by the gauge. The base pressure of the system using only the ion pump was 5×10^{-9} Torr; after the addition of the sublimation pump, the base pressure was 5×10^{-10} Torr.

Gases were admitted to this system from a stainless-steel gas handling system through a UHV variable leak valve. All gases were passed through cryogenic traps immediately before admission to the system. A dry ice/acetone trap was used for NO and a liquid-nitrogen trap for O_2 and CO. The samples of NO were prepurified and stored in glass bulbs. Oxygen was used directly from the lecture bottle in which it was supplied.

In some cases the Pt substrate was spotwelded to three short platinum wires which, in turn, were spotwelded to tantalum flaps attached to copper current feedthroughs; in other cases the Pt substrate was spotwelded directly to the tantalum flaps. Sample temperatures were measured with a chromel-alumel thermocouple spotwelded to the back of the substrate. The thermocouple was calibrated in the temperature range 1050–1325 K against an optical pyrometer and the calibration was extrapolated linearly to room temperature. Temperatures below room temperature were derived directly from the NBS thermocouple calibration table. The substrate could be heated resistively to 1400 K or cooled to about 80 K by adding liquid nitrogen to a reservoir outside the vacuum system and surrounding the copper feedthroughs in the sample-mounting flange.

The single-crystal Pt substrate had previously been used by McCabe and Schmidt (*5*). The crystal was a disc, about 7 mm in diameter and 1 mm thick. Both surfaces had been oriented to within 1° of the (111) direction by X-ray back reflection and both front and back surfaces of the crystal were polished. The crystal had undergone several cycles of annealing in vacuum at 1700 K followed by oxidation in 10^{-6} Torr O_2 at 1400 K to remove impurities such as sulfur, phosphorus, and calcium. An AES spectrum of the crystal was taken prior to mounting it in the IRRAS system. The spectrum showed small amounts of carbon, oxygen, and chlorine, presumably due to atmospheric contamination. There was a small peak at 92 eV which is assignable to either platinum or silicon. The fact that this peak remained constant in intensity in a depth profile and the fact that there was no evidence of a silicon peak between 1605 and 1620 eV led us to conclude that the crystal surface was not significantly contaminated with silicon. It was therefore assumed that the platinum surface was free of all nonoxidizable impurities.

It has been reported by many investigators (*5–10*) that platinum forms a stable surface oxide on exposure to oxygen at high surface temperature (>850 K). This oxide has been shown to produce new binding states for H_2 and CO (*5, 10*) and its presence may also alter the bonding between NO and platinum. It has further been shown (*7*) that the surface oxide is inert to hydrogen exposure at temperatures below 900 K. It has more recently been suggested (*11*) that this so-called stable platinum oxide is actually a product of the reaction of oxygen with silicon impurities in the platinum. For samples which had been shown to be free of Si, oxide formation has not been possible. For samples on which oxide formation is possible it has been found to decompose at about 1250 K. Since the substrates used in our experiments were not contaminated with silicon there should be no problems with surface oxide formation. Even if a surface oxide were formed we should expect it to be completely removed in our cleaning procedure.

The crystal was cleaned prior to each experiment by heating for 10 min in 5×10^{-7} Torr O_2 at 1173 K. For the experiments in which the NO dosage was relatively low ($\leq$ 10 L), the O_2 was pumped out and the crystal was heated briefly to 1400 K in UHV and allowed to cool in UHV to the temperature chosen for the experiment. The IRRAS

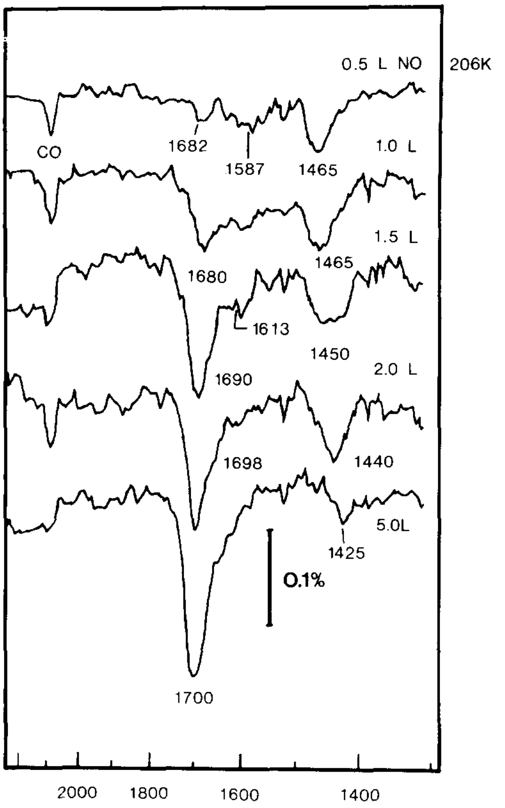

FIG. 1. IRRAS spectra of NO on Pt (111) single crystal. The temperature was maintained at 206 K. These spectra were measured in a vacuum system, the base pressure of which was 5×10^{-9} Torr. NO dosage is expressed in Langmuirs.

spectrum of this clean substrate was subtracted from subsequent spectra and the difference spectrum so obtained was attributed to the adsorbate. For those experiments in which the exposure to NO was large, i.e., when the pressure of NO was $>10^{-3}$ Torr, the background spectrum was recorded in 5×10^{-8} Torr of O_2, after which the O_2 was pumped out and the substrate was heated briefly to 1400 K. The NO was then admitted to the system as the substrate was cooling.

In order to verify that the platinum substrate used in the IRRAS experiments exhibited the chemisorption properties of a clean (111) surface of platinum, the IRRAS spectrum and the TPD spectrum of a 10 L exposure of CO were measured. These spectra, shown in Fig. 3 of Ref. (*3*) are in excellent agreement with the EELS spectrum of CO on Pt (111) reported by Hopster and Ibach (*12*) and the previously reported TPD spectra (*12, 13*).

We also report in this paper the spectrum of an adsorbate formed on polycrystalline platinum foil which we believe to have a predominantly (110) surface structure. This foil had the dimensions 10 × 10 × 0.25 mm. Prior to any IRRAS investigation the foil was cleaned for 5 hr at 1173 K in 5×10^{-6} Torr O_2 and then annealed for 24 hr in vacuum at 1355 K. After the IRRAS spectra had been obtained, the foil was demounted, transferred to a separate vacuum system, and examined by AES. The results were very similar to those found for the single-crystal substrate. The only significant impurities were superficial amounts of C and O, presumably from atmospheric contamination.

RESULTS AND DISCUSSION

We turn first to the spectra of NO on single-crystal Pt (111). The series of spectra shown in Fig. 1 were measured in a vacuum system, the base pressure of which was 5×10^{-9} Torr. The spectra shown in Figs. 2 and 3 were measured in an improved system with a base pressure of 5×10^{-10} Torr. The same substrate was used for both sets of measurements and the treatment of the substrate was essentially the same. The spectra shown in Fig. 1 have traces of a feature at ca. 2000 wavenumbers which has been ascribed to CO impurity. There is no evidence of this in the spectra shown in Fig. 2. Further, the spectra shown in Fig. 1 appear to show absorption features between 1450 and 1700 cm^{-1} which are apparently not present in the spectra shown in Fig. 2. These features between 1450 and 1700 cm^{-1} have previously been observed (*2*) in a high-pressure system and were shown, by isotopic substitution, to be attributable to a nitrogen-containing species. It is interesting to note that the IRRAS spectra obtained

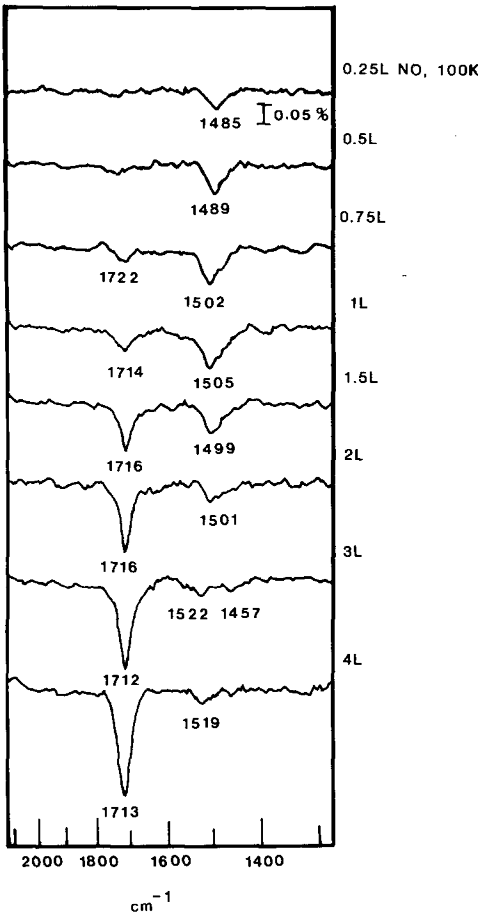

FIG. 2. IRRAS spectra of NO on Pt (111) single crystal. The temperature was maintained at 100 K. The substrate was mounted in a vacuum system, the base pressure of which was 5 × 10^{-10} Torr. NO dosage is expressed in Langmuirs.

under clean conditions are very similar to the EELS spectra (*14*) obtained under similar experimental conditions. The spectra shown in Fig. 3 demonstrate that there are frequency shifts when CO is coadsorbed with the NO.

Turning now to the spectra shown in Figs. 4 and 5 which were measured at higher adsorbant pressures under stirred-tank conditions, we note that the intermediate features are considerably more evident. Indeed, in Figs. 4d and 5c the band at 1631 cm^{-1} is very prominent.

The spectra of NO adsorbed on the polycrystalline foil, which we believe has principally a reconstructed (110) surface, are in many ways similar to the EELS spectra reported by Gorte and Gland (*15*). The series of spectra shown in Fig. 6 were measured at 160 K and show the development of the IRRAS spectrum of the adlayer with increasing coverage. There is only one prominent feature in the spectrum which shifts from about 1610 cm^{-1} at low coverage to 1688 cm^{-1} at high coverage. The spectra shown in Fig. 7 were measured under conditions very similar to those in Fig. 6 except that the temperature was maintained at 270 K. At low coverage (0.5 L) the spectra are quite similar in that there is a single relatively sharp feature at about 1610 cm^{-1}. However, at higher coverage this feature diminishes in intensity and a broad and substantial absorption feature grows in,

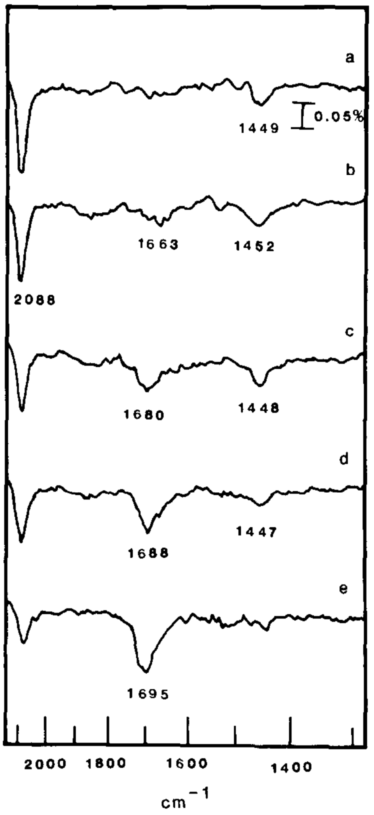

FIG. 3. IRRAS spectra of an adsorbate formed on Pt (111) single crystal with 1 L of CO followed by the indicated doses of NO: (a) 0.75 L, (b) 1 L, (c) 1.5 L, (d) 2 L, (e) 5 L. All experiments conducted at 100 K.

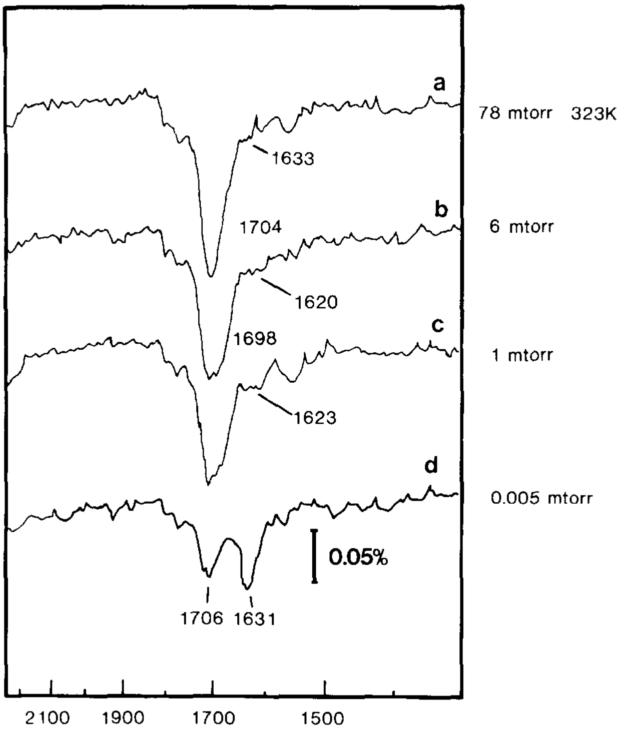

FIG. 4. IRRAS spectra of NO adsorbates in equilibrium with high pressure gas-phase NO over single-crystal Pt (111). Temperature of the experiment was 323 K.

stretching from the apparent absorption maximum at 1632 cm^{-1} all the way to about 1850 cm^{-1}. These results parallel those obtained by Gorte and Gland (cf. Figs. 2 and 3 of Ref. (*15*)). The spectra shown in Fig. 8 exhibit an even more pronounced absorption feature at 1767 cm^{-1} which appears to grow in and then disappear as the sample is heated in stages. The spectra obtained at 473 K under pressures of NO up to 1 Torr which was shown as Fig. 4 of Ref. (*3*), exhibit an even stronger feature at 1773 cm^{-1}. Indeed, at the highest pressure this 1773 cm^{-1} feature dominates the spectrum of the adsorbate. The results on the polycrystalline foil do, we believe, provide an essential clue to the understanding of the spectrum of NO on Pt and its relationship to the structure of the adsorbate. Our spectra show quite clearly that there are essentially two separate features; one which shifts from 1600 to 1680 with increasing coverage and one which sometimes appears at ca. 1775 cm^{-1} and sometimes does not. It does not appear in the spectra measured at 160 K

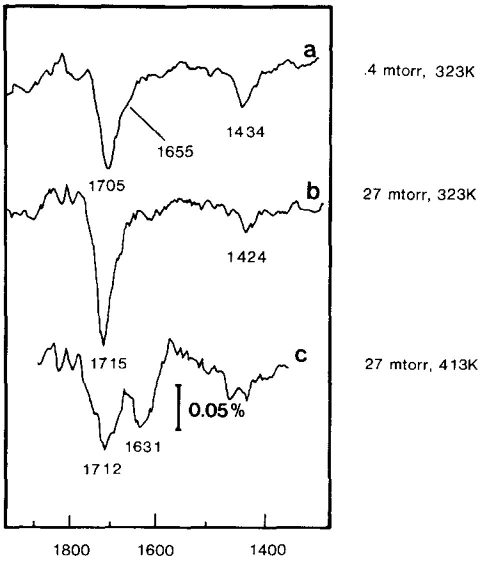

FIG. 5. IRRAS spectra of NO on single-crystal Pt (111) showing the effect of increasing the substrate temperature.

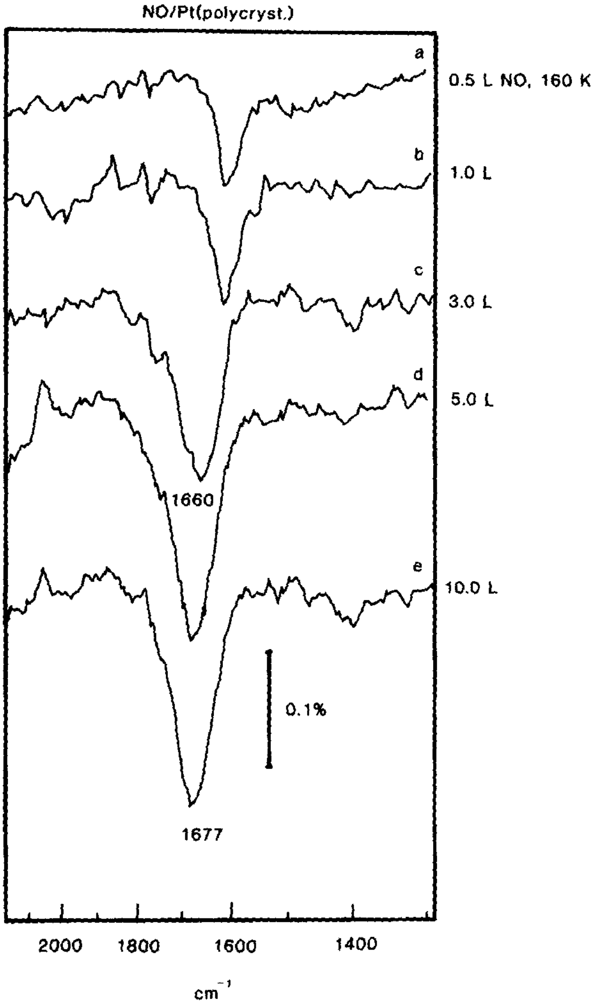

FIG. 6. IRRAS spectra of NO on Pt foil at 160 K at increasing dosage of NO.

but there is evidence of it in spectra measured at 270 K and higher temperatures. It is apparent from the work of Gorte and Gland (*15*) that there are structural changes between these two temperatures and it appears that the most likely explanation of the spectral observations is that they are correlated with these structural changes. Since the reconstructed Pt (110) surface is thought to have a ridged appearance, i.e., to be two-dimensionally anisotropic, we believe that in the low temperature form the adsorbate is anisotropically structured in chains parallel to the ridges. If molecules adsorbed on adjacent sites within a chain are assumed to interact and the chains not to interact, this will explain the shift from 1610 to 1680 cm^{-1} with increasing coverage. To explain the further shift to 1775 cm^{-1} requires more complex interactions which we believe result when chain structures interact and coupled two-dimensional adstructures are built up. The behavior of all the spectra obtained on the polycrystalline foil is understandable in these terms. The vibrationally coupled structures can be disturbed either by the removal of adsorbed species by increasing temperature or reducing pressure, or by displacement of NO molecules by impurities such as dissociatively adsorbed NO or adsorbed CO. The displacement by adsorbed CO shows clearly in the contrast between Figs. 8a and 8e; the CO is clearly evident from its own spectral adsorption. In Fig. 6 we note the wavenumber shift as the interacting structures are built up at 160 K. The conditions for the development of the 1775 cm^{-1} feature are less clear; indeed, it is only in the spectra which we have previously shown as Fig. 4 of Ref. (*3*) that we see this feature in its fully developed form although it appears as a somewhat less intense band in Fig. 8 and in Figs. 2 and 3 of Ref. (*15*). Since we are assigning this vibrational feature to coupled two-dimensional arrays of adsorbed NO, we conclude that only at relatively high temperatures and high pressures are these arrays in any sense fully formed.

We now return to the spectra of NO on the single-crystal Pt (111) surface. From our understanding of the spectra on the reconstructed (110) surface, we now believe the structure of the NO adlayer on Pt (111) to be two-dimensional, in contrast with our assertion in a previous paper (*2*) where we used a one-dimensional interacting structure to explain our observations on NO adlayers at high temperatures and in the presence of high pressure NO gas. We recognize the band at ca. 1465 cm^{-1} as being due to isolated NO molecules on the surface and that at 1700 cm^{-1} to be due to relatively large-scale two-dimensional structures (islands). The appearance of features intermediate between these extreme wavenumbers is attributable either to partially formed ad-structures or to island structures which have been partially destroyed, either by loss of adsorbed molecules or by

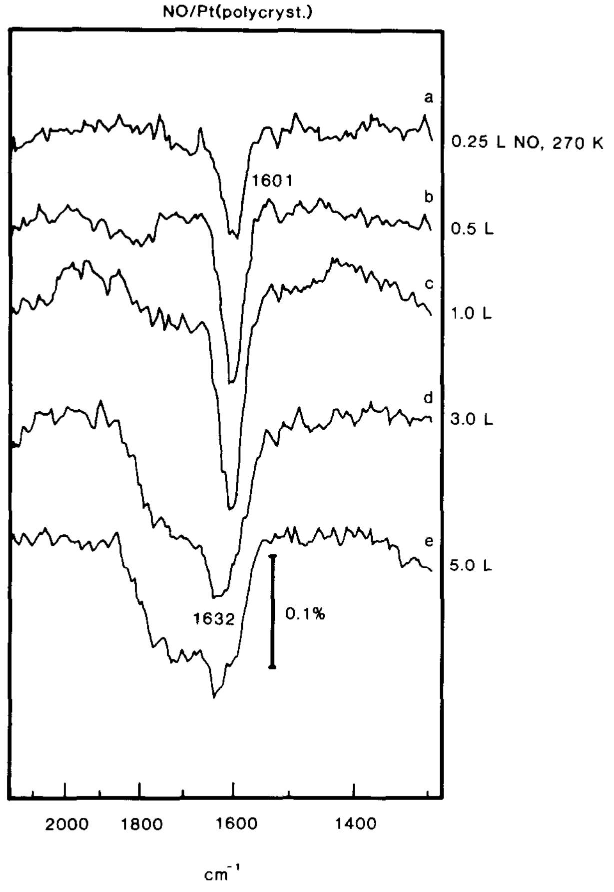

FIG. 7. IRRAS spectra of NO on Pt foil at 270 K at increasing dosage of NO.

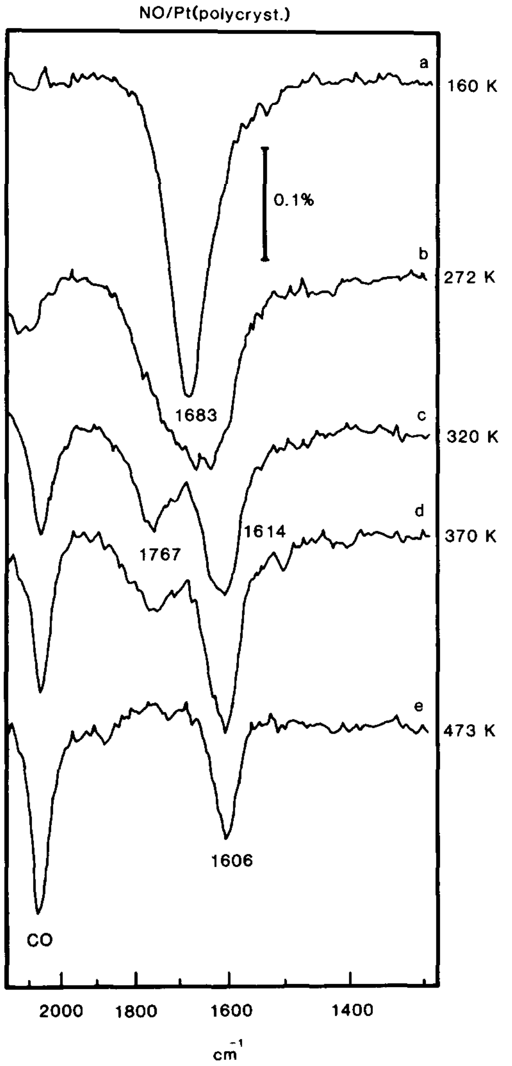

FIG. 8. IRRAS spectra of NO on Pt foil. The adsorbate was established at 160 K with a 10 L dose and is shown in curve (a), cf. Fig. 6e. The adsorbate was flashed to successively higher temperatures and returned to 160 K to obtain the spectra shown in curves (b)–(e). Note the band due to CO impurity.

adsorption of an impurity. The conditions under which we observe these intermediate features are fully consistent with this explanation. The appearance of the band at 1631 cm^{-1} in Figs. 4d and 5c at high temperature and reduced pressures is consistent with the break-up of island structures through removal of an adsorbed species. The appearance of the intermediate features which are apparent in Fig. 1 is consistent with the fact that these spectra were obtained under less than clean conditions as is evidenced by the appearance of the characteristic CO adsorption band. The spectra shown in Fig. 2, which were obtained under considerably cleaner conditions, show no evidence of these intermediate features.

MODEL CALCULATIONS

Pt (111) Surface

The basic model we have used to interpret our observations is first, that each NO molecule adsorbed on a Pt (111) surface has an intrinsic principal NO stretching force constant which has the same value for every NO molecule in the adlayer and second, that NO molecules adsorbed on contiguous sites are vibrationally coupled and this effect shows up as an interaction force constant coupling the NO stretching coordinates of each pair of contiguously adsorbed molecules. A direct implication of this model is that all NO molecules are adsorbed on equivalent sites but, in order to apply the model, it is not necessary to stipulate whether these are linear or bridged sites. The spectra we have previously obtained of adlayers formed from mixtures of ^{14}NO and ^{15}NO convincingly support the assumption of strong vibrational coupling between NO molecules adsorbed on contiguous sites (*16*).

The computational problem was simplified by factoring out the NO stretching mode from all the other modes of the system which lie at much lower wavenumber. Trial calculations with an assumed force field for the complete vibrational problem showed that this approximation should not introduce errors of more than two or three wavenumbers. This simplification allows us to treat exactly the coupling among a relatively large number of adsorbed NO molecules since we need consider only the NO stretching mode for each molecule. Moreover, the use of the approximation that the NO stretching mode may be factored out from the vibrational problem and that only nearest-neighbor interactions are important makes the problem relatively insensitive to geometrical factors. It is not necessary to know the length of the NO bond, the distance between NO adsorption sites nor the angle the NO molecule makes with the surface plane. For the calculations reported in the following, we considered an array of up to 400 adsorption sites in a hexagonal close packed configuration. In each case, 100 molecules were considered; the coverage was varied by changing the size of the substrate. Occupied sites were determined by calculating their x, y coordinates from a pair of random numbers. Edge effects were eliminated by using periodic boundary conditions so that all adsorption sites were equivalent, i.e., all had six nearest neighbor sites. Once the detailed coverage of the surface was determined for a particular calculation, the matrix of the coupled vibrational problem was set up by entering the principal NO stretching force constant in the diagonal matrix element corresponding to each occupied site and the interaction force constant in each off-diagonal matrix element corresponding to a pairwise coupling of two NO molecules adsorbed on adjacent sites. It is at this stage of the calculation that the morphological details of the substrate must be taken into account. For example, on a hexagonal close packed substrate, each adsorbed NO molecule may have up to six nearest neighbors with which it is coupled whereas on a square array the maximum number of nearest neighbors would be four. It is immaterial in this calculation whether every Pt atom has an NO adsorbed on it at saturation or only every alternate atom as appears to be the case in NO on Pt (111) which has been reported to exhibit a p(2 × 2) LEED pattern (*14*) at saturation. All that is necessary is that the interaction force constant be representative of the coupling between nearest neighbors.

The vibrational energies of the NO adlayer are then obtained by diagonalizing the matrix. The relative intensities of the vibrational transitions are also found from the eigenvectors of this matrix if we assume that in the initial (uncoupled) representation each adsorbed NO molecule has the same oscillator strength.

The principal NO stretching force constant was taken to be 9.9126 md/Å giving a wavenumber of 1500 cm^{-1} for the NO stretching mode of an isolated NO molecule on the surface, i.e., for one with no neighbors with which to interact. An interaction force constant of 0.510 md/Å was chosen to give a limiting wavenumber of about 1716 cm^{-1} for the infrared active mode of an extended ad-structure. The results of this calculation are shown graphically in Fig. 9.

Reconstructed Pt (110) Surface

The detailed morphology of the NO adlayer on a reconstructed Pt (110) surface is at this time somewhat obscure and for this

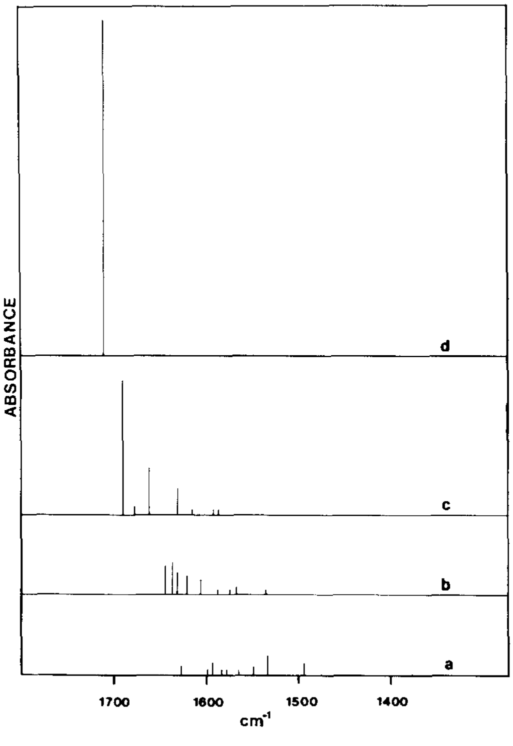

FIG. 9. Calculated spectra of an NO adsorbate on Pt (111) assuming a principal NO stretching force constant of 9.9126 md/Å and an interaction force constant of 0.510 md/Å coupling NO molecules adsorbed on contiguous sites.

reason any interpretation of the vibrational spectra must be speculative. Gorte and Gland (*15*) were able to show that the (2 × 1) LEED pattern of a reconstructed Pt (110) substrate remained unchanged with NO coverage up to about 30% (dosage ca. 1 L) over the temperature range 100–500 K. At coverage between 30 and 65% of saturation and at temperatures between 175 and 275 K a c(4 × 8) structure was found and at higher temperature and higher coverage the LEED pattern indicated a (1 × 1) surface structure suggesting a structural change in the underlying substrate. The TPD spectrum of NO from the Pt foil used for the present studies, illustrated in Fig. 10, matches very well that measured by Gorte and Gland (*15*) and since the IRRAS spectra we have measured also match their EELS spectra, we believe it to be reasonable to assume that the periodicity of the NO adlayer in our experiments is similar to that determined by them. Figure 11a illustrates the surface morphology of Pt (110) and Figs. 11b and 11c illustrate two possible structures for the (2 × 1) reconstruction. The structure shown in Fig. 11c has alternate rows of Pt atoms removed; that shown in Fig. 11b has the rows alternately displaced in opposite directions. From the work of Gorte and Gland, it appears that all the spectra shown in Fig. 6, which were measured at 160 K, should correspond with the observed (2 × 1) LEED pattern. A plausible structure of this adlayer is illustrated in Fig. 12b. This structure is shown on a substrate like the one sketched in Fig. 11b although alternate (2 × 1) structures could be suggested on this substrate other than the one shown in Fig. 11c. In any case, the essential feature of this structure is that the adsorbed NO molecules are arranged in linear arrays. We believe that the feature in the spectra shown in Fig. 6a at ca. 1610 cm^{-1} corresponds to an isolated NO molecule, i.e., one with no nearest neighbors, and the feature in Fig. 6e at ca. 1677 cm^{-1} corresponds to the ir active mode of an extended linear array of adsorbed NO molecules. We adopted the same procedure for the model calculations as we did for NO adsorbed on the Pt (111) surface and factored out the NO stretching mode. In order to have the calculated wavenumber of a single adsorbed molecule equal to 1610 cm^{-1} it was necessary to adopt a principal NO stretching force constant of 11.420 md/Å rather than the value of 9.9126 md/Å which we used for the NO adsorbed on the Pt (111) surface. We assumed the value of the interaction force constant to be 0.510 md/Å, i.e., the same as on the Pt (111) surface, and we allowed this interaction force constant to couple the NO stretching coordinates of each pair of nearest neighbors in the linear array of NO molecules. For a linear array of 50 NO molecules we calculated the strongly allowed infrared transition to be at 1680 cm^{-1}.

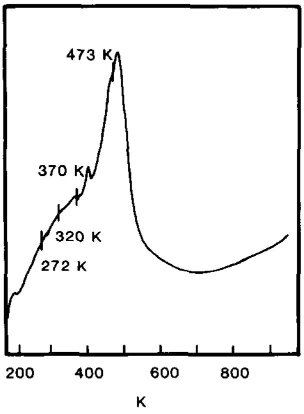

FIG. 10. TPD spectrum of a saturation coverage of NO on Pt foil. Heating rate about 10 K/s. Indicated temperatures correspond to those to which the adsorbate was flashed in order to obtain the spectra shown in Fig. 8.

We then carried out a similar calculation for a double linear array of 100 NO molecules, i.e., two parallel arrays each containing 50 NO molecules. Every NO molecule in each linear array was assumed to be coupled vibrationally with its neighbors in its own array and, in addition, each was assumed to be coupled to the corresponding NO molecule in the other linear array with the same interaction force constant. The

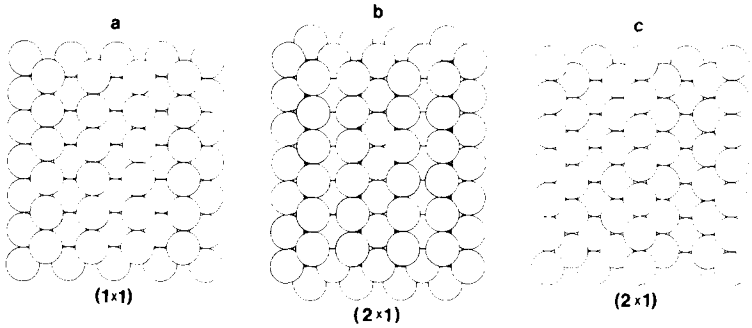

FIG. 11. Pt (110) structures: (a) bulk periodicity; (b) and (c) possible surface structures for the (2 × 1) reconstruction.

principal and interaction force constants were taken as 11.420 and 0.510 md/Å, respectively. The strongly allowed infrared transition for an adsorbate with this configuration was calculated to be 1715 cm^{-1}. Since this calculated wavenumber seemed much too low to match the experimental observation of a band at ca. 1775 cm^{-1} at high temperature and high coverage we tried yet another model for the vibrational structure of the NO adlayer on Pt (110). We assumed a 10 × 10 array of NO molecules on a square lattice, cf. Fig. 12a. Each NO molecule was assumed to be vibrationally coupled with its four nearest neighbors with an interaction force constant of 0.510 md/Å and to have a principal NO stretching force constant equal to 11.420 md/Å. This configuration is calculated to have its strong infrared band at 1748 cm^{-1} which is closer to the observed absorption maximum than the value calculated for the double linear array.

Gorte and Gland (*15*) have noted that at temperatures in the range 335 to 450 K and at coverages above 30% the LEED pattern indicates a (1 × 1) surface structure and, since the 1775 cm^{-1} feature shows clearly only in the spectra in Figs. 8c and 8d and in Fig. 3 of Ref. (*3*), all of which were obtained at high coverage and high temperature, it seems quite reasonable to assume that the structural features giving rise to the 1775 cm^{-1} absorption also give rise to the (1 × 1) LEED pattern. It seems reasonable to conclude that in the observation of a restored (1 × 1) LEED pattern on the reconstructed (2 × 1) surface lies implicit the idea that, under high-temperature high-coverage conditions, there is a phase change in the surface structure of the Pt substrate, presumably induced by the presence of the NO adsorbate. That such a phase change should be so facile and apparently reversible strongly suggests that the structure of the reconstructed Pt (110) surface is similar to that shown in Fig. 11b rather than that shown in Fig. 11c. The establishment of the latter (2 × 1) structure requires the removal of Pt atoms from the surface whereas the establishment of the (2 × 1) structure shown in Fig. 11b requires a simple lateral displacement of Pt atoms and, in that case, the reestablishment of the (1 × 1) structure would require only a simple reverse displacement. Of course, the observation of a (1 × 1) structure with adsorbed NO on the Pt surface implies that there is at least one NO adsorbed per unit cell of the (1 × 1)

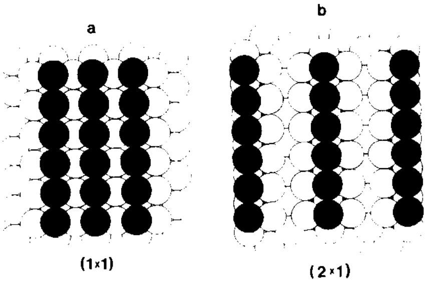

FIG. 12. Possible structures for the NO adsorbate on Pt (110): (a) at high coverage; (b) at low coverage.

structure shown in Fig. 11a. The simplest assumption is to postulate just one adsorbed NO molecule per unit cell and to imagine the adsorbate to be structured somewhat like that sketched in Fig. 12a. An NO molecule adsorbed in such a structure could easily be expected to interact strongly with four nearest neighbors and hence its vibrational spectrum might reasonably be modeled by the calculation which gives 1748 cm^{-1} for the infrared active NO stretching mode.

What now remains is to explain the broad high wavenumber wing which is developed in many of the spectra of NO on the (110) surface, e.g., in the spectra shown in Figs. 6c, 6d, and 8b and in the spectral curves d and e of Fig. 3 in Ref. (*3*). For lack of a better explanation, we correlate this feature with the observation by Gorte and Gland of a c(4 × 8) structure at intermediate temperatures and intermediate coverage. The suggestion we derive from the spectra is that the c(4 × 8) pattern is developed in the transition from the (2 × 1) structure which we describe vibrationally as linear (one-dimensional) coupled arrays and the (1 × 1) structure which we associate with the two-dimensional coupled arrays. With such a large periodicity as (4 × 8), the adsorbate–substrate structure must be fairly complex. We believe it to represent a relatively stable transition stage intermediate between the (2 × 1) linear and (1 × 1) two-dimensional ad-structures, the complexity of which derives from a cooperative shift in the Pt atoms of the substrate and NO molecules of the adsorbate from one relatively simple structure to the other.

CONCLUSIONS

The overall conclusion we reach is that NO adsorbed on Pt surfaces is strongly coupled vibrationally and that the interaction is short range, coupling only those NO molecules adsorbed on contiguous sites. There is a suggestion of a longer range coupling in some of the spectra; in Fig. 2 it is apparent that a low wavenumber wing develops on the 1500 cm^{-1} band as the coverage is increased and we attribute this to the increasing contribution of coupling through next-nearest neighbor interactions to the wavenumber of the NO stretching mode as surface coverage is increased. However, these longer range effects are much less than the very dramatic short-range coupling which shifts the NO stretching mode through over 200 cm^{-1}. The origin of the vibrational coupling is unclear to us at present. Dipole–dipole coupling has been used (*17, 18*) to explain a wavenumber shift with coverage of the 2100 cm^{-1} band of CO on Pt (111). In that case the total shift is only about 35 cm^{-1} which is understandable in terms of an interaction force constant of about 0.1 md/Å (*17*). In the theory of dipole–dipole coupling, the interaction force constant is proportional to the square of the derivative of the dipole moment with respect to the normal coordinate of the isolated molecule (*19*). Therefore, if the proposed interaction force constant of 0.510 md/Å for NO on Pt were to be explained by dipole–dipole interaction, $|\partial\mu/\partial q|^2$ for the NO stretching mode, and hence the infrared intensity of the NO stretching mode, would have to be more than five times larger than the corresponding value for CO. Our observations show that NO is a much weaker infrared absorber than CO and we are therefore led to the conclusion that the origin of the vibrational interaction cannot lie in dipole–dipole coupling. A convenient way to compare the value found for the interaction force constant in the present work with values in other NO-containing species is through the splitting between the symmetric and antisymmetric modes in a system containing two NO molecules. In the present case the splitting is 77 cm^{-1}; in $(NO)_2$ dimer in the gas phase the observed splitting is 72 cm^{-1} (*20*), it is 130 cm^{-1} for $(NO)_2$ dimer formed on chromia (*21*) and 25–100 cm^{-1} in a variety of inorganic dinitrosyl complexes (*22*). Thus we conclude that the vibrational coupling of NO adsorbed on Pt surfaces is as large as in NO dimer, even though in the latter case the NO molecules are directly bonded whereas in the former they, presumably, connected only through the metal surface.

The conclusion to which we have been led is that the coverage dependent shifts in the spectrum of NO on Pt are due to strong short-range interactions between adjacent NO molecules rather than to the change over from bridge-bonded to linear adsorption sites. This contrasts with the accepted interpretation of the spectrum of CO adsorbed on Pt, in which case, the two principal bands at 2100 and 1850 cm^{-1} are assigned to linear and bridged structures and the shift in each with coverage is thought to be relatively small. Moreover, the vibrational coupling of adsorbed CO may be quantitatively understood in terms of dipole–dipole interactions without postulating any special short-range coupling through the metal substrate. The fact that our understanding of the behavior of NO on Pt surfaces is so different from CO is remarkable. Possibly some clue to the difference is to be found in the elementary fact that NO has unpaired electrons and may behave more like a radical. Whatever the explanation, we believe that the further study of NO adsorbates on catalytic surfaces may lead to some insight into the mechanisms of heterogeneous catalysis.

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