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Infrared Spectra of ^{14}NO and ^{15}NO on a Low-Area Pt Surface at Elevated Temperatures

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Infrared spectra of NO adsorbed on an annealed polycrystalline Pt surface have been measured at temperatures between 300 and 673 K and under pressures of gas-phase NO between 10^{-3} and 1 Torr. The spectra show that the NO adsorbate is in equilibrium with the gas phase at elevated temperatures. A model based on strong vibrational coupling between NO molecules adsorbed on adjacent Pt atoms is proposed to explain the observed spectra.

INTRODUCTION

Techniques for the measurement of infrared reflection absorption spectra (IRRAS) have now been developed to the point where the sensitivity of the measurement is comparable with that attainable in electron energy loss spectroscopy (EELS). The spectral range of IRRAS is at present instrumentally restricted to the measurement of transitions above ~1000 cm^{-1} and therefore generally does not allow us to observe bending modes or substrate–adsorbate stretching modes which are readily observable in EELS. But, in contrast with EELS and other electron and ion spectroscopies, the IRRAS technique can be applied in the presence of gases in the pressure range 10^{-3}–10^{3} Torr (1 Torr = 133.3 N/m^2) and in the temperature range 0–1000 K, which are temperature and pressure ranges often desirable for the study of kinetics of heterogeneously catalyzed reactions at gas–solid interfaces.

In a previous paper (*1*) we gave a preliminary report of the observation of the IRRAS spectrum of an adsorbate obtained when an annealed polycrystalline Pt foil was exposed to gas-phase NO at a pressure of 50 Torr. In experiments carried out at 300 K we were able to show that the spectrum of the adsorbate changed markedly as the pressure of NO over the surface was reduced to 0.05 Torr. The pressure-induced changes in the adsorbate spectrum were only partially reversible.

In the present paper we describe the extension of these measurements to elevated temperatures, the spectrum of an adsorbate formed from ^{15}NO which gives the expected isotopic shifts for an adsorbed NO molecule, and a series of studies which we believe show that the gas and adsorbed phases of NO are in equilibrium at temperatures above ~450 K. We further propose a model for the structure of the adsorbate which is consistent not only with our observed IRRAS spectra but also with previous low-energy electron diffraction (LEED) (*2, 3*) and EELS (*2*) studies.

EXPERIMENTAL

The details of the spectrometer used for these experiments have been described elsewhere (*4–6*). The sample cell was constructed from type 316 stainless steel, the outlet port was liquid-nitrogen trapped, and the inlet was trapped with a dry ice–acetone bath. The cell windows and the inlet and outlet ports were sealed to the body of the cell with Viton "O"-rings. In all the experiments reported in this paper the sample cell was operated under stirred-tank conditions (*7*); gas pressures in the sample

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cell could be adjusted in either the inlet or pumping lines and in this way stirred-tank conditions could be maintained as gas pressures were changed. The cell was fitted with a thermocouple gauge which was used for the measurements of the gas pressures reported in this paper.

The substrate, a piece of Pt foil 5 × 25 mm, was spot welded to Pt rods which were connected by heavy stainless-steel sleeves to tungsten feed-throughs. The Pt foil could be heated resistively to over 1300 K. Substrate temperatures were monitored with a Pt/Pt–Rh thermocouple spot welded to the foil. The thermocouple calibration was checked by measuring a few high temperatures with an optical pyrometer. The temperature of the main body of the sample cell was monitored with a second thermocouple. Even when the platinum foil was maintained at 1300 K for periods as long as an hour, the temperature of the cell wall did not rise above ~325 K. Thus, in all the experiments in which the substrate was maintained at elevated temperature, there was a large temperature gradient across the gas in the cell and under these conditions it is not meaningful to ascribe a temperature to the gas phase over the adsorbates.

The cleaning procedure we adopted for the substrate was as follows. The foil was heated at 1300 K for ca. 15 min in 10^{-2} Torr of O_2 to remove oxidizable impurities. This treatment leaves an oxide surface which was removed by heating the foil at 650 K in 10^{-2} Torr H_2 for 15 min. Presumably, this reduction in H_2 leaves the Pt surface covered with a hydrogenic adlayer. For some of the experiments, we carried out the oxidative step of the cleaning at lower temperatures (650 K) for 1–2 hr. This, we believe, produces a less heavily oxidized and cleaner surface but we did not find our results to depend on the method of cleaning. In all these cleaning steps the oxygen or hydrogen was flowed through the sample cell under stirred-tank conditions. In some test experiments we discovered that this procedure gave the cleanest and most reproducible substrate surfaces. The cleaning procedure was repeated prior to each set of experiments.

There was no provision in the reactor to monitor surface cleanliness or surface periodicity. We did, however, demount several sample foils for examination by AES and XPS. These spectra showed that there was substantial contamination of the foils by carbon, especially those that had been cleaned in O_2 at the higher temperature. No evidence of calcium contamination was found.

The sample of ^{14}NO was obtained from Matheson. The infrared spectrum showed it to contain traces of NO_2 and N_2O; it was purified prior to our experiments by reacting with $FeSO_4$ to form the familar brown complex (*8*) which was decomposed by heating *in vacuo* to give NO. The infrared spectrum of the purified NO showed no detectable impurities. The sample of ^{15}NO was obtained from Prochem and was found to contain $^{15}N_2O$ as a major impurity. The impurity was separated by low-temperature distillation.

At the beginning of each experiment the spectrum of the reduced Pt surface was first scanned with the Pt at 600 K in 10^{-2} Torr H_2 to reduce possible contamination. This spectrum was stored digitally and subtracted from each subsequent spectrum to give a difference spectrum, presumably the spectrum of the NO adlayer since we have been unable to detect an infrared spectrum of hydrogen on Pt(111) in the wavelength region scanned. To establish the NO adsorbate we cut off the supply of hydrogen and pumped the reactor down to the base pressure, which was $\sim 10^{-5}$ Torr. We then introduced the NO and adjusted the flow rate to establish the desired pressure of NO in the system. Sometimes we found the NO to be adsorbed under these conditions; generally the results were irreproducible and we found it preferable to heat the substrate for a few seconds to 1100 K in the presence of NO and then return the system to lower temperature. This, we found, gave very reproducible spectra and presumably reproducible adsorbate structures. Probably, in this brief heating, the hydrogen adlayer and any NO are desorbed and the new adlayer is predominantly NO bonded directly to a clean Pt surface. We discount the possibility that the NO reacts with the hydrogen adlayer since the spectral behavior is completely unchanged when D_2 is substituted for H_2 in the reduction of the surface (*1*).

For measurements at high temperature we used two power supplies to furnish the current to heat the substrate. The first power supply was adjusted to give the correct current and voltage such that, under steady-state conditions, the substrate temperature was about the desired value. The second power supply was used to heat the foil to establish the adsorbate structure. When the second power supply was turned off, the foil returned to the desired base temperature, or close to it since we did notice that the resistance of the substrate was affected slightly by the deposition of adsorbates.

RESULTS

We carried out a series of experiments with the substrate at elevated temperatures; the general procedure was as follows. The NO adsorbate was established by heating the substrate briefly to ~1100 K in 0.065 Torr NO and then returning it to the base temperature. A series of spectra was then measured as the pressure of the gas-phase NO was reduced in a stepwise manner. A typical sequence of such spectra measured at a base temperature of 473 K is showed in Fig. 1. Note, that there are marked changes in the spectrum with changing pressure, presumably reflecting decreased coverage of the substrate as the pressure is reduced. The pressure of NO was returned to 0.065 Torr for the last spectrum shown in Fig. 1. Although there are some differences between the first and last spectra in this sequence (for example, the band at ~1325 cm^{-1} appears stronger in the last spectrum), the main features at ~1700 cm^{-1} are the same within experimental uncertainty. We found, quite generally, that at substrate temperatures above ~450 K, the restoration of the original pressure gave an adsorbate spectrum virtually identical with the original one. In other words, the changes in the spectrum of the adsorbate induced by changes in the gas pressure of the adsorbant appear to be completely reversible at these temperatures. This apparent equilibrium between gas and adsorbate at elevated temperatures contrasts strongly with the behavior at room temperature where, as we previously reported (*1*) and have confirmed in this present study, the desorption and readsorption of NO from the gas phase is *not* a reversible process.

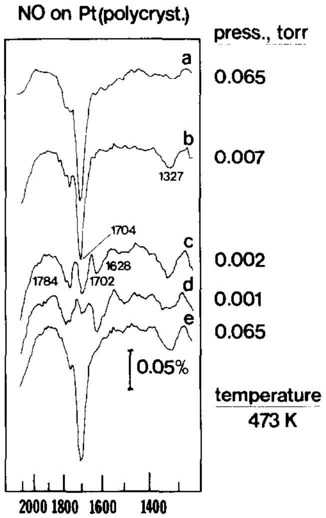

FIG. 1. Spectra of NO on annealed polycrystalline Pt at 473 K showing changes as the pressure of NO over the surface is reduced. Note the apparent reversible behavior when the pressure is restored to 0.065 Torr.

We also measured a series of spectra at different substrate temperatures but at constant gas pressure. In Fig. 2 we show such a series of spectra taken at a gas pressure of 0.065 Torr. The apparent desorption of NO with increasing temperature is also reversible when the temperature is lowered as

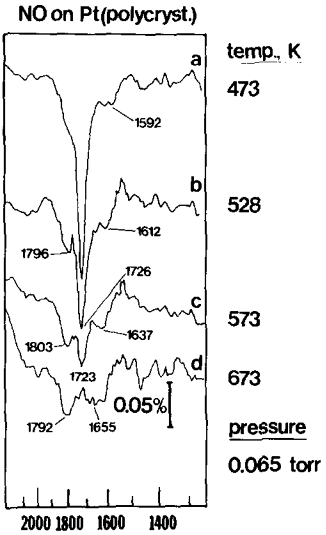

FIG. 2. Spectra of NO on annealed polycrystalline Pt. The gas pressure was maintained at 0.065 Torr and the temperature was raised in stepwise fashion from 473 to 673 K. When the temperature was returned to 473 K, the system behaved reversibly.

long as the base temperature stays above ~450 K. We have made an extensive survey of the behavior of the NO–Pt system in the pressure and temperature ranges covered in Figs. 1 and 2 and find first, that the results are very reproducible and second, that there are no obvious features which do not show in the two cross-sections illustrated in Figs. 1 and 2.

The results we found at substrate temperatures above ~450 K stand in marked contrast to the room temperature results we reported previously (*1*). In particular, at higher temperature, the peak absorbance of the feature at ~1725 cm^{-1} is about twice what it is at room temperature and, at the higher temperatures, desorption and adsorption appear to be reversible processes where as at room temperature they are not. We have therefore examined carefully the behavior of the spectrum of the NO adsorbate between room temperature and 473 K. Our results are summarized in Fig. 3. The letters on the spectra show the sequence in which they were measured; the measurement conditions are specified in the legend to the figure. In Fig. 3 we have shown the wavenumber of the absorption maximum in each spectrum. Note, in particular, that these absorption maxima show hysteresis;

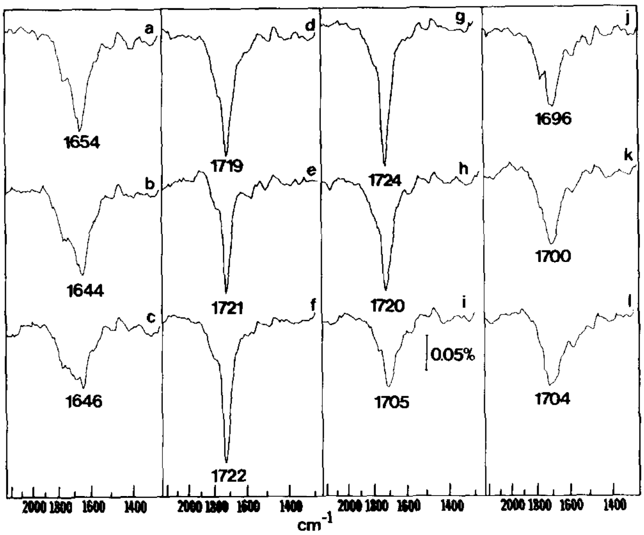

FIG. 3. Behavior of the spectrum of the NO adsorbate as the temperature is varied between 473 and 298 K. The adsorbate was initially established by heating the substrate briefly to 1075 K in 0.065 Torr of NO. The spectra were taken in sequence at the following substrate temperatures: (a) 378 K; (b) 398 K; (c) 423 K; (d) 448 K; (e) 473 K; (f) 448 K; (g) 423 K; (h) 398 K; (i) 378 K; (j) 348 K; (k) 323 K; and (l) 298 K.

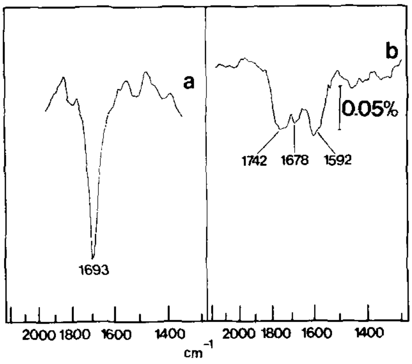

FIG. 4. Spectra of an adsorbate on polycrystalline Pt formed from ^{15}NO. The observed isotope shifts are summarized in Table 1. The conditions of the experiment were the same as those used to obtain Fig. 2a.

for example, in Fig.s 3b and h, which were both recorded at 400 K, the absorption maxima differ by ~80 cm^{-1}.

We also measured the spectrum of an adsorbate formed from ^{15}NO to ascertain which of the features in the spectrum could unambiguously be assigned to nitrogen-containing species; the results are summarized in Fig. 4. Since we had only a small sample it was not possible to make a complete set of measurements with ^{15}NO. But the spectra in Fig. 4 do clearly show the four important features at 1742, 1693, 1678, and 1592 cm^{-1}.

DISCUSSION

The results of the experiments with ^{15}NO, although preliminary, do establish conclusively that the major features in the spectra of the adsorbate at 1785, 1725, 1700, and 1630 cm^{-1} are all assignable to nitrogen-containing species. The calculated ^{14}N–^{15}N isotope shift for an isolated molecule is 1.8% of the ^{14}NO vibrational wavenumber and, in the approximation that the NO stretching frequency may be split out from all other modes of the adsorbed NO molecule, we should expect the isotope shift of adsorbed NO to be the same percentage of the observed wavenumber. The measured isotope shifts are summarized in Table 1 and compared with the values calculated in this simple approximation.

TABLE 1

Isotope Shifts of Major Features in the Spectrum of NO on Polycrystalline Pt in cm^{-1}

Observed ^{14}NO	Wavenumber ^{15}NO	Observed $\Delta\nu$	Calculated $\Delta\nu$
1784	1746	38	32
1724	1693	31	31
1701	1677	24	30
1628	1592	36	29

We have explored the dependence of the calculated isotope shifts on assumed geometry of the adsorbed NO, considering both linear and bent configurations, and on the values taken for the Pt–N stretching and Pt–NO bending force constants. Generally, we find that the calculated isotope shift of the NO stretching mode is quite insensitive to these assumptions and, in view of the uncertainties in our measured shifts (ca. 5 cm^{-1}), it seems that further interpretation of the isotope shifts is unwarranted at this time.

The most puzzling feature of our observations is the behavior of the band at ca. 1725 cm^{-1} when the temperature of the substrate is reduced from ~450 K to 350 K (cf. Fig. 3). The peak absorbance drops by a factor of two, the adsorption maximum shifts to the red, and the band appears to be somewhat broadened due to the appearance of a shoulder or shoulders on the low wavenumber side. It seems inconceivable to us that the coverage of NO, which obviously decreases with increasing temperature (cf. Fig. 2), should also decrease with decreasing temperature! Our first thought was that the NO exists in two states on the surface: a high-temperature form which is linear and a low-temperature form which is bent. The linear form would have a larger component of the dipole transition moment normal to the metal surface and would therefore have a greater intrinsic intensity under the IRRAS selection rules (9). To explore this possibility further, we measured the integrated absorption intensities

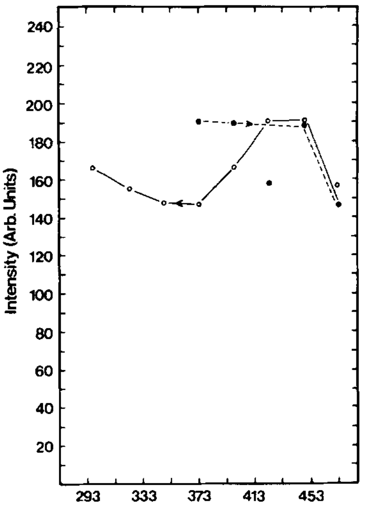

FIG. 5. Integrated intensities between 1914 cm^{-1} and 1535 cm^{-1} measured from the sequence of spectra shown in Fig. 3. Points corresponding to increasing temperature are shown as solid circles.

between 1914 and 1535 cm^{-1} for the series of spectra shown in Fig. 3. Our results are summarized in Fig. 5. We experienced some difficulty in determining exactly where to draw the baseline in these spectra and therefore we estimate the uncertainty in these integrated areas to be ~20%. Although there do appear to be some small changes in intensity as the temperature is varied, the overall picture suggests that the integrated intensity is almost independent of substrate temperature, at least within the uncertainty of our measurement. This result, together with the observation that the changes in the spectrum do not occur at a single temperature, as might be expected if there were a phase transition between a linear and bent form of NO, suggest that the structural changes in the adsorbate responsible for the temperature effects we observe are not attributable to two distinct chemical states of NO on the surface but rather to changes in aggregation and ordering.

Ibach and Lehwald reported the EELS spectrum of NO on Pt(111) measured at 160 K under uhv conditions (*2*). They observed two features in the NO stretching region: one at 1516 cm^{-1} which was observed at low coverage and a second at ca. 1718 cm^{-1} which was observed at high coverage. At intermediate coverage both features were observed. The feature at 1516 cm^{-1} was found to shift to ca. 1484 cm^{-1} as surface coverage was increased. Ibach and Lehwald assigned the loss at 1516 cm^{-1} to the NO monomer and that at 1718 cm^{-1} to a dimer. They also reported some experiments in which a Pt(111) surface at 230–300 K was exposed to 5 L doses of NO at a dosing pressure of 5×10^{-8} Torr. Under these conditions the 1718 cm^{-1} loss peak was observed but, as a function of time, the 1718 cm^{-1} loss peak decreased in intensity and the one at 1484 cm^{-1} grew in until finally there was only a single feature in the NO stretching region at 1516 cm^{-1}. We expect the annealed polycrystalline platinum to have a surface which is mostly Pt(111) (*10*) and, if this is indeed the case, our results should correlate with those ob-

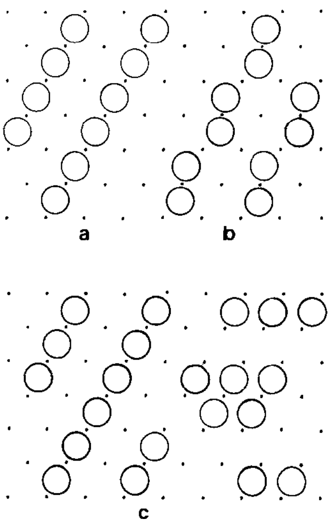

FIG. 6. Possible structures of the NO adsorbate on Pt(111). (a) is consistent with a p(2×1) LEED pattern. (b) shows alternate NO molecules slightly displaced through steric interactions which we believe would give similar spectra to (a). (c) shows a disordered structure in which many of the linear arrays of adsorbed NO molecules are much shorter than in (a) or (b). In these structures we have shown the NO in a bridged configuration but equivalent structures could be drawn with the NO adsorbed in a linear configuration.

tained by Ibach and Lehwald (*2*). Ibach and Lehwald also made LEED studies of the NO adsorbate structure and found that, at exposures greater than 0.6 L, a diffuse p(2 × 2) pattern was developed. Such a pattern would be consistent with either a p(2 × 2) or a p(2 × 1) adsorbate structure.

We believe that the previous observations can be correlated with those described in this paper if one assumes a model for the NO-adsorbate structure at high coverage similar to those illustrated in either Figs. 6a or b. The number of possible structures may be compounded if the NO is slightly bent from the linear configuration and we have not explored all these possibilities in an exhaustive way. But the essence of our model is that, under the high-temperature and high-dosage conditions employed in our experiment, the linear arrays of NO are broken up by collision of gas-phase molecules with the surface. The linear arrays are reformed when the substrate is heated to a temperature at which the adsorbed NO becomes easily mobile. We envision the broken chain structure as something similar to that illustrated in Fig. 6c in which the arrays of NO molecules adsorbed on adjacent sites are relatively small containing two, three, four, or five NOs with structural discontinuities separating the arrays (*11*).

The interpretation of the observed spectra then requires the assumption of an interaction force constant coupling the NO stretching coordinates of NO molecules adsorbed on adjacent Pt atoms. With this assumption, we set up a normal-coordinate calculation in which we considered the NO stretching mode to be uncoupled from the other modes and calculated the vibrational wavenumbers of all the NO stretching modes of various arrays of NO molecules adsorbed on the surface. We also calculated the oscillator strengths of all these NO stretching modes.

TABLE 2

Calculated Wavenumbers and Calculated Oscillator Strengths per NO (Shown in Parentheses) for the NO stretching Modes of Interacting Assemblies of NO Molecules[a]

1	2	3	4	5	6	7	8	9	10
1518	1630	1674	1695	1707	1714	1719	1722	1724	1726
(4.861)	(4.861)	(4.597)	(4.426)	(4.308)	(4.224)	(4.160)	(4.110)	(4.069)	(4.036)
	1397	1518	1588	1630	1656	1674	1686	1695	1702
	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
		1343	1444	1518	1568	1604	1630	1648	1663
		(0.169)	(0.290)	(0.348)	(0.378)	(0.395)	(0.405)	(0.411)	(0.415)
			1316	1397	1465	1518	1557	1588	1611
			(0)	(0)	(0)	(0)	(0)	(0)	(0)
				1301	1365	1426	1477	1518	1550
				(0.029)	(0.064)	(0.089)	(0.105)	(0.116)	(0.124)
					1292	1343	1397	1444	1484
					(0)	(0)	(0)	(0)	(0)
						1285	1328	1374	1418
						(0.009)	(0.022)	(0.033)	(0.042)
							1281	1316	1357
							(0)	(0)	(0)
								1288	1308
								(0.003)	(0.009)
									1275
									(0)

[a] The number of NO molecules in each unit is shown in the table heading. Units are cm^{-1} for wavenumbers and 10^{-40} cgs for oscillator strengths.

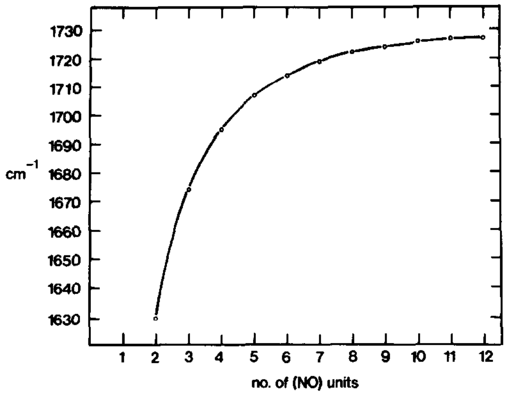

FIG. 7. Plot of the calculated wavenumber of the strongly allowed NO stretching mode vs the number of NO molecules in an array (cf. Table 2).

The details of the calculation are as follows: the N–O distance was taken as 1.2 Å and the adsorbed NO molecules were assumed to lie parallel to one another with a separation of 2.774 Å, i.e., the Pt–Pt distance. The NO stretching force constant was taken as 10.13 mdyn/Å and the interaction force constant between two adjacent NO molecules was taken to be 1.55 mdyn/Å. All other interaction force constants were assumed to be zero. The calculation of the oscillator strength followed simply through the application of a normal–coordinate transformation and the assumption of an oscillator strength of 4.86×10^{-40} cgsu for an isolated adsorbed NO molecule, corresponding to an effective charge of -0.15 e on the oxygen atom and $+0.10$ e on the nitrogen atom.

The results of these calculations for linear arrays of NO molecules, such as illustrated in Fig. 6a, are summarized in Table 2. The wavenumber of an isolated NO molecule is calculated to be 1518 cm^{-1} matching the feature observed by Ibach and Lehwald (*2*) in their low-coverage EELS spectrum. There are two NO stretching modes for the array of two NO molecules. One is at 1630 cm^{-1} and is polarized parallel to the NO bond and allowed in the IRRAS spectrum by both the normal–coordinate and the IRRAS selection rules (*9*). The linear array of three molecules has two NO stretching modes allowed in the IRRAS spectrum, the more intense one at 1674 cm^{-1}. As the number of NO molecules in the linear array is increased, the calculated wavenumber of the strongly allowed mode approaches a limiting value of ca 1727 cm^{-1} (cf. Fig. 7), and the oscillator strength approaches a limiting value of $\sim 4.0 \times 10^{-40}$ cgsu/NO molecule (cf. Fig. 8). The calculated wavenumbers and oscillator strengths are exactly the same as those given in Table 2 for arrays with bends or kinks such as those illustrated in Fig. 9.

In the high-temperature region above 450 K the adsorbate is structured in relatively long chains at high coverage and, as coverage is decreased, either by reducing the pressure or raising the temperature, the chains become, on the average, shorter and shorter. This result is consistent with the observations summarized in Fig. 1. As the pressure is reduced to 0.002 and to 0.001 Torr at 473 K, the feature at 1725 cm^{-1}, which we assign to the relatively long chains, shifts to the red and the feature, at ca. 1630 cm^{-1}, assigned to an adjacent pair of NO molecules, increases in intensity. At 0.001 Torr a band at ca. 1500 cm^{-1} is also beginning to develop, suggesting the presence of isolated NO molecules in the adsorbate strcuture. A similar interpretation can be made of the spectra shown in Fig. 2

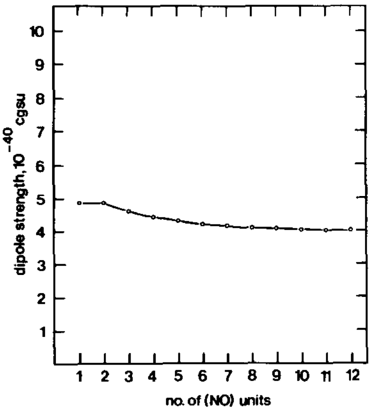

FIG. 8. Plot of the calculated dipole strength of the strongly allowed NO stretching mode vs the number of NO molecules in an array (cf. Table 2).

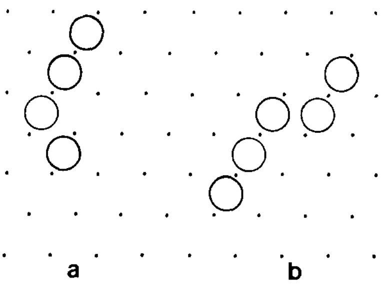

FIG. 9. Structures showing (a) bends and (b) kinks in the NO chains. The results are shown in Table 2.

which result when the temperature is increased at constant pressure.

At temperatures below ~450 K under the high-pressure conditions of our experiment, the results are consistent with there being a considerable fraction of the adsorbed NO molecules in small groups. Hence the features at 1700–1630 cm^{-1}, which are attributable to groups of two to five adjacent NO molecules, predominate. The spectra in Fig. 3 are readily understandable in terms of such a model if the number of groups of two to five NO molecules varies relative to the number of groups of six to nine. The hysteresis suggests that equilibrium is not fully attained in the time of our experiments which was about 15 min.

The EELS results of Ibach and Lehwald are interpreted in terms of our model as follows; we assume that at low coverage the surface is first covered in a p(2 × 2) pattern as shown in Fig. 10. Such an adsorbate structure would give a calculated wavenumber of 1518 cm^{-1} at low coverage (cf. Table 2). Adsorption of another NO would be in one of the interstices in the structure and would produce a three-molecule array. We should expect a wavenumber of 1674 cm^{-1} for such a structure, shifting to 1725 cm^{-1} as coverage increased. However, one should note that at coverages high enough that this feature could be clearly detected, there would be a significant fraction of five and seven NO arrays which have calculated wavenumbers of 1707 and 1719 cm^{-1} and it is possible that the 1674 feature might not be detected.

We have also calculated the wavenumbers of a number of other adsorbate conformations using exactly the same geometrical and force-constant parameters. A group of three NO molecules arranged in a triangle on adjacent sites has a calculated wavenumber of 1734 cm^{-1}. If another NO molecule is adsorbed next to this array, the wavenumber shifts to 1790 cm^{-1} which matches the feature we observe at ca. 1790 cm^{-1} in many of our spectra.

The fundamental basis of the model we have used to explain our observations is the postulation of a strong local interaction between the stretching modes of two NO molecules absorbed on adjacent sites. We have carried out a few calculations using a Urey–Bradley force field to model steric interactions for a number of assumed geometries. We conclude that, to attribute the interaction between NO stretching modes to steric effects would require the assumption of unreasonably large steric forces (*12*).

The 1.55 mdyn/Å NO interaction force constant we have assumed gives a calculated split of 233 cm^{-1} between the symmetric and antisymmetric stretching modes of the two adjacent NO molecules (cf. Table 2). This should be compared with an observed splitting of 72 cm^{-1} in $(NO)_2$ (*13*) and an observed splitting of 60–150 cm^{-1} in a variety of inorganic complexes (*14*).

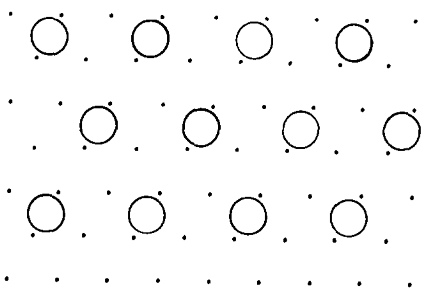

FIG. 10. Structure showing a p(2 × 2) array which, in the present model, would give a calculated wavenumber of 1518 cm^{-1} in agreement with the low-coverage observations of Ibach and Lehwald (*2*).

Thus the postulated interaction force constant coupling adjacent adsorbed NO molecules seems to be unusually large. It seems to us that it reflects in some way the interaction of the odd electron in the NO molecule with electron density in the metal. Also, since the coupling falls off sharply with separation of the adsorbed NO molecules, it appears that this electron density is quite localized. The sense of the positive interaction force constant is such that a simultaneous stretching of the two NO bonds, which leads to a simultaneous compression of the Pt–N bonds, gives a configuration of higher energy than one in which one NO bond is extended and the other compressed.

The wavenumber of the isolated NO molecule suggests that it is adsorbed in a bridging site (*15*) and we have shown it in that way in Figs. 6, 9, and 10. If this is indeed the case, two adjacent adsorbed NO molecules are bonded to a common Pt atom which may account for the large interaction force constant. The difference between the splitting we observed and that observed in inorganic complexes suggests that the chemical binding of NO to a bulk Pt surface is different from that found in essentially covalent inorganic complexes.

The model we have used to explain our observations differs from that adopted by Thiel *et al.* (*16*) to explain very similar observations in their study of the EELS spectrum of NO on Ru, and the effect on the NO spectrum of coadsorbing CO along with the NO. However, it is clear that, with slightly different force constants, our model would explain thier results. The question must remain open as to which model is correct but we believe that planned studies at higher resolution and higher sensitivity will allow us to seek some of the weaker features calculated in Table 2 and allow us to choose between the two models.

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11. In ordinary circumstances one would not expect ΔH to be a strong function of temperature and therefore higher temperature would favor the more entropic form. It is therefore surprising that the higher temperatures favor the longer "chains" of adsorbed NO molecules. However, it is quite possible that the short chains are better ordered since we cannot distinguish the presence of kinks and bends with the present model.

12. We have calculated the dipole–dipole coupling of two NO oscillators with the assumed dipole transition moments and find that this gives a splitting of the order of 1 cm^{-1} between two NO stretching modes.

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