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# An Infrared Study of the Adsorption of NO on Silica-Supported Platinum over a Wide Temperature Range

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Infrared spectroscopy has been used to study the adsorption of NO over a wide temperature range (130 to 473 K) on high- and low-area silica-supported platinum. Three distinct states of adsorbed NO have been detected, called A, B, and C, having NO stretching frequencies near A-1785, B-1690, and C-1620 $cm^{-1}$. The A state, which is favored at ambient temperatures (325 K in the ir beam) has been assigned to linear PtNO whereas the C state, which is relatively more important at low coverages at 325 K, or during heating to 473 K, has been attributed to bent PtNO, possibly at step or kink sites where electron donation to the nitrosyl would be expected to be more facile. The B state is most populated at low temperatures (~140 K) and during warm-up to 325 K this irreversibly converts to the A and C states. The B state is also more populated at 325 K in the presence of gas-phase NO, it partially changes to the A and C states following evacuation, and has been assigned to a weakly held form of NO on an unspecified Pt site. On high-area $Pt/SiO_2$ samples a slight degree of dissociation of NO occurs at high surface coverages, giving rise to a new PtNO band at 1710 $cm^{-1}$ which has also been attributed to linear PtNO on a partially oxidized Pt surface. Heating adsorbed NO from 325 to 500 K results in the near quantitative conversion to gaseous $N_2$ and adsorbed oxygen. Finally, the spectra observed in this work are similar to those which have been previously reported using electron energy loss spectra (EELS) for NO adsorbed on Pt(110) or using infrared reflection absorption spectra (IRRAS) for NO on polycrystalline Pt foils but are different from that of NO on Pt(100) or Pt(111).

The vibrational spectrum of NO adsorbed on platinum has been extensively studied. Electron energy loss spectra (EELS) of NO on various single-crystal surfaces have been obtained by several groups (*1–5*). Infrared reflection absorption spectra (IRRAS) of NO on both single crystal and polycrystalline surfaces have been reported by Overend *et al.* (*6–10*) and Hayden (*1*), and transmission ir spectra using supported Pt catalysts have been published by Brown and Gonzalez (*2*), Primet *et al.* (*13*), Ghorbel and Primet (*14*), De Jong *et al.* (*15*), and by Fang and White (*16*). The adsorption of NO on Pt has also been studied many times using nonvibrational techniques [representative references in 1981–1983 include (*17–22*)].

The vibrational spectra reported have been quite complex, generally exhibiting two bands due to an NO stretching mode between 1800 and 1400 $cm^{-1}$, the relative intensities of which are a function of surface coverage, and the frequencies of which depend on the type of Pt surface used (polycrystalline bulk Pt, single-crystal Pt or supported Pt). Moreover, the spectra also vary according to the temperature of adsorption, the pressure of NO in contact with the surface, or the pretreatment conditions of the catalyst. Generally speaking, a high-frequency band (1700–1820 $cm^{-1}$) which has been most prominent at high surface coverages has been assigned to NO adsorbed as a linear species, whereas the low-frequency band (1400–1660 $cm^{-1}$) which is relatively

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more prominent at low surface coverages, has been assigned to NO adsorbed either in a bent configuration or as NO bridge bonded to two Pt atoms.

In most of the work involving bulk Pt samples under UHV conditions, the NO adsorption has been carried out initially at low temperature (~100 K) and the vibrational spectra obtained were very different from those obtained using supported samples at ambient temperature. In order to probe the reasons for these differences, we have studied, for the first time, the ir spectra of NO adsorbed on oxide-supported platinum over a wide range of conditions of temperature (130 to 473 K) and pressure. Silica was used as the support since it is well known that this material is relatively unreactive vis-à-vis NO adsorption. We have also briefly examined the effect of metal surface area on the spectra. Our results show that the variability of the spectra of NO on Pt depends much more on the temperature of adsorption than on the spectroscopic technique used to study this system, or on the crystal face examined, except in the unique case of the Pt(111) surface.

## EXPERIMENTAL

Two types of catalyst sample, termed high area (HA) and low area (LA) were used in this work. Both were prepared by impregnating dry Cab-O-Sil silica (HS-5 grade, 320 $m^2g^{-1}$) with $H_2PtCl_6$ dissolved in anhydrous acetone. In both cases, 200 mg of the dry $H_2PtCl_6/SiO_2$ catalyst were pressed into disks, 25 mm in diameter, and the reduced catalysts contained 16.2% Pt by weight. The reduction procedure at 673 K in $H_2$ for the high-area sample has been described (*23, 24*), whereas the low-area sample was precalcined in air at 350°C for 1 h prior to reduction.

Infrared spectra were obtained using a modified Perkin–Elmer 13G presample chopped ratio-recording spectrometer. Because the silica background changes appreciably in the region 2000–1300 $cm^{-1}$ (below 1300 $cm^{-1}$ the silica is totally absorbing), a $SiO_2$ disk was placed in the reference beam of the spectrometer. This disk, in its own cell, had been degassed at 673 K under vacuum and gave a nearly perfect cancellation in the spectral region of interest, although a sloping background still persisted because of the differing scattering characteristics of the two samples. We have previously determined that the real sample temperature under ambient conditions is about 325 K for "black" supported metal samples in this spectrometer, under vacuum conditions (*24, 25*).

The cell used for ambient-temperature studies has been described (*23*): its volume was 300 ml so that a dose of 1 Torr corresponds to the addition of 16 $\mu$mol of gas or 100 $\mu$mol $g^{-1}$ of $Pt/SiO_2$. The variable-temperature cell which was used for low-temperature measurements has also been described (*26*) and spectra were recorded after the following sequence: cooling with a slush bath in the cell's Dewar in the presence of 10 Torr of He, evacuation of He, addition of a dose of NO, readdition of He, placing the cell in the ir beam.

The cell used for variable-temperature studies in the range 325–673 K simply consisted of a 10-cm-length Pyrex tube, 32 mm i.d., which had an epoxy-sealed IRTRAN 2 window at one end and a Viton-A O-ring-sealed polycrystalline $BaF_2$ window at the other end with a compression fitting to hold the assembly together. A single vacuum attachment was at one end of the cell and the sample disk was mounted in the middle of the cell which was surrounded by a Nichrome wound furnace of about 7 cm length. Temperatures were measured with a sheathed thermocouple in the furnace windings and all temperatures reflect the furnace temperature which will certainly differ from the actual sample temperature.

The microbalance experiments were carried out using a Sartorius Model 4433 instrument ($10^{-7}$ g sensitivity). Pressure measurements were made with a McLeod gauge on a system with a total volume of

2.3 liters. The 50-ml-volume Hg-filled McLeod gauge was isolated from the main system during all processing and was only exposed to the system for final pressure measurements during pyrolysis experiments. The maximum quantity (mg) of hydrogen (300 K), oxygen (300 K), and nitric oxide (325 K) irreversibly adsorbed per gram of the high-area catalyst was: $H_2$ = 0.248; $O_2$ = 3.94; NO = 5.54. On the low-area catalyst, $O_2$ chemisorption corresponded to 1.54 mg per g of catalyst.

Of the order of 20 different high-area catalyst samples were used in this work and each catalyst was regenerated many times ($H_2$ at 673 K) for additional use. Our spectra were very reproducible. Fewer experiments were carried out using low-area samples since our objective was simply to compare the spectra, but these results were equally reproducible.

## RESULTS

The infrared spectrum of NO adsorbed at 325 K on the high-surface area sample as a function of dosage is shown in Fig. 1. These spectra showing an intense band near 1785 $cm^{-1}$ (which we call band A) and a weaker band near 1620 $cm^{-1}$ (band C) have been observed by others under similar reaction conditions using silica or other oxides as a support (*12–16*), albeit not as intense as those shown in Fig. 1. We also observed a weak shoulder near 1690 $cm^{-1}$ (band B), and at the highest coverage an additional shoulder appeared at 1710 $cm^{-1}$ (band B′).

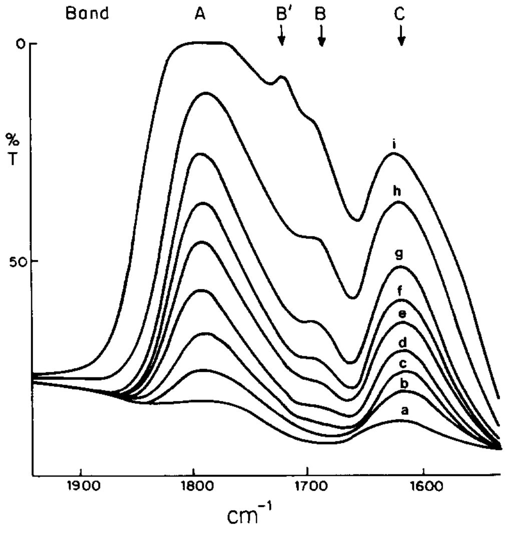

FIG. 1. Infrared spectra of NO on high-area Pt at ambient temperature (325 K). In each case the indicated dose of NO (μmol per gram of sample) was added for about 30 min and the cell was evacuated for 10 min prior to recording the spectrum: (a) background; (b) 1.1; (c) 0.9; (d) 1.5; (e) 1.9; (f) 2.6; (g) 15; (h) 23; (i) 500 (excess).

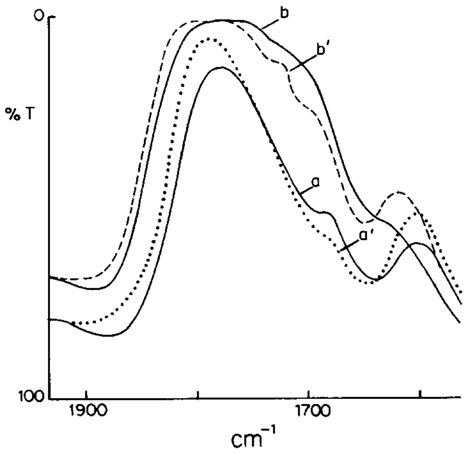

FIG. 2. Solid curves, ir spectra of NO adsorbed on Pt at 325 K before evacuation for (a) 88 μmol $g^{-1}$;' (b) 480 μmol $g^{-1}$. Dashed curves, (a′) and (b′), after evacuation for 10 min.

The frequency of band A was relatively constant with coverage, whereas that of C shifted gradually from about 1600 to 1620 $cm^{-1}$ with increasing coverage. Likewise, band B started out near 1680 $cm^{-1}$ at low coverage. For the same coverage, all peaks shifted by about 35 $cm^{-1}$ to lower wavenumber when 99% $^{15}NO$ was used.

The spectra shown in Fig. 1 were recorded after evacuation for 5 min or longer after each dose of NO was added (longer evacuation times had no effect). However, the spectra were slightly different if the cell had not been evacuated (Fig. 2), the major difference being that before evacuation the A and C bands were less intense and at slightly lower wavenumber than after evacuation, whereas the B band was slightly more intense but at essentially the same frequency.

The spectra of NO adsorbed on the low-area sample were similar to those shown in Figs. 1a to g except that band C was always less intense than for the HA sample, and at saturation the band B′ was not observed. A typical spectrum is shown in the bottom curve of Fig. 3 for near saturation coverage.

When NO was adsorbed on a sample which had been cooled to about 130 or 170 K, a completely different spectrum was observed. The spectra for low- and high-area samples are shown in Figs. 3 and 4, and the most prominent feature is a band near 1680 $cm^{-1}$. However, upon warming to ambient temperature, the spectrum gradually converted to that which was observed following adsorption at ambient temperature and this did not change when the sample was recooled.

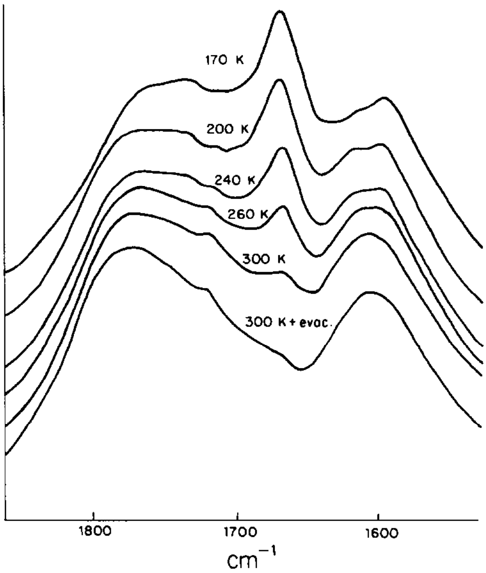

FIG. 4. Same as Fig. 3 but with NO initially adsorbed at 170 K on high-area Pt.

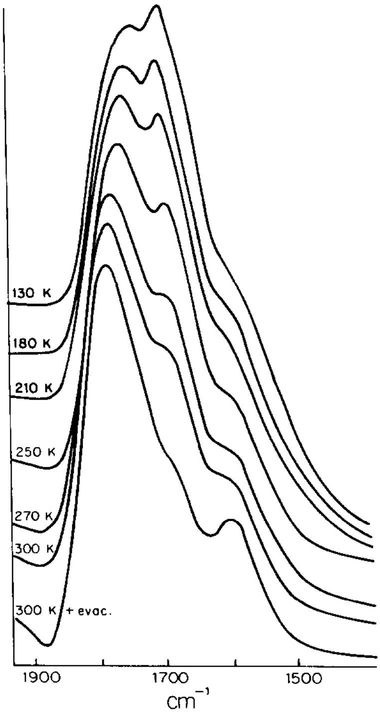

FIG. 3. Infrared of NO adsorbed on low-area Pt at 130 K and the spectral changes during warm-up to ambient temperature under static vacuum. For the bottom curve the cell had been evacuated for 10 min after reaching 300 K.

Other studies have shown that NO dissociates on Pt at temperatures above 473 K, or that NO on Pt at 300 K desorbs and/or dissociates when the sample is heated from 300 K (or lower temperature) up to 473 K. The spectra observed in this work, following adsorption at saturation coverage and heating of the cell during evacuation over a 1-h period from 325 to 525 K, were the reverse of the sequence shown in Fig. 1. That is, band B′ disappeared first, then B, and band C intensified relative to A, and finally the A and C bands disappeared more or less in unison.

Pyrolysis to 500 K as described above, but with no pumping (i.e., into static vacuum at 325 K) lead to the same spectral changes but the gas phase was composed of mainly $N_2$ with traces of NO and $N_2O$. Using the vacuum microbalance during such a pyrolysis sequence under static vacuum, we have verified that within ±5% error that the stoichiometry can be represented as

$$NO_{ads}(325\ K) \xrightarrow{\text{heat to 500 K}} \tfrac{1}{2}N_2 + O_{ads}$$

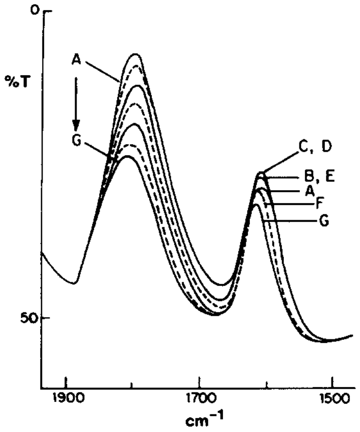

FIG. 5. Excess NO was adsorbed on low-area Pt at 325 K, excess was evacuated for 10 min, and the sample was subsequently heated in 10 min under static vacuum to 443 K. Thereafter, with no change in temperature, successive scans (A–G) were carried out over the indicated spectral region every 2 min.

We show (in Fig. 5) the spectra observed after a relatively rapid heating (~15 min) from room temperature to a registered temperature of 443 K where thereafter the temperature was held constant. Repetitive scans were carried out every 2 min. The spectra clearly show that although the A band steadily decreases in intensity that of the C band first increases, then decreases, in intensity.

In a separate experiment, $^{15}NO$ was adsorbed at saturation coverage and, following evacuation of excess NO, the cell was left under static vacuum for 1 h. The ir spectrum did not change following evacuation or during the 1-h period, but a MS analysis after 1 h revealed that traces of $^{15}NO$ and $^{15}N_2$ in equal quantities were present. The quantity of $N_2$ was about 1% of that which was detected after pyrolysis at 500 K.

## DISCUSSION

Our vacuum microbalance data is consistent with the notion that the mole ratio of chemisorbed $O_2/H_2$ should be 1 : 1; i.e., mass O/mass H = 15.9, as was found by experiment (3.94/0.248). Assuming a 1 : 1 ratio of adsorbed oxygen atoms and surface Pt atoms and that the average area (*27*) of each surface Pt atom is 8.4 Å$^2$ (average for 100, 110, and 111 planes), the resultant areas per gram of platinum are calculated to be 76.9 m$^2$g$^{-1}$ for HA and 30.0 m$^2$g$^{-1}$ for LA. The important point is that the metal surface area of the high-area sample is about 2.5 times greater than that of the low-area sample.

The ir spectra obtained in this work of NO on Pt at ambient temperature (325 K in our case) are similar to those reported by De Jong *et al.* (*15*) who also used a silica support. A similar spectrum was found for alumina-supported Pt (*13, 14*) although the band at 1620 cm$^{-1}$ was partially masked by a band due to NO adsorbed on the support. Brown and Gonzalez (*12*) found a single band at 1760 cm$^{-1}$ for NO adsorbed on a 6% Pt/$SiO_2$ catalyst whereas Fang and White (*16*) using a 2% Pt/$TiO_2$ sample (anatase) reported relatively weak peaks near 1763 and 1700 cm$^{-1}$ and a very weak band near 1617 cm$^{-1}$. Before discussing assignments we will describe the results obtained using macroscopic or bulk Pt samples.

### *Bands A and C*

The vibrational spectra obtained using single-crystal or polycrystalline Pt foils have been very complex and only a brief summary can be given. In most studies the initial Pt-sample temperature was anywhere from 95 to 323 K, and the Pt was then subjected to a heating program with or without recooling to the original low temperature before recording the subsequent spectra. This is an important point because we have also clearly shown (Figs. 1, 3, 4) that the initial temperature of adsorption is a very important parameter. Therefore, given the number of variables we will only attempt to summarize the main conclusions, and the observations relevant to this work.

A. Almost all spectra show, at some coverage, a high-frequency (H) and low-frequency (L) $\nu$(NO) band for NO adsorbed on Pt.

B. Except for Pt(100), L is relatively more intense at low coverage and H at high coverage. At very low or very high coverages, H or L, respectively, are sometimes not observed.

C. For intermediate coverages at low temperature during heating, the H band decreases in intensity and the L band increases. It does not appear to matter whether the sample is subsequently recooled to the original low temperature for recording of the spectra (as also found in this work).

D. For Pt(111), the L band is near 1480 ± 40 $cm^{-1}$, and the H band is near 1710 ±10 $cm^{-1}$.

E. For Pt(100) [5 × 20 or 1 × 1], the L band is always the dominant feature, 1650 ± 40 $cm^{-1}$, although a weak H band at high coverage at 140 K, or for any coverage at 300 K is observed near 1800 $cm^{-1}$.

F. The spectra for NO on Pt(110) or polycrystalline Pt foils are remarkably similar. At high coverage and at 100–160 K, the major single broad band is at 1677–1690 $cm^{-1}$ [Fig. 6e of Ref. (*10*) and Fig. 2 of Ref. (*4*)]. We also observe a major peak (Figs. 3 and 4) in this region for low-temperature initial adsorption. After heating NO on Pt at 100 K to ambient temperature, the EELS spectra show a strong H band at 1770 and a weaker L band at 1620 $cm^{-1}$. In the IRRAS case, heating NO initially adsorbed (10 L exposure) at 160 to 320 K gave rise to a strong L band at 1614 $cm^{-1}$ and a weaker H band at 1767 $cm^{-1}$ (Fig. 8c, Ref. (*10*); i.e., the intensity ratio of the H and L bands was reversed compared to the EELS experiment, and compared to this work, but the authors in Ref. (*10*) acknowledged that there was also adsorbed CO as an impurity).

G. Heating NO on Pt(110) or polycrystalline Pt foil from ambient temperature to 435 K (Fig. 2 of Ref. (*4*)) or 473 K (Fig. 8e of Ref. (*10*)) caused the H band to diminish in intensity at a faster rate than the L band; the latter at some intermediate temperature appeared to intensify. Qualitatively, we found similar behavior (Fig. 5).

The infrared spectra obtained by us are remarkably similar to those obtained under a wide range of conditions of temperature and coverage to those obtained by EELS (*4*) for Pt(110) and by IRRAS (*10*) for polycrystalline Pt foil. The high-wavenumber band (1760–1790 $cm^{-1}$) for NO on these and all other Pt surfaces has always been assigned to linear PtNO (*1–16*) and we concur. However, the low-wavenumber band [1600–1690 $cm^{-1}$, or near 1490 $cm^{-1}$ for Pt(111)] in most of the EELS and IRRAS studies has been assigned to NO adsorbed on twofold bridge sites. It has further been assumed that for steric reasons the bridged form is less favorable at high coverages, thus accounting for observation B above. Exceptionally, Pirug *et al.* (*2*) assigned a band in the region 1615–1660 $cm^{-1}$ for NO on Pt(100) to a bent PtNO species. We believe that a NO frequency in this spectral region (our band C) must be attributed to a bent PtNO since, to our knowledge, no known bridged nitrosyl has an NO stretching frequency above 1550 $cm^{-1}$, let alone in the range 1600–1690 $cm^{-1}$ (*2, 28, 29*). This band is more intense at low coverages relative to the high frequency or A band, and for steric reasons we would also expect the linear species to be favored at high coverages and the bent form at low coverages.

It is perhaps significant that the C state is relatively more populated on the HA sample than on the LA sample, *all other conditions being equal.* If we assume that the HA sample contains more surface Pt atoms with a low coordination number (steps and kinks) than the LA sample, then according to Blyholder (*30*) these atoms would be more capable of donating electrons to a surface species than the highly coordinated Pt atoms in the low index planes. Since it is well known (*31*) that the bent form requires more charge donation from the metal to the nitrosyl than the linear form then the above experimental observation can be reconciled. That step or kink sites are also more populated at low surface coverages has also been demonstrated in recent NO/Pt molecular beam studies (*21, 22*).

Finally, Dunn *et al.* (*10*) considered a model which was independent of the site geometry (bridged or linear) or configuration (linear or bent) for NO on polycrystalline Pt [assumed to be reconstructed Pt(110)]. They showed that the spectral changes with coverage could be accounted for by assuming various degrees of coupling between the vibrational modes of molecules first in linear chains on a Pt(110) surface, and eventually between two-dimensional arrays of these chains. This model certainly provides an interesting alternative interpretation for the spectral changes observed, at least for a single-crystal surface.

### *Bands B and B′*

We have observed a weak shoulder at 1690 $cm^{-1}$ (band B) at all but the lowest coverages at 325 K on the HA and LA samples, and a second weak band (B′) at 1710 $cm^{-1}$ which only appeared at saturation coverages on the HA sample. In a subsequent paper we will present strong evidence (*32*) in support of assigning the B′ band to NO adsorbed on a partially oxidized Pt surface, the oxygen arising from a limited dissociation of NO to $N_2$ and PtO at saturation coverages. De Jong *et al.* (*15*) also reported limited dissociation of NO on $Pt/SiO_2$ at ambient temperatures and recall that we found traces of $N_2$ in the gas phase after saturation adsorption at 325 K. Further, although NO is not reported to dissociate on Pt(111), Pt(110), or Pt(100) at ambient temperature, it does apparently dissociate on surfaces containing steps and kinks (*17, 21, 33*).

We have noted that the B band is relatively more intense at 325 K before evacuation of the cell (even if there was no detectable NO in the gas phase) and that after evacuation its intensity decreases and bands A and C intensify (Figs. 2 and 3). Following NO adsorption on samples which had been precooled to 130–170 K (Figs. 3 and 4) the B band is the dominant spectral feature. During warm-up to 325 K this band irreversibly diminishes in intensity and the A and C bands intensify; the spectrum at 325 K is exactly the same as was observed if the initial adsorption had been carried out at 325 K and it did not change on subsequent recooling.

After warm-up there was no detectable NO in the gas phase and we acknowledge that the decrease in the intensity of band B was greater than the increase in the intensity of the bands A and C. This could be due to differences in extinction coefficients, or, since our low-temperature cell contains many metal parts (*26*) it is possible that if some NO desorbed it could have readsorbed on the cell walls. In addition, bandwidths and peak heights change with temperature, as does the background spectrum of silica in this region. Therefore, the trends noted above cannot be interpreted quantitatively but we believe that data overwhelmingly demonstrates that there are three adsorbed states for NO on $Pt/SiO_2$, two of which (A and C) are stable up to and slightly beyond 325 K, and another (B) which is only appreciably stable at low temperature. State B must correspond to a weakly held form of NO. Its frequency, which is very different from that of gaseous NO (1876 $cm^{-1}$), would suggest that it is assignable to a linear or bent Pt NO and not to physisorbed NO. Further speculation is not warranted.

Our low-temperature spectra and the spectral change observed on warming to ambient temperature are almost identical to those reported in the EELS of NO on Pt(110) [Fig. 2 of Ref. (*4*)]. Further, Dunn *et al.* [Figs. 6e and 8 of Ref. (*10*)] also found a band at 1683 $cm^{-1}$ for NO on a Pt foil at 160 K and observed that on flashing to 320 K (with subsequent recooling to 160 K) this band was replaced by a doublet at 1767 and 1614 $cm^{-1}$. In this case, the intensity ratio of 1767/1614 was approximately the reverse of that observed by us or by Gorte and Gland (*4*), but the fractional coverage was unknown and CO was present as an impurity. Again we conclude that NO on Pt/$SiO_2$ behaves very much as it does on Pt(110) or on bulk polycrystalline Pt.

Finally, the ir spectra of NO on Pt/$Al_2O_3$ (*13, 14*) and Pt/$SiO_2$ (*15*) in the region 1850–1650 $cm^{-1}$ are very similar to ours for the low surface area sample (Fig. 3) in that in addition to the intense A band, a shoulder near 1700 $cm^{-1}$ corresponding to our B band is clearly evident. No comment or assignment of this feature was made in the above studies. On the other hand, Fang and White (*16*) found a relatively more intense B band using 2% Pt/$TiO_2$ and, by analogy with the EELS data they assigned the B band to NO on Pt(111) sites and the A band to NO on Pt(110) sites. We cannot confirm or refute this assignment. However, all of their spectra were recorded with NO present in the gas phase and we have shown that the intensity of the B band is accentuated relative to that of the C band under these conditions.

## ACKNOWLEDGMENTS

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## REFERENCES

*1*. Ibach, H., and Lehwald, S., *Surf. Sci.* **76,** 1 (1978).
*2*. Pirug, G., Bonzel, H. P. Hopster, H., and Ibach, H., *J. Chem. Phys.* **71,** 593 (1979).
*3*. Gland, J. L., and Sexton, B. A., *Surf. Sci.* **94,** 355 (1980).
*4*. Gorte, R. J., and Gland, J. L., *Surf. Sci.* **102,** 348 (1981).
*5*. Gorte, R. J., and Schmidt, L. D., *Surf. Sci.* **111,** 260 (1981).
*6*. Dunn, D. S., Severson, M. W., Golden, W. G., and Overend, J., *J. Catal.* **65,** 271 (1980).
*7*. Dunn, D. S., Golden, W. G., Severson, M. W., and Overend, J., *J. Phys. Chem.* **84,** 336 (1980).
*8*. Golden, W. G., Dunn, D. S., and Overend, J., *J. Catal.* **71,** 395 (1981).
*9*. Severson, M. W., and Overend, J., *J. Chem. Phys.* **76,** 1584 (1982).
*10*. Dunn, D. S., Severson, M. W., Hylden, J. L., and Overend, J., *J. Catal.* **78,** 225 (1982).
*11*. Hayden, B. E., *Surf. Sci.* **131,** 419 (1983).
*12*. Brown, M. F., and Gonzalez, R. D., *J. Catal.* **44,** 477 (1976).
*13*. Primet, M., Basset, J. M., Garbowski, E., and Mathieu, M. V., *J. Amer. Chem. Soc.* **97,** 3655 (1975).
*14*. Ghorbel, A., and Primet, M., *J. Chem. Phys.* **73,** 89 (1976).
*15*. De Jong, K. P., Meima, G. R., and Geus, J. W., *Appl. Surf. Sci.* **14,** 73 (1983).
*16*. Fang, S. M., and White, J. M., *J. Catal.* **83,** 1 (1983).
*17*. Park, Y. O., Masel, R. I., and Stolt, K., *Surf. Sci.* **131,** L385 (1983).
*18*. Mummey, M. J., and Schmidt, L. D., *Surf. Sci.* **109,** 29, 43 (1981).
*19*. Gorte, R. J., Schmidt, L. D., and Gland, J. L., *Surf. Sci.* **109,** 367 (1981).
*20*. Kiskinova, M., Pirug, G., and Bonzel, H. P., *Surf. Sci.* **136,** 28 (1984).
*21*. Campbell, C. T., Ertl, G., and Segner, J., *Surf. Sci.* **115,** 309 (1982).
*22*. Lin, T. H., and Somorjai, G. A., *Surf. Sci.* **107,** 573 (1981).
*23*. Morrow, B. A., and Ramamurthy, P., *J. Phys. Chem.* **77,** 3052 (1973).
*24*. Morrow, B. A., and Moran, L. E., *J. Catal.* **62,** 294 (1980).
*25*. Morrow, B. A., St. Onge, A., and Sont, W., *J. Catal.* **62,** 304 (1980).
*26*. Morrow, B. A., *J. Sci. Instrum.* **43,** 487 (1966).
*27*. Benson, J. E., and Boudart, M., *J. Catal.* **4,** 704 (1965).
*28*. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," 3rd Ed. Wiley, New York, 1972.
*29*. Su, C. C., and Faller, J. W., *J. Organomet. Chem.* **84,** 53 (1975).
*30*. Blyholder, G. J., *J. Phys. Chem.* **68,** 2772 (1964); Blyholder, G. J., and Allen, M. C., *J. Amer. Chem. Soc.* **91,** 3158 (1969).
*31*. Eisenberg, R., and Meyer, C. D., *Acc. Chem. Res.* **8,** 26 (1975).
*32*. Morrow, B. A., McFarlane, R. A., and Moran, L. E., *J. Phys. Chem.*, in press.
*33*. Gland, J. L., *Surf. Sci.* **71,** 327 (1978).