Adsorption of Nitric Oxide on Y-Type Zeolites. A Low-Temperature Infrared Study

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Abstract: Nitric oxide was adsorbed on Cab-O-Sil and on HY, decationated Y, NaY, and CaY zeolites at −190, −150, −130, and −73°. The resulting infrared spectra indicate that three different types of adsorbed species were produced: adsorbed N_2O_2, adsorbed NO, and the products of the disproportionation reaction of NO. One trans and two cis forms of N_2O_2 were found on the surfaces. These were identified by comparing their ir spectra with the spectra of matrix-isolated N_2O_2, and by examining their adsorption properties at different coverages and temperatures. Two adsorbed NO species were observed. They were assigned to coordinately bonded NO^+ and NO^- because of the line position shifts relative to free NO and the binding strength with the surface. The disproportionation of NO was not observed on any zeolite at −190°, but it did occur at higher temperatures. The results suggest that N_2O_2 is an intermediate in the disproportionation reaction but that other factors are also involved.

It is known that at 0° or lower temperatures nitric oxide disproportionates on zeolites to produce N_2O and NO_2.[1] In our early studies of this reaction at −78°, we found that it was reasonable to assume adsorbed N_2O_2 as a reaction intermediate;[2] however, since the ir spectra in that study were taken at room temperature, the adsorbed N_2O_2 was never observed. A direct observation of adsorbed N_2O_2 would help to establish the mechanism for the disproportionation reaction.

Furthermore, the paramagnetic properties of the nitric oxide molecule have been used as a probe to explore the electrostatic and magnetic fields in zeolites.[3-6] It was found that at −196° often only a small fraction of the total NO introduced could be detected by epr techniques. One purpose for the present investigation was to determine the state of the nitric oxide that was not observed by epr techniques.

Among the anticipated species which could be produced by adsorption, the dimer, N_2O_2, has been studied as a solid, liquid, and as individual molecules isolated in an inert matrix.[7-9] It has recently been detected in the gas phase by ir techniques.[10] One might also expect to find the monomer weakly bonded to the surface, since Solbakken and Reyerson[11-13] have shown that a considerable amount of NO is held in a paramagnetic state on silica gel and alumina at temperatures from −92° to 0°.

Experimental Section

High surface area silica and four different forms of Y-type zeolites (NaY, CaY, HY, and decationated Y) were studied. The silica (Cab-O-Sil M-5) was supplied by the Cabot Co. of Boston, Mass. The sodium form of the Y-type zeolite was supplied by the Linde Co. (Lot No. 11007-73). The calcium and ammonia forms of the Y-type zeolites were obtained by exchanging the NaY with the desired cation in a nitrate solution. The exchange procedure was reported in an earlier paper.[5] HY and decationated Y were obtained by degassing NH_4Y to 400 and 650°, respectively. In the formation of HY the ammonium ions decompose, producing NH_3 and a proton which is bound to a lattice oxide ion. Upon subsequently heating the sample to 650°, the resulting decationated Y zeolite is formed as the OH groups are removed as water. Before adsorption, CaY, NaY, and Cab-O-Sil were degassed to 400 or 500°.

Two different cold cells were designed and constructed. The structure of cold cell A is shown in Figure 1. It is essentially a conventional ir cold cell for taking a solid-phase spectrum of a low boiling point compound. The new option here is that a zeolite sample can be degassed inside the cold cell. The cold cell consists of a glass dewar with a copper-to-glass seal and a copper block cooling tip which was soldered onto the seal with silver solder (Englhard silver 301 which contains 72% Ag and 28% Cu). A zeolite paste was spread onto a platinum wire gauze to make a thin sample film (~10 mg/cm²). The platinum wire gauze was pressed against the block by a copper lip with screws to ensure good thermal conductivity between the sample and the heat sink (or source, during degassing). Liquid nitrogen or other coolants were in direct contact with the copper block. For degassing the sample, the light output of two 1-kW projector lamps was focused onto the copper lip and block. The temperature of the copper block was monitored by a (Pt + 10% Rh)-Pt thermocouple. The degassing temperature was controlled by regulating the voltage across the projector lamps. The maximum temperature that could be reached was 490°. The major advantage of this type of cell is that it has a high cooling efficiency. The only bottleneck for thermal conduction is between the sample and the platinum wire.

Cold cell B consists of a fused-quartz degassing arm and an ir cell arm. The sample film on platinum wire gauze was mounted in a stainless steel frame which could be maneuvered back and forth in the cell between the two arms. The ir cell arm was embedded in a styrofoam dewar. During ir measurements the sample compartment of the cell was dipped in liquid nitrogen, but the CaF_2 windows were protected from frost by styrofoam sleeves and two small heating coils. The major advantage of this cell is that a very high degassing temperature can be reached.

The temperature of the samples in both cells A and B was measured by means of a copper–constantan thermocouple which was welded onto the platinum gauze. Ir spectra of NO adsorbed on CaY, NaY, HY, and Cab-O-Sil were taken in cold cell A at −190, −130, and −73°. These temperatures were maintained by using liquid nitrogen, a solid–liquid pentane slush, and a Dry Ice–isopropyl alcohol mixture, respectively. The NO was sprayed on the precooled samples. The ir spectra of the zeolites and Cab-O-Sil were also taken in cold cell B with only liquid nitrogen as the coolant. Since the contact between the glass cell wall and the stainless steel frame was rather poor and the thermal conductivity of stainless

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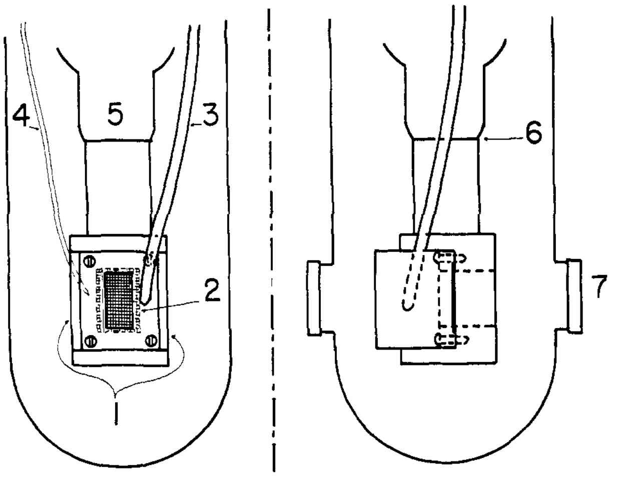

Figure 1. Cold cell A: (1) surfaces for collecting heating radiation, (2) platinum wire gauze, (3) tubing for introducing gas to be adsorbed, (4) (Pt + 10% Rh)–Pt thermocouple, (5) liquid nitrogen reservoir, (6) copper-to-glass seal, (7) CaF_2 windows.

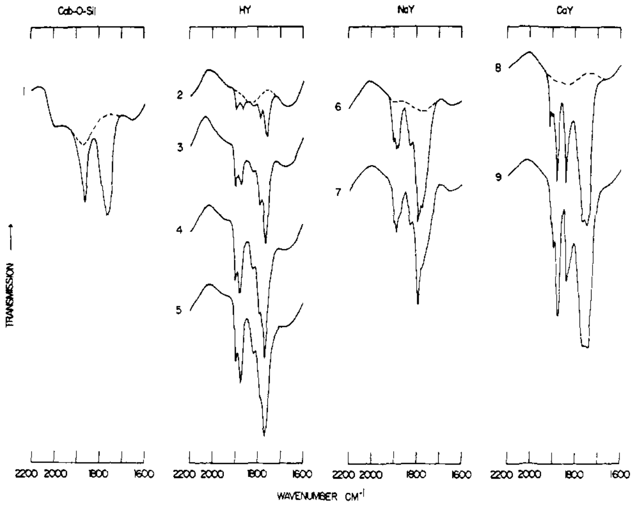

Figure 2. Spectra produced by adsorbing NO at −190°: (1) on Cab-O-Sil; (2, 3, 4, and 5) on HY with increasing quantity of NO adsorbed; (6) on NaY; (7) part of adsorbed species of (6) was evaporated; (8 and 9) on CaY with increasing quantity of NO adsorbed.

steel is small, it took about 1 hr to cool down the sample completely. The NO gas was introduced at about the time when the sample reached −150°. A dead volume between two stopcocks was used to control the amount of gas introduced.

A Beckman IR-12 spectrophotometer was used for the measurements. The programming of the slit width was such that a minimum resolution of 3 cm^{-1} was maintained.

Results

At low temperatures the ir spectra produced by adsorption of NO on Y-type zeolites were very complex. Several species were produced in every Y-type zeolite. The relative concentration of adsorbed species depended on the temperature of the sample, the pressure of NO gas, and the cation in the particular zeolite sample. For some zeolites, a relatively simple spectrum can be obtained with a low NO pressure. The temperature of the sample and the pressure of NO gas were used as variables to resolve overlapping spectra. The unique features of the low-temperature ir spectra after adsorption of NO on zeolites all appeared in the range of 1700–2200 cm^{-1}. In the cases where adsorbed N_2O_3 was produced, ir absorption was also observed in the lower frequency region (to be specific, for NaY they appeared at 1305 and 1550 cm^{-1}, and for CaY they appeared at 1305 and 1570 cm^{-1}). These peaks, which exist in the room-temperature spectra as well, have been analyzed in a previous paper;[2] therefore, they are not shown in the figures and tables of this paper.

(1) Spectra Produced by Adsorbing NO on Cab-O-Sil and Zeolites at −190°. The dotted lines in Figure 2 are spectra of the degassed sample before the adsorption of NO. The positions of the lines in Figure 2 are tabulated in Table I.

Table I. Infrared Absorption Induced by Adsorbing NO on Cab-O-Sil and Y-Type Zeolites at −190°

Substrate	Line positions, cm^{-1}
Cab-O-Sil	1768, 1870
HY	1765, 1790, 1820, 1870, 1890, 1900
NaY	1750, 1775, 1795, 1825, 1880, 1890, 1900
CaY	1750, 1770, 1790, 1845, 1884, 1902, 1917

Curve 1 is a spectrum following adsorption of NO on Cab-O-Sil. The quantity of NO sprayed was about 7 × 10^{-4} mol, but a large portion of it condensed on the copper block and the actual quantity of adsorbed NO was small. A pair of peaks was observed at 1768 and 1870 cm^{-1}.

Curves 2, 3, 4, and 5 are spectra produced by spraying NO on HY. The amount of NO sprayed increased progressively from curve 2 to curve 5. Most of the NO sprayed on HY and the other zeolites was condensed on the sample instead of on the copper block. The amount of NO needed to produce curve 3 was about 7 × 10^{-5} mol. Six lines at 1765, 1790, 1820, 1870, 1890, and 1900 cm^{-1} were observed. The 1890-cm^{-1} line is not completely resolved, but its existence can be inferred from curve 3.

Curve 6 was observed for NaY immediately after 4 × 10^{-5} mol of NO was sprayed onto the sample. Curve 7 is the spectrum of the same sample taken 5 min later. Seven peaks can be seen. They are at 1750, 1775, 1795, 1825, 1880, 1890, and 1900 cm^{-1}. The 1750-cm^{-1} line is not completely resolved. By comparing curves 6 and 7 one can see that the intensity of the 1775- and 1880-cm^{-1} peaks decreased relative to the 1795- and 1890-cm^{-1} peaks during the time lapse.

The spectrum following adsorption of NO on CaY is depicted in curve 8. The amount of NO sprayed onto the sample was about 5 × 10^{-5} mol. The seven peaks observed are at 1750, 1770, 1790, 1845, 1884, 1902, and 1917 cm^{-1}. Curve 9 is a spectrum of the sample with 1 × 10^{-4} mol of NO sprayed on it.

(2) Spectra Produced by Adsorbing NO on Zeolites at −130°. The vapor pressure of NO is higher at this temperature, and its pressure in the cell is completely determined by the adsorption equilibrium. Throughout this series, the pressure of NO was kept low so that only strongly adsorbed species could be seen. The spectra of NO adsorbed on HY, NaY, and CaY are shown in Figure 3, and the positions of peaks are tabulated in Table II.

Curve 1 is the spectrum produced when HY was in contact with 1 Torr of NO gas. Three peaks were produced; their positions are at 1750, 1780, and 1910 cm^{-1}.

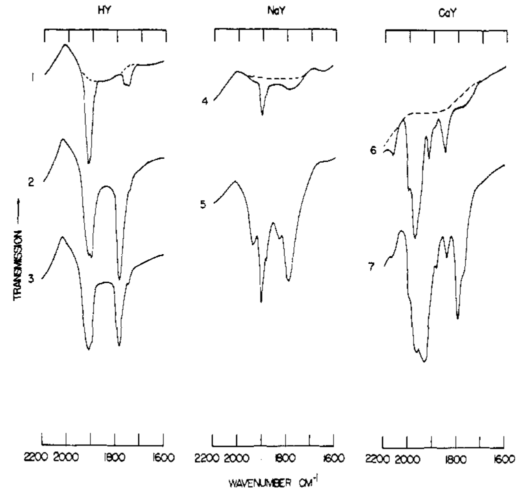

Figure 3. Spectra produced by adsorbing NO on zeolites at −130°: (1) HY in 1 Torr of NO gas; (2) HY in 10 Torr of NO gas; (3) sample warmed to a higher temperature; (4) NaY in 1 Torr of NO gas; (5) NaY in 20 Torr of NO gas; (6) CaY in 1 Torr of NO gas; (7) CaY in 20 Torr of NO gas.

The peak at 1910 cm^{-1} is much more intense than the others. After the pressure of the NO was raised to 10 Torr, a new peak was observed at 1895 cm^{-1} (curve 2). Curve 3 shows that as the temperature of the sample was raised the 1780- and 1895-cm^{-1} peaks started to fade away simultaneously. The 1910-cm^{-1} peak remained to higher temperatures.

Table II. Infrared Absorption Induced by Adsorbing NO on Y-Type Zeolites at −130°

Substrate	Pressure of NO 1 Torr	 10–20 Torr
	Line positions, cm^{-1}	
HY	1750, 1780, 1910	1750, 1780, 1895, 1910
NaY	1900	1750, 1780, 1790, 1825, 1870, 1880, 1900, 1930
CaY	1845, 1917 1970, 2000, 2130	1770, 1790, 1840, 1885, 1935, 1970, 2000, 2140

When NaY was in contact with 1 Torr of NO, the spectrum shown in curve 4 was observed. The major peak is at 1900 cm^{-1}. After the pressure of NO was raised to 20 Torr, more peaks were produced, as shown in curve 5. The positions of the peaks are at 1750, 1780, 1790, 1825, 1870, 1880, 1900, and 1930 cm^{-1}. The 1930-cm^{-1} peak grew with time, and it did not disappear even after the sample was warmed up to room temperature. The 1930-cm^{-1} peak together with peaks at 1550 and 1305 cm^{-1} (observed but not shown in the spectrum) are due to adsorbed N_2O_3.[2]

Curve 6 is the spectrum produced when CaY was in contact with 1 Torr of NO. The peaks are at 1845, 1917, 1970, 2000, and 2130 cm^{-1}. The 1970-cm^{-1} peak grew with time. At a pressure of 20 Torr of NO, the peaks were at 1770, 1790, 1840, 1885, 1935, 1970, 2000, and 2140 cm^{-1} (curve 7). The 1935 cm^{-1} peak grew at the expense of the 1970-cm^{-1} peak. As the sample was warmed up to room temperature, every peak faded away except the one at 1935 cm^{-1}.

(3) Spectra Produced by Adsorbing NO on Zeolites at −73°. At this temperature, only CaY under high NO pressure produced an ir absorption peak which was not observed in the room-temperature spectra reported in the earlier study.[2] As shown by curve 1 of Figure 4, for CaY under 140 Torr of NO a peak was produced at 1788 cm^{-1}. The broad features at the higher frequency are due to gas-phase NO and adsorbed N_2O_3. Curve 2 is the spectrum of NaY under 430 Torr of NO. No peak in the 1788-cm^{-1} region was produced.

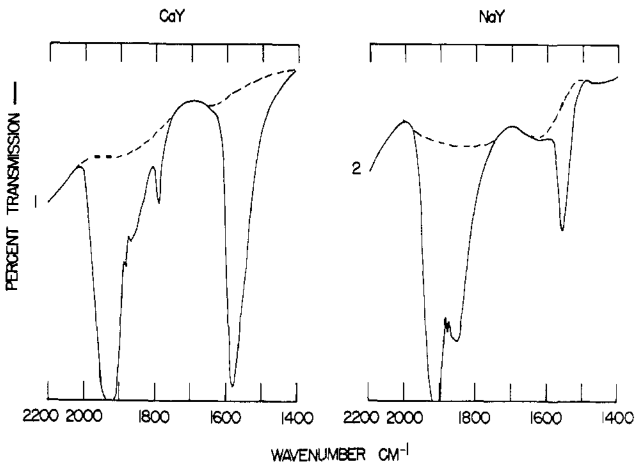

Figure 4. Spectra produced by adsorbing NO on zeolites at −73°: (1) CaY in 140 Torr of NO; (2) NaY in 430 Torr of NO.

At −73° with high NO pressure, the disproportionation proceeded very rapidly. In all the spectra taken, a strong N_2O_3 absorption was the dominating feature. It is possible, therefore, that weak lines could be masked by the strong N_2O_3 absorption in the region around 1900 cm^{-1}.

(4) Spectra Taken with Cold Cell B. The cold cell B was constructed mainly because the preparation of decationated Y required degassing the NH_4Y to 650°, which is beyond the limit of cold cell A. HY, decationated Y, NaY, and CaY were studied in cold cell B. The NO was introduced when the sample was approximately at −150°. The spectra obtained are presented in Figure 5, and the positions of the lines are tabulated in Table III. Spectra are here recorded in absorbance, since some lines are better defined in this mode and the line intensity is linearly proportional to concentration.

Table III. Infrared Absorption Induced by Adsorbing NO on Y-Type Zeolites Near −150°

Substrate	Line positions, cm^{-1}
HY	1770, 1790, 1890, 1900
Decationated Y	1730, 1795, 1840, 1900
NaY	1790 (with br sh down to 1740) 1825, 1900 (with br sh down to 1870)
CaY	1555, 1750, 1770, 1850, 1890, 1917, 1970 2000, 2150

Curve 1 is the spectrum produced by adsorption of NO on HY. The main features are the 1770-, 1790-, 1890-, and 1900-cm^{-1} peaks. Curves 2, 3, and 4 are spectra of decationed Y with different amounts of NO adsorbed on the surface. The peaks at 1730, 1795, and 1900 cm^{-1} all grew with increasing amounts of NO, but there were no simple proportional relationships between them. There is also a small peak at 1840 cm^{-1}.

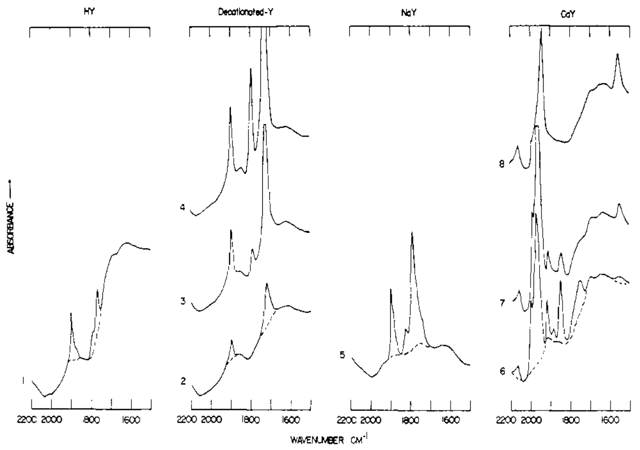

Figure 5. Spectra produced by adsorbing NO on zeolites at $-150°$: (1) on HY; (2, 3, and 4) on decationated Y with NO dosage increasing progressively; (5) on NaY; (6, 7, and 8) on CaY with sample temperature raised slowly.

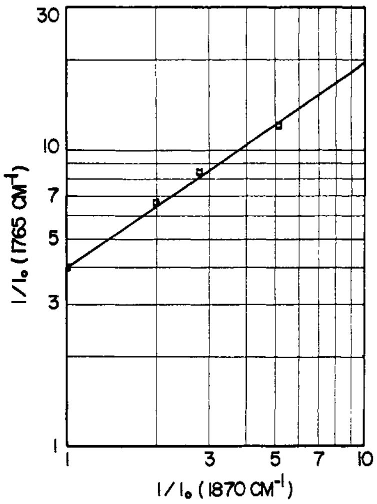

Figure 6. Intensity correlation of 1765 cm^{-1} *vs.* 1870 cm^{-1} peaks which are due to *cis*-N_2O_2 species adsorbed on HY.

The spectrum observed following adsorption of NO on NaY is shown in curve 5. This spectrum has the same set of lines as curve 6 of Figure 3, but the relative intensities are different, The 1790-, 1825-, and 1900-cm^{-1} lines can be seen clearly, but the 1750-, 1775-, 1885-, and 1890-cm^{-1} peaks are not resolved.

Curve 6 is the spectrum observed for CaY following NO adsorption. The peaks are at 1750, 1770, 1850, 1890, 1917, 1970, 2000, and 2150 cm^{-1}. The 1750- and 1770-cm^{-1} lines are not well resolved. As time elapsed the 1970-cm^{-1} line grew at the same rate as the 2245-cm^{-1} line (not shown, but due to adsorbed N_2O produced by the disproportionation reaction of NO). Curve 7 shows that soon after emptying out the liquid nitrogen, the peaks at 1750, 1770, 1850, 1890, and 1917 cm^{-1} all diminished, but the 1970-cm^{-1} peak was not changed. Curve 8 shows that as the sample warmed up the 1935- and 1555-cm^{-1} peaks grew at the expense of the 1970-cm^{-1} peak.

Discussion

Assignment of the Ir Absorption Peaks. The infrared absorption produced by adsorbing NO on zeolites at low temperature can be attributed to three groups, *i.e.*, adsorbed N_2O_2, adsorbed NO, and products of the disproportionation reaction of NO. Basically, the assignments have been made in the following manner. Those peaks coming in pairs with their absorption positions near to those of matrix-isolated *cis*-N_2O_2 are assigned to *cis*-N_2O_2; those lone peaks near 1750 cm^{-1}, which are near to the absorption band of matrix isolated *trans*-N_2O_2, are assigned to adsorbed *trans*-N_2O_2. In principle, the peaks in the 1750-cm^{-1} region could also be assigned to NO molecules which are strongly bonded to the surface;[11] however, since the peaks only existed at temperatures below $-130°$, the species must be very weakly held on the surface. The possibility of a strongly bonded species is thus ruled out. Other peaks, identified in the previous study,[2] are due to the products of the disproportionation reaction. The remaining ones are assigned to adsorbed NO. The justification for this will be further discussed in subsequent sections.

(1) Lines Due to Adsorbed N_2O_2. In an inert matrix, at liquid helium temperatures, isolated N_2O_2 exists as one trans form and two cis forms. The *trans*-N_2O_2 has only one adsorption peak in the midinfrared region, and it is at 1764 cm^{-1}. One cis species absorbs at 1785 and 1870 cm^{-1}, whereas the other absorbs at 1776 and 1870 cm^{-1}. All bands have rather narrow line widths. At higher temperatures, N_2O_2 exists in an aggregated form for which the absorption lines become broad. Their positions are at 1768 and 1876 cm^{-1}.[9]

The form of the species produced on the surface very much depends on the properties of the substrates. On relatively inert Cab-O-Sil, the N_2O_2 spectra could only be observed at $-190°$; both the position and the line width of the spectra shown in curve 1 of Figure 2 resemble those of the aggregated N_2O_2 in the inert matrix.

In zeolites the situation was more complex. As one can see from the data of the last section, as long as the quantity of the sprayed NO was small, many relatively narrow lines were formed. Obviously, on the active surface N_2O_2 was adsorbed as individual molecules even at much higher temperatures than 4°K. In HY at $-190°$, among six peaks produced four of them appeared in pairs. We assigned the 1765- and 1870-cm^{-1} lines to adsorbed *cis*-N_2O_2 species A, and the 1790- and 1890-cm^{-1} peaks to adsorbed *cis*-N_2O_2 species B. Species A and B are due to *cis*-N_2O_2 adsorbed either on different types of sites or the same type of sites but with different configurations, thus the bond strengths and angles of *cis*-N_2O_2 are slightly different. The letters A and B do not have particular implications.

Although the 1765-cm^{-1} line is close to the absorption position of matrix-isolated *trans*-N_2O_2, it is still assigned to a cis species, since the growth patterns of the 1765- and 1870-cm^{-1} peaks correlate quite well. In a spectrum, if two peaks belong to the same species, their transmission should obey the following equation

$$\ln I/I_0 = (\epsilon/\epsilon') \ln I'/I_0'$$

Here I/I_0 is the transmission of one peak, I'/I_0' is the transmission of the other peak, and ϵ/ϵ' is the ratio of their extinction constants. In other words, on log–log paper a plot of the transmission of peak 1 *vs.* the transmission of peak 2 will give a straight line. Figure 6 is such a plot for the peaks at 1765 and 1870 cm^{-1}, and a straight line is obtained. The data for this plot were taken from curves 2, 3, 4, and 5 of Figure 2.

The correlation between the 1790- and 1890-cm^{-1} bands is not obvious in the $-190°$ spectra. Owing to serious overlap, the 1890-cm^{-1} line is virtually unseen for high NO coverages. At $-130°$, however, the relatively unstable species A cannot form on HY, and the evidence for the existence of the adsorbed *cis*-N_2O_2 species B is more obvious. Though the overlap between the 1895- and 1910-cm^{-1} peaks prevents one from making an intensity plot of the 1780-cm^{-1} peak *vs.* the 1895-cm^{-1} peak, it is quite clear from comparing curves 1, 2, and 3 of Figure 5 that these two peaks grow and fade together.

It was observed that the line positions of the peaks change slightly for samples at different temperatures. For example, on HY the *cis*-N_2O_2 species B absorbs at 1780 and 1895 cm^{-1} at $-130°$, but the same species absorbs at 1790 and 1890 cm^{-1} at $-190°$. Such a shift may partly be due to the multilayer adsorption. Since $-190°$ is well below the normal boiling point of $-152°$ for NO, it is conceivable that multilayer adsorption occurred on the surface at larger NO concentrations. Thus the environment of N_2O_2 adsorbed at $-190°$ and at $-130°$ would be different. Indeed, the 1765- and 1870-cm^{-1} peaks could be due to a second layer of condensed *cis*-N_2O_2. In some cases, the difference in the line position at different temperatures may partly be due to the overlap of several lines. The apparent peak position then depends on the relative intensity of the various lines.

The spectra produced by adsorption of NO on NaY, CaY, and decationated Y are basically the same as that for HY. The only difference is that some of the lines were very close to each other for NaY, CaY, and decationated Y; hence, the spectra were less well resolved than in the HY case.

In NaY for the spectra recorded at $-190°$, the 1750-cm^{-1} line is assigned to adsorbed *trans*-N_2O_2. The 1775- and 1880-cm^{-1} lines are assigned to adsorbed *cis*-N_2O_2 species A, and the 1795- and 1890-cm^{-1} peaks are assigned to adsorbed *cis*-N_2O_2 species B. The covariance of the intensity for a pair of lines due to adsorbed *cis*-N_2O_2 can be clearly seen from curves 6 and 7 of Figure 2.

In CaY as in NaY the 1750-cm^{-1} line is assigned to the adsorbed *trans*-N_2O_2. The 1770- and 1884-cm^{-1} pair along with the 1790- and 1902-cm^{-1} pair are assigned to the adsorbed *cis*-N_2O_2 species, A and B. The covariance of the intensity of the lines in the pairs can be followed in curves 8 and 9 of Figure 2. The most interesting feature about CaY is that at high NO pressure *cis*-N_2O_2 can exist on its surface up to $-73°$. In curve 1 of Figure 4, one can see that a peak was produced at 1788 cm^{-1} under 140 Torr of NO. The high-frequency counterpart of this peak is completely covered by the spectra of products from the disproportionation reaction and the NO gas. No adsorbed N_2O_2 was observed in the other Y-type zeolites at $-73°$.

Decationated Y was only studied following adsorption at $-150°$. The most distinguishing feature of the spectra produced by adsorbing NO on decationated Y is a strong absorption at 1730 cm^{-1}. This position is relatively far away from the observed absorptions of the matrix-isolated and the zeolitic *cis*-N_2O_2. In addition, no equally shifted high-frequency line was observed in spectra 2, 3, and 4 of Figure 5. Hence, the line at 1730 cm^{-1} cannot be assigned to an adsorbed *cis*-N_2O_2. Since the 1730-cm^{-1} line disappeared quickly as the temperature of the sample was raised, the species responsible for it was weakly held on the surface. It appears most probable that it is due to the adsorbed *trans*-N_2O_2. The 1795-cm^{-1} line and a portion of the 1900-cm^{-1} line are assigned to the adsorbed *cis*-N_2O_2 species B. From curves 2 and 3 of Figure 5 one can see that the 1900-cm^{-1} line actually formed before the appearance of the 1795-cm^{-1} line, but the latter grew more rapidly and surpassed the former. As one can see from curve 2, Figure 3, for the HY sample the lines due to adsorbed NO and the high-frequency line of *cis*-N_2O_2 are so close to each other that their separate existence is just barely detected. It is conceivable that in decationated Y they become completely unresolved. We believe that the 1900-cm^{-1} peak of decationated Y has two components. One is due to adsorbed *cis*-N_2O_2, the other one is due to the adsorbed NO which will be discussed in a subsequent section.

(2) Lines Due to Products of the Disproportionation Reaction of NO. The disproportionation reaction did not occur at $-190°$ on any zeolite. The ir absorption of N_2O, which is a sure sign of the occurrence of the disproportionation reaction, started to appear only after the liquid nitrogen was removed and the sample was warmed. The reaction proceeded readily on CaY at -150, -130, and $-73°$ and on NaY at -130 and $-73°$. No significant reaction was detected in HY under all the conditions used. For decationated Y, which was only studied at $-150°$ and under low coverage, no significant reaction was observed.

The disproportionation reaction produced adsorbed N_2O, N_2O_3, NO_2^+, etc. The ir absorption of these species has been reported in detail in the previous paper[2] and only a small fraction of those known lines are shown here. In spectra reported here the absorption at 1930 cm^{-1} is due to adsorbed N_2O_3 on NaY, and the absorption at 1555 and 1935 cm^{-1} is due to adsorbed N_2O_3 on CaY.

For CaY at low temperatures new products were found. In curve 6, Figure 3, one may observe that at $-130°$ there was a peak at 1970 cm^{-1} which grew along with the 1935-cm^{-1} peak of adsorbed N_2O_3. At $-150°$, the 1935-cm^{-1} peak did not appear, but the 1970-cm^{-1} peak, along with the absorption due to adsorbed N_2O (at 2245 cm^{-1}), grew with time (curves 6 and 7, Figure 5). We take the above observation as evidence that the 1970-cm^{-1} peak is a product of the disproportionation reaction. The 1970-cm^{-1} peak does not have a counterpart in all of the ir region which was observed (from 1350 to 3800 cm^{-1}, including the 1500-cm^{-1} region where the adsorbed N_2O_3 has a peak). This rules out the possibility of assigning it to an adsorbed N_2O_3 on a different type of site. Since N_2O has been produced, the 1970-cm^{-1} peak should belong to some adsorbed NO_2, according to the stoichiometry. The 1970-cm^{-1} peak is assigned to NO_2 which is bonded to the surface with partial loss of an electron. This is consistent with the vibrational frequency of NO_2^+ in N_2O_5, which is shifted to much higher wave numbers relative to free NO_2.[14] Curve 8 of Figure 5 shows that after the coolant was removed and the temperature of the sample started to rise, the adsorbed NO_2^+ reacted with the NO gas to produce N_2O_3, *i.e.*, the 1555- and 1935-cm^{-1} peaks increased at the expense of the 1970-cm^{-1} peak. In CaY, two other new peaks appeared at 2000 and 2140 cm^{-1} (curves 6, 7, and 8 of Figure 5), which were only observed at −150° or higher temperatures. As the coolant of the sample was removed, these two peaks disappeared at slightly higher temperatures than the 1970-cm^{-1} peak. These are likewise assigned to NO_2 on still more positive sites.

(3) **Lines Due to Adsorbed NO.** After marking away those lines due to adsorbed N_2O_2 and products of the disproportionation reaction, there are two relatively weak lines left in each spectrum upon adsorption of NO on the zeolites at −190°. Their positions are 1845 and 1917 cm^{-1} for CaY, 1825 and 1900 cm^{-1} for NaY, 1820 and 1900 cm^{-1} for HY, and 1840 and 1900 cm^{-1} for decationated Y. The growth of these two lines was not related to the rest of the lines in the spectra and they were not related to each other. At −130° in the spectra of HY and NaY the peaks in the 1900-cm^{-1} region grew significantly faster than any other spectral lines. This confirms that the 1825- and 1900-cm^{-1} peaks in NaY and the 1820- and 1900-cm^{-1} peaks in HY are not pairs.

Free NO absorbs at 1870 cm^{-1}, and it is generally recognized that more anionic NO absorbs at lower wave numbers, while more cationic NO absorbs at higher wave numbers.[14-16] The two independent peaks that are formed on zeolites apparently are due to coordinatively bonded nitric oxide which is weakly held at two different sites. The line in the vicinity of 1900 cm^{-1} is due to NO bonded on a relatively positive site such as a cation; the line in the vicinity of 1830 cm^{-1} is due to NO bonded on a relatively negative site such as an oxide ion associated with an aluminum tetrahedra. The latter conclusion is supported by the observation that this peak had the largest intensity in CaY and the smallest intensity in HY. In HY the proton may more effectively balance the negative charge through the formation of hydroxyl groups.

An attempt was made to observe the infrared spectrum of the particular NO that was studied in earlier work by means of epr spectroscopy.[3-5] A maximum spin concentration of 10^{-5} mol/g of zeolite was detected for decationated Y, and for low coverage essentially all of the nitric oxide was in the observed paramagnetic state at −196°. Adsorption of comparable amounts of nitric oxide onto decationated Y in infrared cell B did not produce any detectable infrared peaks. The coordinatively bonded NO having infrared absorption in the region around 1900 and 1830 cm^{-1} is not detected in the epr spectrum. These species may be paramagnetic but held at sites where the crystal-field interaction is weak. This could result in very short relaxation times and a broad spectrum. Indeed, Solbakken suggested that the paramagnetic nitric oxide, observed on alumina by a static technique, was not subject to strong crystal-field perturbations.

Table IV. Infrared Absorption (cm^{-1}) of Adsorbed NO in Y-Type Zeolites

Adsorbed species	Temp of adsorption, °C	Substrate			
		HY	Decationated Y	NaY	CaY
NO^+	−130	1910		1900	1917
	−150	1900	1900	1900	1917
	−190	1900		1900	1917
NO^-	−130			1825	1845
	−150		1840	1825	1850
	−190	1820		1825	1845
trans-N_2O_2	−130	1750		1750	
	−150		1730	1750	1750
	−190			1750	1750
cis-N_2O_2 Species A	−130				1770
					1885
	−150	1770		1770	1780
		1890		1880	1890
	−190	1765		1775	1770
		1870		1880	1884
cis-N_2O_2 Species B	−73				1788
	−130	1780		1780	1790
		1895		1880	1902
	−150	1790	1795	1790	1790
		1890	1900	1890	1902
	−190	1790		1795	1790
		1890		1890	1902
NO_2^+	−130				1970
					2000
					2140
	−150				1980
					2000
					2150

All of the assignments are summarized in Table IV.

Mechanism for the Disproportionation Reaction of NO. In this study there are several interesting observations which may be related to the disproportionation reaction of NO. (1) At −190° no catalytic disproportionation reaction occurred in any one of the zeolites studied. (2) The appearance of adsorbed N_2O_2 is not always accompanied by the disproportionation reaction. In HY, though the adsorbed N_2O_2 was observed in large quantities, the disproportionation reaction was always very limited. (3) *cis*-N_2O_2 was observed on CaY up to −73°. (4) CaY and NaY can catalyze the disproportionation reaction much better at −130 than at −78°. The NO pressure required to obtain the same result at −130° was only one-fifth that at −78°.

The first observation is different from that previously reported by Barrer,[1] who believed the disproportionation reaction of NO to proceed at liquid nitrogen temperature. The reason for the discrepancy is evident when one realizes that in the previous investigation a method was used which could not discriminate between the reaction which occurred at liquid nitrogen temperature and the reaction which occurred during the warm-up of the sample.

Since the reaction rate increased significantly as the sample temperature dropped from −78 to −130°, it seems unlikely that the reaction should become undetectably slow at −190°. We attribute the absence of the disproportionation reaction at −190° to the multilayer condensation. In the condensed phase, NO dimerizes completely to N_2O_2, and the multilayer condensation will limit the contact between adsorbed N_2O_2 and gaseous NO molecules. Thus the oppor-

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tunity for the reaction

$$]\ldots N_2O_2 + NO \longrightarrow]\ldots NO_2 +]\ldots N_2O$$

is limited. Here, it is inferred that adsorbed N_2O_2 is the key intermediate for the disproportionation reaction; however, the adsorbed N_2O_2 on HY did not contribute at all to the disproportionation reaction. This indicates that the function of the zeolite in the catalyzed reaction may be more than just to bring three NO molecules together at one site. The unique ability of certain zeolites to catalyze the reaction may be partly due to the stabilization of N_2O_2 in a particular configuration. At the present time there is still not enough evidence to decide which particular adsorbed N_2O_2 species contributes most to the disproportionation reaction.

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Lanthanide Shift Reagents. A Survey

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Abstract: A quantitative study of the action of trivalent lanthanide chelate complexes of 2,2,6,6-tetramethylheptane-3,5-dione, $Ln(dpm)_3$, Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, on the pmr spectra of 4-vinylpyridine, 4-picoline *N*-oxide, and *n*-hexyl alcohol is reported. Upfield substrate ligand resonance shifts are obtained for the systems involving Pr, Nd, Sm, Tb, Dy, and Ho, while downfield shifts are observed for Eu, Er, Tm, and Yb. A linear dependence of the observed shifts on the $[Ln(dpm)_3]/[\text{substrate}]$ ratio for values of this quantity less than 0.2 is observed. The shift ratios are found to correlate with calculated geometric factor ratios for 4-vinylpyridine, and the signs of the shifts correlate qualitatively with magnetic anisotropy data in the literature, indicating a dipolar origin of the resonance displacements. A survey of the relative proton resonance broadening abilities of the various lanthanide chelates is also presented.

Following the discovery by Hinckley[1] that large isotropic shifts $\Delta\nu^{\mathrm{iso}}$ are produced for the proton resonances of cholesterol when this molecule is placed in solutions of the dipyridinate of tris(dipivaloylmethanato)europium(III), $Eu(dpm)_3(py)_2$,[2] considerable interest has been shown[3–19] in lanthanide "shift reagents."[20] Major discoveries include: (1) the finding that shift reagents cause isotropic shifts in a variety of functional organic molecules including alcohols,[1,3–5,7–9,15,16,18] amines,[3,10,13,15,18] ketones,[3,11,14,18] aldehydes,[3,18] sulfoxides,[6,17] and esters;[12,13,15,18,19] (2) the observation[3] that $Eu(dpm)_3$ is more efficient in effecting such shifts than is $Eu(dpm)_3(py)_2$, presumably owing to the lack of competition with pyridine for coordination sites; (3) the discovery[4] that $Pr(dpm)_3$ causes upfield shifts of larger magnitude than the downfield displacements induced by $Eu(dpm)_3$ and the observation[13] of shifts for substrates in the presence of dpm complexes of Sm, Tb, Ho, and Yb as well; (4) the introduction[10] of the chiral chelate, tris[(+)-3-pivaloylcamphorato]europium(III), a shift reagent for the determination of enantiomeric purity; (5) the observation that certain other lanthanide complexes[4] as well as β-diketonate chelates with less bulky substituents[18,21] than $Ln(dpm)_3$ are inefficient as shift reagents, very likely owing to the lack of a preferred orientation of the substrate molecule when the stereochemical rigidity and the bulky substituents of the chelate rings are absent; (6) the finding[19] that partially fluorinated chelates of a similar variety are superior shift reagents because of propitious solubility and Lewis acidity characteristics.

While the action of shift reagents is generally attributed to a through-space dipolar[22,23] interaction, a through-bond Fermi contact interaction has been considered to contribute in some cases.[5,8] Dipolar shifts are proportional to magnetic susceptibility anisotropy,[23–25]

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