

Electron Spin Resonance Study of Nitric Oxide Adsorption on Linde Type Y Zeolites

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Abstract: Interaction between NO and Linde Type Y zeolites was examined. The zeolites sealed with NO initially exhibit broad, ill-defined esr spectra. On standing at room temperature for several days, the spectra become sharp and well defined, indicating a crystal field modification. The analyses of the resulting spectra revealed a clear dependency upon zeolitic cations, of the lifting of the degeneracy in the NO π orbitals. The origin of the crystal field modification is proposed to be a formation of NO⁺ and NO₂⁻ ions. The proposal has been substantiated by photoinduction of NO₂ in the modified materials, by the effect of introducing NaCl into zeolites, and by reduction of Ni(II)-Y zeolites by NO leading to a formation of Ni(I) ions.

Linde Type Y synthetic zeolite is a crystalline aluminosilicate, the empirical formula of which may be given as Na_x(AlO₂)_x(SiO₂)_y. A representative value of the ratio, x/y , is 1/2.4. The crystal structure of this material has been determined and described by many authors.¹ The well-known "molecular sieve" property is due to the interconnecting channels and cavities outlined by a three-dimensional network of oxygen sharing AlO₄ and SiO₄ tetrahedrons. The Na cations are not directly involved in the network and can be easily exchanged with other kinds of cations. In dehydrated Y-type zeolite these cations are found predominantly at two types of sites, site I and site II (see Figure 1). The cations at site I enjoy an octahedral coordination to six oxygens and are, therefore, well hidden and well shielded. The cations at site II, on the other hand, are coordinated to only three oxygens in a pyramidal form and are displaced into the main zeolitic cavities. Consequently they are not well shielded and create very large electric fields extending into the cavities.

Nitric oxide (NO) is a stable and unique radical. In spite of its unpaired electron, the molecule exhibits no paramagnetism in its ²Π_{1/2} ground state owing to the exact cancellation between the orbital magnetic moment and the spin magnetic moment of the electron. The esr signal of the spin-only paramagnetism should become observable, therefore, if the orbital moment of the electron is quenched, *i.e.*, if the degeneracy among the π orbitals is removed by its environment. One might surmise that the electric field associated with the zeolitic cations might bring about such quenching of the orbital moment. Superoxide ion, O₂⁻, is also a ²Π radical. An esr study of O₂⁻ generated and stabilized within zeolitic cavities showed that its orbital moment is indeed substantially quenched by the cationic field.²

Reported here is the result of our esr investigation of the interaction between NO and Linde Type Y zeolites. Since this work was begun, esr spectra of NO adsorbed on zeolites have been reported by Lunsford³ and by Gardner and Weinberger.⁴ The spectra they observed, however, are not as well resolved as those of NO adsorbed on MgO⁵ and hence hampered a detailed

characterization. Our study has led not only to the observation of a well-resolved esr signal of NO, but also to the discovery of unique crystal field modification resulting from a much stronger interaction between NO and the zeolitic structure.⁶ The origin of the modification is proposed to be a formation of NO⁺ and NO₂⁻ ions. The proposal has been substantiated by photoinduction of the esr signal due to NO₂ within such material, by the effect of introducing NaCl into zeolites, and by reduction of Ni(II)-Y zeolites by NO leading to a formation of Ni(I) ions.

Experimental Section

Laboratory-synthesized iron-free zeolites were used throughout the experiment. Zeolites were activated in esr sample tubes at 500° for 18 hr connected to a vacuum system maintained at 1×10^{-3} mm. A desired amount of NO, monitored by a pressure reading, was then introduced through the vacuum manifold. Hydrated zeolites showed none of the signals described below.

The notation Na-Y will be used to designate Linde Type Y (sodium) zeolite, and Ni (65%)-Y, for example, to designate Linde Type Y zeolites with 65% of the original Na⁺ ions replaced by Ni²⁺ ions through exchange process.

All the esr measurements were done at liquid nitrogen temperature (77°K) with a X-band spectrometer. The microwave frequency locked to the loaded cavity was 9.10 GHz.

Preliminary Observation

At room temperature, freshly activated Na-Y, Ba-Y, and Zn-Y (~0.1 g) sealed with NO gas (~2/3 atm) in Pyrex tubes (2.5 mm i.d. and 200 mm long) appeared white and gave no esr signals. However, when cooled to 77°K, the samples became intensely purple and showed a strong but broad and ill-defined esr signal similar to those reported by Lunsford³ and Gardner, *et al.*⁴ Both the coloration and the signals are attributed to NO molecules whose π -orbital degeneracy has been lifted upon adsorption on the zeolitic cations. It was soon found that, on standing at room temperature for 3~4 days, the signal observable at 77°K became much sharper and in the case of Ba-Y and Zn-Y, even the hyperfine interaction with ¹⁴N nucleus became resolved. It was further found that this process could be hastened either by heating the sample to ~200° or by increasing the amount of NO initially sealed with a given amount of zeolite. Pumping on this "NO-treated" zeolite at room temperature quickly (within 5

(1) See, for example, a review article by J. V. Smith, 2nd International Conference on Molecular Sieve Zeolites, Worcester, Mass., Sept 1970.

(2) P. H. Kasai, *J. Chem. Phys.*, **43**, 3322 (1965).

(3) J. H. Lunsford, *J. Phys. Chem.*, **72**, 4163 (1968).

(4) C. L. Gardner and M. A. Weinberger, *Can. J. Chem.*, **48**, 1317 (1970).

(5) J. H. Lunsford, *J. Chem. Phys.*, **46**, 4347 (1967).

(6) A part of the present report has been presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., 1968.

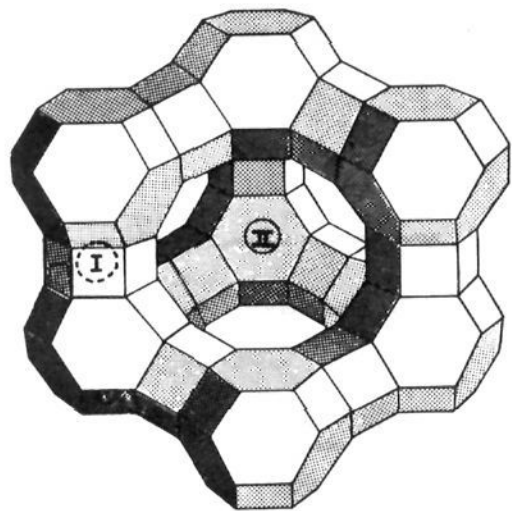


Figure 1. A view into a large cavity of Linde Type Y zeolite. Silicon and aluminum atoms are at the corners of the linked polyhedrons, and oxygen atoms are at the centers of the edges. The cation positions, site I and II, are indicated.

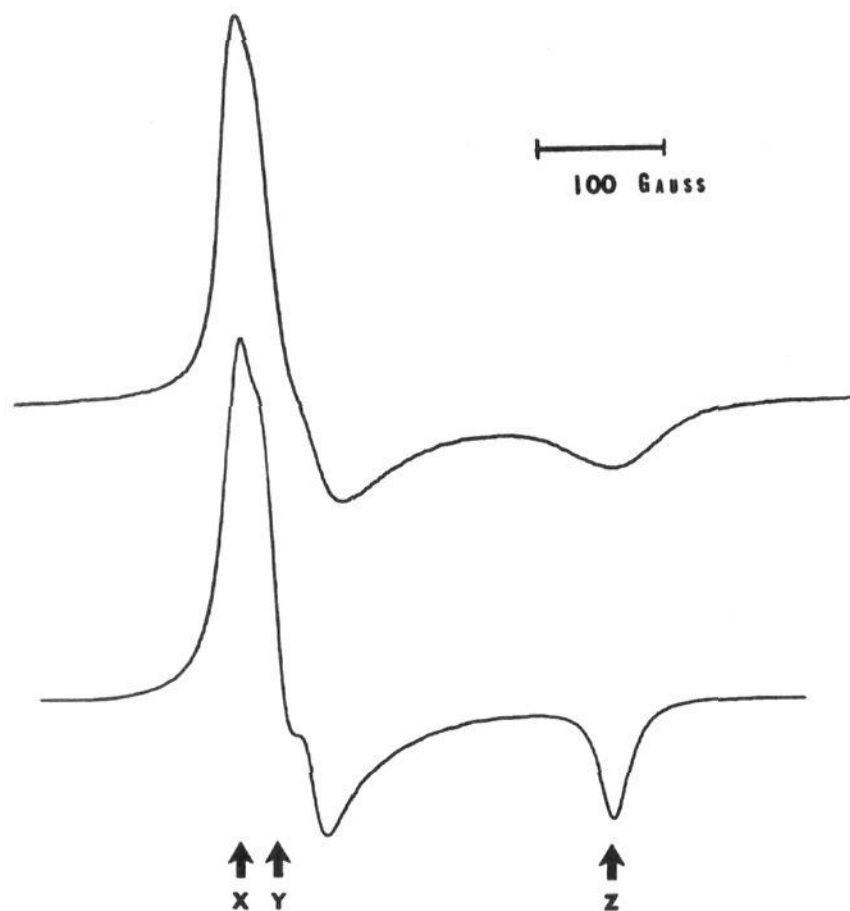


Figure 2. Observed (a, upper) and simulated (b, lower) spectra of NO adsorbed on "NO-treated" Na-Y.

min) produced a sample which no longer showed any esr signal, nor the purple coloration when cooled to 77°K. However, introduction of a small amount of NO into this "NO-treated-then pumped" sample gave immediately the strong, well-resolved esr signal of NO molecules. Clearly, some permanent chemical or physical modification has occurred within zeolites as a result of the NO treatment.

We shall first present the analysis of the sharp NO signals exhibited by the "NO-treated" zeolites. The nature of the NO treatment will be discussed subsequently.

Analysis of the ESR Spectra of NO

Figures 2a, 3a, and 4a show the sharp esr spectra of NO exhibited by NO-treated Na-Y, Ba-Y, and Zn-Y, respectively. The triplet feature, indicated for the *y* components of the Ba-Y and Zn-Y signals, is due to the hyperfine interaction with ^{14}N nucleus ($I = 1$). This

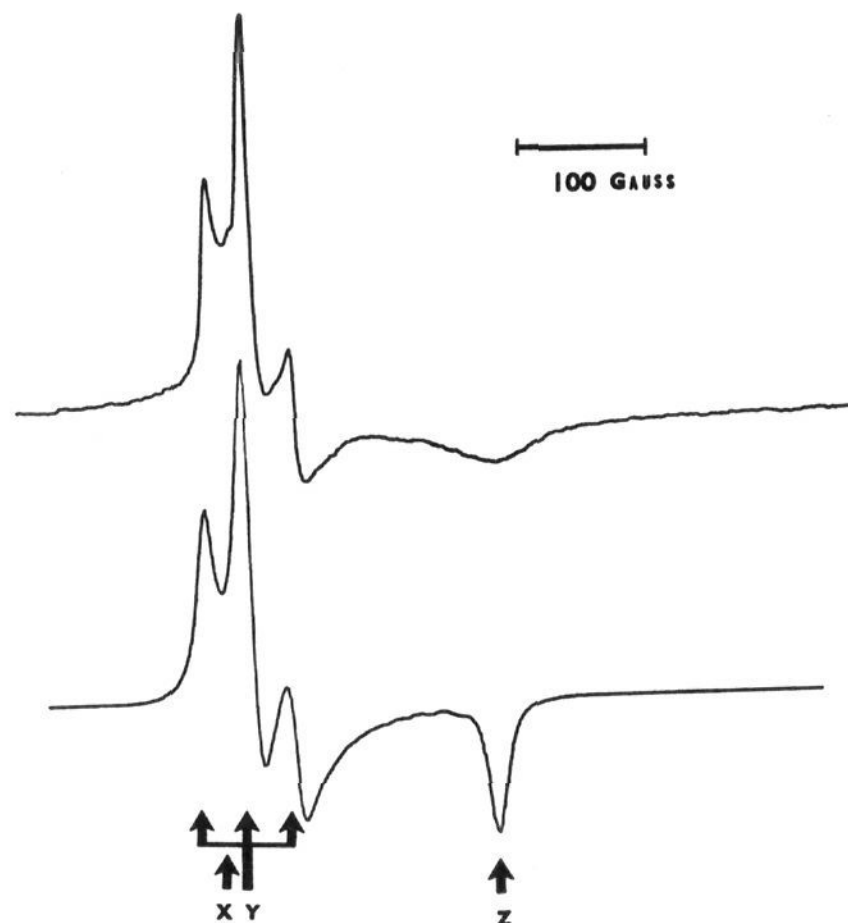


Figure 3. Observed (a, upper) and simulated (b, lower) spectra of NO adsorbed on "NO-treated" Ba-Y.

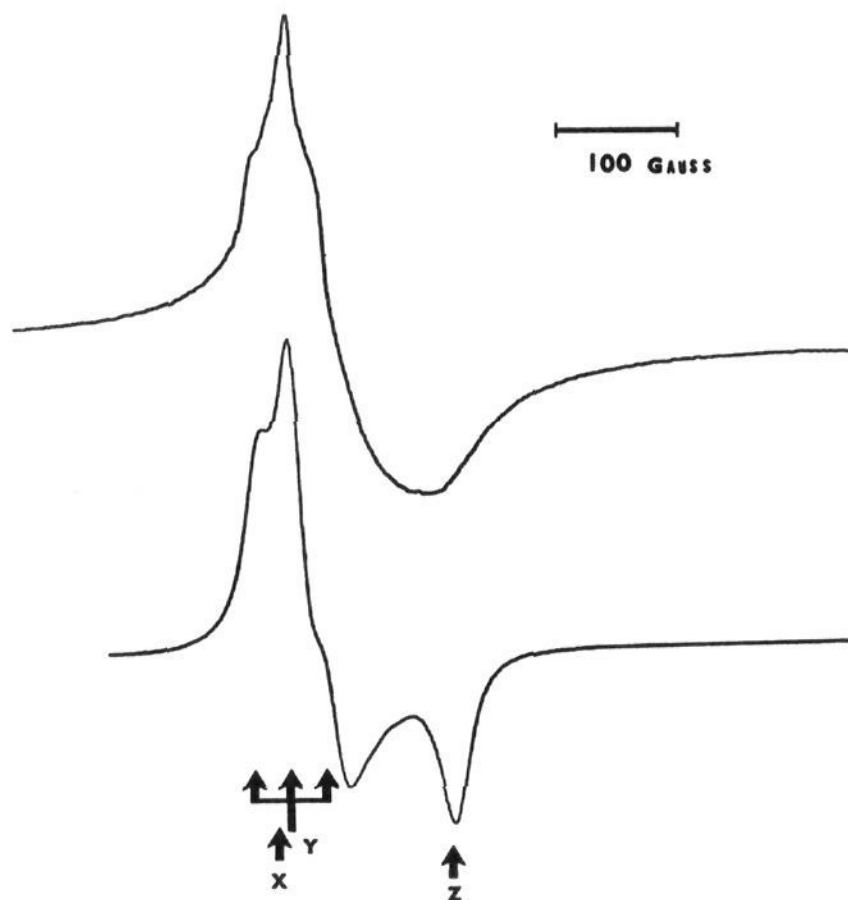


Figure 4. Observed (a, upper) and simulated (b, lower) spectra of NO adsorbed on "NO-treated" Zn-Y.

has been confirmed by the use of NO gas enriched with ^{15}N ($I = 1/2$) isotope (see Figure 5). Apparently, the hyperfine interactions in the directions of other principal axes are too small to be resolved. A high resolution obtained with Ba-Y and Zn-Y can be attributed to: (1) the absence of hyperfine interaction with the cations, and (2) the stronger attraction (hence less thermal motion) by the divalent cations. This difference of affinity is also demonstrated by the fact that the Ba-Y and Zn-Y samples become purple at Dry Ice

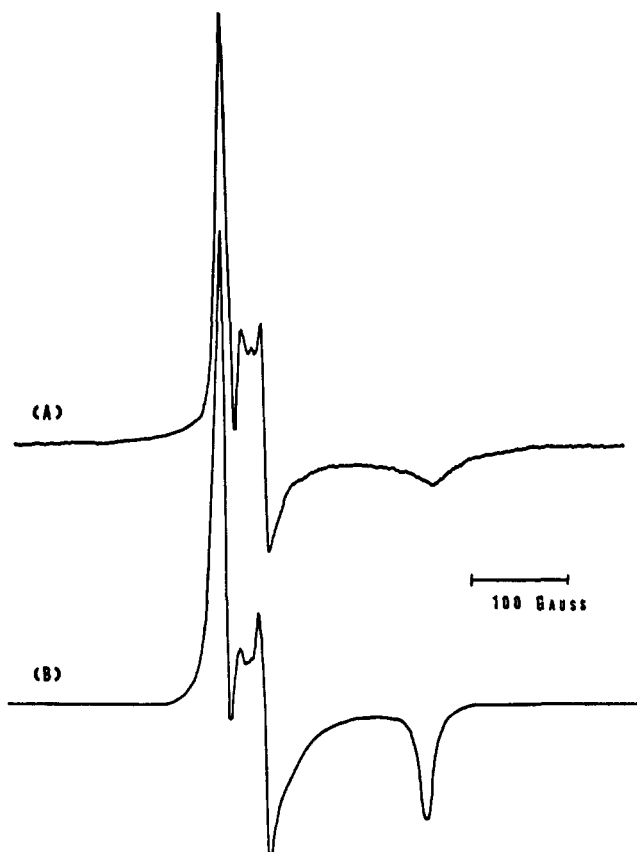


Figure 5. Observed (A) and simulated (B) spectra of ^{15}NO adsorbed on "NO-treated" Ba-Y. The simulation was done by using the set of parameters obtained for ^{14}NO (Table I) making necessary adjustment for the isotope substitution.

temperature (-78°) while the Na-Y sample remains white at that temperature.

Let us say that the unpaired electron of NO molecules adsorbed on zeolitic cations occupies the antibonding orbital π_y^* . Figure 6 shows schematically the valence p orbitals of NO molecules in such a state. Note that the originally degenerate π and π^* orbitals are split into π_x and π_y , and π_x^* and π_y^* orbitals, respectively. The treatment of the spin-orbit coupling interaction, in a manner similar to that employed for the analysis of O_2^- generated in alkali halides,⁷ gives the following expressions for the principal g tensor of NO molecules.

$$g_x = 2.0023 + 2(\lambda/\Delta) - (\lambda/\delta)^2 + (\lambda/\delta)(\lambda/\Delta) \quad (1a)$$

$$g_y = 2.0023 - (\lambda/\delta)^2 - (\lambda/\delta)(\lambda/\Delta) \quad (1b)$$

$$g_z = 2.0023 - 2(\lambda/\delta) + (\lambda/\delta)^3 \quad (1c)$$

Here λ is the spin-orbit coupling constant and is estimated to be ~ 0.01 eV for NO from the interval between its $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states. On the basis of these expressions, the g tensors and the hyperfine tensors were assessed from the observed spectra. The results are tabulated in Table I. Figures 2b, 3b, and 4b are the spectra simulated by a computer program based upon these assignments.⁸ The largest discrepancy between the observed and the simulated spectra is seen, in every case, near the g_z region. The broadness of the observed

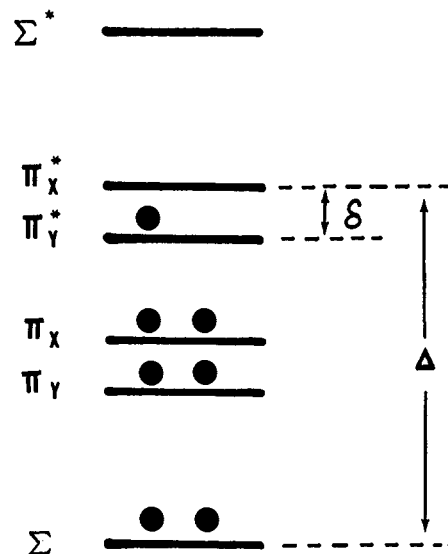


Figure 6. Valence orbitals of NO adsorbed on zeolites.

Table I. g Tensors and the Hyperfine Coupling Tensors (^{14}N) Observed with NO Adsorbed in Linde Type Y Zeolites^a

Zeolites	g_x	g_y	g_z	A_x	A_y	A_z
Na-Y	1.986	1.978	1.83	~ 0	29	~ 0
Ba-Y	1.999	1.995	1.89	~ 0	34	~ 0
Zn-Y	2.000	1.998	1.93	~ 0	30	~ 0

^a The accuracies for the g values are ± 0.001 for g_x and g_y and ± 0.01 for g_z . The hyperfine coupling constants are given in gauss and are accurate to within ± 1 G.

signal in this region, we believe, is not due to the unresolved hyperfine components but rather due to a high sensitivity of the g_z value to a small scatter in the π -orbital separation, δ . The agreement in the $g_x \sim g_y$ region is excellent and clearly warrants that $A_x \leq 5$ G.

When the distribution of an unpaired electron around a magnetic nucleus possesses an axial symmetry, the hyperfine coupling tensor to that nucleus can be given by $A_{||} = A_{\text{iso}} + 2A_{\text{dip}}$, and $A_{\perp} = A_{\text{iso}} - A_{\text{dip}}$. A_{iso} represents the isotropic interaction related to $|\Psi(0)|^2$, and A_{dip} represents the anisotropic interaction related to $\langle 1/r^3 \rangle$ of the electron measured from the nucleus. It so happens that, for a nitrogen 2p atomic orbital, $A_{\text{iso}} \cong A_{\text{dip}}$. A_{iso} in this case arises from the "inner core polarization" caused by the spin density in the p orbital. Thus if a radical contains a nitrogen, and the molecular orbital of the unpaired electron involves a 2p orbital of the nitrogen but not its 2s orbital, the largest hyperfine interaction with the ^{14}N nucleus is expected along the direction parallel to the p orbital, and the coupling constants along the two other principal axes would be very near zero. This has indeed been found to be the case for radicals such as $\text{H}_2\text{C}=\text{N}\cdot$ ⁹ and NF_2 .¹⁰ The hyperfine coupling tensor observed with NO also falls in this category. The comparison of the coupling constant observed on Ba-Y along the y axis with that expected for a pure p orbital¹¹ shows that the antibonding π orbital in NO contains 64% of the nitrogen 2p_y orbital.

(9) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1938 (1962).

(10) P. H. Kasai and E. B. Whipple, *Mol. Phys.*, **9**, 497 (1965).

(11) J. R. Morton, J. R. Rowlands, and D. H. Whiffen, *Nat. Phys. Lab. (U. K.), Circ.*, No. BPR-13.

(7) W. Kanzig and M. H. Cohen, *Phys. Rev. Lett.*, **3**, 509 (1959).

(8) P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Amer. Chem. Soc.*, **91**, 4364 (1969).

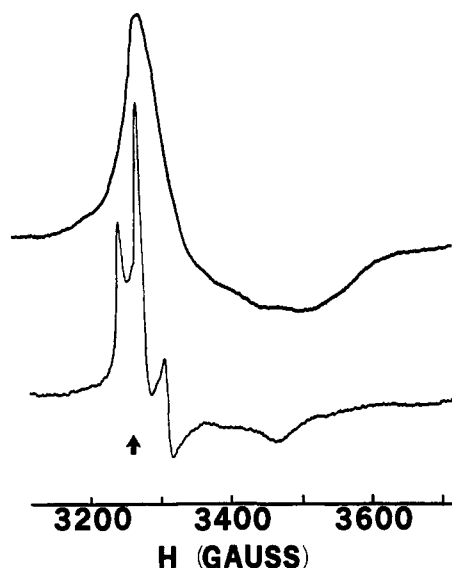


Figure 7. ESR spectra of NO introduced to freshly activated Ba-Y (upper trace) and that introduced to "NO-treated" Ba-Y. The arrow indicates the position corresponding to $g = 2.0023$.

Almost an identical conclusion had been reached by Dousmanis¹² from the analysis of the hyperfine structure in the gaseous spectrum.

It is particularly interesting to note that the g tensors observed for NO on Ba-Y and Zn-Y are very similar to those observed by Lunsford with NO adsorbed on MgO ($g_x = g_y = 1.996$, $g_z = 1.89$)⁵ and on ZnO ($g_x = g_y = 1.999$, $g_z = 1.94$),¹³ respectively.

Integration of the esr signals showed that the number of NO molecules responsible for the signal is approximately 10^{19} per gram of zeolite. This figure corresponds to about one NO molecule per five unit cells or 40 cavities and to about $1/20$ of the NO molecules sealed within the sample tubes.

NO Treatment

We shall define the NO treatment as sealing freshly activated zeolites with NO gas, letting it stand at room temperature for 1 week, and finally pumping on it at room temperature until it no longer exhibits purple coloration nor the esr signal when cooled to 77°K.

The esr spectra of NO introduced to freshly activated Ba-Y and that introduced to NO-treated Ba-Y are compared in Figure 7. A similarly dramatic sharpening of the esr signal was found with Na-Y and Zn-Y after the NO treatment. This sharpening of the signal implies improved uniformity in the crystal field to which the NO molecules responsible for the esr signal are subjected. Intensity measurements showed that there is no major change in the number of NO molecules displaying the signal. We have further learned that the modification brought about by the NO treatment survives through such treatment as exposure to air, exposure to moisture, or even vacuum activation at 300° overnight. Vacuum activation at 400° overnight finally returned the sample to the original state, whereupon the esr signal of newly introduced NO appeared broad and ill defined. When a NO-treated sample was heated to 400° in a sealed tube, a layer of brown gas was formed above the

(12) G. C. Dousmanis, *Phys. Rev.*, **97**, 967 (1955).

(13) J. H. Lunsford, *J. Phys. Chem.*, **72**, 2141 (1968).

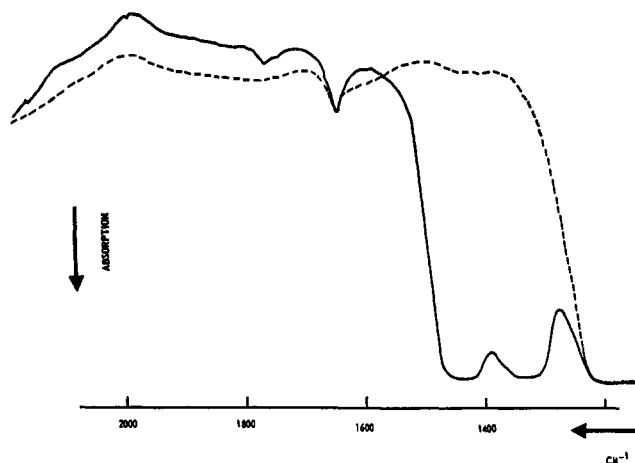


Figure 8. Infrared spectra of "NO-treated" Ba-Y (solid line) and nontreated Ba-Y (dotted line).

zeolite. When cooled back to room temperature, the gas was reabsorbed, and the sample exhibited the esr spectrum characteristic of NO.^{14,15}

To determine the nature of the modification caused by the NO treatment, parallel X-ray diffraction and infrared spectral studies were performed. No significant difference was detected between the X-ray powder patterns of the treated and nontreated zeolites. The infrared spectra, however, revealed two extremely broad absorption bands at around 1400 cm^{-1} in NO-treated zeolites. See Figure 8. Parallel to the esr observation, these bands at $\sim 1400\text{ cm}^{-1}$ grow slowly with time during NO treatment and, once created, are not removable by pumping at room temperature nor by activation at 300°. Vacuum activation at 400° was necessary to remove these bands completely.¹⁶ Thus, in summary, the following is the known nature of the elements responsible for the NO treatment. (1) They are not paramagnetic. (2) They are tenaciously held by zeolites. (3) They can produce NO₂ when heated. (4) They possess strong infrared absorption bands at around 1400 cm^{-1} . (5) Their presence results in a sharpening of the esr signal of NO.

Adsorption isotherm study of NO on various zeolites has been made earlier by Addison and Barrer.¹⁷ Based on the mass balance, and the density of the gas evolved, they concluded that, upon adsorption on zeolites, NO undergoes a disproportionation reaction $4\text{NO} \rightarrow \text{N}_2\text{O} + \text{N}_2\text{O}_3$ nearly to completion at temperature below 0°, and that, while the resulting N₂O can be removed quantitatively below 150°, N₂O₃ stays occluded in zeolites past 200°.

Comparison of our observations with those of Addison and Barrer suggests that N₂O₃ or its equivalent, generated by the disproportionation reaction, is responsible for the NO treatment. However, N₂O₃ is known to dissociate easily into NO and NO₂. Both NO and NO₂ would surely be detected by esr if such dissociation oc-

(14) C. B. Colburn, R. Ettinger, and F. A. Johnson, *Inorg. Chem.*, **2**, 1305 (1963).

(15) T. M. Pietrzak and D. E. Wood, *J. Chem. Phys.*, **53**, 2454 (1970).

(16) A detailed infrared study of NO adsorption on Y-type zeolites has been recently reported by C. C. Chao and J. H. Lunsford, *J. Amer. Chem. Soc.*, **93**, 71 (1971). They too observed the strong, persistent doublet at $\sim 1400\text{ cm}^{-1}$ and assigned the bands to nitrate ions resulting from the reaction between NO and the framework oxygen.

(17) W. E. Addison and R. M. Barrer, *J. Chem. Soc.*, 757 (1955).

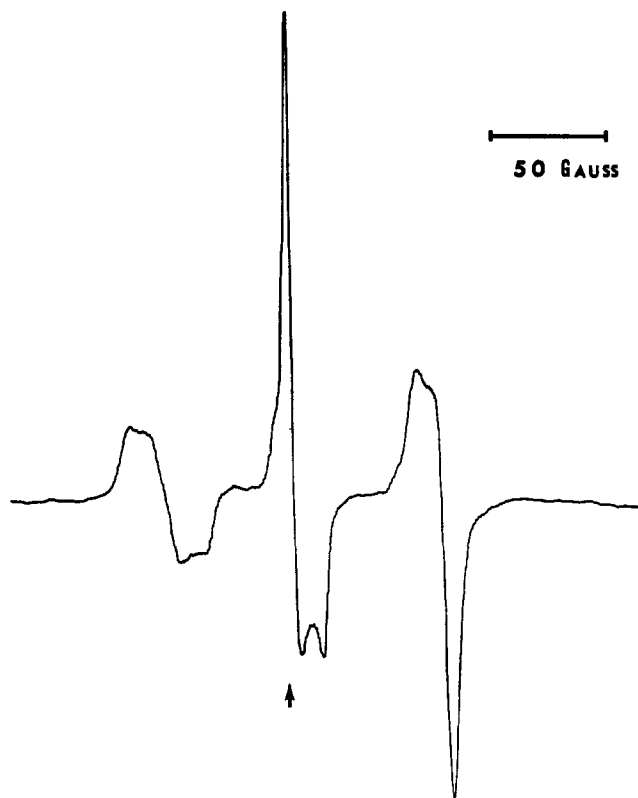


Figure 9. ESR spectrum obtained when "NO-treated" Ba-Y was irradiated with uv at 77°K. The spectrum is due to NO₂ and disappears completely when the sample is warmed to 50°. The arrow indicates the position corresponding to $g = 2.0023$.

curs in the NO-treated zeolite. We propose, therefore, that N₂O₃ formed by the disproportionation reaction is ionized to yield NO⁺ and NO₂⁻ and that a proper redistribution of these additional cations and anions results in the improved uniformity of the zeolitic crystal field. This model also explains both the diamagnetism and the tenacious affinity of the elements responsible for the NO treatment. The infrared absorption bands near 1400 cm⁻¹ observed with NO-treated zeolite can be attributed to NO₂⁻ associated with the cations and/or NO⁺ associated with the framework oxygen adjacent to Al. Dinitrogen trioxide, nitrogen dioxide, the nitrite ion, and the nitrate ion are all known to have characteristic stretching bands in this region. The built-in polar structure between the semishielded cations and the negatively charged framework is believed to be the driving force toward the formation of the ionic pairs, NO⁺ and NO₂⁻.

Photoelectron Transfer

As stated earlier, the NO-treated zeolite as such does not exhibit any esr signal. However, a strong esr signal was found to appear when such material was irradiated with uv light (GE, AH-6) at 77°K (Figure 9). The spectrum is immediately recognized as that of NO₂ condensed on zeolites. Once created, the photoinduced signal was stable as long as the sample was maintained at liquid nitrogen temperature. It decayed gradually at room temperature ($T_{1/2}$ = several hours) and disappeared completely when annealed at 50° for 30 min. The process was repeated several times without any apparent decrease in the intensity of the signal initially

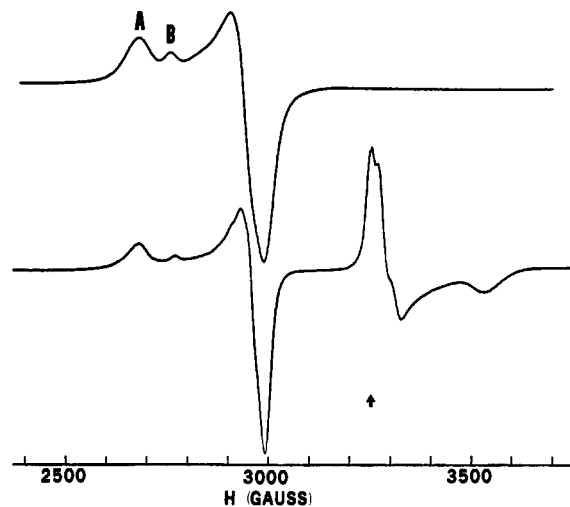
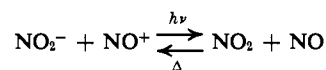


Figure 10. ESR spectra of Ni (65%)–Y reduced by NO (a, upper) and Ni (5%)–Y reduced by NO (b, lower). The spectrometer gain for the trace (b) was five times that used to obtain the trace (a). Note the presence of the NO₂ signal in the trace (b). The arrow indicates the position corresponding to $g = 2.0023$.

photoinduced at 77°K. Zeolites are strong adsorbents for NO₂. A separate experiment showed that Ba-Y which had directly adsorbed NO₂ possesses a strong esr spectrum due to NO₂, and overnight evacuation at 300° is required to remove the signal completely. Clearly the NO₂ signal photoinduced in the NO-treated zeolite is a feature unique to the material. The reversible process may be written as



The facility and the completeness of the reversibility, however, suggest a proximity and some unique arrangement of the ionic pairs NO₂⁻ and NO⁺ within the zeolitic structure. The absence of the NO signal in Figure 9 may be attributed to the degeneracy of the π orbitals not being lifted at these sites.

Effect of NaCl Occlusion

The ionization potential of NO is 9.25 eV, while the electron affinity of NO₂ is ~ 3.8 eV. If, as proposed above, the internal polarity of zeolite is instrumental in effecting an electron transfer between such species, and stabilizing the resulting ions, it is quite possible that an electrolytic molecule such as NaCl might "dissolve into zeolite" in an ionized form. The energy required to dissociate a NaCl molecule into Na⁺ and Cl⁻ ions is 6 eV. If this indeed happens, the extra cations and anions so introduced might also bring about the "NO-treatment" effect upon the esr signal of NO. We, therefore, made slurries of Na-Y and Ba-Y, respectively, each containing 8 wt % of NaCl. The mixtures were heated to dryness and vacuum activated at 500° for 18 hr. The X-ray diffraction patterns of the materials thus prepared were exactly the same as those of Na-Y and Ba-Y, respectively, and showed no evidence of NaCl phase. When a small amount of NO ($1/6$ atm) was introduced to these samples, they displayed immediately the sharp, well-resolved esr signals identical with those observed with NO-treated Na-Y and Ba-Y, respectively.

Ni⁺ Ion in Ni-Y

The facility with which the proposed electron-transfer process appears to occur in zeolites eventually led us to examine the possibility of reducing some of the multivalent zeolitic cations to their lower valence states. As can be evidenced in Figure 4a and Table I, the esr spectrum of NO adsorbed in Zn-Y shows, among those observed, the strongest interaction with the cations. The NO treatment of Zn-Y, however, did not produce monovalent zinc ion, Zn⁺. The second ionization potential of Zn atom is 17.89 eV, as compared to 9.95 eV for Ba atom. Shown in Figure 10a is the spectrum of Ni (65%)–Y, sealed with $\frac{2}{3}$ atm of NO and kept at 100° for 3 hr. The second ionization potential of Ni atom is 18.2 eV, and Ni (65%)–Y itself does not exhibit any esr signal. The signals observed in Figure 10 are, therefore, assigned to monovalent nickel ions Ni⁺ located at two different sites, A and B. Their respective *g* tensors are assessed as follows.

$$g_{||}(\text{A}) = 2.430 \pm 0.005$$

$$g_{\perp}(\text{A}) = 2.171 \pm 0.002$$

$$g_{||}(\text{B}) = 2.346 \pm 0.005$$

$$g_{\perp}(\text{B}) = 2.171 \pm 0.002$$

The exact origin for the two sites is not as yet known. The both sets of *g* values are similar to, but distinctly different from, those of Ni⁺ ions observed earlier in Ni-Y treated with Na vapor.¹⁸ In the case of Na-vapor treatment, most of the Ni²⁺ ions are reduced to nickel metals, and the esr signal due to Ni⁺ ion was weak and severely obscured by the broad background signal caused by the metallic phase.

In a tetragonally distorted octahedral ligand field, the *g* tensor of an ion with 3d⁹ configuration (e.g., Cu²⁺ and Ni⁺) can be given by the following relations.

$$g_{||} = 2 + 8\lambda/\Delta E_{||}$$

$$g_{\perp} = 2 + 2\lambda/\Delta E_{\perp}$$

Here λ is the spin-orbit coupling constant of the ion, and $\Delta E_{||}$ and ΔE_{\perp} are the respective energy separations of the d_{xy} and d_{xz} (or d_{yz}) orbitals from the lowest orbital, $d_{x^2-y^2}$. The spin-orbit coupling constant of Ni⁺ ion is smaller than that of Cu²⁺ ion. In spite of this, the *g* values of Ni⁺ ions produced by NO are significantly larger than those of Cu²⁺ ions in Cu, Na-Y¹⁹ and Cu, Mg-Y,²⁰ and also those of Ni⁺ ions produced by Na vapor. The indicated smaller energy separations $\Delta E_{||}$ and ΔE_{\perp} must be caused by the presence of NO⁺ ions.

The total concentration of Ni⁺ ions produced in Ni (65%)–Y by NO reduction was measured to be 1×10^{20} /g. This figure corresponds to one Ni⁺ ion per four cavities and is in exact agreement with the number of Ni²⁺ ions expected at site II in Ni (65%)–Y assuming preferential occupation of site I by Ni²⁺ ions.

The envisaged electron-transfer reaction, $\text{NO} + \text{Ni}^{2+} \rightarrow \text{NO}^{\cdot+} + \text{Ni}^+$, was also found to be reversible. Evacuation of the NO-treated Ni (65%)–Y at 200° for 18 hr resulted in a decrease of the Ni⁺ signal by a factor

of 10, but no signal due to Ni metal resulting from a disproportionation reaction $2\text{Ni}^+ \rightarrow \text{Ni}^0 + \text{Ni}^{2+}$ was detected.

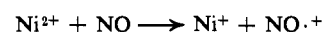
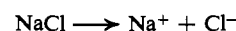
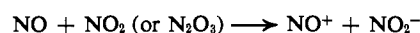
When oxygen was introduced into Ni (65%)–Y reduced by NO, the Ni⁺ signals disappeared instantly. The phenomenon was found to be completely reversible. The Ni⁺ signal was restored to its original intensity by evacuation at room temperature. The disappearance of the signal, therefore, is attributed to the broadening caused by the paramagnetism of oxygen molecules. Note that we must also conclude that the NO⁺ and Ni⁺ system in zeolite is chemically inert toward oxygen.

Another interesting aspect is that Ni (65%)–Y reduced by NO does not exhibit any esr signal due to NO, even though it is supplied in excess. Apparently when the reduction of Ni²⁺ ions, presumably at site II, occurs to the extent described above, the sites formerly capable of lifting the degeneracy of NO orbitals are no longer available. A collateral observation is that Ni (65%)–Y reduced by an excess amount of NO does not show the purple coloration when cooled to 77°K. An esr spectrum of Ni (5%)–Y reduced with NO is shown in Figure 10b. It appears that even at this low level of exchange, a small fraction of the divalent cations is at site II. The concentration of Ni⁺ ions produced here is about $\frac{1}{5}$ of that obtained with Ni (65%)–Y, and, in this case, a well-resolved signal due to NO is also observed.

Final Remarks

Esr spectra of radical cations resulting from adsorption of polynuclear aromatic molecules on various zeolites have been reported by several authors.²¹ The mechanism for the formation of the radical cations has been pictured as electron transfers to the zeolitic cations, or to tricoordinated aluminum ions in the case of activated NH₄-Y, and a direct correlation between the ionizing power of zeolites and their catalytic activities has been advocated. One difficulty in this approach has been the fact that the maximum number of cation radicals, $\sim 10^{19}$ /g, obtainable with polynuclear aromatics is at least one order of magnitude smaller than the number of electron-accepting centers within zeolites. The discrepancy, we believe, is caused by the clogging of zeolite channels resulting from a strong affinity between the large aromatic cations and the negatively charged framework. The ionization potential of anthracene which has given one of the highest yield is 7.55 eV. NO, in spite of its much larger ionization potential (9.25 eV), appears to be capable of reducing all the Ni²⁺ ions at site II. Thus a treatment by NO of Ni (65%)–Y produced zeolite containing 10^{20} Ni⁺ ions/g. It sets forth a clear warning against usage of large aromatic molecules for the purpose of "titrating" acceptor centers within zeolites.

Finally let us discuss what we believe is the most important conclusion of the present study. The reactions discussed in the preceding sections are



(18) J. A. Rabo, C. L. Angell, P. H. Kasai, and V. Schomaker, *Discuss. Faraday Soc.*, **41**, 328 (1966).

(19) A. Nicula, D. Stamires, and J. Turkevich, *J. Chem. Phys.*, **42**, 3684 (1965).

(20) J. T. Richardson, *J. Catal.*, **9**, 178 (1967).

(21) D. N. Stamires and J. Turkevich, *J. Amer. Chem. Soc.*, **86**, 749 (1964); J. T. Richardson, *J. Catal.*, **9**, 172 (1967).

As written, they are endothermic reactions. Yet, each one of them has been found or indicated to proceed easily within zeolites. The most noteworthy aspect common to all of these reactions is that they result in an increase in the number of ions inside the zeolite. We then immediately recall the strongly polarized internal structures of zeolites. As stated earlier, the cations at site II are shielded only on one side. By reason of symmetry, many of the $(\text{AlO}_2)^{-1}$ units within the framework must also be shielded unevenly. This polarization would, of course, be more pronounced in zeolites with divalent cations. We should also note that, because of the open network structure of zeolites, the separations between the positively charged regions and the negatively charged regions are large and often encompass the void spaces constituting the channels and cavities. Introduction of additional cations and anions into these void spaces with a proper arrangement should then bring about an increase in the Madelung energy of the crystal. We believe it is this gain in the Madelung energy which offsets the endothermicity of the reaction cited above. Thus zeolites may be viewed as a "solid state electrolytic solvent." Its

ionizing power is of such magnitude that not only does it "dissolve" a strong electrolyte such as NaCl in its ionized state, but also accommodates two different molecules A and B in their charge-transfer state, A^+ and B^- . As an extreme example one may cite the formation of Na_4^{3+} centers when Na-Y is treated with Na vapor.¹⁸ The reaction within zeolite can be simply expressed as



Catalytic properties of Y-type zeolites for a variety of organic reactions are well known and have been the subjects of many investigations.²² The observed activity has been attributed to the electric field associated with the cations, to the acidity of the hydroxyl groups incorporated within the structure, or to the combined effect of both. It is quite conceivable that some of these reactions are catalyzed through a charge-transfer state formed as a direct manifestation of the electrolytic property discussed above.

(22) See, for example, a review article by J. A. Rabo and M. L. Poutsma, 2nd International Conference on Molecular Sieve Zeolites, Worcester, Mass., Sept 1970.

Polarized Single-Crystal Absorption Spectra of Pyrazine and Tetramethylpyrazine

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Received December 11, 1971

Abstract: Polarized absorption spectra have been measured at room temperature on the (101) crystal face of pyrazine and on the (001) crystal face of tetramethylpyrazine to 2150 Å on a quartz microspectrophotometer. Absolute crystal intensities have been estimated from Lambert's law plots of optical density vs. crystal thickness. The absolute intensities and dichroic ratios observed for pyrazine and tetramethylpyrazine crystals are very close to those expected from an oriented gas model of noninteracting molecules and confirm theoretical predictions regarding the polarizations of the first three electric dipole allowed pyrazine singlet-singlet transitions. Second-order dipole-dipole calculations predict the small magnitude of intermolecular effects observed in the crystal spectra.

Although the azabenzenes are a class of polyatomic molecules whose electronic spectra have been investigated in great detail,¹ no reports have appeared in the literature describing the polarized singlet absorption spectra of these compounds in the pure crystalline state. In this paper, we report polarized absorption spectra on single crystals of pyrazine and tetramethylpyrazine measured at room temperature to 2150 Å on a microspectrophotometer. Particular emphasis has been directed in this study toward accurate measurement of absolute crystal intensities so that any intensity modifications caused by intermolecular interactions may be analyzed and interpreted.

There has recently been a good deal of activity devoted to measurement of polarized crystal spectra for heteroaromatic systems of biological interest both by

direct absorption²⁻⁵ and by reflection techniques.^{6,7} Since a major aim of this work has been the derivation of free-molecule transition moments from linear dichroism measurements, it has been important to assess the extent to which intermolecular interactions in the crystal affect crystal transition intensities and dichroic ratios. Pyrazine is a heteroaromatic system in which free-molecule transition moments are limited by symmetry to three mutually orthogonal directions. Polarized single-crystal spectra may easily distinguish the three alternative polarizations for particular transitions, and deviations of measured intensities from those ex-

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(3) W. A. Eaton and T. P. Lewis, *ibid.*, **53**, 2164 (1970).

(4) T. P. Lewis and W. A. Eaton, *J. Amer. Chem. Soc.*, **93**, 2054 (1971).

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(6) H. H. Chen and L. B. Clark, *J. Chem. Phys.*, **51**, 1862 (1969).

(7) P. R. Callis and W. T. Simpson, *J. Amer. Chem. Soc.*, **92**, 3593 (1970).

(1) K. K. Innes, J. P. Byrne, and I. G. Ross, *J. Mol. Spectrosc.*, **22**, 125 (1967).