

Interactions of Ammonia with a NiO(100) Surface Studied by High-Resolution Electron Energy Loss Spectroscopy and Temperature Programmed Desorption Spectroscopy

Ming-Cheng Wu, Charles M. Truong, and D. Wayne Goodman*

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Received: November 23, 1992; In Final Form: January 26, 1993

Interactions of ammonia with well-defined NiO(100) films prepared on Mo(100) have been investigated using combined high-resolution electron energy loss spectroscopy (HREELS)/temperature-programmed desorption (TPD). The results show that ammonia is bonded to the surface cations of NiO(100) via the nitrogen lone pair of the molecules, with an accompanying transfer of electrons to the surface cations. At low coverages ($\theta < 0.2$ monolayer), there are strong repulsive interactions between adsorbates, resulting in a marked decrease in the apparent activation energy of desorption. Three distinct desorption states are observed below monolayer coverages. The presence of bilayers of ammonia following NH_3 adsorption at 90K is also indicated. The HREELS data show that the umbrella mode of ammonia exhibits great charge sensitivity and that the frequency of this mode remains unchanged as a function of NH_3 exposure. This result has an important implication in that the frequency of the umbrella mode can be utilized as a fingerprint of the nature of the cations of oxide materials, independent of the ammonia adsorption geometry and coverage.

I. Introduction

Interactions of ammonia with well-defined solid surfaces under ultrahigh vacuum (UHV) conditions have recently received considerable attention due to the importance of industrial catalytic processes such as ammonia synthesis. Ammonia has an electron lone pair on the nitrogen atom which acts as a donor ligand that bonds to metal atoms both in organometallic compounds¹ and on surfaces.^{2,3} Accordingly, the bonding configuration and adsorption geometry of NH_3 to single-crystal metal surfaces have been a focus of intensive research^{2–17} for the past decade.

Several studies using ultraviolet photoelectron spectroscopy (UPS)^{4–10} have shown that the lone pair orbital ($3a_1$) of ammonia is strongly perturbed when adsorbed on metal surfaces. This perturbation is presumed to arise because of the bonding of the nitrogen atom of ammonia to the substrate, with an accompanying electron transfer from the $3a_1$ lone pair to the substrate. Work function measurements^{2,4–7} have shown that the apparent dipole moment of ammonia, deduced from the work function change, increases relative to that of NH_3 in gas phase, indicating a charge transfer between the adsorbate and the substrate. The marked decrease in work function following NH_3 adsorption^{2,4–7} is consistent with the conclusion that ammonia is bonded via the nitrogen atom with the hydrogen atoms directed away from the surface.

The information relevant to the bonding configuration of ammonia to metal surfaces has also been obtained from electron-stimulated desorption ion angular distribution (ESDIAD) measurements. ESDIAD studies performed on several transition metal surfaces^{2,18–24} showed a “halo”-like H^+ pattern at submonolayer coverages, indicating that the NH_3 is bonded via the N atom with its molecular axis oriented perpendicular to the surface.

The adsorption of ammonia to a number of transition-metal surfaces, such as Ru(001),^{3,11} Pt(111),¹² Fe(110),^{13,14} Ni(110),¹⁵ Ag(110),¹⁶ and Ag(311),¹⁷ has also been a subject of high-resolution electron energy loss spectroscopy (HREELS) investigations. No such studies, however, have been reported on well-defined metal oxide surfaces. The HREELS spectra of NH_3 adsorbed on these metal surfaces at monolayer coverages exhibited a number of loss features in the 300–4000 cm^{-1} spectral region. A predominant loss feature found between 1050 and 1170 cm^{-1} is due to excitation of the NH_3 symmetric deformation mode ($\delta_s(\text{NH}_3)$), and some weaker loss features observed in the frequency ranges of 1580–1650, 3200–3320, and 3340–3400 cm^{-1}

arise from the NH_3 asymmetric (degenerate) deformation ($\delta_a(\text{NH}_3)$), symmetric stretch ($\nu_s(\text{NH}_3)$) and asymmetric (degenerate) stretch ($\nu_a(\text{NH}_3)$), respectively. The NH_3 rocking ($\rho(\text{NH}_3)$) mode and the nitrogen–metal stretching ($\nu(\text{N-M})$) mode have been observed in the lower frequency range (300–700 cm^{-1}) in several of these studies.^{3,13,15,17}

An intriguing feature revealed in these EELS studies is the frequency shift of the $\delta_s(\text{NH}_3)$ mode (the umbrella mode) as a function of coverage for NH_3 chemisorbed on transition-metal surfaces.^{3,12–14} By analogy to the results obtained from coordination compounds,¹ the observed frequency shift is interpreted to be due to a net transfer of electrons from the ammonia to the metal surface atoms.³ As the coverage of ammonia increases, the electron richness of these surface atoms is also increased, resulting in a red shift in the frequency of the umbrella mode. This interpretation is consistent with the trend observed for coordination compounds with regard to the charge on the metal atom.¹ The variation in the frequency of the umbrella mode also correlates well with the change of the work function found for these systems.^{2,4–7} The sharp decrease in the work function following initial NH_3 adsorption is explained as a consequence of enhancement of the dipole moment of the molecules that originates from a transfer of electrons to the substrate.^{2,4–7}

As part of a continuing study of relatively complex organic species chemisorbed on insulating metal oxides, we report here the results of a combined HREELS/temperature-programmed desorption (TPD) investigation of ammonia adsorption on NiO(100) films. The focus of our studies is to investigate the adsorption geometry of ammonia on NiO(100) and to explore the nature of bonding between ammonia and the insulating oxide surface. The differences and similarities between NiO(100) and metal surfaces with respect to ammonia adsorption will be addressed.

Our approach to the study of oxides involves the following procedure: (1) preparation of well-defined, ultrathin metal oxide films on a single-crystal refractory metal surface; (2) spectroscopic characterization of adsorbates chemisorbed on these well-characterized oxide films utilizing combined HREELS/TPD. Such an approach allows us to employ various surface-sensitive spectroscopies such as HREELS, Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED) without difficulties associated with surface charging during charged particle measurements due to the insulating nature of oxide materials. Studies of thin oxide films have another advantage

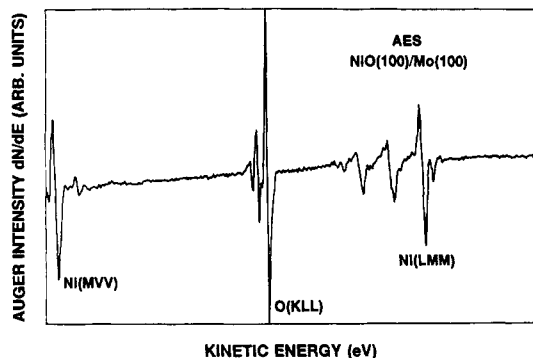


Figure 1. Auger spectrum of a ~ 20 monolayer (ML) NiO(100) film grown on Mo(100) at 300 K.

over their bulk counterparts in that a temperature gradient while heating, caused by poor thermal conductivity of oxides, is avoided. This property allows precise temperature control in thermal desorption studies.

In the application of HREELS to adsorbates on ionic substrates, however, a great difficulty encountered is that the accompanying vibrational spectra are dominated by losses due to excitation of surface optical phonons. Since the intense multiple phonon losses generally extend over a wide vibrational frequency range of the HREELS spectra, it is not practical to observe directly adsorbate losses (which are several orders of magnitude smaller in intensity than the phonon losses) in the $0\text{--}4000\text{ cm}^{-1}$ spectral range. In recent studies,^{25,26} we have developed a new approach to acquiring HREELS data in order to circumvent the difficulties associated with these phonon losses. By utilizing a high-energy incident electron beam, this new approach enables the direct observation of weak loss features due to the excitation of adsorbates without serious interference from intense multiple surface optical phonon losses.

II. Experimental Details

These studies were carried out utilizing an ultrahigh vacuum (UHV) system, described elsewhere,^{25,26} with capabilities for HREELS, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and TPD and for sample heating and cooling. The sample temperature measurement and the crystal cleaning procedure have been described elsewhere.²⁷

Thin NiO films were prepared by depositing Ni onto Mo(100) in a controlled oxygen atmosphere, followed by annealing in oxygen ambient. Nickel deposition was performed via thermal evaporation of a high-purity ribbon tightly wrapped around a tungsten filament. The film stoichiometry was adjusted by tuning the flux of Ni evaporation, which was monitored by a mass spectrometer mounted in line with the metal source, at an oxygen pressure of 7×10^{-7} Torr. The growth of the films was controlled at a rate of approximately one monolayer (ML) per minute, and the films were typically 20 ML thick. Displayed in Figure 1 is the Auger spectrum acquired following the film synthesis which shows features essentially identical to those from single-crystal NiO(100).²⁸ The structural studies using LEED show that the NiO films prepared using the above approach exhibited an excellent (1×1) LEED pattern indicative of the long-range order of the films. The detailed studies regarding film synthesis and characterization are described elsewhere.²⁹

Anhydrous ammonia (99.99%, Matheson Gas Products, Inc) was used in the adsorption study and was further purified in the manifold via freeze-pump-thaw cycles prior to introduction of the adsorbate into the vacuum chamber. In the TPD experiments, a diirreational gas doser was used to introduce the molecules to the crystal surface; however, the exposure of ammonia was performed via backfilling the UHV chamber for HREELS measurements. Ammonia surface coverage is reported with respect to the saturation coverage. The saturation or monolayer coverage (ML) of NH_3 on NiO(100) deduced from the TPD spectra is assumed to be $\theta = 1$. This value is used to calibrate

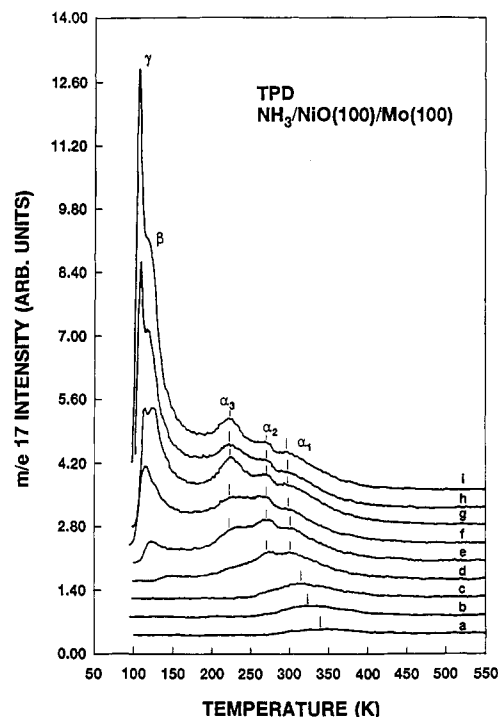


Figure 2. TPD spectra of ammonia adsorbed on NiO(100) surfaces at 90 K as a function of coverage (ML): (a) 0.07; (b) 0.14; (c) 0.18; (d) 0.47; (e) 0.80; (f) 1.22; (g) 1.64; (h) 1.96; and (i) 2.50. The desorption states designated as α_1 , α_2 , α_3 , β , and γ are indicated.

the ammonia coverage which was calculated by measuring the NH_3 -TPD peak area.

The HREELS spectra were acquired using an electron beam with a primary energy of $E_p \approx 50$ eV and an incident angle of 60° with respect to the surface normal. The other parameters used in obtaining the EELS spectra presented here were the following: spectral resolution (full width at half maximum of elastically reflected electron beam), $80\text{--}100\text{ cm}^{-1}$; typical count rate in the elastic peak of the clean surfaces, 50 000 Hz.

Because of the low signal levels encountered in our HREELS measurements an optimal Fourier filtering technique³⁰ has been utilized to remove high-frequency random noise and spikes in the HREELS spectra. All HREELS spectra reported below have been smoothed using this Fourier filtering technique.³⁰

The temperature-programmed desorption spectra were obtained at a linear heating rate of 5 K/s using a quadrupole mass spectrometer.

III. Results

A. Temperature Programmed Desorption Spectroscopy. The adsorption of ammonia on NiO(100) films was examined using TPD. The evolution of various desorption features as a function of NH_3 exposure was followed by monitoring several masses ($m/e = 2, 14, 17$). Displayed in Figure 2 are thermal desorption spectra of the parent molecule. No desorption signal was observed for masses other than the parent peak and its fragments, indicating reversible adsorption of ammonia on NiO(100) surfaces at 90 K under UHV conditions. Negligible decomposition of ammonia on Ru(001),^{2,3} Pt(111),⁴ Fe(111), Fe(100),⁶ Fe(110),⁷ Ni(110),^{8,9} and Ni(111)¹⁰ following NH_3 adsorption at ~ 100 K has also been reported and only at adsorption temperatures exceeding room temperature does significant dissociation occur on Fe(110)⁷ and Ni(110).³¹

At desorption temperatures exceeding 150 K, TPD spectra ($m/e = 17$) were characterized by the presence of three distinct desorption features with maxima at 299, 269, and 224 K, designated as α_1 , α_2 , and α_3 states, respectively. These three desorption states appear to fill sequentially in the order $\alpha_1 \rightarrow \alpha_2 \rightarrow \alpha_3$ with increasing NH_3 exposure. While the α_2 and α_3 states

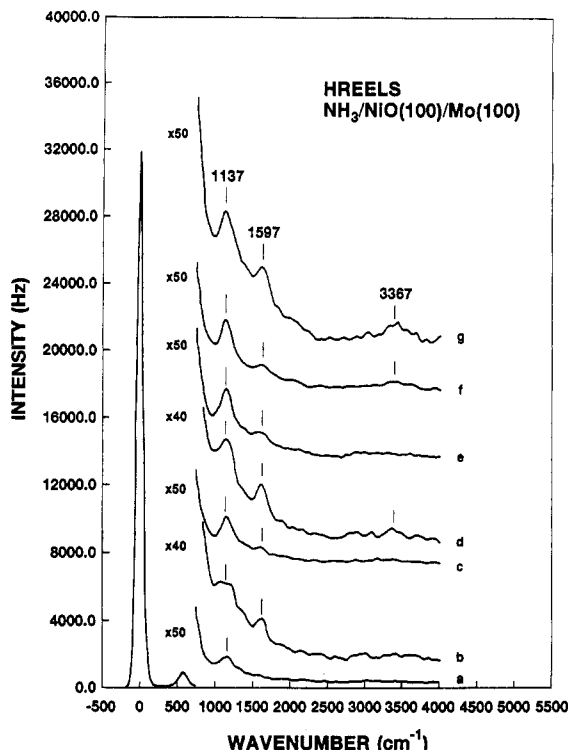


Figure 3. HREELS spectra of ammonia adsorbed on a ~ 20 ML NiO(100) film at 90 K as a function of NH_3 coverage (ML): (a) 0.00; (b) 0.20; (c) 0.27; (d) 0.33; (e) 0.40; (f) 0.53; and (g) 0.67. The spectra were collected at $E_0 \approx 50$ eV and at the specularly reflected beam direction. Spectra b and d were acquired at an angle of 8° off the specular direction. The HREELS spectra have been smoothed using a Fourier filtering technique.

remain unchanged with respect to their peak maxima as the NH_3 exposure is varied, the α_1 state behaves quite differently. The peak maximum shifts from 343 K at low exposure ($\theta = 0.07$ ML) to 299 K at a coverage approaching saturation of the first layer, as shown in Figure 2.

Further exposure to ammonia results in the appearance of two new features at lower temperatures. The sharp desorption feature (γ state) at 109 K, whose peak intensity increases continuously with increasing NH_3 exposure, apparently arises from condensed multilayers of ammonia. The peak (β state) at 125 K, which appears approaching saturation at coverages greater than 2 ML, can be explained as arising from the desorption of bilayers of the molecules. Assuming first-order kinetics and a preexponential factor $\nu = 1 \times 10^{13}$ Hz, the activation energy of desorption of this bilayer is deduced to be 7.4 kcal/mol using Redhead's peak maximum method.³² This value is slightly lower than the previously reported activation energy (9.0 kcal/mol) for the desorption of the second layer of ammonia.⁴

B. Electron Energy Loss Spectroscopy. Adsorption of ammonia on thin NiO(100) films has been further investigated using HREELS. Displayed in Figures 3 and 4 is a set of HREELS spectra of ammonia adsorbed on a ~ 20 monolayer NiO film at 90 K as a function of exposure. Exposing the sample to NH_3 at 90 K gives rise to a number of distinct loss features in the 750–4000 cm^{-1} region. The losses observed at 1137 and 1597 cm^{-1} are due to excitations of the NH_3 symmetric deformation, $\delta_s(\text{NH}_3)$, and asymmetric (degenerate) deformation, $\delta_a(\text{NH}_3)$, respectively.^{3,11–17} The spectra b and d, acquired at an angle 8° off the specularly reflected beam direction, clearly show the enhancement of the $\delta_a(\text{NH}_3)$ mode relative to the $\delta_s(\text{NH}_3)$ (umbrella) mode, indicating the nondipole nature of this vibrational feature. Previous HREELS studies^{11,12} have shown that the umbrella mode is strongly dipole allowed, whereas remaining vibrational modes of the molecule are predominantly excited by impact scattering. The symmetric and asymmetric stretching modes, which are barely perceptible in the 3000–3500 cm^{-1} region

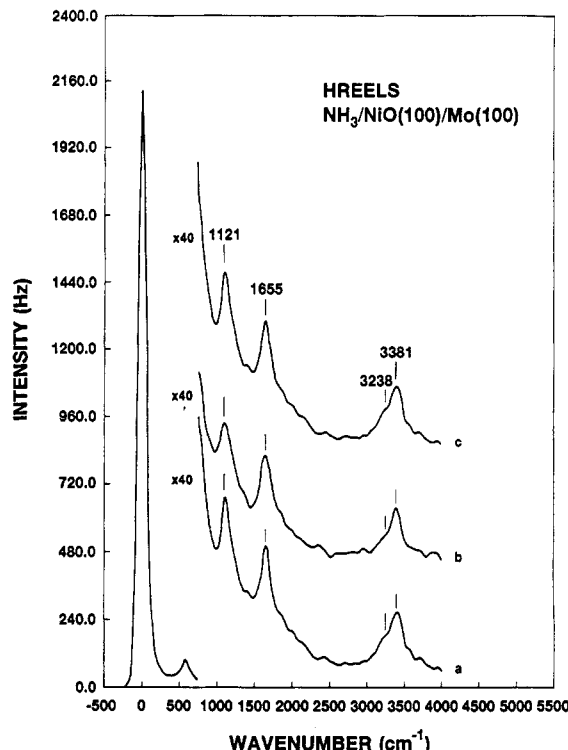


Figure 4. HREELS spectra of ammonia adsorbed on a ~ 20 ML NiO(100) film at 90 K as a function of NH_3 coverage (ML): (a) 1.33; (b) 3.33; and (c) 6.67. The spectra were collected at $E_0 \approx 50$ eV and at the specularly reflected beam direction. The HREELS spectra have been smoothed using a Fourier filtering technique.

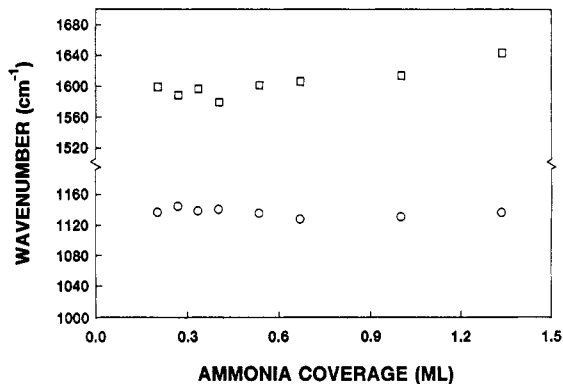


Figure 5. Frequencies of the $\delta_s(\text{NH}_3)$ mode (O) and of the $\delta_a(\text{NH}_3)$ mode (□) versus NH_3 coverage.

at low exposures, become more intense as the coverage is increased. At high NH_3 exposures, a loss feature with a maximum at 3381 cm^{-1} and a shoulder at ~ 3238 cm^{-1} is evident, as shown in Figure 4, which can be unambiguously attributed to the asymmetric ($\nu_a(\text{NH}_3)$) and symmetric ($\nu_s(\text{NH}_3)$) stretching modes, respectively.^{3,11–17}

Plotted in Figure 5 are the frequencies of the $\delta_s(\text{NH}_3)$ and the $\delta_a(\text{NH}_3)$ modes versus NH_3 coverage. The asymmetric deformation mode exhibits a blue shift in loss energy by approximately 40 cm^{-1} when the ammonia coverage exceeds one monolayer, whereas the coverage dependent shift is not observed for the symmetric deformation within an experimental error of 10–15 cm^{-1} . The latter feature has important implications and will be discussed in the following section.

The evolution of the losses as a function of the annealing temperature has also been examined using HREELS, as shown in Figure 6. No dramatic changes occur upon annealing to higher temperatures; however, the intensities of all loss features decreases concurrently, indicating the desorption of ammonia multilayers. The $\delta_a(\text{NH}_3)$ loss feature also shifts slightly to a lower loss energy upon annealing, consistent with that shown in Figure 5 in which this mode is blue-shifted as the NH_3 coverage is increased.

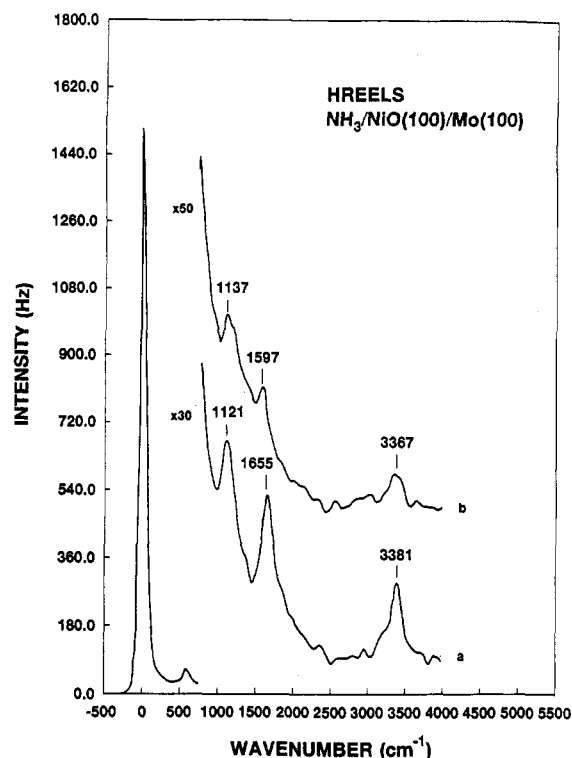


Figure 6. HREELS spectra of ammonia adsorbed on a ~ 20 ML NiO(100) film at 90 K at different annealing temperatures: (a) 90 K; (b) 150 K. The surface coverage of ammonia is 3.33 ML. Note that the $\delta_s(\text{NH}_3)$ mode shifts downward slightly in frequency upon annealing to 150 K. The spectra were collected at $E_0 \approx 50$ eV and at the specularly reflected beam direction. The HREELS spectra have been smoothed using a Fourier filtering technique.

IV. Discussion

A. Repulsive Interactions at Low Coverages. The kinetics of desorption of ammonia on NiO(100) has been studied using TPD. The TPD-peak maximum of the α_1 state shifts continuously toward lower temperatures as the NH_3 coverage is increased. A similar behavior has been observed for ammonia adsorbed on several transition-metal surfaces, such as Ru(001)² and Ni(111).¹⁰ In order to obtain the coverage dependence of the activation energy of desorption, E_d , Benndorf and Madey² have carried out a calculation based on thermal desorption analysis. Their results showed that E_d decreases significantly with increasing ammonia coverage. The variation of E_d as a function of NH_3 coverage was interpreted to be due to repulsive lateral interactions between neighboring NH_3 dipoles. These results are not surprising because the dipole moment associated with ammonia (the gas phase value of $\mu = 1.47$ D) is rather large and becomes larger when the molecule is adsorbed on metal surfaces. The increase in the dipole moment for ammonia chemisorbed on some transition metal surfaces indeed has been observed and explained as arising from charge transfer between the molecules and the metal substrates. The oriented molecules in the α_1 state² thus experience a strong dipole-dipole interaction, which results in a marked decrease in E_d as the NH_3 coverage is increased.

In the present studies, an equation analogous to that derived by Benndorf and Madey² is utilized to obtain the activation energy of desorption, E_d , from the TPD spectra. Assuming first-order kinetics for NH_3 in the α_1 state and a preexponential factor of $\nu = kT/h$ with k and h assuming the usual significance, namely Boltzmann's and Planck's constants, we obtained the following equation:²

$$E_d = -RT \ln (\Delta P(t)/\nu \int \Delta P(t) dt)$$

where $\Delta P(t)$ represents the change of the NH_3 partial pressure during the thermal desorption measurements and R the gas constant.

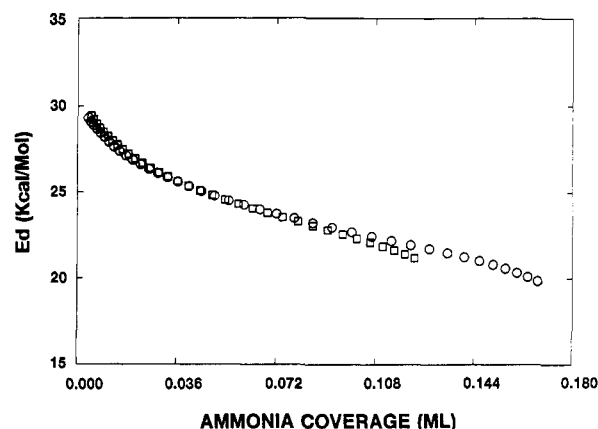


Figure 7. Coverage dependence of E_d calculated from spectra b and c of Figure 2. The overall agreement in E_d between spectrum b (circles) and spectrum c (square) is excellent.

Plotted in Figure 7 is the coverage dependence of E_d calculated from spectra b and c of Figure 2 based on the above equation. The marked decrease in the activation energy of desorption with an increase in NH_3 coverage clearly indicates a strong repulsive interaction between the adsorbates in the α_1 state. The great similarity in the coverage dependence of E_d between the present case and the case studied by Benndorf and Madey² suggests that ammonia is bonded to NiO(100) via the nitrogen atom and that the molecules in the α_1 state are adsorbed with its molecular axis oriented perpendicular to the surface. Further support for the binding configuration of NH_3 on NiO(100) comes from HREELS measurements which follow.

Likewise, it is tentatively proposed that the 3-fold axes of the adsorbates on NiO(100) in the α_2 and α_3 states are inclined toward the surface with their dipole moments oriented in random directions. This adsorption geometry of the molecules in the α_2 and α_3 states is consistent with the TPD results (Figure 2) which show essentially constant desorption peak maxima of the α_2 and α_3 states with an increase in NH_3 coverage. This indicates relatively weak dipole-dipole interactions between the NH_3 molecules in these states. In the work of Benndorf and Madey,² the constant desorption peak temperature of the α_2 state is accompanied by a lower dipole moment (derived from the work function change) as compared with that of the molecules in the α_1 state.

B. Second Layer and Multilayer Ammonia. TPD spectra shown in Figure 2 reveal the presence of bilayers and multilayers of ammonia following NH_3 adsorption at 90 K. The binding energy of the bilayers deduced from the TPD spectra using Redhead's peak maximum method is in agreement with those of the bilayers found for ammonia on several transition metals.^{2,4} The molecules in the second layer are then proposed to bond to those in the first layer via 3-fold hydrogen bonding; i.e., each second-layer ammonia molecule in the reverse umbrella geometry is surrounded by three ammonia neighbors in the first layer. The formation of hydrogen bonding in the second layers and multilayers also alters slightly the frequency of the asymmetric deformation, as shown in Figure 5.

C. Charge Sensitivity of the $\delta_s(\text{NH}_3)$ Mode. Ammonia in the first layer is bonded to the surface cations of NiO(100) via the nitrogen atom, accompanying a transfer of electrons from the $3a_1$ lone pair of the molecules to the Ni^{2+} cations. Recent theoretical work of Cain et al.³³ supports this bonding configuration. Band calculations show that upon approach of NH_3 toward a surface cation site of NiO(100), the $\text{Ni}3d_{z^2}$ orbital electrons interact strongly with those of the NH_3 lone-pair orbital, whereas the remaining Ni 3d orbitals are essentially unaltered. Since previous studies using IR¹ and HREELS^{3,12-14} have demonstrated great charge sensitivity of the umbrella mode, the $\delta_s(\text{NH}_3)$ frequency will be likely altered when ammonia is adsorbed on NiO(100). This is indeed the case in that the frequency of this mode obtained

in our HREELS experiments is blue shifted by 187 cm^{-1} relative to that in gas-phase ammonia (950 cm^{-1}).³⁴

Infrared spectra of coordination compounds have shown some interesting trends regarding the charge on the metal cation.¹ The $\delta_s(\text{NH}_3)$ frequency is very charge sensitive and shifts upward with an increase in charge on the metal cations. The average value of this frequency is 1158 cm^{-1} in the $\text{M}(\text{NH}_3)^{2+}_6$ compounds, 1333 cm^{-1} in the $\text{M}(\text{NH}_3)^{3+}_6$ compounds, and some intermediate values in the $\text{M}(\text{NH}_3)^{2+}_4$ compounds, where M represents the metal cation of the compounds. The difference in the frequency of the umbrella mode between different cations was found to be insignificant if the charge on these cations was held constant.¹ The $\rho(\text{NH}_3)$ and $\nu(\text{N-M})$ modes are also very charge sensitive and show marked blue shifts in frequency as the charge on the cation increases. Comparing our HREELS data to those obtained from coordination compounds reveals immediately that the $\delta_s(\text{NH}_3)$ frequency of the molecules chemisorbed on NiO(100) is very similar to those observed in the $\text{M}(\text{NH}_3)^{2+}_6$ compounds. Noting that the cations of NiO bear a formal charge of $2+$, this result is not surprising.

On the other hand, the coverage-dependent shift of the $\delta_s(\text{NH}_3)$ frequency is not observed in the present study, as shown in Figure 5. This behavior contrasts with that found for ammonia chemisorbed on several transition-metal surfaces in which the $\delta_s(\text{NH}_3)$ mode exhibited a red-shift by $\sim 100\text{ cm}^{-1}$ in frequency as the NH_3 exposure was increased.^{3,12-14} To explain this apparent discrepancy, we first compare the results obtained from ammonia chemisorbed on metal surfaces to those from coordination compounds. This comparison leads immediately to an explanation that the frequency change observed in ammonia/metal systems arises from changes of charge on the surface atoms. With an increase in ammonia coverage, each surface atom becomes more negatively charged due to a net transfer of electrons from the lone pair of ammonia to the surface atoms. In contrast with the metal cases, the electronic structure of the cations in nickel oxide is rather localized due to the nature of insulating ionic solids. The electrons from the lone pair of the molecules are then held at the corresponding cation site, and further lateral charge transfer to the neighboring cations is limited. The observed constant frequency of the umbrella mode below monolayer coverages further indicates that repulsive interactions between ammonia molecules at low coverages do not alter the frequency of this vibrational mode.

These results have an important implication in that the frequency of the umbrella mode of ammonia can be utilized as an indicator to detect the presence of certain types of cation (acidic) sites of oxide catalysts independent of the ammonia adsorption geometry and coverage. It is noteworthy that the frequency change of the umbrella mode has been previously used to investigate the acidity of a number of oxide catalysts,³⁵ but the validity of these investigations has not been sufficiently proved. Finally, it should be pointed out that since the $\rho(\text{NH}_3)$ and $\nu(\text{N-M})$ modes are also charge sensitive for ammonia in coordination compounds, these charge-sensitive modes of ammonia are expected to serve as fingerprints characteristic of the nature of cations of oxide materials, independent of the ammonia coverage.

V. Conclusions

Interactions of ammonia with well-defined NiO(100) films prepared on Mo(100) have been investigated using combined HREELS/TPD. The results are summarized as follows:

- (1) Ammonia undergoes reversible adsorption on NiO(100) surfaces at 90 K under UHV conditions and bonds to the surface cations of NiO(100) via the nitrogen lone pair of the molecules, accompanying a transfer of electrons to the surface cations.
- (2) At low coverages ($\theta < 0.2$ monolayer), strong repulsive interactions between adsorbates are observed, which result in a marked decrease in the apparent activation energy of desorption.

Three distinct desorption states are evident below monolayer coverages. The presence of the bilayer of ammonia following NH_3 adsorption at 90 K is also indicated and a bonding configuration for this bilayer proposed.

(3) The HREELS data show that the umbrella mode of ammonia exhibits great charge sensitivity and that the frequency of this mode remains unchanged as a function of NH_3 exposure. This result has an important implication in that the frequency of the umbrella mode can be utilized as a fingerprint of the nature of cations of oxide materials, independent of the ammonia adsorption geometry and coverage.

Acknowledgment. We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Science and the Gas Research Institute.

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