A FT-IRAS study of ammonia adsorbed on Ru(0001)

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The interaction between ammonia and Ru(0001) has been studied by means of Fourier-transform infrared reflection absorption spectroscopy (FT-IRAS). Chemisorption of NH₃ on Ru(0001) enhances the IR cross section of the umbrella mode of the molecule. For the first adsorption layer, changes in the IR intensity of the umbrella mode correlate with variations in the orientation of the molecules observed in ESDIAD and work function measurements. Formation of hydrogen bonds between first- and second-layer NH₃ molecules reduces drastically the IR cross section of the umbrella mode of chemisorbed ammonia.

1. Introduction

In recent years, major technological advances have made Fourier-transform infrared reflection absorption spectroscopy (FT-IRAS) a very useful tool for studying the adsorption of molecules on metal surfaces. The technique can give direct information about the nature of the chemisorption bond, orientation of the adsorbed molecule, adsorption sites, lateral interactions between adsorbates and the presence of surface reaction intermediates [1–3]. In some cases, the vibrational frequencies of an adsorbate are sensitive to the morphology of a surface, allowing FT-IRAS to be used to monitor phase transitions [4,5] or other types of surface reconstructions [5,6]. Although many FT-IRAS studies have appeared investigating the vibrational spectra of CO on metal surfaces [1–7], only a very limited amount of work has been reported for other adsorbed molecules. In the present article, we show the results of a FT-IRAS investigation of ammonia adsorption on Ru(0001).

Previous thermal desorption studies [8,9] indicate that chemisorbed ammonia desorbs from Ru(0001) in a broad feature that appears between 150 and 350 K. Surfaces saturated with ammonia show additional desorption peaks at ~ 115 K (multilayer) and 135 K (second layer). The saturation coverage of chemisorbed ammonia on Ru(0001) was estimated [8] to be approximately 0.25 molecules per Ru surface atom. The results of electron stimulated desorption ion angular distribution (ESDIAD) and work function measurements indicate that at low coverages (θ_{NH₃} ≤ 0.15) ammonia bonds via the N atom, with its symmetry axis parallel to the surface normal and the H atoms pointing away from the Ru(0001) substrate [8]. For coverages close to saturation of the first layer (θ_{NH₃} ≈ 0.25), the symmetry axes of chemisorbed NH₃ are no longer perpendicular to the surface, but are, to some extent, tilted or inclined toward the metal [8]. This reorientation lowers repulsive dipole–dipole interactions. The ESDIAD data [8] suggest that the second layer of NH₃ adsorbs on top of the first via three-fold hydrogen bonding, with the N-end of each second layer molecule interacting simultaneously with hydrogens of three molecules bonded to the Ru(0001) substrate (see fig. 8 in ref. [8]).

2. Experimental

The ultra-high vacuum system used in this study has been described in detail previously [10].
The apparatus was equipped with capabilities for FT-IRAS, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED) and temperature programmed desorption (TPD). The IRAS experiments were carried out employing a Mattson Cygnus 100 spectrometer in a single reflection mode at an 85° incident angle. All the infrared spectra were recorded at a resolution of 4 cm⁻¹ with a liquid-nitrogen-cooled mercury cadmium telluride detector covering a frequency range from 4000 to 900 cm⁻¹.

The Ru(0001) crystal was cleaned following procedures reported in the literature [8,9]. Surface cleanliness was verified by AES and by obtaining CO thermal desorption spectra that are characteristic of the clean surface [11]. The crystal was mounted on a manipulator capable of resistive heating to 160 K and cooling to 80 K. A W–5%Re/W–26%Re thermocouple was spot-welded to the sample edge for temperature measurements. A heating rate of 5 K/s was used in the TPD experiments.

In this work, ammonia coverages are reported with respect to the number of Ru(0001) surface atoms (1.57 × 10¹⁵ atoms/cm²). One admolecule per substrate surface atom corresponds to \( \theta_{\text{NH}_3} = 1 \). It has been estimated that the first layer of NH₃ on Ru(0001) has a saturation coverage of \( \theta_{\text{NH}_3} = 0.25 \) [8] and thus \( \theta_{\text{NH}_3} = 1 \) corresponds to a surface covered with four layers of NH₃. This value was used to calibrate ammonia coverages determined by measuring the area below the NH₃ TPD peaks.

3. Results

Fig. 1 shows a series of infrared and TPD spectra for ammonia on Ru(0001). The surface was exposed to NH₃ at 80 K, followed by IR spectra acquisition and subsequent thermal desorption. The TPD spectra are in good agreement with results reported in the literature [8]. Saturated surfaces show desorption peaks at 115 (multilayer or \( \gamma \) state), 135 (second layer or \( \beta \) state), 180 and 290 K (chemisorbed species, \( \alpha_2 \) and \( \alpha_1 \) states).

At low NH₃ exposures, the infrared spectra were characterized by the presence of a sharp peak in the 1050–1150 cm⁻¹ region (symmetric deformation mode, \( \delta \)) and the absence of any
appreciable signal in the 1550–1650 (asymmetric deformation mode) and 3200–3400 cm$^{-1}$ (N–H stretching mode, $\nu$) regions. The peak position of the umbrella mode decreased by ~40 cm$^{-1}$ when $\theta_{\text{NH}_3}$ was increased from 0.05 to 0.25.

Fig. 2 illustrates the effect of NH$_3$ exposure on the integrated IR intensity of the umbrella mode ($\delta$). The data show a non-linear dependence of the IR cross section with NH$_3$ coverage. Initially, a monotonic enhancement in the intensity with increasing coverage was observed, with a maximum at $\theta_{\text{NH}_3} \approx 0.15$ (NH$_3$ exposure of ~0.5 L, saturation of the $\alpha_1$ state). A further increase in coverage to $\theta_{\text{NH}_3} = 0.25$ (NH$_3$ exposure of ~1 L, saturation of the first layer of ammonia on Ru(0001) [8]) produced a reduction of ~50% in the IR intensity. Population of the second layer reduced drastically the cross section of the umbrella mode in chemisorbed NH$_3$. For a film with 2 layers of ammonia ($\theta_{\text{NH}_3} = 0.5$) no signal was observed in the region between 1000 and 1200 cm$^{-1}$. The signal reappeared when NH$_3$ films with thickness in excess of 5 layers were deposited on Ru(0001). For NH$_3$ coverages from 1.5 ML up to 25 ML (6–100 NH$_3$ layers), we observed a linear relation between IR intensity and NH$_3$ coverage.

The infrared spectrum displayed in fig. 1 for an NH$_3$ exposure of 10 L is in excellent agreement with that reported for solid ammonia [12]. The existence of two peaks in the 1050–1150 cm$^{-1}$ region indicates the presence of metastable phases in the film [12]. In the past, it has been established that metastable solid phases are produced when ammonia gas is deposited on substrates at liquid nitrogen temperature [12]. The IR spectrum of a 10 L exposure shows peaks with similar intensity for the N–H stretching and umbrella modes. An identical result is observed in the spectra of solid and liquid ammonia [12,13]. In contrast, ammonia chemisorbed on Ru(0001) shows a much larger cross section for the umbrella mode than for the N–H stretch.

Curve a in fig. 3 shows an infrared spectrum acquired at 80 K after exposing the Ru(0001) surface to 7 L of ammonia. The resulting surface
contained approximately five layers of NH₃ (i.e., \( \theta_{\text{NH}_3} \approx 1.3 \)). Flashing to 150 K induced desorption of the \( \gamma \) and \( \beta \) states, leaving only chemisorbed NH₃ on the surface (\( \theta_{\text{NH}_3} \approx 0.25 \)), with an IR spectrum (curve b) that shows appreciable signal only in the umbrella mode region. A dose of 1 L of NH₃ to this surface at 80 K saturated the second layer and eliminated the signal in the IR spectrum (curve c). A final flashing of the surface to 150 K produced desorption of the second layer and the reappearance of signal in the umbrella mode region of the IR (curve d).

Fig. 4 shows infrared spectra acquired after dosing different amounts of D₂O on top of a saturated layer of chemisorbed ammonia (\( \theta_{\text{NH}_3} \approx 0.25 \)). In these experiments, our objective was to investigate the effects of hydrogen bonding using a molecule different from NH₃. At the low temperature conditions kept during the experiments, it is likely that ammonia was not displaced from the Ru(0001) surface by D₂O. In fig. 4, it is clear that a significant reduction in the cross section of the umbrella mode occurred after dosing small amounts of D₂O. After a 1 L exposure of D₂O, the ammonia signal disappeared completely! This behavior is identical to that seen in fig. 1 after population of the second layer of ammonia. In both cases, the formation of hydrogen bonds led to a decrease in the IR intensity of the umbrella mode.

4. Discussion

Theoretical studies for ammonia adsorbed on different metal surfaces suggest bonding through the N, with N–H bond lengths and HNH bond angles that are very close to those seen in the free molecule [14]. In general, the bond between ammonia and a metal surface is essentially due to a transfer of electrons toward the surface from the N-lone pair of the molecule, plus an electrostatic interaction between the dipole moment of the adsorbate and the charge distribution of the metal substrate [14–16]. For the \( \alpha_1 \) state of ammonia on Ru(0001), work function measurements and ESDIAD data [8] indicate adsorption via the N-lone pair, with the H atoms pointing away from the substrate and the molecular axis parallel to the surface normal. Among the vibrational modes of NH₃ in this adsorption geometry, one can expect that only the umbrella mode (\( \nu_3(A_u) \) in gas phase [17]) will generate the large dipole moment perpendicular to the surface that is necessary to produce an appreciable cross section in infrared spectroscopy. Our FT-IRAS results are consistent with this expectation. At \( \theta_{\text{NH}_3} \leq 0.15 \), the infrared spectra show a peak at \( \sim 1110 \text{ cm}^{-1} \) (umbrella mode) and no appreciable signal in the 3200–3350 cm\(^{-1}\) region (N–H stretch). The IR results are in qualitative agreement with previous HREELS studies for ammonia chemisorbed on Ru(0001) [9,18], which show that the umbrella mode is strongly dipole allowed, whereas the remaining vibrational modes of the molecule are predominantly excited by impact scattering.

Our IR results show a decrease of \( \sim 40 \text{ cm}^{-1} \) in the peak position of the umbrella mode (\( \delta \))
when $\theta_{\text{NH}_3}$ increases from 0.05 to 0.25. An identical behavior has been observed in HREELS studies of NH$_3$ on Ru(0001) [9]. The frequency shift of the $\delta$ mode correlates with a decrease in the work function of the surface [9]. This agrees with trends observed in inorganic complexes, where an increase in the electron density of the metal center leads to a lower $\delta$ frequency [9].

The data in figs. 1 and 2 for chemisorbed ammonia indicate a maximum in the IR intensity of the umbrella mode when the $\alpha_1$ state is saturated (NH$_3$ exposure $\sim 0.5$ L, $\theta_{\text{NH}_3} = 0.15$). Population of the $\alpha_2$ state results in a decrease of the $\delta$ signal. This is probably a consequence of a change in the orientation of the molecules on the Ru(0001) surface. Results of ESDIAD [8] indicate that in the $\alpha_1$ state the NH$_3$ molecules are bonded with their symmetry axes perpendicular to the surface. In contrast, when the $\alpha_2$ state is present, the symmetry axes of the NH$_3$ species are to some extent inclined toward the surface [8]. This reorientation reduces the perpendicular component of the dipole moment associated with the umbrella mode. As a result, the IR cross section of NH$_3$ molecules in the $\alpha_2$ state is considerably larger than that of molecules in a saturated layer of ammonia ($\theta_{\text{NH}_3} = 0.25$). Interestingly, the change in IR intensity of the $\delta$ mode at $\theta_{\text{NH}_3} = 0.15$, also matches variations in the work function of Ru(0001) with ammonia coverage [8]. For the $\alpha_1$ state, the decrease in the work function is linear with coverage. The work function continues to decrease as the $\alpha_2$ state populates, but with decreasing slope.

Population of the second layer of ammonia drastically reduces the IR intensity of the umbrella mode of chemisorbed ammonia. For a film with 2 layers of ammonia no signal is observed in the 1050–1150 cm$^{-1}$ region. To explain this phenomenon, we must consider first the bonding configuration of the second layer of ammonia. Results of LEED and ESDIAD [8] indicate that the NH$_3$ molecules in the second adsorption layer are bonded to those in the first layer via hydrogen bonds. The N-end of each second-layer molecule interacts with the hydrogens of three molecules bonded to the Ru(0001) substrate [8]. Similar threefold hydrogen bonding is observed in the cubic modification of solid ammonia [8,19]. A film with 2 layers of ammonia has a very large fraction of the first- and second-layer molecules oriented with their symmetry axes normal to the surface [8]. For these molecules excitation of the umbrella mode is dipole allowed. However, they show an IR absorbance that is much smaller than that of the $\alpha_1$ state of chemisorbed ammonia. This behavior can be explained by assuming: (1) a reduction in the IR cross section of the $\alpha_1$ and $\alpha_2$ states as a consequence of the formation of hydrogen bonds with the second layer, and (2) a relatively small IR cross section for the molecules in the second adsorption layer.

The results of figs. 1–3 indicate that adsorption in the $\alpha_1$ state enhances the IR cross section of the umbrella mode of ammonia. For chemisorption on metal surfaces, the presence of an image dipole can modify to a large extent the vibrational properties of a molecule [3,20]. Thus for example, the dynamical dipole moment of CO chemisorbed on Cu(100) and Ni (100) ($\mu \approx 0.25$ D) is twice as large as for the free molecule ($\mu = 0.1$ D) [20]. One can expect that a molecule with a very large dipole moment in gas phase like ammonia ($\mu = 1.7$ D), will induce a large image dipole in the metal surface. In fact, theoretical studies indicate that the electrostatic interaction between the charge distribution of NH$_3$ and the image charge in the metal is primarily responsible for the adsorption energy of the molecule [16]. It is possible that a Ru-H interaction could enhance the dynamical dipole moment (and IR cross section) associated with the umbrella mode of NH$_3$ molecules adsorbed in the $\alpha_1$ state. Formation of hydrogen bonds between the first- and second-layer molecules would prevent the Ru-H interactions, reducing significantly the IR cross section of chemisorbed ammonia. The second layer (and subsequent physisorbed layers), on the other hand, are above the Ru surface by at least 1 ammonia layer. This significantly reduces the image dipole enhancement of the NH$_3$ cross section and results in the lack of observable IR intensity until a film thickness of $\sim 5$–6 layers is obtained.

The data in figs. 3 and 4 indicate that hydrogen bonding can introduce large changes in the
IR spectrum of chemisorbed ammonia. In principle, the formation of hydrogen bonds can modify the IR cross section of a vibrational mode by: (1) introducing additional mechanical stress in the vibration; (2) changing the nature of the interaction between the chemisorbed species and metal substrate, altering the dynamical dipole moment of the admolecule; and (3) reorienting the adsorbed molecule. Evidence for (3) has been presented in a recent IR study of D\textsubscript{2}O on Ni(110) [21], where in the first layer, the D\textsubscript{2}O molecules show no detectable intensity in the O–D stretch region of the IR spectrum. Adsorption of the second layer “switches on” the IR signal. These results have been interpreted [21] in terms of a model in which the D\textsubscript{2}O molecules in the first layer are adsorbed with their molecular planes parallel to the Ni(110) surface (making the O–D stretch inactive for absorption in the IR). Adsorption of the second layer of D\textsubscript{2}O introduces hydrogen bonding, reorienting the chemisorbed molecules and “turning on” the IR signal [21]. This model conflicts with previous UPS [22] and ESDIAD [23] results that indicate the formation of chemisorbed water dimers, bound through hydrogen bonding and oriented with their molecular planes in a tilted configuration with respect to the Ni(110) surface. The fact that these water dimers do not show detectable intensity in the O–D stretch region of the IR is consistent with our present results, in which no signal was detected for the N–H stretch of chemisorbed NH\textsubscript{3}. In the first layer of D\textsubscript{2}O/Ni(110) and NH\textsubscript{3}/Ru(0001), the O–D and N–H stretches are substantially tilted with respect to the surface normal, and thus exhibit relatively small dipole moments perpendicular to the substrate. In ref. [21], the appearance of IR signal for D\textsubscript{2}O/Ni(110) coincides with the beginning of the second layer and likely with the formation of a bilayer structure [22,23]. According to the bilayer model (which is based on LEED, UPS and ESDIAD results [22,23]), the D\textsubscript{2}O molecules in the second layer are attached to those in the first via three-fold hydrogen bonding. In this model the O–D bond is perpendicular to the surface and thus should be very active in the IRAS.

Regarding the results and interpretation of ref. [21], it is noteworthy that our data in fig. 4 for D\textsubscript{2}O adsorption onto a chemisorbed layer of NH\textsubscript{3} show no D\textsubscript{2}O stretching features for exposures up to 2.0 L. The hydrogen bonding interactions between the D\textsubscript{2}O and the chemisorbed NH\textsubscript{3} layer make a parallel configuration between the planes of the D\textsubscript{2}O molecules and the surface very unlikely. All together the similarities between the IR results for the D\textsubscript{2}O/Ni(110) and NH\textsubscript{3}/Ru(0001) systems suggest a common mechanism for the modification of the cross section of the O–D and N–H stretches in the infrared spectrum.

5. Conclusions

The infrared spectrum of ammonia chemisorbed on Ru(0001) is characterized by the presence of a sharp peak in the 1050–1150 cm\textsuperscript{-1} region (umbrella mode) and the absence of any appreciable signal in the 3200–3400 cm\textsuperscript{-1} region (N–H stretching mode). The variation of the IR intensity of the umbrella mode with NH\textsubscript{3} coverage is not linear. In the first adsorption layer, the changes in IR intensity correlate with changes in the orientation of the admolecules observed in ESDIAD and work function measurements. It appears that chemisorption on Ru(0001) enhances the IR cross section of the umbrella mode of ammonia. On the other hand, formation of hydrogen bonds between first- and second-layer NH\textsubscript{3} molecules reduces drastically the IR cross section of chemisorbed ammonia. A film with 2 layers of ammonia shows no signal in the infrared spectrum.

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References

[2] A.M. Bradshaw and E. Schweizer, in: Advances in Spec-