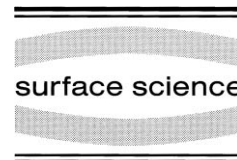




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Identification of a vibrational Stark shift within an adsorbate layer: NH₃ on Ru(001)

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Abstract

Using high-resolution electron energy loss spectroscopy we investigated the coverage-dependent vibrational properties of ammonia chemisorbed on Ru(001). With increasing coverage we find a drastic red shift of 100 cm⁻¹ for the ammonia symmetric deformation mode. Based on results for ammonia layers containing different isotopic species, such as NH₃ as well as partially and totally deuterated ND_xH_{3-x}, this red shift can be identified as a dominantly static shift (no dynamical coupling). Based on DFT model calculations, the origin of this shift can be understood as a Stark shift due to the electric fields produced by the static NH₃ dipoles within the adlayer. Calculations for isolated ammonia and for ammonia adsorbed on small Ru clusters, both in the fields of neighboring electric dipoles, can well reproduce the sign and magnitude of the observed red shift and for this molecular system allow a clear distinction between pure electrostatic and adsorption-induced (chemical) effects. We show that as a consequence of the electric field, the ammonia molecule opens the H–N–H angle and a softening of the symmetric deformation mode occurs. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ammonia; Density functional calculations; Electron energy loss spectroscopy; Field effect; Ruthenium; Vibrations of adsorbed molecules

Electric fields have significant impact on the geometric, electronic and vibrational properties of gas-phase molecules, as well as on chemisorbed molecules [1–4]. However, a clear experimental distinction between different possible origins – e.g.,

charge transfer versus electrostatic field induced – was possible on surfaces for only a few systems for which electric field effects have been proposed to play an important role [5–8]. Such a strict distinction is often impossible (especially for atomic adsorbates) since charge distribution and electrostatic fields are closely related to each other. Both quantities have to be calculated self-consistently, as has been discussed in detail by Wang et al. [8]. Additionally to the interest in internal

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electric fields, new interest in external electric fields has grown based on the observation of STM induced modifications of admolecule surface bonds [7].

Here we report on a strong vibrational Stark shift within an adsorbate layer. For ammonia adsorption on Ru(001), a coverage-dependent down shift of about 100 cm^{-1} is found for the symmetric deformation (umbrella) mode. Based on isotopic exchange experiments combined with density functional cluster calculations, it is identified as static shift induced by the electric field generated by the surrounding molecules.

Ammonia adsorption on metal surfaces has attracted considerable interest already in the early stages of surface science as a prototypical adsorption system which exhibits hydrogen bonding, and because of its relevance for industrial catalytic processes such as ammonia synthesis. On Ru(001) it has been the subject of several studies [9–14]. It was shown that ammonia adsorbs at 80 K molecularly with multilayer desorption around 115 K, bilayer desorption around 140 K and molecular ammonia desorption for the monolayer over a broad temperature range from 150 to 350 K [10,12]. Derived from changes in the electron stimulated desorption ion angular distribution (ESDIAD) pattern and the occurrence of a second desorption maximum within the monolayer desorption regime, two different NH_3 species, α_1 and α_2 , were proposed [12]. An electron energy loss spectroscopy (HREELS) study found an intense symmetric deformation mode δ_s which shifts down nearly linearly with coverage [14]. This shift has been related to the workfunction decrease of 2.3 eV with NH_3 coverage but interpreted as a consequence of charge transfer from the adsorbate to the metal substrate [14]. Based on this proposal they expected strong coverage-dependent shifts for the frustrated translation of the molecule perpendicular to the surface (T_z mode) and the frustrated rotations as well. At that time both modes were not detectable [14].

The HREELS experiments reported here were performed in a two-chamber UHV system described previously [15]. Briefly, it is equipped with standard four grid LEED optics, quadrupole mass spectrometer, Ar^+ -ion sputter gun, different

dosing facilities, X-ray source, and hemispherical analyzer for XPS, and an HREEL spectrometer (Delta05, VSI). Here a resolution of about 8 cm^{-1} with count rates in the range of 10^5 – 10^6 s^{-1} for the specular beam was used. Sample preparation was performed by noble gas sputtering, oxygen adsorption–desorption cycles, and annealing to 1570 K in standard fashion.

HREEL spectra for dilute NH_3 and ND_3 layers which have been adsorbed at 90 K and annealed to 250 K are shown in Fig. 1, respectively. The three strong modes at 3255 (2362), 1130 (872), and 140 (135) cm^{-1} for NH_3 (and ND_3) are attributed to the three dipole active modes of ammonia adsorbed on high symmetry sites and oriented normal to the surface with C_{3V} symmetry. The modes correspond to the symmetric N–H stretch, the NH_3 symmetric deformation mode, and the T_z mode, respectively. The latter is identified here for the first time. Previous studies with lower energy resolution could not detect this mode because of its low energy and consequent vicinity to the tail of the elastic peak. Also the N–H stretching modes have been resolved in the past

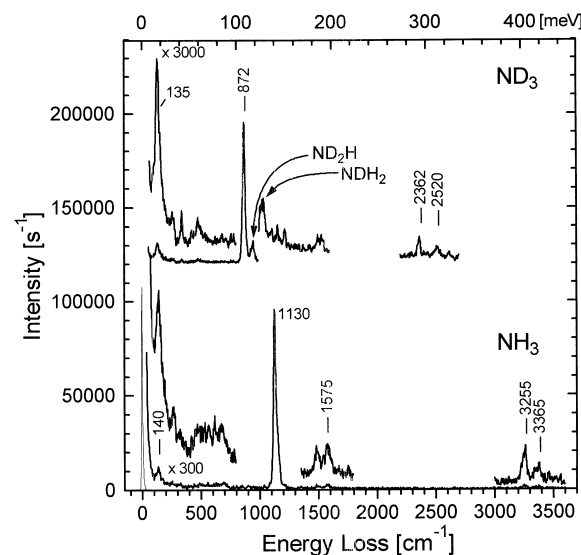


Fig. 1. HREEL spectra for a dilute ammonia layer on Ru(001) ($\theta_{\text{NH}_3} = \frac{1}{3}\theta_{\text{sat}}$). The layers were prepared by adsorption at 90 K followed by annealing to 250 K. A primary electron energy of 4 eV and specular scattering conditions ($\theta_{\text{in}} = 60^\circ$) with an energy resolution of 8 cm^{-1} were used.

only close to saturation coverage. Due to vibrational excitation by electron impact scattering additional ammonia modes at 3365 (2520) and 1575 cm^{-1} are visible. They correspond to the doubly degenerate asymmetric N–H stretch and NH_3 deformation modes. This assignment is supported by the observed isotopic shifts. Weak features in the ND_3 spectrum in the 950–1050 cm^{-1} range can be assigned to the ammonia umbrella mode of ND_2H and NDH_2 remainder species due to isotopic exchange within the dosing line, as was verified by additional experiments with isotopic mixtures. The weak mode at 1490 cm^{-1} which is visible in both spectra is ascribed to the internal stretch of CO contamination within the layer, with a relative coverage below 5%. Note that compared with the thorough work by Parmeter et al. 10 years ago [14], the experimental resolution here is increased by nearly one order of magnitude. At the same time the sensitivity is significantly improved: the resolved N–H stretches, the degenerated deformations and the frustrated translations could not be detected at similar submonolayer coverages before.

Based on a comparison of the observed vibrational spectra with calculated frequencies for a $\text{NH}_3\text{Ru}_{14}$ cluster [16], particularly in view of the rather low frequency of the T_z mode, ammonia adsorption in the three-fold hollow site is concluded for the α_1 species at low coverages. Details of the vibrational structure will be discussed elsewhere [17]; here we focus on the properties of the ammonia umbrella mode in comparison to the external T_z mode. Fig. 2 displays the enlarged energy loss region from 1000 to 1200 cm^{-1} for a sequence of annealing steps after bilayer adsorption. Annealing leads to molecular NH_3 desorption and a remaining NH_3 submonolayer close to equilibrium. This procedure was chosen instead of dosing an increasing amount of NH_3 at 90 K, since it was found that at low temperatures second-layer adsorption starts before monolayer completion [14]. The umbrella mode δ_s is the dominating peak in Fig. 2. On the higher frequency side a second peak is discernible for annealing temperatures below 260 K. It shows a similar frequency shift with annealing temperature as the dominant umbrella mode. It is present for ammonia cover-

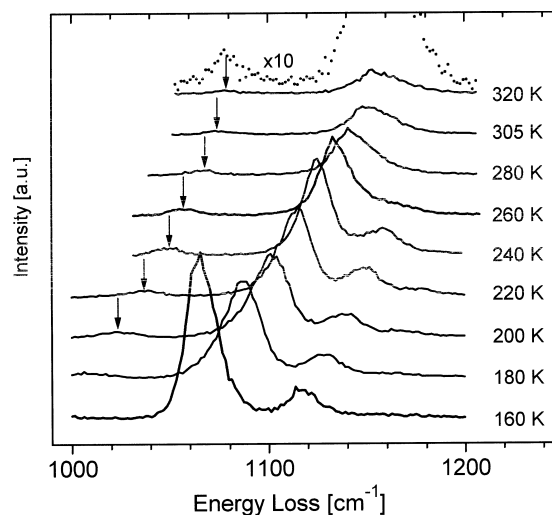


Fig. 2. HREEL spectra in the energy range of the symmetric deformation (umbrella) mode for increasing ammonia coverage (from top to bottom). All layers contain a few percent of NH_2D beside the majority NH_3 species; prepared by adsorption at 90 K and annealing to the indicated temperatures.

ages above half a monolayer and is accompanied with a strong mode at 358 cm^{-1} . These additional modes are interpreted as the umbrella and the T_z modes, respectively, of a second species ($\alpha_2\text{-NH}_3$) adsorbed at the ontop position [17]. For the following discussion of the Stark shift, a distinction between α_1 and α_2 species is not substantial since we deal with long-range dipole forces. Clearly an up-shift of the frequency with increasing annealing temperature and therefore decreasing coverage can be seen in Fig. 2. It is summarized in Fig. 3: Within the monolayer, the NH_3 umbrella mode shifts up from 1060 to 1160 cm^{-1} with increasing annealing temperature. In Fig. 2 an additional weak peak, indicated by arrows, can be identified. It corresponds to the umbrella mode of a NH_2D minority species (about 5%) in the NH_3 dosing gas. It shifts from 984 to 1080 cm^{-1} as marked in Fig. 3. Approximate NH_3 coverages as determined by thermal desorption are indicated at the top of Fig. 3. Also note that none of the other vibrational modes shows any significant frequency shift.

The observed red shift might have different physical origins which can be divided into two categories: either dynamical coupling of the indivi-

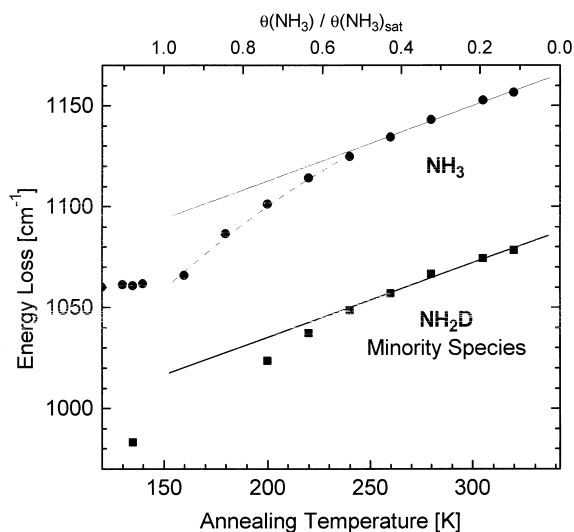


Fig. 3. Frequencies of the NH_3 and NH_2D symmetric deformation mode for the α_1 species as function of annealing temperature. The corresponding ammonia coverage is indicated at the top axis.

dual oscillators, i.e., the presence of dispersion, or static lateral interactions. Experimentally it is possible to differentiate between static and dynamical shifts by analyzing the dispersion of the vibrational modes and determining the dynamical coupling constants. Here we have chosen a different way by using partly deuterated molecules. By preparing a layer which, besides the majority species NH_3 , contains also chemically identical minority species with different eigenfrequencies (in our case NH_2D), vibrational coupling can be switched off for the minority species. As seen in Fig. 3, the majority as well as the minority species show parallel shifts with coverage. From lowest coverage on, the frequency ratio $\delta_s(\text{NH}_3)/\delta_s(\text{NH}_2\text{D})$ for the symmetric deformation mode of the two isotopes is constant ($=1.07$). Therefore we rule out any significant dynamical coupling for this mode. The shift of this mode is clearly identified as a predominantly static shift.

So far, we have discussed the umbrella mode. For all other modes, especially the frustrated translation T_z , no significant shift (within about 5 cm^{-1}) with coverage is observed. Note that the external T_z mode is more sensitive to changes in the NH_3 surface chemisorption bond than the

internal umbrella mode. We therefore propose that the static shift for NH_3 on $\text{Ru}(001)$ is a result of the electrostatic dipole–dipole interaction and of the response of the adsorbate bonds to it. Since the dipole field vanishes only slowly with $1/r^3$ compared with any short ranging electronic modifications due to charge transfer, this interpretation would also explain why a shift of the umbrella mode is already visible at low coverages where the mean separation between ammonia molecules is rather large, and why the shift is continuous with coverage rather than stepwise as one could expect for a short-range coordination-dependent effect.

A distinction of vibrational shifts due to adsorption-induced changes of the surface electronic structure (chemical interactions) versus electrostatic interactions due to the dipole fields of the coadsorbates might be difficult, especially for atomic adsorbates, because any change of the charge distribution will lead, e.g. via generation of electrostatic dipoles, to altered electric fields at the surface and vice versa. However, a molecule with a large intrinsic dipole moment which is only slightly modified upon adsorption facilitates the separation into chemical and electrostatic interactions. In this case, the electrostatic field at the adsorbate is determined mainly by the superposition of the dipole fields of the surrounding molecules (properly accounting for the image charges). Clearly, this simple concept is only meaningful if the dipole moment due to the adsorption-induced charge redistribution is small compared to the intrinsic molecular dipole moment found, e.g., in the gas phase. For ammonia on $\text{Ru}(001)$ we will use this picture to estimate the order of magnitude of such a Stark shift.

To verify that a Stark effect within the adsorbate layer, in fact, can explain the large shift found for the umbrella mode DFT model calculations for a single ammonia molecule within an electric field of neighboring dipoles, and for ammonia adsorbed on small Ru clusters ($\text{NH}_3\text{—Ru}$ and $\text{NH}_3\text{—Ru}_4$), have been performed. The calculations were carried out with the ParaGauss program [18], a parallel implementation of the LCGTO-DF technique [19]. The basis sets were taken from a previous investigation of NH and NH_3 species adsorbed on $\text{Ru}(001)$ [16,20]. However, in con-

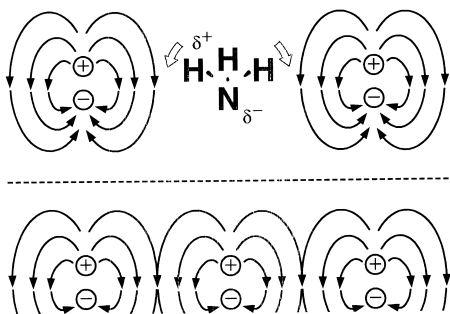


Fig. 4. Sketched structure used in the calculations for the dipole-induced changes for gas-phase ammonia.

trast to these studies the gradient-corrected functionals proposed by Becke [21] and Perdew [22] are used here. By the use of unsupported ammonia molecules, the Stark effect on the adsorbate can be widely separated from adsorbate–substrate interaction-induced effects. Furthermore, the use of electric dipoles instead of neighboring molecules prevents any possible lateral adsorbate–adsorbate interaction mediated effects to superpose the pure electrostatic mechanism.

Gas-phase ammonia has a strong dipole moment of 1.47 D [23]. It will be modified upon adsorption by the interaction of the nitrogen lone pair orbital with the metal surface and also by electronic screening. The latter can be described as the formation of an image dipole. However, to separate the influence of the electric field on the intramolecular properties from those of the chemisorption, we start with the calculations for gas-phase ammonia in the electric field of neighboring dipoles generated by charges fixed in space, as indicated in Fig. 4. The results are summarized in Table 1. In the absence of external electric fields

Table 1
Structural parameters together with calculated and experimentally determined frequencies^a

	No field	High coverage	High coverage + image fields
Exp: δ_s (cm^{-1})	1160	–	1060
δ_s (cm^{-1})	1039	905	960
ν_s [cm^{-1}]	3367	3380	3374
\angle HNH (deg.)	106.5	108.4	107.7

^a For details see text.

the calculation yields the ammonia symmetric deformation and symmetric N–H stretch modes at 1039 and 3367 cm^{-1} , in good agreement with previous DF calculations [24] for an optimized geometry with an H–N–H angle of 106.5°. The calculation with three neighboring dipoles at a distance of $2/\sqrt{3} a$ (with $a=2.70$ Å being the lattice constant of Ru) which reflects the geometric structure at ammonia saturation coverage, yields deformation and stretch modes of 905 and 3380 cm^{-1} , respectively. This high coverage simulation corresponds to an imposed electric field of 0.43 V/Å along the ammonia symmetry axis. The softening of 134 cm^{-1} found for the symmetric deformation mode is accompanied by an opening of the H–N–H angle to 108.4°, which is in line with the orientation of the added electric field (see Fig. 4). The N–H bond length, on the other hand, is unaffected by the dipole field within 0.002 Å. Adding the image dipoles of both, the ammonia molecule and the three surrounding dipoles (with an N–N_{image} distance of 4.4 Å corresponding to an on-top N–Ru distance of 2.2 Å as typically encountered here and in previous model cluster calculations [16]), leads to a reduction of the opening of the ammonia umbrella H–N–H angle by 0.7°, again together with a hardening of the symmetric deformation mode by 55 cm^{-1} . Both trends are in perfect accordance with the reduced field strength of 0.27 eV/Å at the center of the ammonia molecule due to the image dipoles.

Similar strong Stark shifts are found for ammonia adsorbed on-top of a single Ru atom, 1165 down to 1078 cm^{-1} , and on-top of a tetrahedral Ru₄ cluster, 1121 down to 1012 cm^{-1} for the low to the high coverage geometry, respectively.² Again, the softening of the umbrella mode is accompanied by an opening of the H–N–H angle from 107.7 to 109.0° for the NH₃–Ru model and from 107.9 to 109.5° for the NH₃–Ru₄ model. Although the modeling of the surface is strongly

² Note that no stable ammonia species could be found for the hollow site in agreement with previous DF model cluster calculations with much larger Ru clusters [16,25] where, at most, a very weakly bound ammonia molecule was observed but in variance to DF repeated slab calculations [26] which show the hollow site adsorption complex [with $z(\text{N–Ru})=1.9$ Å] to be more stable.

simplified, we believe that the changes induced by the additional electric field are satisfactorily described. As for gas-phase ammonia, we find a strong Stark shift for the symmetric deformation mode of 109 cm^{-1} , again accompanied by an opening of the ammonia umbrella.

These simple calculations for an isolated NH_3 molecule and NH_3 bonded to one or four Ru atoms clearly demonstrate that the down shift of the umbrella mode observed experimentally can be explained with respect to both, sign and order of magnitude, by a Stark shift due to the field of the neighboring adsorbate dipoles. However, for a detailed analysis one has to consider the simplifications adopted. Besides the rather small size of the cluster used in the calculations, only the next neighbor dipoles have been taken into account. It is possible to sum up the long-ranging dipole fields of the individual entities in a periodic arrangement of point dipoles, although they only decay slowly with $1/r^3$. This results in an electric field for the full monolayer which is about 2.2-times higher than the field due to the next neighbor dipoles only. On the other hand, depolarizing effects and any tilting of the ammonia C_3 axis away from the surface normal which both decrease the effective dipole moments are not considered here. Actually, at higher coverages the vibrational data indicate a symmetry breaking due to ammonia tilting [17], which can be understood as a response to the strong electrostatic dipole–dipole repulsion.

To summarize, we presented a high-resolution vibrational study for NH_3 and ND_3 adsorption on Ru(001), demonstrating a strong Stark shift within the adlayer: the symmetric deformation mode exhibits a 100 cm^{-1} red shift with increasing coverage. Based on isotopic experiments, the red shift can be identified as a static shift (no significant contribution due to dynamical coupling). Calculations for gas-phase ammonia and for ammonia adsorbed on a Ru_4 cluster in the field of neighboring NH_3 dipoles demonstrate that the ammonia molecule opens the H–N–H angle as a consequence of the imposed electric field, and that indeed softening of the symmetric deformation (umbrella) mode in the order of magnitude observed experimentally arises from such a field.

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