# Adsorption-Induced Bending of a Triatomic Molecule: Near-Edge X-Ray Absorption Fine-Structure Spectroscopy Investigation of $N_2O$ Adsorbed on Different Ni(111) Surfaces

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A monolayer of $N_2O/Ni(111)$, a submonolayer species, and a monolayer of $N_2O/Ni(111) + O\ p[2 \times 2]$ were studied using near-edge x-ray absorption fine-structure spectroscopy. From the polarization dependence we derive bent $N_2O$ molecules for the monolayer species whereas the two other species remain linear upon adsorption. Using the $X\alpha$-scattered-wave method the polarization dependence of the three $\pi^*$ resonances was calculated explicitly for linear and bent $N_2O$ molecules. The calculations reproduced the experimental results quantitatively, yielding a bond angle of 165° for the monolayer species. [S0031-9007(96)00447-4]

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The most prominent application of *near-edge x-ray-absorption fine-structure* (NEXAFS) spectroscopy is the determination of the orientation of molecular adsorbates. For highly symmetric molecules the polarization dependence of certain absorption resonances is evaluated in terms of symmetry selection rules using simple group theoretical considerations. This method was described in detail by Stöhr and Outka [1]. The group theoretical approach, however, fails if the symmetry of the molecule is reduced [2,3]. In this Letter we report the first clear example of such a case, namely, the adsorption induced bending (i.e., symmetry reduction) of a linear polyatomic molecule, nitrous oxide ($N_2O$) which is weakly chemisorbed on Ni(111). We shall demonstrate that the polarization dependence of the NEXAFS spectra can be interpreted *only* by using explicit calculations of the transition dipole moments (TDM).

Nitrous oxide is a linear triatomic molecule in the gas phase [4]. It contains two nitrogen atoms in different chemical environments: the *central* ($N_c$) and *terminal* ($N_t$) nitrogen atoms which can be clearly distinguished by all core level spectroscopies. The NEXAFS measurements presented here are part of a comprehensive study on the adsorption of $N_2O$ on Ni(111) and on Ni(111) + O $p[2 \times 2]$ [5]. Thermal desorption spectra reveal three clearly separated adsorption species on the clean Ni(111) surface: (1) *multilayers* with a desorption temperature of ≈70 K, (2) a *monolayer* species which desorbs at ≈92 K, and (3) a third species, clearly discernible from the monolayer and containing about 10% of a monolayer, which desorbs at ≈100 K, and which will be referred to as *dilute layer* in the following. The rather low desorption temperature and the x-ray and UV photoelectron spectra (negligible binding-energy shifts of all peaks with respect to the gas phase) clearly indicate molecular adsorption with weak chemisorptive bonding to the Ni surface [5].

The experiments were performed at the SX 700-I monochromator at the BESSY storage ring (Berlin) using a photon energy resolution of ≈0.8 eV at the N 1*s* edge and ≈1.2 eV at the O 1*s* edge, respectively. The energy was calibrated to better than 0.2 eV using the Ni 3p photoelectron peak. Photon absorption was measured recording the Auger yield with a spherical sector analyzer (CLAM 2) with the energy window (12 eV wide) set at 382 eV (N 1*s*) and 510 eV (O 1*s*), respectively. Nitrous oxide multilayers were prepared by dosing through a leak valve and a stainless steel capillary which ended about 1 cm in front of the sample. Monolayers and dilute layers were prepared by heating the sample to 85 and 95 K, respectively, according to the thermal desorption spectra [5]. The O $p[2 \times 2]$ precoverage was prepared by saturating the cold (90 K) surface with adsorbed oxygen (≈20 Langmuir) followed by annealing at 800 K for 30 sec. On the O-precovered surface only a saturated $N_2O$ monolayer was prepared. Data evaluation included subtraction of a constant offset due to higher order radiation, division by an $I_0$ signal representing the incident photon flux, and by subtraction of the (properly attenuated) spectra from the clean surface. For determination of peak intensities the spectra were normalized to the intensity difference between energies below and far above the ionization threshold ("edge jump").

NEXAFS spectra of the different adsorbate states are displayed in Figs. 1 and 2. The dotted spectra were recorded at an angle of incidence of 70° with respect to the surface normal (i.e., polarization vector almost per-

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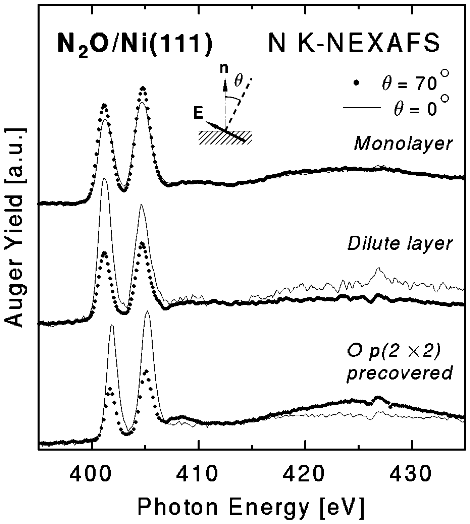

FIG. 1. N K-NEXAFS spectra of three (sub-)monolayer species of $N_2O$/Ni(111). The spectra shown as solid lines were recorded at normal incidence of the synchrotron radiation ($\theta = 0°$, polarization parallel to the surface) while the dotted spectra were measured at grazing incidence of the light ($\theta = 70°$, polarization almost perpendicular to the surface).

pendicular to the surface) and the spectra represented by solid lines were recorded at normal incidence (polarization vector parallel to the surface). The structure visible at ≈426 eV in some of the N spectra is due to the Ni 2*p* edge excited by second order synchrotron radiation which could not be completely eliminated by background subtraction. Gaseous nitrous oxide is dissociated very easily by soft x rays following the Auger decay of core holes [6]. We also observed rapid dissociation in multilayers of $N_2O$/Ni(111) [5]. However, the three species shown in Figs. 1 and 2 were found to be much less sensitive to soft x rays, which can be explained by rapid delocalization of the x-ray induced holes into the substrate due to the substrate-adsorbate coupling.

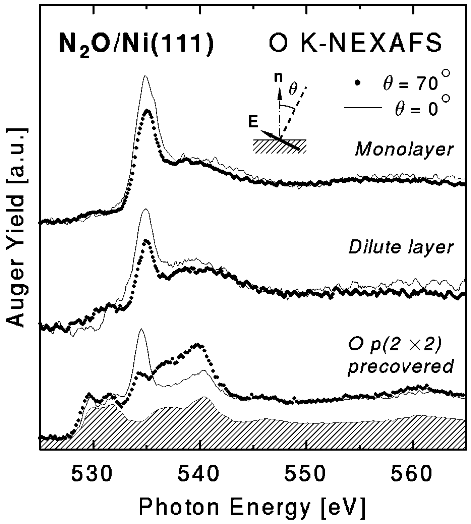

FIG. 2. O K-NEXAFS spectra of the three (sub-)monolayer species investigated corresponding to those in Fig.1. The shaded spectrum at the bottom shows the NEXAFS signal from the O $p[2 \times 2]$ precoverage.

The nitrogen spectra (Fig. 1) show two intense resonances which are assigned to the transition from the 1*s* orbitals of the terminal and the central nitrogen atom, respectively, into the first unoccupied molecular orbital ($3\pi^*$). For the monolayer and the dilute layer their energies (401.2 and 404.8 eV) coincide with those measured for free and condensed $N_2O$ molecules [7,8] as expected for a weakly coupled adsorbate. A small (0.2 eV) but systematic shift is observed in the $N_c$ $1s \rightarrow 3\pi^*$ (and O $1s \rightarrow 3\pi^*$) resonances of the monolayer and the dilute layer when comparing the spectra recorded at $\theta = 0°$ and $\theta = 70°$, respectively. At least in the case of $N_c$ this shift is most likely due to the $N_t$ $1s \rightarrow 3s\sigma$ Rydberg resonance, which is located at the leading edge of the $N_c$ $1s \rightarrow 3\pi^*$ resonance at 404.8 eV and preferentially contributes to this peak at normal incidence [9]. A more detailed discussion of this interesting finding will follow in a subsequent publication [5]. The N $1s \rightarrow 3\pi^*$ resonances of $N_2O$/Ni(111) + O $p[2 \times 2]$ are shifted by ≈0.7 eV ($N_t$ $1s \rightarrow 3\pi^*$) and 0.5 eV ($N_c$ $1s \rightarrow 3\pi^*$), respectively, to higher photon energies. These shifts indicate a different chemisorptive bond as compared to that on the clean surface and the differential shift suggests that the $N_2O$ molecules are bound to the Ni surface via the $7\sigma$ orbital (which is predominantly located on the terminal N atom) as observed earlier by Bornemann [10] and as found also for other substrates like Ru(001) [11,12] or Pt(111) [13]. In the N-K edge spectra of the complete monolayer and of the monolayer on O-precovered Ni(111) the relative intensities of the $\pi^*$ resonances are very similar to those in the spectra of free molecules hence indicating molecular adsorption without significant dissociation. The spectra of the dilute layer are somewhat different (see below).

The O-K NEXAFS spectra (Fig. 2) of all three species show one dominant resonance which is identified as O $1s \rightarrow 3\pi^*$ excitation. The energy (534.6 eV) again coincides with the value for the free molecule [7] within experimental error; the only qualitative difference to the spectra of free $N_2O$ is a small shoulder at ≈531 eV, which can be attributed to small amounts of molecular and/or atomic oxygen as discussed below. In the case of oxygen precovered nickel the oxygen spectra are superpositions of the spectra of $N_2O$ and the O $p[2 \times 2]$ precoverage which is shown as shaded spectrum at the bottom of Fig. 2. In this case the resonance is slightly shifted by 0.3 eV to lower energy again indicating a different chemisorption state as for the N-K spectra.

Significant differences of relative intensities are visible in the spectra of the *dilute layer* as compared to the other preparations: the $N_t$ $1s \rightarrow 3\pi^*$ resonance shows a significantly higher intensity for normal incidence. Comparison to multilayer spectra suggests radiation damage. However, since the intensities do hardly change following long-time exposure to soft x rays (thermal) dissociation during the preparation process is more feasible. The enhanced first $\pi^*$ resonance in normal incidence indicates molecular nitrogen to be coadsorbed with its molecular axis essentially perpendicular to the surface [14]. The other possible fragment of $N_2O$, nitric oxide, can be ruled out since the pronounced shape resonance of NO at 414.5 eV [14] is not observed. In the oxygen spectra the low energy shoulder at 531 eV indicating atomic or molecular oxygen [15] is increased as compared to the monolayer. Both findings clearly suggest formation of some $N_2$ and $O/O_2$ by dissociation during the adsorption process. Note that this dissociated species is a minority only (1%–2% of a monolayer) and hence does not play any role in the discussion below.

Next we address the polarization dependence of the NEXAFS spectra. The solid and dashed lines in Fig. 3 show the ratio of intensities $I_{\theta=0}/I_{\theta=70}$ [for normal (0°) and grazing (70°) incidence of the radiation] as a function of the angle between the molecular axis and the surface normal. The curves were calculated according to Ref. [1] for $\pi^*$ resonances of linear molecules adsorbed on a threefold or higher symmetric substrate. They differ by the assumed *polarization factor* which takes into account the incomplete polarization of the exciting radiation. The horizontal arrows indicate the experimental intensity ratios derived from the $\pi^*$ resonances in the spectra shown in Figs. 1 and 2. For the dilute layer ($I_{\theta=0}/I_{\theta=70} = 1.5$) and for $N_2O$ on the O-precovered surface ($I_{\theta=0}/I_{\theta=70} \approx 2$) the ratios derived from the N and O spectra coincide exactly, indicating an average tilt angle of 45° and 30°–35°, respectively.

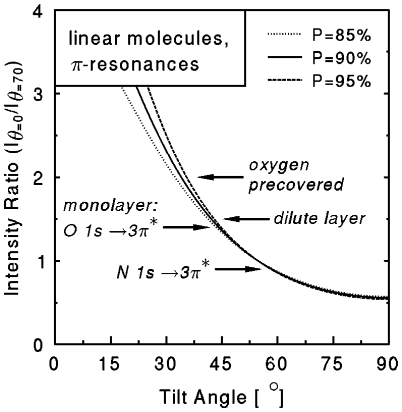

FIG. 3. Calculated ratios of intensity for normal ($\theta = 0°$) and grazing ($\theta = 70°$) incidence for $\pi$ resonances of linear molecules on a threefold or higher symmetric substrate as a function of the tilt angle between the molecular axis and the surface normal. Solid and dashed lines take into account different polarization factors of the synchrotron radiation. The horizontal arrows indicate the experimental values for the different preparations of $N_2O/Ni(111)$.

The most striking result of the present study is found in the monolayer spectra: The intensity ratios in the N ($I_{\theta=0}/I_{\theta=70} = 0.9$) and O ($I_{\theta=0}/I_{\theta=70} = 1.4$) spectra *disagree significantly*. The former ratio indicates a tilt angle of ≈60° whereas the latter indicates a tilt angle of ≈45° with respect to the surface normal. We emphasize that this result is incompatible with a linear molecule. As it appeared so unexpected we repeated the experiment twice with the same result in two additional beam times in order to rule out artifacts or impurity influences. We can also exclude effects from coadsorption of fragments of $N_2O$ ($N_2$ and/or NO), since the relative intensities of the $N_t$ and $N_c$ $\pi^*$ resonances are in full agreement with gas phase spectra. The only remaining explanation for the observed polarization dependence is a bending of the molecule due to the chemisorptive bond and perhaps the interaction with neighboring molecules. To verify this we conducted $X\alpha$ scattered wave calculations [16], which are described in the following.

For the calculations we used the interatomic distances of the free molecule, 1.126 Å ($N_t$-$N_c$) and 1.191 Å ($N_c$-O), respectively, and tested bond angles of 180° (linear), 165°, 150°, and 120°. The last two angles can be ruled out since the calculated energy splitting of the $\pi^*$ resonances due to the reduced symmetry should be clearly observable with the present energy resolution. We used a muffin-tin potential with overlapping atomic spheres (≈20%) and a touching outer sphere centered at the "center of gravity" of the atomic valence charges. An $\alpha$ value of 0.7 was used in all regions. With the $N_t$ and $N_c$ excitation the transition matrix elements were calculated using a simplified transition state with no electrons in the final states [17]. For the O 1$s$ excitation, however, this approximation caused artifacts which disappeared when the correct transition state was employed (self-consistent potential with half an electron in the final state orbital calculated for each core to bound-state resonance).

The bending of the linear $N_2O$ molecule leads to a reduction of the symmetry from $C_{\infty v}$ to $C_s$. The twofold degenerate $\pi$ orbitals are split into more or less energy separated $a'$ and $a''$ orbitals (e.g., $3\pi \rightarrow 7a', 3a''$). For the 165° bond angle the calculated energy splitting of ≈0.6 eV is markedly smaller than the experimentally observed linewidth of the resonances. Hence the experimentally measured intensity ratios $I_{\theta=0}/I_{\theta=70}$ of the "$3\pi^*$" resonances are in fact due to the sum of the intensities of the $7a'$ and $3a''$ resonances:

$$|\langle 3\pi|\hat{\mathbf{r}}|X1s\rangle|^2 \approx |\langle 7a'|\hat{\mathbf{r}}|X1s\rangle|^2 + |\langle 3a''|\hat{\mathbf{r}}|X1s\rangle|^2, \quad (1)$$

where $X$ is one of $N_t$, $N_c$, or O. To compare theoretical and experimental results we assumed the (bent) $N_2O$ molecules only to be aligned and not to be changed in their electronic structure by the Ni(111) surface. This appears to be justified because we deal with weak chemisorption [5,10] as mentioned above. With the geometry shown in Fig. 4 and taking into account the azimuthal averaging of intensities due to the threefold symmetry of the substrate the polarization dependence can be expressed in terms of the polar angle of incidence ($\theta$) and the inclination angle of the N-N axis of the molecules ($\alpha$),

$$I(\theta, \alpha) \propto \tfrac{1}{2}[(d_{x'a'} \cos\alpha + d_{y'a'} \sin\alpha)^2 + d^2_{z'a''}] \sin^2\theta + (d_{x'a'} \sin\alpha - d_{y'a'} \cos\alpha)^2 \cos^2\theta \,. \quad (2)$$

Using this equation and the dipole transition-matrix elements $d$ from the $X\alpha$–scattered-wave calculations the intensity ratios displayed in Fig. 4 were calculated. In this case perfect linear polarization of the synchrotron radiation was assumed. It can be seen that for values of $\alpha$ between 13° and 40° (indicated by the shaded area) the experimental observation of $I_{\theta=0}/I_{\theta=70} < 1$ for the nitrogen resonances and $I_{\theta=0}/I_{\theta=70} > 1$ for the oxygen resonance is correctly predicted. Comparison with the intensity ratios determined for the monolayer of $N_2O/Ni(111)$ ($N_t$, $N_c$: 0.9, O: 1.4) leads to an average $\alpha$ value of 30° ± 10°. The very similar intensity ratios for the $N_t$ and $N_c$ resonances are also reproduced correctly and therefore corroborate the assumption of a bent molecule.

The most important question remaining is why the $N_2O$ molecules are bent and why no bending occurs for the dilute layer and the O $p[2 \times 2]$ precovered substrate. The solution of this puzzle could be the very high electron density of the Ni(111) surface which is significantly lowered by preadsorbed oxygen. Peyerimhoff and Buenker showed, using Hartree-Fock calculations, that a bent geometry is energetically favorable if the LUMO ($3\pi^*$) orbital is partly filled [18]. They also predicted that at a bonding angle of 165° the energies of the occupied molecular orbitals remain almost unchanged. This would explain why the UV-photoelectron spectra show no significant differences as compared to the linear molecule [5].

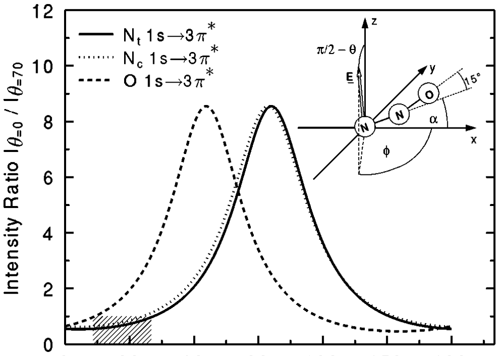

FIG. 4. Calculated ratios of intensity for normal ($\theta = 0°$) and grazing ($\theta = 70°$) incidence for the $\pi$ resonances of bent $N_2O$ (165°) on a threefold or higher symmetric substrate as a function of the angle between the N-N axis and the surface.

Recently, Adachi and co-workers [9] found gaseous nitrous oxide to be bent following excitation of N 1$s$ electrons into the $3\pi^*$ orbital. In our experiments, however, this “dynamic” bending is not observable since the time scale of the photoabsorption is much faster than the time scale of molecule bending. Hence we propose that the $3\pi^*$ orbital becomes (partially) filled prior to the NEXAFS excitation by a $7\sigma$-donation/$3\pi$-back-donation bonding mechanism. This occurs only on the clean Ni surface because of the high electron density in the substrate. For very low coverages (≤10%) partial dissociation occurs leading to (probably coadsorbed) linear molecules as in the case of the O-precovered surface and as for $N_2O/Ru(001)$ [11]. The bonding mechanism, however, appears to be more complicated than the here used Blyholder-type [19] since $N_2O$ on oxygen precovered Ni(111) is probably more strongly bound but does not show significant bending.

Finally we stress that the occurrence of molecular bending of tri- (or more) atomic molecules upon chemisorption may be an important effect both for the understanding of chemisorption and chemical (e.g., catalytic) reactions on surfaces, as well as for the interpretation of spectroscopic results, and that adequate calculations are required for a detailed understanding.

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