NO, ADSORPTION ON Ni(100): A COMPARISON OF NO, WITH CO, ADSORPTION

H. GEISLER, G. ODÖRFER, G. ILLING, R. JAEGER, H.-J. FREUND

Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, Universitätsstrasse 150, 4630 Bochum, Fed. Rep. of Germany

G. WATSON, E.W. PLUMMER

Department of Physics, University of Pennsylvania, Philadelphia, PA 10104, USA

M. NEUBER and M. NEUMANN

Fachbereich Physik, Universität Osnabrück, Barbarastrasse 7, 4500 Osnabrück, Fed. Rep. of Germany

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 NO_2 adsorption has been studied on Ni(100) at temperatures between 90 and 400 K via HREELS, ARUPS, XPS and NEXAFS. It is shown that NO_2 dissociates at low temperatures and small exposures forming atomic oxygen and molecularly adsorbed NO. HREELS data of NO/Ni(100) in comparison with those of NO + O/Ni(100) indicate that the molecular axis of NO in the coadsorbed layer is tilted away from the surface normal. After saturation of the dissociative adsorption NO_2 will chemisorb on the surface. This has been followed by HREELS and XPS. NEXAFS data indicate that the chemisorbed NO_2 moiety is adsorbed with the molecular plane perpendicular to the surface plane and the nitrogen end down. At high NO_2 exposures and at low temperatures physisorbed N_2O_4 is formed on top of this relatively complex chemisorbed layer. It is likely that the molecular plane of N_2O_4 is oriented parallel to the metal surface.

The adsorption of NO_2 on Ni(100) is compared with other NO_2 adsorption systems, and it is shown in comparison with the HREELS data of another triatomic, i.e. CO_2 , that the vibrational spectra represent finger prints of the adsorption geometry of these triatomic molecules.

1. Introduction

Only recently have surface scientists shown interest in the adsorption of triatomic oxides, while in many other fields reaching from environmental to economic studies triatomic oxides like NO₂ [1], CO_2 [2], and SO_2 [3] have been in the center of interest. While CO₂ is a rather inert, i.e. chemically inactive molecule, and represents the thermodynamic sink in many natural processes, NO₂ and SO₂ are very active, for example in atmospheric chemistry [2,3]. The different valence electron structure of the three oxides dictates the different reactivities of the species. However, the electronic structures are interrelated via the following isoelectronic series: CO₂⁻, NO₂, NO₂⁻, SO₂. We mention this interrelation because upon interaction of CO₂ and NO₂ with a solid surface the

molecules may take up electrons and form the corresponding anionic species. This may lead, for example in the case of CO_2 , to a dramatic increase in the reactivity of the species because it becomes "NO₂-like".

Koel and coworkers [4–6] have published a series of interesting papers where they have studied NO₂ adsorption on a set of transition metal surfaces. CO₂ has been studied by several groups [7–13]. We have demonstrated [7–11] that on several transition metal surfaces CO₂ chemisorbs at low temperatures via formation of a bent anionic CO₂ species. The bent species dissociates at low temperatures into adsorbed CO and O. At lower temperatures the bent species can be stabilized on the surface and it may react with species coadsorbed on the surface to form new products [14]. Surface reactions of this type may point the way to chemically active CO_2 . The study of SO_2 adsorption applying the full power of surface science techniques has started only recently also by several groups [15–17], but we shall focus for the remaining part of the paper on CO_2 and NO_2 .

It is the purpose of this paper to report new electron spectroscopic results for the system $NO_2/Ni(100)$ which represent additional evidence that will corroborate some of the ideas put forward in Koel's papers [4–6], and to use this knowledge to compare and correlate the results on NO_2 adsorption with those on other triatomics, in particular CO_2 . In the following we show that the vibrational spectra of chemisorbed CO_2 and NO_2 exhibit common features characteristic of similar bonding geometries, which are in turn confirmed via NEXAFS data.

2. Experimental details

The experiments have been carried out in three different vacuum systems. The NEXAFS and ARUPS data were recorded using synchrotron radiation from the storage ring BESSY in Berlin. The HREELS data have been taken in UHV systems (Philadelphia and Bochum) equipped with a Leybold ELS22 system with a typical resolution of 8 meV. The preparation chambers of the systems contain facilities for low energy electron diffraction (LEED) and thermal desorption spectroscopy (TDS).

The sample was spot-welded to two tungsten rods which were connected with a liquid nitrogen reservoir such that the sample could be cooled below 95 K, and heated by electron bombardement on the reverse side of the crystal as well as by direct heating, i.e. passing current through the crystal.

The Ni(100) surface was prepared by repeated cycles of Ne and Ar ion etching and heating to 1000 K. Care had to be exercised to make sure that water contaminants in the gas supplies were avoided. While NO₂ was introduced into the vacuum chamber all filaments and ion pumps had to be turned off.

The NEXAFS spectra were recorded by monitoring the nitrogen and oxygen Auger yields in a 12 eV wide window centered at 511 and 380 eV, respectively, as a function of photon energy. The Auger electron emission was detected at an angle out of the incidence plane so as to minimize direct photoemission features and to allow maximum variation of the incidence angle. The latter was varied by rotating the sample relative to the light beam. With a dwell time of 0.5 s/data point and 400 data points per 60 eV typically two scans were taken to achieve reasonable signal to noise ratios at the nitrogen edge. The NEXAFS spectra presented here are difference spectra and have been normalized to the absorption step height as was done previously [10].

3. Results and discussion

3.1. HREELS and ARUPS data

Fig. 1 shows a set of HREEL spectra taken under specular scattering conditions for various NO₂ exposures at 115 K. Even at the lowest accessible temperature in this study a small exposure of 1 L always led to NO₂ dissociation on the surface as indicated in spectrum b. This spectrum shows five bands, i.e. two at low frequency and three at high vibrational frequency. This situation is very similar to the one found for oxygen NO coadsorption of Pt(111) which has been studied by several groups [18,19]. Our results which have been obtained in the same UHV system used in this study have been published elsewhere [20]. We know from this previous study [20] that the three bands between 1400 and 1900 cm^{-1} are due to stretching vibrations of several different NO species. The species giving rise to the peak at 1840 cm⁻¹ are NO molecules adsorbed in the proximity of coadsorbed oxygen atoms. The species giving rise to the features at 1430 and 1600 cm⁻¹ are NO molecules adsorbed in different sites and packing density. On a Ni(100) surface there are three high symmetry adsorption sites, namely fourfold hollow, twofold bridge, and on-top, associated with an increasing stretching frequency for NO molecules adsorbed in those sites. In contrast to other chemisorbed closed shell diatomic molecules like CO and N2, NO with its unpaired

electron can assume two equilibrium geometries at low coverage. NO may either be linearly coordinated, i.e. with its molecular axis oriented perpendicular to the surface plane, or take a bent coordination where the molecular axis is inclined with respect to the surface plane. These two different coordination modes are well known for NO transition metal complex chemistry [21]. The stretching frequencies associated with such bent species range from slightly below 1600 cm^{-1} overlapping the regions characteristic for the twofold and the linear on-top coordinations up to 1880 cm⁻¹. Therefore, without further experimental results it is very difficult to give a definite assignment of the various bands. However, as discussed in detail in ref. [20], from the broad low frequency bands at 370-440 cm⁻¹ and 650 cm⁻¹ (which is really a superposition of two bands at 610 and 690



Fig. 1. HREEL spectra (a) of a clean Ni(100) surface exposed to (b) 1 L NO₂, (c) 15 L NO₂, (d) 100 L NO₂ at T = 115 K. The spectra were taken under specular conditions.

Table 1

System	ν _{M-mol}	δ_{bend}	<i>v</i> _{sym}	v _{as}	Ref.
$NO_2/O + Ni(100)$	430 ^{a)}	741	1247	1530	[This work]
$NO_2/O + Pt(111)$	460 ^b	795	1270		[5]
$NO_2/Pt(111)$	295	795	1180	1560	[4]
NO ₂ /Au(111)		800	1180		[6]
NO ₂ (gas)		750	1318	1618	[34]
CO ₂ /Ni(110)	410	750	1130		[7]
$CO_2/Na + Pd(111)$	282	744	1210	1530	[11]
CO ₂ /Re(0001)		650	1230	1625	[12]
$CO_2/K + Pt(111)$		820	1340	1600	[13]
CO_2^{δ} (LiCO ₂)		750	1330	1569	[35]

HREELS loss positions in cm⁻¹ for NO₂ and CO₂ chemisorbates (gas phase NO₂ data as well as data for $CO_2^{\delta-}$ (LiCO₂) are given for comparison)

^{a)} For $p(2 \times 2)O/Ni(100)$ we find a Ni–O vibration at 420 cm⁻¹ and for $c(2 \times 2)O/Ni(100)$ a Ni–O vibration at 370 cm⁻¹.

^{b)} Bartram et al. [5] has assigned this energy loss at 460 cm⁻¹ to the Pt-O vibration.

cm⁻¹) combined with NEXAFS data on NO and NO + O/Ni(100) adsorbates we may draw the following conclusions: The broad band centered at 1430 cm^{-1} is due to linear and bent NO in twofold hollow sites. The 370 cm^{-1} is due to the oxygen-metal stretching mode in a $c(2 \times 2)O/$ Ni(100) layer. The 440 cm^{-1} band represents the metal-NO stretch in the linear species, the 630 cm^{-1} is due to the frustrated rotations (bending modes) of bent NO [20]. The relatively narrow band at 1600 cm⁻¹ must be caused by linear on-top NO molecules, because this is the dominant species at high NO coverage and is known from NEXAFS to be bound perpendicular to the surface plane [22]. The relatively high frequency of NO adsorbed close to coadsorbed atomic oxygen suggests that NO is terminally bonded. For this

species there are two experimental evidences that indicate a bent coordination, i.e. the appearance of a frustrated rotation near 610 cm⁻¹ and a tilt angle of 45° determined via NEXAFS [20]. Summarizing the evidences from spectrum (b) in fig. 1 we may conclude that NO₂ dissociates into adsorbed NO and atomic oxygen. The population of the surface sites by NO after dissociation is similar to the situation we find when we expose a clean Ni(100) surface to 0.5 L NO, except that the loss at 1840 cm⁻¹ exhibits a higher intensity which is due to the oxygen atoms formed in the process of NO₂ dissociation. We see that even at 95 K the NO produced via dissociation exhibits some mobility on the surface.

Spectrum (c) in fig. 1 shows the result of a higher NO_2 exposure at low temperature. Clearly,

Table 2					
HREELS loss positions in cm ⁻¹	for adsorbed, gaseous	, and solid N ₂ O ₄ . (OT = overtone,	CB = combination	mode)

System	NO ₂ rock	NO ₂ wagg	NO ₂ bend	NO ₂ sym	OT bend	NO ₂ asym	CB b-s	OT sym	CB as-s	Ref.
$N_2O_4/Pt(111)$			795	1290	1545	1770	2055			[4,5]
$N_2O_4/Au(111)$		440	770	1280	1535	1755	2055			[6]
$N_2O_4/Ru(001)$	340	440	760	1270		1750				[26]
N ₂ O ₄ /Ni(100)	385	478	766	1274	1516	1742	2024	2516	3000	[This work]
N ₂ O ₄ (gas)	385	430	750	1261		1748				[36]
N_2O_4 (solid)	369	439	737	1253		1730				[36]

the spectrum has changed considerably with respect to low coverage, and we shall show in the following that the additional bands are due to molecularly adsorbed NO_2 . This can most conveniently be done by comparison with the previously published data by Bartram et al. [4-6] as well as with the frequencies of gaseous NO₂, and gaseous and condensed N₂O₄ listed in tables 1 and



Fig. 2. HREEL spectra of NO₂ (left panel) and CO₂ (right panel) adsorbate systems. The geometries deduced for molecularly adsorbed NO₂ and CO₂ are schematically indicated.



Fig. 3. Typical geometries of triatomic oxides coordinated to metal surfaces.

2. Fig. 2 (left panel) shows some typical spectra from the literature [4-6] together with those of the present study. From top to bottom we compare various systems, namely $NO_2 + O/Pt(111)$, $NO_2/$ Ni(100), NO₂/Au(111), and NO₂/Pt(111). It is clear that we expect three internal NO₂ vibrations which may immediately be assigned as O-N-O bending (around 800 cm⁻¹), symmetric N-O stretch (near 1250 cm^{-1}) and asymmetric stretch (close to 1550 cm^{-1}). The molecule-metal stretching mode could cause a loss in the range from 300 to 450 cm^{-1} . It is basically the coordination mode (see fig. 3), i.e. whether NO_2 is nitrogen, oxygen, or mixed nitrogen-oxygen coordinated, that determines the position of the metal molecule loss. In addition to the metal molecule loss, the coordination mode also influences the relative intensities of the internal NO₂ losses as shall be discussed in detail in a subsequent section, where we compare the NO₂ spectra with the CO₂ HREEL spectra (right panel of fig. 2) [7,11]. The geometries which are deduced from this comparison, and which are completely in line with the conclusions of Bartram et al. [4–6], are shown in fig. 3 and schematically indicated in fig. 2. From this comparison, we conclude that $NO_2/Ni(100)$ is nitrogen coordinated.

In order to examine the NO_2 adsorption in slightly greater detail we have carried out ARUPS and NEXAFS (see below) measurements on this system. At this point we only discuss the photoemission results. The set of photoelectron spectra is shown in fig. 4. Here we concentrate on spectrum (e) which has been taken under conditions where no N_2O_4 was present on the surface. Of course, the presence of NO and oxygen cannot be avoided. If we compare spectrum (e) with spectrum (c) of a NO/O coadsorbate we may identify the peaks marked with arrows as mainly due to molecular NO_2 . A reasonable assignment of the peaks can be found by comparison with the gas



Fig. 4. Angle resolved photoelectron spectra of a Ni(100) surface exposed to NO, NO₂ and O+NO. (a) Clean surface, (b) 12 L NO, (c) 12 L NO/c(2×2)O, (d) 3 L NO₂, (e) 30 L NO₂.



Fig. 5. Angle resolved photoelectron spectra of 30 L $NO_2/NO(100)$ and 100 L $NO_2/Ni(100)$ with gas phase NO_2 [23], N_2O_4 [28], theoretical results [24,30] and a spectrum from the literature [29].

phase NO_2 spectrum [23], and additionally with calculations [24] (see fig. 5). Both, the gas phase results as well as the calculated ion state energies are compared with the adsorbate spectra in fig. 5. It appears natural to assign the broad feature around 6 eV binding energy with respect to the Fermi energy to the ionization of the 1a₂ and 4b₂ levels. If this is the case the shoulder below 5 eV binding energy must be due to the 6a1 orbital which is closer in energy to the $1a_2/4b_2$ level in the adsorbate as compared with the gas phase. This relative shift of the $6a_1$ level is caused by the bonding of the molecule to the surface via the nitrogen atom, i.e. via the $6a_1$ orbital (see fig. 8). The relatively wide feature reaching from below 10 eV to above 12 eV must be caused by ionization of the other four outer valence levels of NO_2 . Qualitatively, the photoemission results are in line with the results of the HREELS experiments and support the view that bonding of the molecule occurs via the nitrogen atom.

Spectrum (d) in fig. 1 shows the HREEL spectrum of a condensed N₂O₄ layer. The very high loss intensities are characteristic for such a condensate [25]. The features are shifted with respect to molecular NO₂ chemisorbed on the surface (table 2) and in addition, overtone and combination modes may be identified in the spectrum (indicated with arrows). The N_2O_4 spectrum reported in this study is compatible with those reported in the literature [4-6,26,27]. Complementing the HREELS data we have recorded ARUP spectra of the dimer layer which are shown in fig. 5 together with data from the gas phase [28], from Fuggle and Menzel for $NO_2/W(110)$ [29], and results of theoretical many-body calculations by von Niessen et al. [30]. All results are consistent with the existence of physisorbed N_2O_4 on the surface. Some further evidence about the orientation of the species can be gained from the NEXAFS data which will be discussed below. Before we discuss the NEXAFS spectra in detail we present some independent experimental evidences for the proposed NO₂ coordination modes by comparison with results on CO_2 adsorbates.

Comparison of NO_2 with CO_2 vibrational spectra As alluded to briefly in the introduction, CO_2

chemisorption proceeds under formation of a bent $CO_2^{\delta^-}$ species [7–11]. In the limiting case of a full charge transfer the hypothetical CO_2^- species is isoelectronic with NO₂. It is therefore appropriate to compare the information reported so far for NO₂ with the same information for CO₂. In fig. 2 we have plotted a set of CO₂ vibrational spectra in the right hand panel. The adsorption geometries for CO₂ have been independently deduced [7,11] and are given schematically. The direct comparison of the HREEL spectra of CO₂ and NO₂ reveals some interesting simularities:

(a) For NO₂ and CO₂ adsorption the three limiting cases for coordination of a bent triatomic species as shown in fig. 3 are observed. However, without the presence of coadsorbed species NO₂ appears to be either di-oxygen coordinated (on Au(111)) or mixed oxygen-nitrogen coordinated (on Pt(111)). Only with coadsorbed atomic oxygen present on the surface nitrogen coordinated NO₂ is found [5] (on Pt(111) and Ni(100)). For CO₂ the di-oxygen coordinated species has been found on Ni(110) [7] and proposed to exist on Fe(111) [8]. The carbon coordinated species has been claimed to exist on a Pd(111) surface only when alkali (Na) metal is coadsorbed [11].

(b) The vibrational frequencies of the internal modes of the triatomics adsorbed on the surface are rather similar for NO_2 and CO_2 as judged from table 1. Even the molecule-surface vibrations are relatively close as expected at least for the oxygen coordinated species, with regard to these cases where the assignments are clear. This is entirely reasonable, because the change of force constant ratios is expected to change in a similar fashion for CO_2 and NO_2 if the two species are close to being isoelectronic.

(c) The most interesting observation, however, concerns the relative intensities of the observed losses if we compare NO_2 and CO_2 adsorbed in the same bonding geometry. We find by inspection that the intensity ratios for a given type of coordination are rather similar. This is not unexpected if we consider the similarities of the dynamic dipole moment in corresponding adsorbate geometries.

We feel that the presented comparison of the two sets of data taken from completely indepen-

dent measurements corroborates and strongly supports the given assignment of the coordination type.

3.2. NEXAFS data

Fig. 6 shows a set of NEXAFS spectra taken at the nitrogen edge for different angles of incidence and at different surface temperatures. At the bottom we present an angular series for a relatively high NO₂ exposure at 95K. In this adsorbed layer NO, atomic oxygen, molecular NO₂ and the dimer N₂O₄ are present simultaneously. Above the angular series we show five NEXAFS spectra taken at more elevated temperatures. Spectrum (e) represents the situation where most of the dimer coverage has been removed [5,6]. Spectrum (i) is a spectrum of coadsorbed NO and atomic oxygen. By comparison of the various spectra, we are in a



Fig. 6. NEXAFS spectra of a Ni(100) surface exposed to various amounts of NO₂ at the indicated surface temperatures. Spectra (a)-(d) represent a set where for a given exposure and temperature the light incidence angle has been varied.



Fig. 7. NEXAFS spectra of 6 L NO₂/Ni(100) at T = 90 K for 20° and 90° angle of light incidence. The spectra have been fitted with Student *t*-functions on the basis of the data shown in fig. 6 and the discussion in the text. The insets show the angular variation of the fitted line intensities.

position to identify the constituents of the spectra at low temperature. On this basis we may fit the low temperature spectra. The result is shown for two angles in fig. 7. The insets in fig. 7 show the angular variations of some of the contributing components. For comparison we have included a spectrum of gaseous NO_2 in the figure [31].

We start the discussion of fig. 6 with the spectrum of the adsorbate at elevated temperature (340 K). It is clear from the above discussion that spectrum (i) represents NO and O.

We have used the position of the NO π -signal to achieve the energy calibration necessary to compare with gas phase data. The NO π -signal has been placed to line up with the values of Stöhr and Jaeger [22], i.e. 401.5 eV. They report a shift with respect to gaseous NO (399.7 eV) of 1.8 eV. The lowest energy feature in the gas phase NO₂ spectrum [31] (fig. 7) is situated at 401 eV, i.e. 1.3 eV above gaseous NO [32] and 0.5 eV below chemisorbed NO [22].

The angular dependence of the NO features shown in the inset is consistent with a superposition of the angular dependences observed for a pure NO layer on Ni(100) and NO coadsorbed with oxygen [20]. We shall not consider this case any further here, and refer to ref. [20].

The line with the largest intensity in spectrum (e) of fig. 6 is shifted with respect to adsorbed NO by 1.0 eV. On the absolute energy scale this corresponds to 402.5 eV. Since this spectrum has been recorded at a surface temperature of 130 K where we know from EELS that molecular NO_2 is adsorbed on the surface we assign this peak to molecular NO₂. There are considerable differences with respect to the gas phase spectrum shown in fig. 7. There are two π -signal in gaseous NO₂ due to excitation into the non-degenerate two π -components $6a_1$ and $2b_1$ as shown in fig. 7. The $6a_1$ component, as assigned by Schwarz et al. [33], which is observed at lower excitation energy (401 eV) is about 1.5 eV below the signal of adsorbed NO_2 . The 2b₁ signal is 0.7 eV above the signal of adsorbed NO₂. On the basis of energy considerations it is therefore not clear how to assign the adsorbate feature. However, if we take the information from HREELS into account which indicates that NO₂ is bound nitrogen end down to the surface it is quite obvious that the signal can only result from excitation into the $2b_1$ level, because the $6a_1$ level is active in the bonding with the substrate and therefore doubly occupied. If we assign the signal to the $2b_1$ transition we can use the angular dependence of the NEXAFS signal to determine the orientation of the molecular plane. As shown in fig. 8 the atomic 2p orbitals constituting the $2b_1$ molecular orbital are oriented perpendicular to the molecular plane. In order to excite into this orbital the electric field vector of the light has to be oriented perpendicular to the molecular plane. This means, the intensity of the spectral feature should be maximal at normal incidence if the molecular plane is oriented perpendicular to the surface plane. From the inset in fig. 7 we see that this is indeed the case. At the same time the intensity of the feature at higher excitation energy, the so called σ -shape resonance [32,33] shows minimal intensity. Summarizing this part, we find that the NEXAFS data are compatible with the HREELS results if we assume bonding towards the substrate via the single electron on the nitrogen atom, and an orientation of the molecular NO₂ plane perpendicular to the surface plane.

Spectra (a) through (d) have been taken at various angles of incidence for the lowest surface temperatures reached in this study, i.e. 95 K. In this case we know from HREELS that in addition to dissociated and molecular NO₂ dimerized NO₂, i.e. N₂O₄, is present on the surface. The dominant



Fig. 8. Highest occupied $(6a_1)$ and lowest unoccupied $(2b_1)$ molecular orbitals of NO₂.

 π -signal is due to this species at this temperature. The angular scans indicate that the intense signal is composed of several components, because the maximum shifts to higher excitation energy as the angle of incidence is varied. At the same time there are variations of the relative intensities in the region of the σ -resonances.

A rather simple way to assign the spectrum is to consider what happens to the unoccupied molecular orbitals upon dimerization: The two singly occupied NO₂ $6a_1$ orbitals couple to form a doubly occupied bonding combination and an unoccupied antibonding combination. Only the latter one is available for excitation. In addition the $2b_1$ NO₂ orbitals form bonding and antibonding combinations. Both N_2O_4 orbitals are empty and thus in principle accessible via excitation. However, the planar arrangement of the two NO₂ moieties in N_2O_4 (point group D_{2h}) put symmetry restrictions to the transition moment that govern the excitation intensities. Fig. 9 summarizes the relevant symmetry information. On the left the two initial linear combinations of the N 1s orbitals of N_2O_4 are shown. On the right we have sketched the final unoccupied orbitals of N_2O_4 originating from NO_2 π - and σ -orbitals. π -orbitals are shown at the top, σ -orbitals at the bottom (separated by a horizontal line). In the middle panel a solid line connects the orbitals involved in a dipole allowed transition. The polarization of the allowed transition is given with respect to the molecular coordinate system shown in the left panel. The symbols p and s stand for light polarization perpendicular (p) and parallel (s) to the molecular N_2O_4 plane, respectively. We conclude from this figure that the two combinations of the NO_2 2b₁ orbitals can only be excited if the electric field vector is oriented perpendicular to the molecular plane, while the unoccupied antibonding combination of the NO₂ 6a₁ orbital can be excited with the electric field vector within the molecular plane. In order to connect the symmetry arguments with the experimental observations the energy sequence of the unoccupied orbitals in the presence of the core hole must be known. For the sequence in ground state neutral N_2O_4 von Niessen et al. [30] find the $b_{2u}(2b_1)$ at -0.35 eV, the $b_{1u}(6a_1)$ at 0.62 eV, and the $b_{3g}(2b_1)$ at 1.51 eV. We can guess on the basis

of the following argument that the presence of the core hole will reverse the sequence of the lowest lying orbitals: The unoccupied b_{1u} orbital of N_2O_4 contains some atomic N 2s character (see the s-p-hybrid in fig. 8), while for the b_{2u} and b_{3g} orbitals this is not the case. Therefore upon creation of the core hole on the nitrogen site the less screened 2s electrons will feel a stronger core attraction and lead to a more pronounced stabilization of those molecular orbitals in which they participate. Consequently, we expect an energy sequence of unoccupied π -derived orbitals: $b_{1u} <$ $b_{2u} < b_{3g}$. Going back to the symmetry arguments the polarization dependence upon excitation into the b_{2u} and b_{3g} orbitals is the same but different from the polarization dependence of the b_{1u} excitation. On the basis of the combined evidence we have to assign the low excitation energy feature to the b_{1u} , and the high energy feature to the b_{2u}/b_{3g} excitations. The experimental observation that the b_{1u} excitation has its maximum intensity at normal incidence while the b_{2u}/b_{3g} excitations peak at grazing incidence can be explained by assuming a more or less parallel or tilted orientation of the molecular N_2O_4 plane with respect to the surface plane.

The next step in the analysis is to check this by considering the angular dependence of the σ -shape resonance features. Fig. 9 shows that all N₂O₄ σ -features should be polarized in-plane with the molecule. Unfortunately, the experimental evidence (fig. 7) in this case is not conclusive, because the σ -shape resonances for the three species present on the surface overlap and cannot be separated with sufficient accuracy. It appears though that there is no particularly strong angular dependence of the N₂O₄ features once the expected angular dependence for NO₂ and NO has been subtracted.

We can therefore base our conclusion that N_2O_4 is oriented more or less parallel, i.e. possibly slightly tilted, to the surface plane only on the analysis of the π -features. It must be kept in mind, however, that we cannot exclude, nor determine the tilt angle exactly.

It should also be pointed out that Schwalke et al. [26] propose a more or less perpendicular orientation of N_2O_4 on Ru(001). In the view of



Fig. 9. Some molecular orbitals and symmetries of N_2O_4 (D_{2h}). Left panel: initial orbitals involved in the NEXAFS transitions. Right panel: final orbitals involved in the NEXAFS transitions. Middle panel: polarization of the transitions connecting final and initial orbitals.

these authors the observation of the much less intense NO_2 wagging mode at 440 cm⁻¹ in the HREEL spectrum of the N_2O_4 layer compared with the other four IR active modes suggests this assignment. The intensity of this band is also small for N_2O_4 on Ni(100). Therefore, from the HREELS data alone we would come to the same conclusion as Schwalke et al. However, the independently taken NEXAFS data suggest that this might be incorrect.

4. Summary and conclusions

We have demonstrated in the present study that adsorption of NO_2 on Ni(100) at low temper-

atures proceeds in three steps: At low coverage, HREELS, ARUPS and NEXAFS data show that NO₂ dissociates into adsorbed NO and oxygen. Molecular NO occupies various adsorption sites which are only partly near an atomic oxygen site. Increasing the coverage leads to adsorption of nondissociated, molecular NO2. Comparison with literature data from Koel's group [4-6] and with independent data on CO₂ adsorption [7-14] indicate that the NO_2 molecule is bound via its N atom to the substrate. This conclusion is corroborated by ARUPS measurements where a pronounced shift of the $6a_1$ orbital of NO₂, i.e. the orbital containing the single electron in free NO_2 , with respect to gaseous NO₂ is observed. The NEXAFS spectra of molecular NO₂ taken as a

249

function of the angle of light incidence are compatible with a more or less perpendicular orientation of the molecular plane with respect to the Ni(100) surface. Upon further increase of the coverage at low temperature NO₂ forms dimers (N₂O₄) on the surface. HREELS, ARUPS and NEXAFS data are in line with this conclusion. A more detailed analysis of the angular dependences of the NEXAFS spectra leads us to the conclusion that the N₂O₄ molecular plane is oriented more or less parallel or tilted with respect to the substrate surface, although no indication for any pronounced interaction of N₂O₄ with Ni(100) is found.

Coming back to the primary point made in the introduction concerning the comparison of the adsorption behaviour of different triatomic oxides we have undertaken a detailed comparison of the vibrational spectra of NO₂ and CO₂. It turns out that the spectral features for CO₂ and NO₂ in corresponding adsorption geometries are very similar. In particular, the relative position of the vibrational losses and their relative intensities show similar variations when changing between the adsorption geometries shown in fig. 5. We feel that this comparison lends additional support to the proposed adsorption behaviour. It also shows that CO₂, after some electronic charge has been transfered in the adsorbed state and $CO_2^{\delta-}$ has been formed, exhibits a reactivity similar to NO₂, although not quite as pronounced if we consider for example the dissociation temperature of CO₂ into oxygen and CO (< 200 K) and of NO₂ into oxygen and NO (< 90 K), respectively.

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References

- [1] H. Bosch and F. Janssen, Catal. Today 2 (1988) 369.
- [2] W.M. Ayers, Ed., Catalytic Activation of Carbon Dioxide,

ACS Symposium Series, Vol. 363 (Am. Chem. Soc., Washington, DC, 1988).

- [3] J.G. Calvet, F. Su, J.W. Bottonheim and O.P. Strausz, Atmos. Environ. 12 (1987) 197.
- [4] M.E. Bartram, R.G. Windham and B.E. Koel, Surf. Sci. 184 (1987) 57.
- [5] M.E. Bartram, R.G. Windham and B.E. Koel, Langmuir 4 (1988) 240.
- [6] M.E. Bartram and B.E. Koel, Surf. Sci. 213 (1989) 137.
- [7] B. Bartos, H.-J. Freund, H. Kuhlenbeck, M. Neumann, H. Lindner and K. Müller, Surf. Sci. 179 (1987) 59.
- [8] H.-J. Freund, B. Bartos, H. Behner, G. Wedler, H. Kuhlenbeck and M. Neumann, Surf. Sci. 180 (1987) 550.
- [9] J. Wambach, G. Odörfer, H.-J. Freund, H. Kuhlenbeck and M. Neumann, Surf. Sci. 209 (1989) 159.
- [10] G. Illing, D. Heskett, E.W. Plummer, H.-J. Freund, J. Somers, Th. Lindner, A.M. Bradshaw, M. Buskotte, M. Neumann, U. Starke, K. Heinz, P.L. deAndres, D. Saldin and J.B. Pendry, Surf. Sci. 206 (1988) 1.
- [11] S. Wohlrab, D. Ehrlich, J. Wambach, H. Kuhlenbeck and H.-J. Freund, Surf. Sci. 220 (1989) 243.
- [12] M. Asscher, C.T. Kao and G.A. Somorjai, J. Phys. Chem. 92 (1988) 2711.
- [13] Z.M. Lin, Y. Zhou, F. Solymosi and J.M. White, J. Phys. Chem. 93 (1989) 4383.
- [14] J. Wambach, Thesis, University of Bochum, in preparation.
- [15] U. Köhler and H.-W. Wassmuth, Surf. Sci. 126 (1983) 448.
- [16] D.A. Outka, R.J. Madix, G.B. Fisher and C.L. DiMaggio, Langmuir 2 (1986) 406.
- [17] M.L. Burke and R.J. Madix, Surf. Sci. 194 (1988) 223.
- [18] J.L. Gland, B.A. Sexton and G.B. Fisher, Surf. Sci. 95 (1980) 587.
- [19] M.E. Bartram, B.E. Koel and E.A. Carter, Surf. Sci. 219 (1989) 467.
- [20] G. Odörfer, R.M. Jaeger, G. Illing, H. Kuhlenbeck and H.-J. Freund, Surf. Sci. 233 (1990) 44; see also G. Odörfer, Thesis, University of Bochum (1990.
- [21] R.D. Feltham and J.H. Enemark, Top. Stereochem. 12 (1981) 155.
- [22] J. Stöhr and R. Jaeger, Phys. Rev. B 26 (1982) 4111.
- [23] G.R. Brundle, D. Neumann, W.C. Price, D. Evans, A.W. Potts and D.G. Streets, J. Chem. Phys. 53 (1970) 705.
- [24] J. Schirmer, L.S. Cederbaum and W. von Niessen, Chem. Phys. 56 (1981) 285.
- [25] M.E. Kordesch, W. Stenzel, H. Conrad and M. Sunjic, to be published.
- [26] U. Schwalke, J.E. Parmeter and W.H. Weinberg, J. Chem. Phys. 84 (1986) 4036.
- [27] U. Schwalke, J.E. Parmeter and W.H. Weinberg, Surf. Sci. 178 (1986) 625.
- [28] K. Nomoto, Y. Achiba and K. Kimura, Chem. Phys. Lett. 63 (1979) 277.
- [29] J.C. Fuggle and D. Menzel, Surf. Sci. 79 (1979) 1.
- [30] W. von Niessen, W. Domcke, L.S. Cederbaum and J. Schirmer, J. Chem. Soc. Faraday Trans. II, 74 (1978) 1550.

- [31] C.E. Brion, K.-H. Sze, W. Zhang, J.-M. Li, X-M. Tong, SPIE 911 (1988) 46.
- [32] G.R. Wight and C.E. Brion, J. Electron. Spectrosc. Relat. Phenom. 4 (1974) 313.
- [33] W.H.E. Schwarz, T.C. Chang and J.P. Connerade, Chem. Phys. Lett. 49 (1977) 207.
- [34] E.T. Arakawa and A.H. Nielsen, J. Mol. Spectrosc. 2 (1958) 413.
- [35] Z.H. Kafafie, R.H. Hauge, W.E. Billups and J.L. Margrave, J. Am. Chem. Soc. 103 (1983) 3886.
- [36] I.C. Hisatsune, J.P. Devlin and Y. Wada, J. Chem. Phys. 33 (1960) 714.