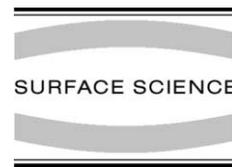




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Electron, photon and thermally induced chemistry in alkali–NO coadsorbates on oxide surfaces

M. Bender^a, O. Seiferth^a, A.F. Carley^{b,*}, A. Chambers^b, H.-J. Freund^{a,*},
M.W. Roberts^b

^a Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

^b Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, UK

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Abstract

The effect of alkali metals on the thermal, photon and electron induced chemistry of nitric oxide at metal oxide surfaces is investigated, using XPS, TPD and IRAS. Alkali nitrosyl salts are observed on both NiO(111) and Cr₂O₃(0001) surfaces, with evidence in the latter case for the presence of a hyponitrite species. Nitrite species are only formed via photon or electron induced reactions. © 2002 Published by Elsevier Science B.V.

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1. Introduction

The activation of surface chemical reactions by photons has been the subject of much recent interest [1–3], although the phenomenon of radiation-induced chemical modification of solid surfaces was well-known, and indeed reviewed, over two decades ago [4].

Deposited metals in general may have a strong influence on photochemical reactions, not only if these processes actually proceed on a deposited

metal aggregate [5] but also if the metal modifies the electronic structure, e.g. the workfunction, of the system more than locally [6]. With respect to the latter the attention has been focussed on the discrimination between direct adsorbate excitation mechanisms and processes driven by the photo-emitted electrons from the substrate. The latter mechanism may be facilitated by alkali metal doping of the substrate since it is known to lower the workfunction. More recently, Feulner et al. [7] have reviewed the involvement of photon-induced core-excited states, and their subsequent Auger decay, in bond-breaking processes.

Recently, the influence of alkali metals on surface photochemistry of coadsorbates as well as the photodesorption of the alkali metal itself has received some attention. In this particular connection oxide surfaces play an important part as

* Corresponding authors. Tel.: +44-1222-874139; fax: +44-1222-874030 (A.F. Carley). Tel.: +49-30-8413-4104; fax: +49-30-8413-4102 (H.-J. Freund).

E-mail addresses: carley@cardiff.ac.uk (A.F. Carley), freund@fhi-berlin.mpg.de (H.-J. Freund).

substrates since photodesorption and photoreaction cross sections are considerably higher on those substrates than on pure metals.

Studies on alkali desorption have been reviewed by Madey and coworkers in the context of a problem of astrophysical significance, viz the presence of alkali in the atmospheres of Mercury and the Moon [8]. The question was how the replenishment of alkali in the atmosphere could be established given that there is a rather high abundance despite the life time of alkali in these atmospheres being limited. From Madey's estimates it is clear that photon-stimulated processes occurring on the surface of the planet contribute substantially to the lunar Na atmosphere [8]. Oxides may be considered as models for the planet surface.

Wilde and coworkers [6] have published a series of studies dealing with potassium desorption from $\text{Cr}_2\text{O}_3(0001)$ surfaces as well as the influence of alkali on coadsorbed NO. In the case of alkali desorption they propose a mechanism involving the charge transfer of an electron from the oxide substrate to the adsorbed alkali, which is thought to be positively charged in the adsorbed state. It is obvious that the situation in the adsorbed state will be modified substantially when molecules with electron withdrawing capabilities are also present on the surface and thus the photodesorption of both adsorbed molecules and alkali may change. The influence of an alkali metal (Na) on the chemistry of a variety of molecules has been studied in the absence of photons by infrared spectroscopy [9], providing comparative data on the thermal chemistry. In the present paper we explore the electron and photon driven chemistry of adsorbed NO at alkali metal and alkali-metal doped oxide surfaces, for a variety of oxide surfaces and for strongly varying alkali coverages up to very thick layers representing alkali metal substrates.

2. Experimental

2.1. $\text{Ni}(111)/\text{NiO}(111)/\text{Na-NO}$ system

The nickel oxide work was carried out in a UHV-chamber equipped with a VSW XPS spectrometer, an Omicron LEED system and a Ley-

bold-Heraeus sputter gun [10]. The sample was spot-welded on the sample holder which was attached to a VG cryostat manipulator. Preparation of thin nickel oxide $\text{NiO}(111)$ films on the $\text{Ni}(111)$ sample has already been described elsewhere [11]. The sodium was deposited from a well outgassed SAES getter source, and the sodium coverage was estimated by an empirical extinction model [12] using XPS intensity measurements of the Na(1s) and O(1s) levels. The photochemical conversion was achieved by a Lambda Physik ArF excimer laser with 6.4 eV photon energy.

2.2. $\text{Cr}(110)/\text{Cr}_2\text{O}_3(0001)/\text{Na-NO}$ system

The work on chromium oxide was carried out in a UHV-apparatus consisting of a preparation chamber containing a LEED-Auger unit and a quadrupole mass spectrometer to perform TDS measurements, as well as the SAES-Na-dispenser [13] and a small chamber separated by a gate valve which allows in situ IRAS measurements to be performed.

The chromium oxide was prepared as a thin film supported on a $\text{Cr}(110)$ single crystal according to a recipe published earlier [13–16]. Nitric oxide gas (99.8%) was used without further purification.

2.3. Cs-NO system

Multilayer caesium films were prepared by evaporation from a SAES getter source onto a sample plate maintained at 80 K until the thickness of the film was such that the attenuated signal from the substrate was <5% of that from the uncaesiated surface. Applying a simple attenuation model this leads to an estimate of the thickness of the caesium film as >65 Å i.e. >12 monolayers of Cs, using a value of 26 Å for the mean free path of substrate photoelectrons in Cs [17]. Nitric oxide gas (99.5%; Matheson) was used without further purification. XP spectra were measured using a VG Scientific photoelectron spectrometer which has been described elsewhere [18]. Data acquisition was achieved using commercial software (SPEC-TRA; R. Unwin) and analysed using software and quantification procedures developed in-house [19].

3. Results and discussion

3.1. Ni(111)/NiO(111)/Na–NO system

The system Na/NiO(111)/Ni(111) has already been investigated in some detail [11]. At elevated temperatures the nickel oxide was reduced to nickel metal and the formation of sodium oxide was observed. Thus, the coadsorption of NO at Na/NiO(111)/Ni(111) surfaces was carried out at 90–100 K; at this temperature the reaction between the sodium adsorbate and the nickel oxide substrate is inhibited as far as possible.

In Fig. 1 the workfunction of the sample is shown as a function of sodium coverage. This plot is of importance for the comparison of the coverage to other adsorption experiments of alkali metals on surfaces. Points A through D indicate the four different coverages at which the coadsorption of sodium and NO has been investigated. Besides the case of the clean nickel oxide surface (point A) the investigations have been carried out in the low (point B: $\theta_{\text{Na}} = 0.3$ ML), medium (C: $\theta_{\text{Na}} \approx 1$ ML) and multilayer (D: $\theta_{\text{Na}} \gg 1$) sodium pre-coverage regime.

The adsorption of NO on the clean i.e. non-alkali pre-covered NiO(111) oxide film has been

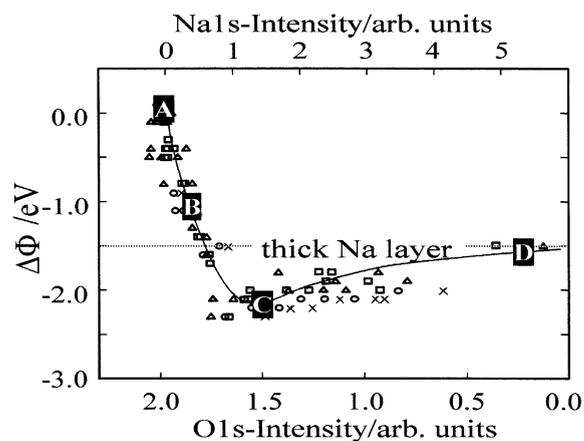


Fig. 1. Workfunction change in the system Na/NiO(111)/Ni(111) as a function of the intensities of the O(1s)- and Na(1s)-signals. (A)–(D) indicate the different sodium coverages at which NO adsorption has been investigated, both before and after laser irradiation: (A) $\theta_{\text{Na}} = 0$ ML; (B) $\theta_{\text{Na}} = 0.3$ ML; (C) $\theta_{\text{Na}} = 1.0$ ML; (D) $\theta_{\text{Na}} \gg 1$ ML.

extensively studied [20], saturation coverage being achieved by a dose of 12 L at 90–100 K. Since the oxide surface is at least partly covered by OH groups the absolute NO coverage may well be less than 1 ML. Fig. 2(a) shows the corresponding XP N(1s) spectrum. O(1s) spectra are not shown since the intense O(1s) emission from the substrate dominates any adsorbate induced feature. The two features at 402.5 and 406.5 eV are due to

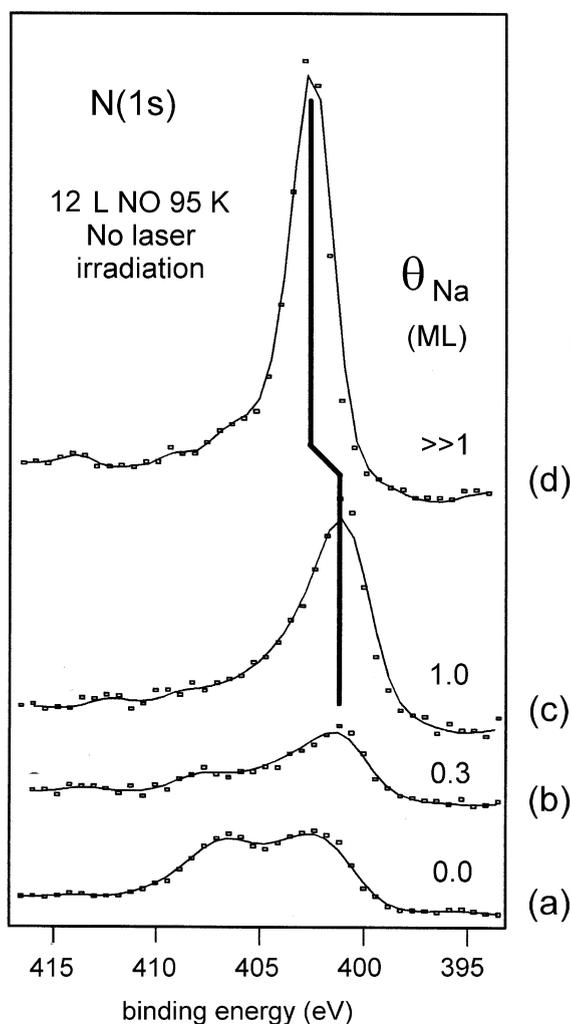


Fig. 2. N(1s) spectra after NO adsorption (12 L) at 95 K, as a function of sodium precoverage: (a) $\theta_{\text{Na}} = 0$ ML; (b) $\theta_{\text{Na}} = 0.3$ ML; (c) $\theta_{\text{Na}} = 1.0$ ML; (d) $\theta_{\text{Na}} \gg 1$ ML. The spectra were measured before laser irradiation.

shake-up processes, i.e. many particle effects upon photoionization as was pointed out by Kuhlbeck et al. [20] for NO on NiO(100). In both cases of NO on NiO(100) and NiO(111) [21] it has been suggested that there is considerable coupling of the core-holes to core excited states leading to intense satellite structure similar to systems with weakly held molecules on metal surfaces [22]. The two features therefore belong to a single chemical species. This was recently confirmed by Woodruff and coworkers [23] using photoelectron diffraction. They could clearly show that both peaks stem from a single species. Also, vibrational spectroscopy (HREELS) [24] shows no evidence for the formation of other chemical species, such as adsorbed N₂O; the latter has been observed on a variety of surfaces [25]. On alkali pre-covered surfaces an equivalent study does not exist.

At the sodium precoverage of 0.3 ML (Fig. 2(b)) a peak is observed at 401.1 eV with a tail to higher binding energies, and the total N(1s) intensity is reduced by about 30% compared to the clean NiO(111) surface. Clearly, the sodium changes the chemistry of the surface. The double peak structure, characteristic of isolated, or monomeric adsorbed NO molecules is attenuated, and a new feature occurs at 401.1 eV.

Fig. 3 shows N(1s) spectra for the surfaces shown in Fig. 2 after laser irradiation by a 6.4 eV excimer laser. As indicated in the figure the incident laser dose ranged between 4.5 and 6.5 × 10¹⁷ cm⁻². In all four cases the desorption cross section was determined in a previous publication [10] to be of the order of 0.1 Å² which is typical for the ineffective quenching of the excited state of the adsorbate on the surface of an insulator. After laser irradiation the original N(1s) signal at 401.1 eV exhibits less intensity but is accompanied by a second signal at 404 eV which is typical for sodium nitrite NaNO₂. For multilayer sodium coverages (point D) the shift of the whole spectrum to higher binding energy by about 1.5 eV is again apparent. Since the shift is found both before and after laser irradiation, a surface photovoltage effect can be ruled out as the origin for this effect.

To identify the chemical distinction between the two nitrogen-containing species the sample characterized by the spectrum at point C was heated.

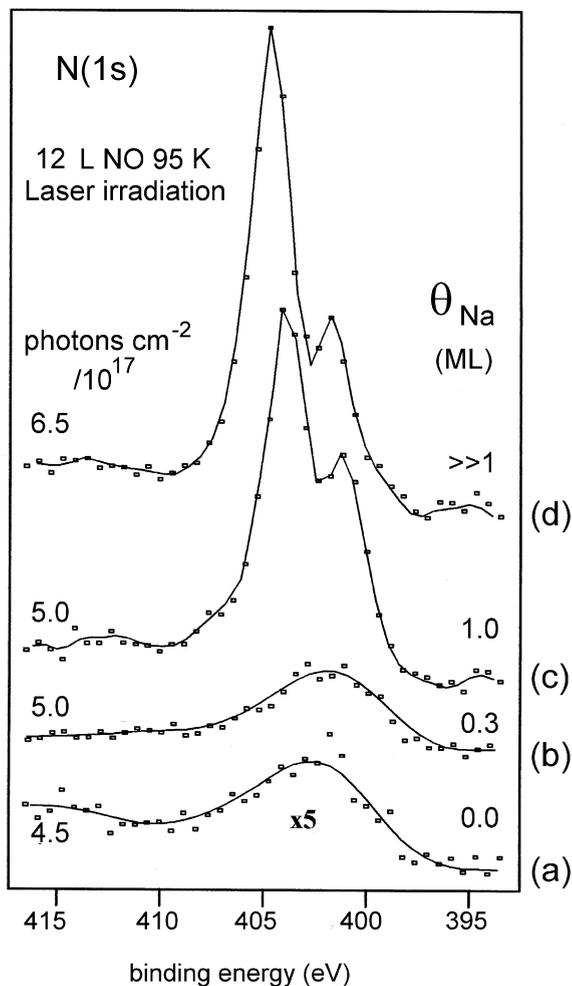


Fig. 3. N(1s) spectra after NO adsorption (12 L) at 95 K, as a function of sodium precoverage: (a) $\theta_{\text{Na}} = 0$ ML; (b) $\theta_{\text{Na}} = 0.3$ ML; (c) $\theta_{\text{Na}} = 1.0$ ML; (d) $\theta_{\text{Na}} \gg 1$ ML. The spectra were measured after laser irradiation ($h\nu = 6.4$ eV). The integrated photon flux is shown by each spectrum.

The resulting N(1s) spectra as a function of temperature are shown in Figs. 4 and 5, for the surface both before and after laser irradiation. We observe that the nitrosyl species desorbs between 300 and 400 K whereas some nitrite species are still present at temperatures as high as 490 K.

Chemistry mediated by electronic transitions also plays an important role in processes which are induced by *electrons* on surfaces [3]. The electrons are usually in the form of an electron beam inci-

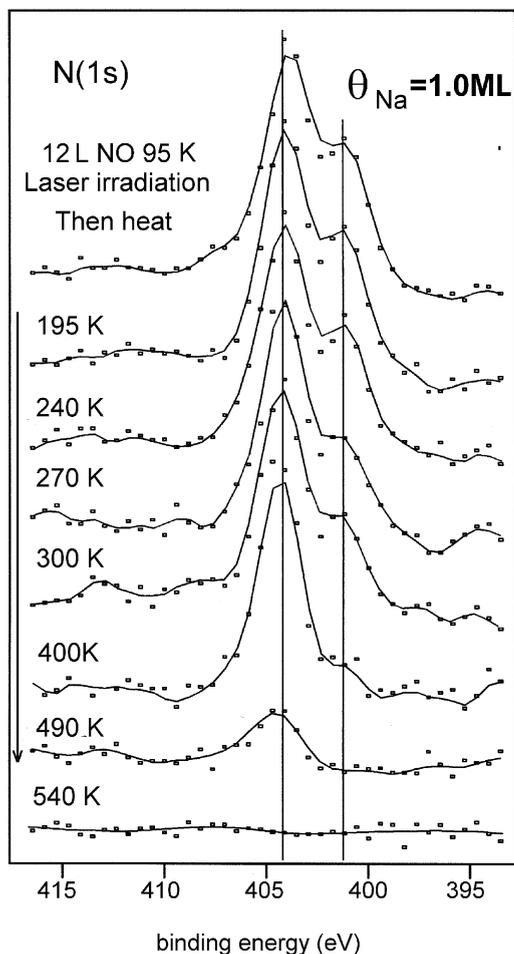


Fig. 4. N(1s) spectra showing the effect of temperature on the adlayer formed after NO adsorption (12 L) at 95 K on the Na-doped NiO(111)/Ni(111) surface (point C: $\theta_{\text{Na}} \approx 1$) followed by laser irradiation.

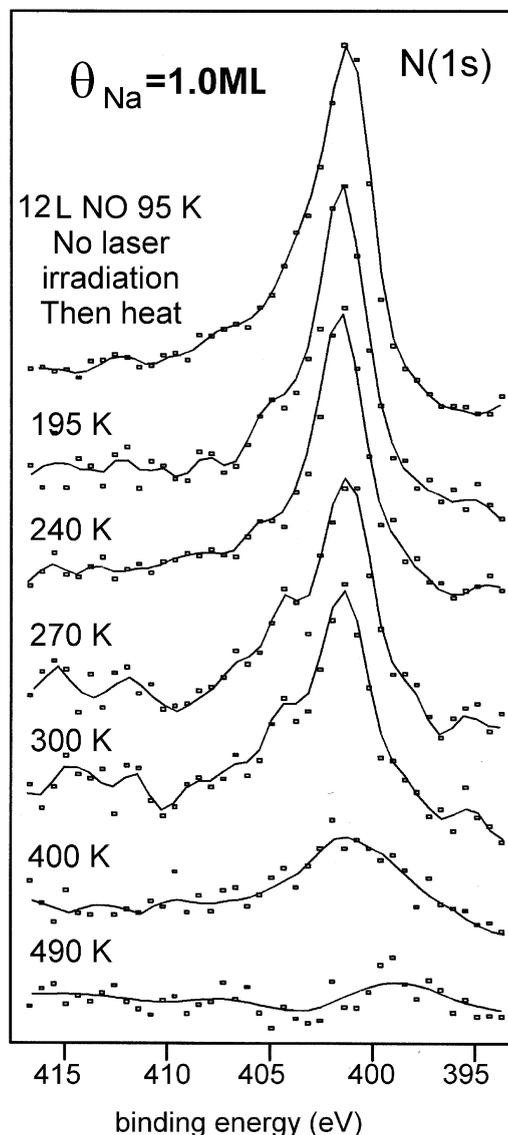


Fig. 5. N(1s) spectra showing the effect of temperature on the adlayer formed after NO adsorption (12 L) at 95 K on the Na-doped NiO(111)/Ni(111) surface (point C: $\theta_{\text{Na}} \approx 1$) without laser irradiation.

dent onto the surface (LEED, EELS, ESDIAD), and indeed electron beam effects are well recognised in these techniques. In contrast to the incident beam energy, which is well defined, secondary scattering processes in the sample give rise to an electron flux which is distributed over a broad energy range, the secondary electron intensity growing rapidly towards zero kinetic energy. What is not often appreciated is that a similar electron flux is also created during photoelectron emission experiments, and these electrons can play an important role in the chemistry observed at the

surface. In the case of CO_2 adsorption at copper surfaces, for example, a species identified as $\text{CO}_2^{\delta-}(\text{a})$ is only observed if a physisorbed CO_2 adlayer is examined by XPS at 80 K and then warmed to 300 K [26]. A similar effect has been reported for K-promoted Cu(110) surfaces [27],

although the authors ascribe it, perhaps incorrectly, to a photon-induced ($h\nu = 660$ eV) chemical reaction.

Since NO desorption has been observed from NiO(1 1 1)/Ni(1 1 1) during XPS measurements [21], the influence of the secondary electron flux was investigated for NO adsorption at Na/NiO(1 1 1)/Ni(1 1 1) surfaces, both with and without prior laser irradiation (Fig. 6). Although there was no significant intensity loss during the timescale of the experiment (300 s XPS measuring time), in sharp contrast to the significant desorption observed from the undoped NiO(1 1 1)/Ni(1 1 1) surface [21], there are indications of changes in spectral shape for both surfaces, intensity being transferred from the NO(a) to the NO₂(a) region. For the unirradiated sample this is reflected more clearly in the development of a weak shoulder at ≈ 404 eV, and for the irradiated surface by a clear decrease in the intensity of the peak at 401 eV. This phenomenon was explored further in a study of NO adsorption at caesium film surfaces (qv post).

3.2. Cr(1 1 0)/Cr₂O₃(0 0 0 1)/Na–NO system

Recently, Wilde et al. have investigated [28] the adsorption of NO on Cr₂O₃(0 0 0 1), using TDS and IRAS to characterize the adsorbates, before they went on to study NO photodesorption from that surface. Briefly, the adsorption is characterized by molecular adsorption exclusively, giving rise to first order desorption at $T_{\max} \sim 330$ K and an NO stretching frequency of 1760 cm⁻¹ shifting to 1782 cm⁻¹ upon increase of coverage. At high coverage (NO)₂ dimers are formed which desorb via formation of N₂O and adsorbed atomic oxygen.

Upon predosing the surface with varying amounts of sodium before exposure to a saturation dose of NO the chemistry changes drastically. Five different Na coverages have been investigated, namely 0.5, 1.0, 1.5, 2.0, 4.0 ML of Na. The two lowest coverages are characteristic for an overlayer which is not yet metallic. At 2.0 ML the transition from a non-metallic to a metallic over-

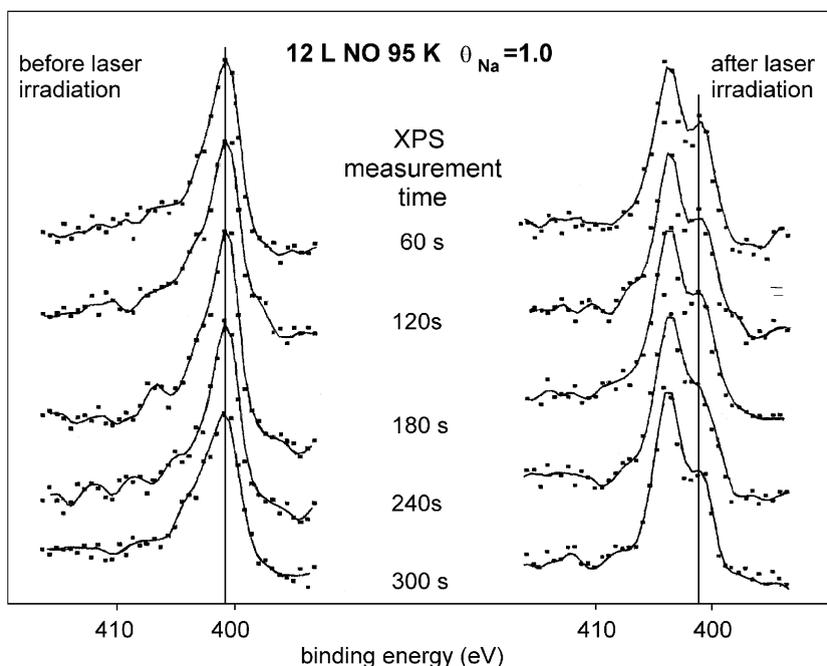


Fig. 6. N(1s) spectra showing the effect of XPS measurement time on the adlayer formed after NO adsorption (12 L) at 95 K on the Na-doped NiO(1 1 1)/Ni(1 1 1) surface ($\theta_{\text{Na}} \approx 1$) both with and without laser irradiation.

layer is just completed. 4.0 ML represents the full metallic Na overlayer. This coverage calibration relies on measurements via photoemission and HREELS published earlier [13,29].

Fig. 7 shows five sets of seven TDS traces taken for different masses, namely C, N, O, CO/N₂, NO, N₂O, CO₂ and NO₂ simultaneously. Each set represents a particular Na coverage as given after exposure to a saturation dose (40 L) of NO at 90 K. The comparison allows us to deduce to what extent NO desorbs molecularly. The latter can only be found before the overlayer has become fully metallic at $T_{\max} = 520$ K. On the other hand we do find already at low Na coverages signals for N ($m/e = 14$) and N₂ ($m/e = 28$) indicative for NO

dissociation and the recombinative desorption of nitrogen atoms. Oxygen remains on the surfaces as Na₂O as has been discussed earlier (Section 3.1). Also, the reaction of the nitrogen atoms with undissociated NO to form N₂O is observed ($m/e = 44$). The carbon dioxide ($m/e = 44$) and carbon ($m/e = 12$) signals are negligibly small. The very small signals stem from reactions with residual CO₂ gas.

The relatively high desorption temperature of molecular NO at 520 K requires attention. On the clean substrate NO molecules desorbed at 330 K. Only with regard to the IRAS data (see below) we are in a position to show that the temperature is shifted due to the formation of charge transfer alkali–NO complexes. We can therefore also rule out the formation of alkali–nitrite salts which have been discussed for K–NO interactions [30,31] and its comparison with decomposition temperatures of KNO₂ on Pt and Fe substrates [32]. The N₂ signal at 420 K strongly increases when reaching 2.0 ML and there is a second N₂ desorption maximum at 560 K once 4.0 ML are reached. In addition, the metallic Na overlayer exhibits strong N₂ signals at 310 and 330 K, as well as near 400, 500, 600 and 700 K. Such N₂ desorption signals on alkali overlayers related to dissociated NO have also been observed for K/Si(111) [33,34] at 310 K and were correlated with alkali multilayer desorption. In the case of Na/Cr₂O₃(1000) multilayer desorption sets in only at 420 K and therefore in the present system N₂ formation and multilayer desorption appear to be uncorrelated.

We will come back to the intense N₂O signals at low temperature which were also observed for the Na free substrate. However, in the present case they are not due to reactive desorption of (NO)₂ dimers but rather to the formation of N₂O already at low temperature, at least for the high Na coverages. Evidence will be presented when the IRAS spectra are discussed.

For metallic overlayers (2 and 4 ML) molecular NO desorption is replaced by an intense high temperature N₂O desorption peak, which we will see in the course of the following discussion is due to the decomposition of a salt, namely iso-sodiumhypodinitrite (Na₂N₂O₂). Oxygen desorption

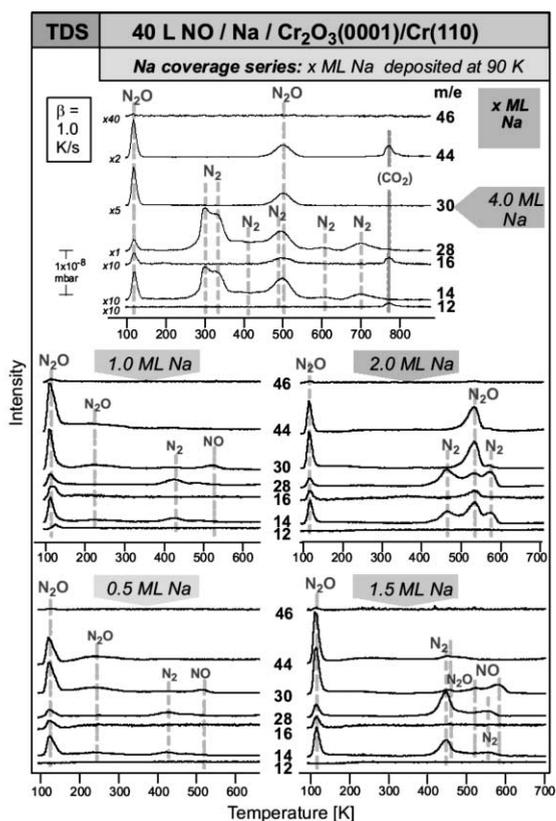


Fig. 7. Thermal desorption spectra recorded after adsorption of 40 L NO at 90 K on sodium-covered Cr₂O₃(0001)/Cr(110) as a function of sodium coverage. The partial pressures of the different masses have been recorded simultaneously.

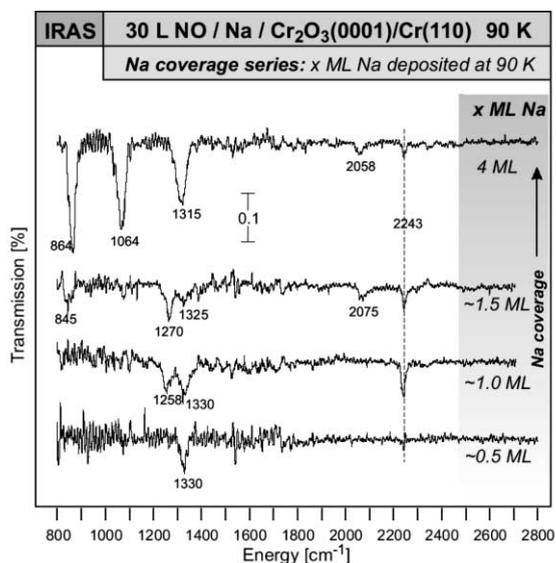


Fig. 8. IR spectra of NO adsorbed (30 L at 90 K) on a sodium covered Cr₂O₃(0001) surface as a function of sodium coverage. The sodium layer was prepared at 90 K.

due to the decomposition of Na₂O, which is formed via various reaction channels is not observed up to the maximum temperature of 800 K. It is not unlikely, also, that part of the Na₂O forms mixed oxides with the substrate chromia.

Fig. 8 shows IRAS spectra recorded of the NO saturation exposure of four of the five Na coverages at 90 K. Very clearly, the very intense signal of the NO stretching frequency on clean Cr₂O₃(0001) at 1760 cm⁻¹ is completely absent. Instead, for the lower Na coverages we find two weak signals near 1300 cm⁻¹ and another weak band at 2243 cm⁻¹. For higher Na coverages we observe three intense bands with maxima at 864, 1064 and 1315 cm⁻¹ and a weak signal at 2243 cm⁻¹. At 2060 cm⁻¹ a weak band is observed for the 1.5 and 4.0 ML exposures.

Further insight is gained by correlating the heating series shown in Figs. 9 and 10 with the above discussed TDS spectra.

The band at 2243 cm⁻¹ appears in all spectra in Fig. 8. It can be identified as the N–N-stretching vibration of weakly bound N₂O molecules $\nu_{\text{gas}} = 2224 \text{ cm}^{-1}$ [35] as observed for N₂O adsorption on Cr₂O₃(0001) [28]. It disappears above 100 K and

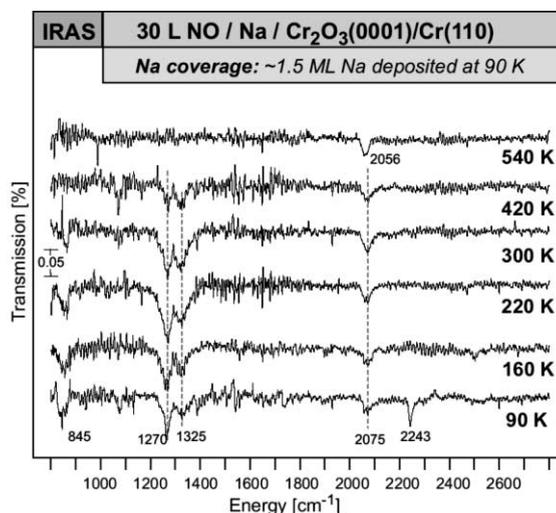


Fig. 9. IR spectra of 30 L NO adsorbed onto ~1.5 monolayer Na deposited at 90 K onto Cr₂O₃(0001) as a function of annealing temperature. The spectra have been recorded after cooling the sample back down to 90 K.

correlates with the desorption features with peak maximum at 110 K. N₂O, therefore, already forms at very low temperature on the surface and is not desorbed via reaction of (NO)₂ dimers. Bands near 1300 cm⁻¹ appear for the 0.5, 1 and 1.5 ML Na coverages after NO exposure. Even though signals near 1300 cm⁻¹ would be consistent with the NO-stretching frequency in N₂O, the bands at 1270 and 1325 cm⁻¹ are too intense and they are present even at 420 K (see Fig. 9). The bands correlate with the NO high temperature desorption at 520 K. NO on K/Si(111) [33] leads to vibrations at 1256 cm⁻¹ and in matrix isolation studies at low temperature Na⁺NO⁻ ion pairs have been identified via vibrations at 1358 cm⁻¹ [36]. We therefore identify these bands with Na⁺NO⁻ salts in different chemical environments.

With higher Na depositions the spectra show the intense bands as discussed. The bands at 864, 1064, 1318 cm⁻¹ disappear simultaneously at about 500 K. The band triplet is very similar to the vibrational spectrum of Na₂N₂O₂ (see Table 1), which can actually be synthesized from NO and Na in liquid ammonia. This salt can be looked at as the sodium salt of the (NO)₂ dimer, where the (NO)₂ dimer forms at sufficiently high NO expo-

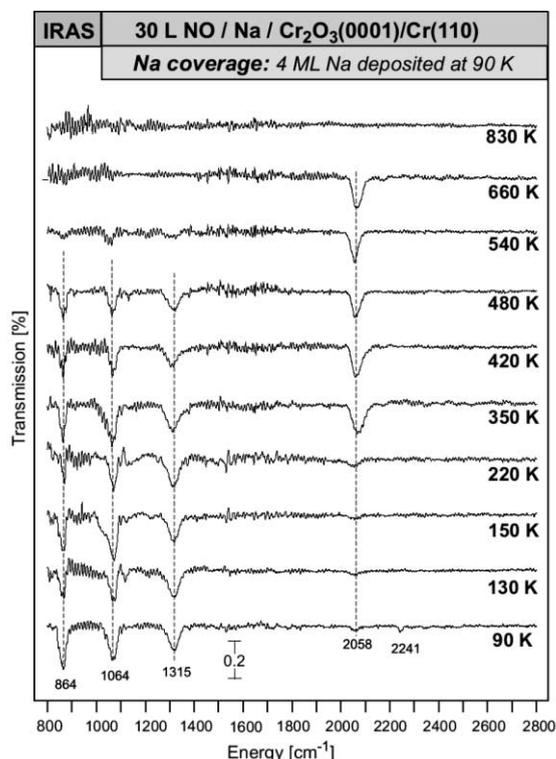


Fig. 10. IR spectra of 30 L NO adsorbed onto ~ 4 monolayer Na deposited at 90 K onto $\text{Cr}_2\text{O}_3(0001)$ as a function of annealing temperature. The spectra have been recorded after cooling the sample back down to 90 K.

sure, which is then immediately transformed into the salt due to the availability of the electrons in metallic sodium. The disappearance of the signal at 500 K is compatible with the thermal decomposition of $\text{Na}_2\text{N}_2\text{O}_2$ according to:



Table 1
Vibrational frequencies (cm^{-1})

Compound	Vibrational frequencies (cm^{-1})			Reference
$\text{Na}_2\text{N}_2\text{O}_2$ (trans)	629	1035		[35,40]
	(m)	(s)		
iso- $\text{Na}_2\text{N}_2\text{O}_2$ (cis)	584	830	1047	[35,39]
	(w)	(s)	(m)	
		(m)	(vs)	
Na_2NO_2	828	1261	1328	[35,38]
NaNO_3	692	831	1405	[35]

This means that on a metallic Na film at 90 K $\text{Na}_2\text{N}_2\text{O}_2$ is formed, which is also supported by XPS data on $\text{Na}/\text{NiO}(111)/\text{Ni}(111)$ [37].

It is interesting to note that concomitantly with the disappearance of the $\text{Na}_2\text{N}_2\text{O}_2$ the band at 2058 cm^{-1} shows a pronounced increase of intensity. We believe this band is due to the presence of NaN_3 ($\nu \sim 2043 \text{ cm}^{-1}$) [38] even though the temperature for disintegration of bulk sodium azide is only 550 K.

3.3. Cs–NO system

Our initial studies of NO adsorption on a caesium film indicated a complex and irreproducible chemistry, which was rationalised by the realisation that the chemistry was influenced markedly by photoelectron-induced processes. Fig. 11 shows the $\text{N}(1s)$ spectra observed when a caesium surface was exposed to NO at 80 K, and spectra recorded

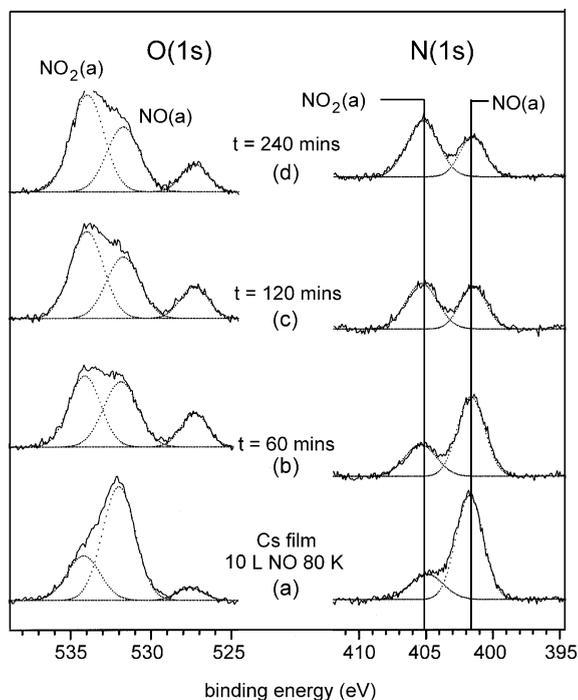


Fig. 11. $\text{N}(1s)$ and $\text{O}(1s)$ spectra for NO adsorbed at a caesium film at 80 K, illustrating the conversion of $\text{NO}(a)$ to $\text{NO}_2(a)$ with X-irradiation: (a) immediately after adsorption of NO (10 L) at 80 K, followed by exposure to X-rays for (b) 1 h, (c) 2 h and (d) 4 h.

after increasing periods of exposure to the X-ray induced secondary electron flux. A clear transfer of intensity from the initially predominant feature at 401.8 eV to the evolving peak at 405 eV is observed, together with a decrease in total N(1s) intensity, a point we shall return to later. As earlier we assign the 402 eV peak to adsorbed NO, possibly present as dimers, and the 405 eV peak to surface nitrite. These assignments are supported by the XPS data published for metal nitrosyls [41] and a range of nitrogen-containing compounds [42] including alkali metal nitrites. Furthermore, the N(1s) binding energy agrees with that observed for methyl nitrite adsorbed on Ag(111) [43] and for the majority surface species on irradiated NaNO_3 [44].

The growth of the N(1s) feature at 405 eV is accompanied by the development of an O(1s) component at 534 eV (Fig. 11), and a quantitative comparison of the intensities of these two features yields an N:O ratio of 1:2, consistent with our identification of a nitrite species. The O(1s) binding energy is also in the range (534.1–534.7 eV) observed for methyl nitrite adsorption on silver [43].

In Fig. 12 is shown evidence that the observed spectral changes are indeed induced by the secondary electron flux and are not simply due to a slow surface reaction. After exposure of the Cs surface to NO at 80 K the surface was left in vacuo for 4 h without irradiation by X-rays. The N(1s) spectrum which was then obtained was identical, within experimental error, to that recorded immediately after NO adsorption. There is no evidence for the presence of $\text{N}_2\text{O}(\text{a})$ at the surface, under any experimental conditions.

Clues to the reaction mechanism come from a detailed quantitative analysis of the curve-fitted data of Fig. 11. The total nitrogen concentration decreases from 1.5×10^{15} to $1.1 \times 10^{15} \text{ cm}^{-2}$ after 4 h irradiation; there is a corresponding decrease in the NO(a) concentration from 1.2×10^{15} to $0.4 \times 10^{15} \text{ cm}^{-2}$ and an increase in the concentration of $\text{NO}_2(\text{a})$ from 0.3×10^{15} to $0.7 \times 10^{15} \text{ cm}^{-2}$. Thus, the decrease in the concentration of NO(a) is equal to the gain in $\text{NO}_2(\text{a})$ plus the nitrogen concentration which is lost from the surface. This is consistent with the following reaction mechanism:

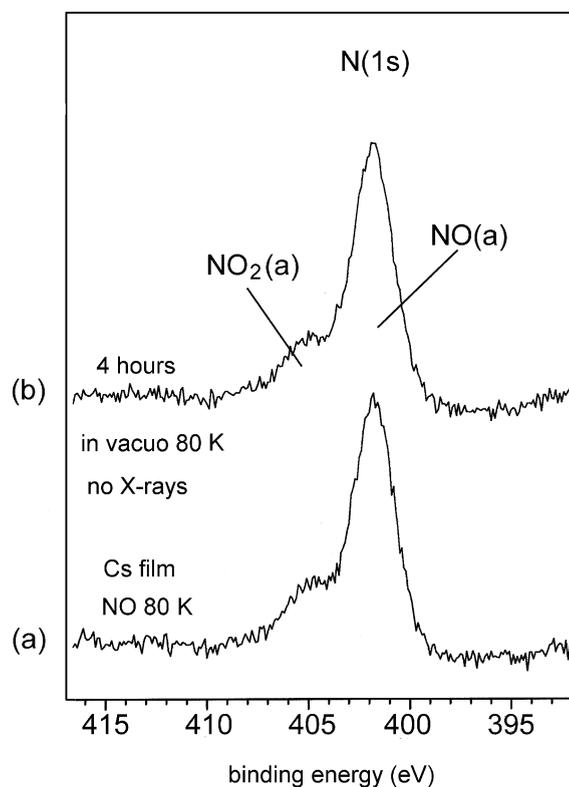
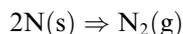
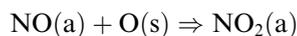


Fig. 12. N(1s) spectra for (a) an NO(a) adlayer (surface nitrogen concentration $\sigma_{\text{N}} = 1.5 \times 10^{15} \text{ cm}^{-2}$) on Cs at 80 K immediately after adsorption, and for (b) a similar adlayer left in vacuo without X-irradiation for 4 h.



where (s) denotes a mobile transient surface species. Clearly the O(s) is scavenged by adsorbed NO species before it can become thermally accommodated with the surface and form a chemisorbed oxygen species. On warming the mixed NO(a)/ $\text{NO}_2(\text{a})$ adlayer to 300 K, the majority of the NO(a) desorbs whilst the surface concentration of $\text{NO}_2(\text{a})$ remains constant.

If a caesium film is exposed to NO at 80 K, and then warmed to 300 K, without examining by XPS at any stage, then a high concentration of NO(a) remains on the surface (Fig. 13); furthermore, this

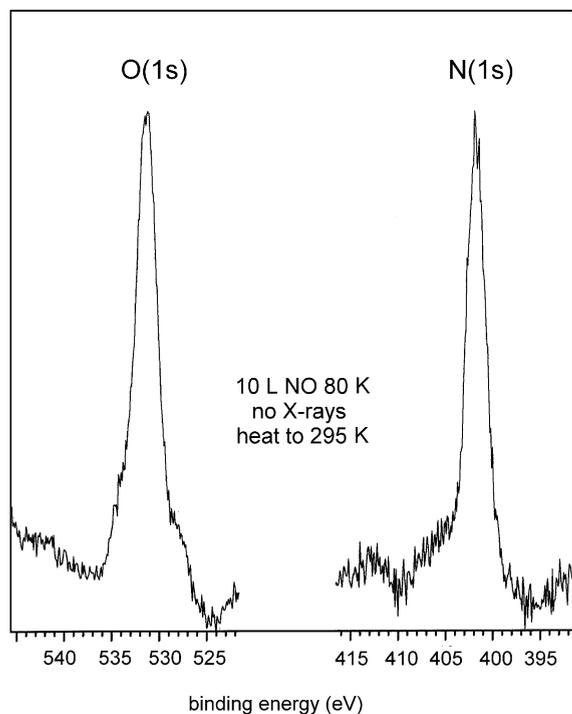


Fig. 13. N(1s) and O(1s) spectra observed after an NO(a) adlayer (10 L NO) formed at 80 K without examination by XPS was then warmed to 300 K ($\sigma_{\text{N}} = 5.6 \times 10^{14} \text{ cm}^{-2}$; O:N = 1.03:1).

species is now stable with respect to irradiation by the secondary electron flux. A possible explanation is that the extensive reconstruction occurring within the Cs film on warming leads to the formation of a discrete caesium nitrosyl compound, analogous to the sodium salt identified earlier, as distinct from surface NO adspecies. The formation of the nitrosyl compound appears to be inhibited when surface nitrite species are first generated at 80 K.

4. Conclusions

We have studied the adsorption and the thermal, electron and photon induced reaction of NO on a variety of alkali-promoted oxide surfaces with XPS, IRAS and TPD. As already evident from previous studies, alkali modification has a strong influence on the reaction of nitric oxide on metal oxide surfaces.

NO adsorbed molecularly and weakly on clean oxide surfaces. On NiO(1 1 1) NO adsorption leads to a complex N(1s) XPS signal which is dominated by multielectron effects. Secondary electron emission only moderately modifies the spectra observed on the clean surfaces, but gives rise to electron stimulated desorption. The presence of an alkali metal, in contrast, does have a pronounced influence on the predominance of surface species and the chemistry is markedly influenced by secondary electron emission induced by X-irradiation. The effect is very similar to the photon stimulated reaction which we have demonstrated in this paper. Independent of Na coverage the formation of a nitrosyl adsorbate is observed, with NO_2 formation being only a minor reaction pathway. Upon exposure to secondary electrons or to photons, the nitrosyl species converts to NO_2 . These findings are corroborated by the results for NO adsorption on thick Cs films, where from an analysis of the N(1s) and O(1s) spectra the stoichiometry of the adsorbed species was determined to be N:O = 1:2.

For NO adsorption on $\text{Cr}_2\text{O}_3(0001)/\text{Cr}(110)/\text{Na}$ surfaces vibrational spectra rule out the possibility of nitrite formation via *thermal* reactions on the surface. Instead, there are clear indications for the formation of the alkali nitrosyl salt $\text{Na}_2\text{N}_2\text{O}_2$ at lower temperatures and the formation of an alkali salt of the $(\text{NO})_2$ dimer, i.e. sodiumhyponitrite $\text{Na}_2\text{N}_2\text{O}_2$. N_2O is released via decomposition of the latter. There are indications for NO dissociation at low temperature which leads to the formation of N_2O , which has desorbed just above 100 K. Our data suggest that the hyponitrite does not form on NiO(1 1 1) and on the thick Cs film. Whether this may be connected with the high tendency of $\text{Cr}_2\text{O}_3(0001)$ to support NO-dimer formation at low temperature, as shown earlier, is not clear at present. We therefore believe, that the formation of nitrite on alkali promoted oxide surfaces is due to electron induced chemistry.

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