THE ADSORPTION OF N₂ ON Fe(111): ANGLE RESOLVED PHOTOEMISSION AND THEORETICAL MODEL STUDIES

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Received 20 November 1986; accepted for publication 4 February 1987

Angle resolved photoelectron spectra excited by synchrotron radiation from the BESSY storage ring have been obtained for adsorbed N₂ on Fe(111) as a function of temperature. The two previously identified phases of molecular N₂, i.e. the γ - and α -phase, can be clearly differentiated by their photoemission characteristics. From the angular profiles the γ -phase can be shown to consist of N₂ molecules oriented perpendicular to the surface plane. The α -phase, on the other hand, shows spectra that are only consistent with N₂ whose axis is strongly inclined from the surface normal. These findings corroborate the conclusions drawn from HREELS and XPS that the N₂ in the α -phase is " π -bonded" to the surface. We also present the results of ab initio generalized valence bond calculations for the A³ Σ_u^+ excited state of the N₂ molecule and suggest that this state of N₂ may be stabilized by the Fe(111) surface resulting in the species responsible for the α -phase. A microscopic model for the " π -bonding" state is proposed.

1. Introduction

Adsorption of molecular nitrogen and its subsequent dissociation into atomic nitrogen on Fe(111) has been studied in some detail in recent years [1-5]. Two weakly chemisorbed molecular N₂ states have been identified mainly via high resolution electron energy loss spectroscopy (HREELS) [6-8], X-ray photoelectron spectroscopy (XPS) [6], and thermal desorption spectroscopy (TDS) [7,8]. In the so-called γ -state, with an adsorption enthalpy of ~ 24 kJ/mol [5], the N₂ molecules are terminally bonded to first layer Fe

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atoms [8]. The slightly more strongly bound α -state, with an adsorption enthalphy of $\sim 31 \text{ kJ/mol}$ [5], which is the precursor to N₂ dissociation on the surface, has been attributed to N_2 π -bonded to the surface [6]. While the y-state has recently been found to have a vibrational N-N stretching frequency of 2100 cm⁻¹ [8], the α -state exhibits an unusually low stretching frequency of 1490 cm^{-1} [6], which in turn was used to infer together with XPS results the π -bonded nature of the state [6]. Even though the cited HREELS and XPS results suggest that the α -state interacts "side-on" with the metal, experimental results that allow conclusions about the geometric structure have so far not been presented. Unfortunately, a LEED structure analysis cannot be undertaken due to the lack of any sharp adsorbate induced pattern for molecular N₂ adsorption on Fe(111). Results of empirical, theoretical calculations [9] indicate that the γ -state is bonded normal, the α -state parallel to the surface. Fig. 1 schematically summarizes experimental and theoretical information available on the $N_2/Fe(111)$ system in the form of a two-dimensional potential energy diagram [9]. The two reaction coordinates represent the tilt angle with respect to the surface normal and the position along the Fe(111) surface (ordinate) with the zero at the bridging AB site as indicated in the upper inset. According to theory [9] and experiment [5] α - and γ -states are separated by an activation barrier, which has been determined experimentally to be approximately 20



Position on Fe(111) surface

Fig. 1. Schematic two-dimensional potential energy diagram [9] for the conversion of $\gamma \rightarrow \alpha N_2$. The insets show the adsorption enthalpies [5] and activation energy [5] of the two species as well as their vibrational N-N stretching frequencies [6-8].

kJ/mol [5]. The separation of α - and γ -states by an activation barrier allows one to selectively depopulate the γ -state at higher (110 K) temperature, while at lower temperature (below 77 K) α - and γ -states are both populated as has recently been clearly demonstrated through HREELS studies [8].

The present paper presents results of UV photoemission experiments undertaken to further elucidate the geometric structure of the α - and γ -state. Via angular resolved photoemission employing polarized synchrotron light we find the γ -state to contain N₂ molecules which are oriented preferentially perpendicular to the surface while in the α -state the N₂ molecules are oriented with their axis strongly inclined with respect to the surface normal. We compare the spectra of the N₂/Fe(111) system with those of the CO/Fe(111) system. Finally a simple theoretical model of the α -state bonding is proposed which suggests future experimental and theoretical studies.

The paper is organized as follows: The next section gives details of the experimental procedure, and in section 3 we discuss the results of our study. The last section contains a synopsis.

2. Experimental and theoretical details

The experiments were performed in a magnetically shielded ultra-high vacuum system (VG, ADES 400) containing facilities for low energy electron diffraction (LEED), Auger electron spectroscopy (AES), residual gas analysis with a quadrupole mass spectrometer, and angle resolved photoelectron spectroscopy (ARUPS). The electron analyser is rotatable in two orthogonal planes and electrons are collected within an acceptance angle of $\pm 1.5^{\circ}$. The resolution was typically 150 meV including monochromator. Excitation of photoelectrons was achieved by synchrotron radiation from the exit slit of a toroidal grating monochromator (TGM) attached to the storage ring BESSY in Berlin. The base pressure in the system was below 10^{-8} Pa. The Fe(111) crystal was spot-welded between two tungsten wires which were spot-welded to two tungsten rods on a sample manipulator. By pumping on a liquid nitrogen reservoir the crystal could be cooled a few degrees below 77 K. Heating was possible either by direct resistive heating or by electron impact onto the reverse side of the crystal.

The surface was cleaned by argon ion bombardment according to ref. [14]. After annealing the cleanliness was checked with AES, and surface order and geometry were established by LEED.

CO and N_2 were admitted to the chamber. At all temperatures used no sharp adsorbate induced LEED patterns were observed. Only the background of the sharp substrate LEED pattern appeared blurred upon adsorption.

The results are shown in figs. 2-5. Usually the spectra have been corrected for photon flux. However, in the case of the photon energy dependent

experiments the spectra were corrected for analyser transmission in addition to flux corrections.

The theoretical calculations on the ${}^{3}\Sigma_{u}^{+}$ state of N₂ were carried out using the perfect pairing approximation of the generalized valence bond (GVB) method [10], which incorporates important electron correlation effects and allows a simple physical description of bonding in terms of correlated orbitals. A standard double zeta basis set was used [11]. Details of such calculations may be found in previous studies [12,13].

3. Results and discussion

Fig. 2 shows photoelectron spectra of the $N_2/Fe(111)$ system at two different temperatures, and we shall discuss the two temperature regimes separately.

The upper panel refers to a surface at a temperature below that of liquid nitrogen temperature (< 77 K) exposed to 2 L N₂. This adsorbate is called low temperature (LT) phase in the following. Spectrum a has been excited with p-polarized light at $\hbar \omega = 32$ eV, and the electron emission angle (θ) was set to 0° (normal emission). The adsorbate induced features in spectrum a at 8.3 and 12.2 eV binding energy are rather pronounced and can be compared with binding energies in other N_2 -transition metal adsorbates (see table 1) [15–19]. The shape and relative intensities are similar to the Ni(110) system [16]. Both, the $3\sigma_g$ and $2\sigma_u$ states are clearly visible in normal emission. The rather high intensity of the $2\sigma_{\rm u}$ emission in the low temperature phase for photon energies between 25 and 45 eV (see fig. 3) in normal emission is due to the reduction of symmetry upon adsorption. As a consequence the σ -shape resonance, which is observed in the gas phase for the $3\sigma_g$ ion state only, is now found in the $2\sigma_u$ region as well (see fig. 3). The spectra have been normalized to the photon flux and analyser transmission. Clearly, the two adsorbate induced features exhibit resonant behaviour in an energy range typically found for other N₂ adsorbates [16,18] corroborating the vertical adsorption geometry suggested previously [8]. For a further determination of the bonding orientation of N_2 for the LT phase using selected angles of collection and light polarization [28] we use spectra b-d of fig. 2. For s-polarized excitation we find an overall pronounced reduction in intensity in normal emission as expected [28]. The σ -states are still most pronounced (spectrum b). Spectra c and d are for s-polarized light with a collection angle of 20° with respect to the normal. In spectrum c the collection is in the plane defined by the surface normal and the polarization vector along the y-axis while in curve d the data are taken in a plane perpendicular to the polarization vector. If the N₂ molecules are standing upright on the surface, curve c should show the σ -states and the even component of the π -states, and only the odd π -state should be excited in

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Fig. 2. Angle resolved photoelectron spectra of N₂ on Fe(111). Upper panel: low temperature (T > 77 K) adsorption; lower panel: high temperature (T = 110 K) adsorption.

spectrum d [28]. Qualitatively, the spectra behave properly, in that the two main peaks are substantially reduced in spectrum d compared to spectrum c. This indicates that the N_2 axis is sticking up from the surface. However, we cannot quantify this statement for mainly two reasons:

(i) There seem to be several peaks in the spectral region of the $2\sigma_u$ ion state, since the position and shape of the 12 eV peak are different in each spectrum (a-d of fig. 2). This situation is similar to other N₂ adsorbates, i.e. N₂/Ni(110) [16], N₂/Ni(100) [18], N₂/W(110) [17], and N₂/Ru(001) [20]



Fig. 3. Spectra in normal emission using p-polarized light as a function of photon energy for the low temperature phase.

where it was suggested that this is due to shake-up processes accompanying valence electron ionization. These processes are likely to occur for weakly chemisorbed adsorbates and to show up energetically in the region of the $2\sigma_u$ ion state [29,30].

(ii) We know that at temperatures below 77 K both states, α - and γ -N₂, are populated, i.e. we have to expect two different chemical species on the surface leading to two overlapping spectra which show, due to possible differing bonding orientations different angular emission characteristics.

To verify that adsorbed CO is not causing the observed extra peaks we show in fig. 4 spectra of CO adsorbed on Fe(111) for reference purposes. The upper panel shows spectra at high coverage (5 L), various collection angles and both polarization directions. The lower panel shows that the shape of the spectrum does not depend on the coverage, since it has been taken at 0.5 L exposure. Note that a recently published HREELS study for the CO/Fe(111) system [31] shows that at a 5 L exposure three different sites are populated, while at a 0.5 L coverage only one type of site (shallow hollow, B) becomes

occupied. Without going into a detailed assignment it is clear by inspection of fig. 4 that the difference between the CO/Fe(111) and the N₂/Fe(111) spectrum is significant, so that there is no danger that coadsorbed CO could contribute to the N₂/Fe(111) spectra without recognition. This is of particular importance for the N₂ adsorbate with low coverage, i.e. the α -phase.

As referred to the introduction we can depopulate the γ -phase, and keep exclusively α -N₂ on the surface by increasing the temperature of the surface to 110 K. By this means, we are able to investigate the photoemission of the α -phase (high temperature (HT) phase) separately and then go back to the above raised questions of whether and how the simultaneous presence of the α - and γ -phase influences the conclusions of the previous paragraph. For this purpose the lower panel of fig. 2 shows spectra (e and f) taken at 110 K. Spectrum e has been collected with p-polarized light in normal emission.



Fig. 4. Reference spectra for CO adsorbed on Fe(111) at two coverages. Upper panel: 5 L at 240 K; lower panel: 0.5 L at 240 K.

Clearly, the spectrum differs considerably from the corresponding spectrum a taken for the low temperature phase. The adsorbate induced features at 7.5 and 11.5 eV are rather weak. In particular, the 11.5 eV feature is hardly visible. This change suggests that the bonding of the N_2 species in the α -phase is different as compared to the γ -phase. If we assume, as was suggested earlier, that the N_2 species is π -bonded to the surface and actually inclined by a large angle from the surface normal, we should expect the π -states of the N₂ molecule to give rise to the most intense peaks in normal emission and p-polarization. A calculation of photoemission intensities for oriented N₂ has been published by Umbach et al. [17]. For this bonding orientation, the σ -states should show the maximum intensities at large off-normal angles for s-polarized incident light. Such a spectrum is shown in curve f of fig. 2. We find two rather intense adsorbate induced features around 8 and 12.3 eV, which by the above arguments have to be assigned to the remnants of the $3\sigma_{g}$ and $2\sigma_{\rm u}$ N₂ ion states. Fig. 5 shows photoelectron spectra of the high temperature phase as a function of photon energy. The geometry chosen for fig. 5a corresponds to spectrum e of fig. 2, i.e. p-polarization and normal emission. The feature peaking around 7.5 eV is observed at all photon energies but there is no clear resonance behaviour detectable. Fig. 5b shows curves corresponding to the geometry in spectrum f of fig. 2, i.e. s-polarization and off-normal emission (60°). At low photon energy, i.e. 27.5 eV, the low binding energy feature dominates, at higher photon energies the 12.3 eV peak dominates the adsorbate induced peaks. The relative intensities of the peaks as a function of photon energy are consistent with the dominance of the $1\pi_u$ ion states at low photon energies and the $2\sigma_{\mu}$ ion state at high photon energies as is also observed in the gas phase. However, unlike the gas phase and the LT $N_2/Fe(111)$ phase none of the supposedly σ -type ion states show a pronounced resonance behaviour. The absence of the shape resonance can be rationalized to a certain extent by considering that the N2 molecule possibly is coordinated to the very "open" metal surface near a C site (see fig. 1). It is expected that the electron in the σ -shape resonance in a free N₂ molecule has a rather large radial extent [32] and becomes strongly influenced when both atoms of the molecule are close to the metal surface. In fact, it would not be too surprising if it were quenched just like Rydberg transitions in molecules are quenched upon formation of a molecular solid [33]. In addition, from comparison of the N–N stretching frequency in the α -phase we expect a N–N bond elongation [6].

Let us now compare the photoemission from the low and the high temperature phases. Comparing spectra a and e of fig. 2 it is found that the α -phase (spectrum e) does not contribute substantially to spectrum a. Therefore it is appropriate to assume that the peak positions and shapes observed are determined by the γ -phase. Note that the population of the α -phase is likely to be even higher at T = 110 K as compared to T < 77 K under the present experimental conditions [8]. Upon changing to s-polarized light the α -phase is likely to contribute to the electron distribution measured at T < 77 K, although the α -phase shows maximum intensity for s-polarization at far off-normal (60°) collection as shown in fig. 2, spectrum f. However, it is not quite clear at present whether the shift of the 12 eV feature in the spectrum of the low temperature phase upon changing the collection angle in s-polarization is a characteristic of the γ -phase, and thus possibly connected with the occurrence of shake-up. Summarizing, we come to the conclusion that the position of the $3\sigma_g N_2$ ion state in the γ -phase is 8.6 eV (table 1), while the position of the $2\sigma_u$ state cannot be definitely given, but lies in the energy range 11.8–12.2 eV (table 1). The position of the $1\pi_u$ state can be taken from spectrum d in fig. 2 (8.3 eV, table 1), since shape and relative intensity (with respect to the d-band) are different from what we would have expected for the σ -emission in the α -phase (spectrum f).

The determination of peak positions for the α -phase is straightforward since the γ -phase has been removed from the surface (fig. 2, lower panel), and the values are listed in table 1. In table 1 comparison is made with the observed peak positions of the present Fe(111) data with other N₂-transition metal adsorbates [12,15]. The binding energies are given with respect to the Fermi energy. However, to compare them with free uncoordinated N₂ [11] we have determined the binding energies relative to the vacuum level by adding the work function of the clean metal and take the work function change due to N₂ adsorption into account whenever possible [17–23]. Table 1 shows an almost constant shift (2.7–2.9 eV) of the $3\sigma_g$ ion state with respect to the gas phase independent of the surface and coordination type. In contrast, the position of the $2\sigma_u$ ion state varies by more than 1 eV for the same set of

| System | 3σ _g | $\Delta 3\sigma_{g}$ | $1\pi_{\rm u}$ | $\Delta 1 \pi_{\mathrm{u}}$ | 2 <i>σ</i> _u | $\Delta 2\sigma_{\rm u}$ | Ref. |
|----------------------------|-----------------|----------------------|----------------|-----------------------------|-------------------------|--------------------------|--------------|
| N ₂ | 15.5 | | 17.0 | • | 18.8 | | [15] |
| $N_2/Pd(111)$ | 8.7 | | 10.3 | | 11.9 | | [16] |
| $N_2/W(110)$ | 7.5 | 2.9 | (7.6) | (4.3) | 11.9-12.1 | 2.6 - 2.8 | [17] |
| $N_2 / Ni(110)$ | 8.1 | 2.9 | 7.8 | 4.7 | 11.8 | 2.5 | [16] |
| $N_2 / Ni(100)$ | 8.3 | | 8.1 | | 12.8 | | [18] |
| $N_2/Ru(001)$ | 7.9 | 2.8 | 7.9 | 4.3 | 12.4 | 1.6 | [19] |
| $N_2/Fe(111) LT$ | 8.6 | 2.9 | 8.3 | 4.7 | 11.8-12.2 | 2.6-3.0 | This work |
| N ₂ /Fe(111) HT | 8.4 | 2.7 | 7.5 | 5.1 | 12.3 | 2.1 | This work |

Binding energies (eV) relative to $E_{\rm F}$ for adsorbates

Table 1

The binding energy difference Δ indicates: $\Delta = E(gas) - E(adsorbate)$.

To compare the adsorbate binding energies with gas-phase energies the work function of the adsorbate covered system has been added to the tabulated values: W(110): 5.3 eV [22], $\Delta\phi = -0.19$ [23]; Ni(110): 4.65 eV [26], $\Delta\phi = -0.1$ [27]; Ru(001): 5.4 eV [21], $\Delta\phi = -0.55$ [19]; Fe(111): 4.3 eV [24], $\Delta\phi_{LT} = -0.30$ [25], $\Delta\phi_{HT} = +0.15$ [25].

systems. The strongest shifts are found for the $1\pi_{\rm u}$ ion state, i.e. between 4.3 and 5.1 eV. The interpretation of these shifts is not unique. Two contributions have to be taken into account, namely a relaxation shift due to stabilization of the ion state through screening by the metal electrons, and a bonding shift [29]. Several theoretical studies have been published that discuss the N_2 transition metal bonding in a linear M-N-N arrangement [12,29,30,34-36]. In contrast to CO-transition metal systems where the shift of the 5σ ion state relative to the 1π state is believed to document the CO-metal bonding [28], while the 4σ ion state stays basically unaffected, both σ ion states of N₂ are thought to be shifted through interaction with the metal. Quantitative calculations in fact show that the lower lying σ ion state has significantly stronger amplitude towards the metal [16,30,34–36]. Therefore the $2\sigma_{\mu}$ ionization should be more sensitive to variations of the metal, the site, etc., as compared to the $3\sigma_g$ ionization for linear N₂ coordination. This allows us to explain the variations of the Δ values for the $2\sigma_u$ ionizations in table 1 and at the same time the constant shifts of the $3\sigma_g$ (2.7–2.9 eV) and the $1\pi_u$ states (4.3–4.7 eV)



Fig. 5. Photoelectron spectra of the high temperature phase. (a) Spectra in normal emission excited with p-polarized light as a function of photon energy. (b) Spectra excited with s-polarized light collected 60 ° off-normal as a function of photon energy.



Fig. 5. Continued.

for supposedly linear coordination. It was shown earlier and is only noted here that a many-body CNDO-Green-function calculation reproduces approximately the tabulated Δ values for Ni–N₂ and allows us to trace them back to relaxation shifts for linear coordination [29]. Since we know from the angle dependent intensity changes (fig. 2), discussed above, that the N₂ molecule is inclined to the surface in the high temperature (α) phase we can now try to use the information gained on the linear N₂-metal systems to deduce information about the bonding in the α -phase. If the N₂ molecule in the α -phase was in a symmetric site, like the one indicated in fig. 1, and thus basically oriented parallel to the (111) surface, we would expect both σ -states to feel the interaction with the surface equally strongly. Therefore, the observation of a shift $\Delta 3\sigma_g$ in line with perpendicular coordination and a $\Delta 2\sigma_u$ value within the variation found for the other metal-N2 system seems to indicate a nonsymmetric coordination site. However, the expected stronger influence of the surface on the $1\pi_u$ derived ion states for a π -bonded N₂ is indicated by the larger $\Delta 1\pi_u$ value observed for the high temperature phase. Hence, a possible coordination site is the C site that binds one end of the N_2 molecule, which then leans over to coordinate its 1π electrons into a B–C edge. Fig. 6a shows schematically such a coordination site. Our bonding proposal would easily explain the observed low coverage (10%–20% of a monolayer) for the α -state [5]: The tilted N₂ molecule "binds" five iron atoms, so that the surface can only accommodate a small number of N₂ molecules. Although this is a rather speculative proposal which cannot be considered as proven, the discussion below suggests that such a geometry may not be unreasonable from bonding requirements.

It has been noted [13,37,38] that for several chemisorption systems, the adsorbate molecule can be considered to be an ion state or excited state molecule stabilized by the substrate. We invoke this hypothesis in the present study for the α -N₂ species and consider which excited states of molecular N₂ might be reasonable candidates to form a surface complex. The lowest excited



Fig. 6. (a) Schematic representation of a possible nonsymmetric bonding site of α -N₂ on Fe(111). (b) Schematic representation of the ${}^{3}\Sigma_{u}^{+}$ excited state of N₂ which can form two covalent bonds towards the metal atoms in the geometry shown in (a). (c) Electron density plots of the GVB orbitals participating in N₂-Fe bonding (see text).



state of N₂ is the $A^3 \Sigma_u^+$ state [39], which has a vibrational frequency of 1460 cm⁻¹ (N₂ ground state ${}^1\Sigma_g^+$: 2360 cm⁻¹) and a bond length of 1.29 Å (N₂ ground state: 1.10 Å) and lies 6.22 eV above the ground state. This state has two attractive features as a candidate for the α -N₂ surface complex: (1) the vibrational frequency is very close to that observed for α -N₂, and (2) the bond length is increased by about 0.2 Å from the ground state - an important ingredient for a potential precursor to dissociation. But, the excitation energy of 6.22 eV requires considerable bonding interactions to stabilize this state. However, two covalent nitrogen-iron single bonds can be formed by the N2 $({}^{3}\Sigma_{n}^{+})$ state; each such bond should contribute a bond energy of about 2.5 eV [40]. This is still not sufficient to counterbalance the 6.22 eV excitation energy and the remaining energy would have to be obtained via several dative bond interactions and electrostatic effects due to polarization. It is not unreasonable, therefore, that the combination of these contributions could yield a species consistent with the known properties of α -N₂. By contrast, we expect the γ -N₂ state to be the ground state of N₂ (${}^{1}\Sigma_{g}^{+}$) weakly bonded to the surface by a single dative interaction.

A schematic representation (in terms of correlated orbitals of σ - and

 π -symmetry) of this state as it might bond to the surface is given in fig. 6b. We note that the state corresponds to a broken " π -bond" with the two resulting dangling orbitals available for forming covalent bonds to the surface. In addition there is the potential for forming several dative bonds in this unique geometrical arrangement. Hence, it appears that the proposed site geometry does offer the considerable bonding interactions which are necessary to stabilize the ${}^{3}\Sigma_{\mu}^{+}$ state.

In fig. 6c, contour plots of the dangling orbitals of the broken bond in the ${}^{3}\Sigma_{u}^{+}$ state are shown together with the correlated lone pair on one of the nitrogen atoms. These are the results of a generalized valence bond calculation [10] which gives a calculated vibrational frequency of 1473 cm⁻¹, a bond length of 1.30 Å and an excitation energy of 5.02 eV, in quite reasonable agreement with experiments for the gas-phase molecule excited state.

It will require considerable further experimental and theoretical work to test the validity of our proposed bonding model for α -N₂, however we feel it may be valuable as a starting point for discussion to have a definite microscopic model in mind.

4. Conclusion

We have shown by angle resolved photoemission the presence of two different molecular N₂ phases on the Fe(111) surface. These findings are in accord with recent HREELS [6-8] and XPS [6] results: At low temperature a γ -phase with lower adsorption energy coexists with an α -phase of higher adsorption energy. The photoemission revealed for the first time information on the bonding orientation of the nitrogen molecule within the adsorbate layers. While the N₂ molecule is bound perpendicular to the surface in the γ -phase, the N₂ bond axis appears to be strongly inclined with respect to the surface normal in the α -phase. A detailed analysis of the energetic shifts of the ion states of the adsorbed molecule with respect to the gas phase indicates a nonsymmetric coordination site (with respect to the internuclear axis) of the N₂ molecule in the α -phase. The σ -shape resonance, observed in the γ -phase as in other N₂-transition metal systems, is not observed in the α -phase. It is argued that due to the interaction of both nitrogen atoms with the surface the σ final state is quenched and thus no longer accessible. Finally a microscopic bonding model is proposed for the α -N₂ state which considers the species to be a stabilized $3\Sigma_{u}^{+}$ state of N₂; stabilized by the high coordination possible at the proposed adsorption site.

Acknowledgements

We thank Dr. M. Golze for helpful suggestions concerning cleaning of the Fe(111) surface and Dr. D. Heskett for useful discussions. This work has been

funded by the German Federal Minister for Research and Technology (BMFT) under contract number 05327 AAB/3, the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

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