

π -Bonded N₂ on Fe(111): The Precursor for DissociationM. Grunze^(a)*Fritz-Haber-Institut der Max-Planck-Gesellschaft, 1000 Berlin 33, Federal Republic of Germany*

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N₂ chemisorbed on Fe(111) is identified by photoelectron spectroscopy and high-resolution electron energy-loss spectroscopy as a π -bonded surface complex in which both nitrogen atoms interact with the metal. This species forms the immediate precursor to dissociation.

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Molecular nitrogen adsorption on transition metals has been studied in detail on various substrates by photoemission and vibrational spectroscopies,¹ and in all cases it has so far been concluded that the molecule bonds mainly via the $3\sigma_g$ and $2\sigma_g$ molecular orbitals in an "end-on" configuration to the surface, i.e., *M-N-N*. Atomic nitrogen adsorption has also been studied widely,² but no experimental data have been reported for the actual surface intermediate in which the breaking of the dinitrogen bond occurs. There is a great practical interest in a better understanding of the dissociation mechanism on a molecular basis, since dissociative nitrogen adsorption has been identified as the rate-determining step in the ammonia synthesis reaction on iron.³

The kinetics of dissociative nitrogen adsorption on Fe(111) have been studied in detail previously⁴; it was concluded that this process proceeds through a molecularly adsorbed species with a rather low activation energy. Later it was found⁵ that this species (α state) is preceded at low temperatures by a more weakly held, physisorbed γ state, which desorbs at about 85 K. In the present work, the α state has been identified as a π -bonded molecule with *both* N atoms interacting with the surface and thus forming the immediate precursor to dissociation. This evidence is based on experimental x-ray photoemission spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (not discussed here) supplemented by calculations for the N 1s core-hole

spectra and high-resolution electron-energy-loss spectroscopy (HREELS) data. N 1s core-level photoelectron experiments using Al *K* α radiation were performed in a Leybold Heraeus photoelectron spectrometer equipped with a rotatable cold finger.⁶ The vibrational data were obtained in a different vacuum system with a high-resolution electron-energy-loss spectrometer. The Fe(111) crystals were cleaned and annealed following previously described procedures.⁷

In Fig. 1, a sequence of N 1s spectra for the three different nitrogen bonding states on Fe(111), denoted by γ , α (molecular), and β (atomic) is displayed. The γ state spectrum (curve *a*) was recorded at 85 K in an ambient of $P_{N_2} = 5 \times 10^{-7}$ mbar and includes emission from some α -N₂,⁵ giving rise to the shoulder at ~ 399 -eV binding energy (E_B). The intensities of the two peaks at $E_B = 405.9$ eV and $E_B \sim 401$ eV depend on the ambient N₂ pressure at $T \geq 85$ K, since γ -N₂ is only weakly adsorbed ($E_{ad} \leq 24$ kJ/mol).⁵ A similar N 1s-doublet structure has been observed by Kishi and Roberts⁸ for N₂ on polycrystalline iron but was interpreted incorrectly as arising from two different adsorption states of N₂. After heating the predosed surface in vacuum to 97 K, all γ -N₂ is desorbed and a single species (α) ($E_{ad} \approx 31$ kJ/mol⁴) characterized by a band at 399.0 eV and some intensity at higher E_B remains on the surface [Fig. 1(b)]. With

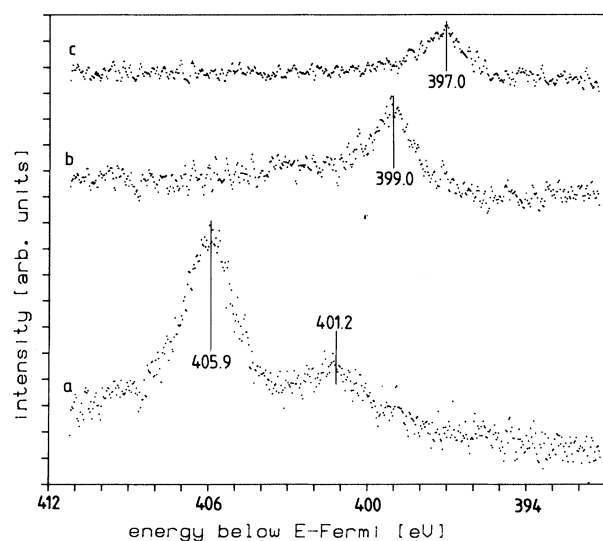


FIG. 1. N 1s core-level spectra for the three different nitrogen species on Fe(111): (a) γ -N₂, (b) α -N₂, (c) atomic β nitrogen.

increasing substrate temperature this α -state band shifts to lower binding energies, indicating a conversion of the α state into the strongly bound atomic β state.⁵ The characteristic N 1s spectrum of atomic β nitrogen is shown in Fig. 1(c). From the integrated XPS band intensities, we estimated the maximum γ -state and α -state populations to be 3.4×10^{14} and 7×10^{13} molecules/cm², respectively.⁵ These values are in fair agreement with the coverage for weakly bound nitrogen on polycrystalline iron reported by Wedler⁹ (γ state) and the α -state nitrogen coverage on Fe(111) reported in Ref. 4.

Curve (a) in Fig. 2 displays the HREELS spectrum from the α state which was obtained after exposing an Fe(111) surface at 110 K to 150×10^{-6} Torr-sec ³⁰N₂. The band at 1490 cm⁻¹ has to be associated with the N-N stretch vibration (whose frequency is significantly lowered with respect to the 2331 cm⁻¹ value of the free molecule), while a weak shoulder at ~ 435 cm⁻¹ is attributed to the M-N vibration of a small fraction of already dissociated molecules. "Off-specular" measurements show that the ν_{N-N} band is dipole active. Subsequent warming to 170 K leads to partial desorption,⁴ while simultaneously part of α -N_{2ad} dissociates giving rise to a band 450 cm⁻¹ [curve (b)]. These results parallel the XPS observations⁵ and demonstrate (i) that the formation of atomic nitrogen occurs through dissociation of the molecular α state, and (ii) that the N 1s levels at 399 and 397 eV indeed have to be associated with molecular (α) and atomic (β) nitrogen, respectively.

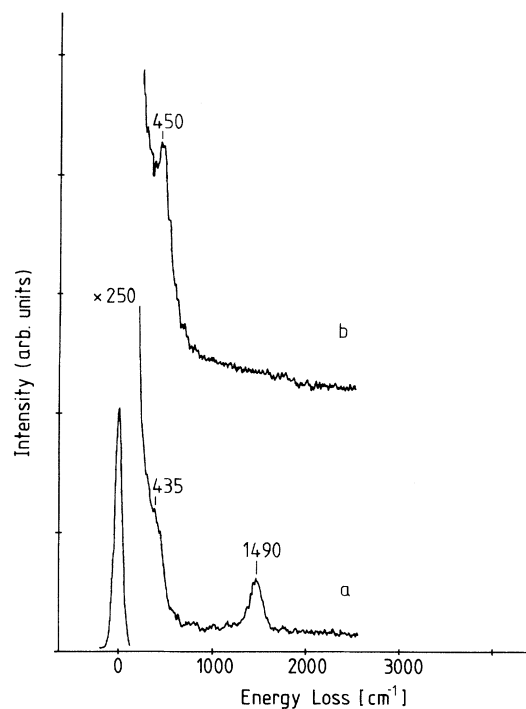


FIG. 2. HREELS data for (a) α -N₂ and (b) atomic β nitrogen on Fe(111).

The observed N-N vibration for the ³⁰N₂ α state at 1490 cm⁻¹ (which would be higher by ~ 30 cm⁻¹ for ²⁸N₂) is extremely low compared to the N₂²⁸ on Ni(110) system, for which $\nu_{N-N} = 2194$ cm⁻¹ was determined,¹⁰ and bonding to the surface in an "end-on" form could clearly be established.¹ Similar high ν_{N-N} values were also reported for all dinitrogen complexes in which the ligand is attached end-on to a metal atom.¹¹ Low N-N frequencies (reaching down to 1255 cm⁻¹) were observed for complexes in which the N₂ molecule was concluded to be bridge-bonded ($M-N=N-M$). Structural analysis of a "side-on" nickel-dinitrogen complex revealed a considerably increased N-N bond length (1.35 Å as compared with 1.10 Å in free N₂), while in the same work it was concluded that ν_{N-N} has to be below 1550 cm⁻¹.¹² Recent work with a Ti complex, in which each of the two nitrogen atoms is attached to two Ti atoms, found $\nu_{N-N} = 1282$ cm⁻¹ and an increased N-N bond length of 1.30 Å.¹³ These data strongly suggest that in the present system *both* N atoms in α -N₂ interact with the metal. In the case of a metal surface the experimental distinction between bridge-bonded and side-on becomes somewhat arbitrary, since certainly both prototypes of coupling will play a role. The Fe(111) surface has a very open structure and side-on bonding does not necessarily imply that the

N_2 molecular axis is parallel to the surface plane. The absence of a N_2 -Ni bending mode, however, rules out a tilted structure in which only one nitrogen atom interacts with the surface. In any case, it can be concluded that the observed low ν_{N-N} for α - N_2 on Fe(111) reflects a considerable weakening of the N-N bond by partial occupation of the antibonding π levels (in a manner similar to the analogous olefin or acetylene transition-metal complexes.¹¹ This is accompanied by an increase of the N-N bond length and consequently a lowering of the activation barrier for dissociation. Additional qualitative support for the electron-acceptor nature of α - N_2 is provided by the observed increase of the work function.⁴

A side-on bonding geometry of α - N_2 also follows from a comparison of the N 1s photoemission data with calculated core-hole spectra for end-on and side-on bonded N_2 . The hole states were calculated within the equivalent-cores approximation, treating the valence electrons self-consistently and augmenting the self-consistent-field solution by configuration interaction using the 300 lowest energy configurations.¹⁴ On this basis, all singly and doubly excited states within the configuration space and their contribution to the spectral function were determined by direct overlap calculations within the sudden approximation.¹⁴ Calculations were carried out for a linear Ni- N_2 and side-on arrangement, varying the Ni- N_2 distance from 1.5 to 2.3 Å. The intramolecular N_2 separation in the linear clusters was kept constant at the gas-phase value of 1.1 Å; in the side-on clusters, extended N-N distances have also been considered in the calculations. For metal- N_2 bond lengths typically found in linear N_2 transition-metal complexes, i.e., between 1.8 and 2.0 Å, the satellites carry as much intensity as the line at lowest binding energy, in agreement with experimental data on linear N_2 complexes.¹⁴ As the N-N bond gets weaker, the satellite peaks gain even more intensity. Figure 3(a) shows a plot of the calculated N 1s spectrum, which was obtained by summing the emission from both nitrogen atoms of a linear Ni- N_2 cluster with a metal- N_2 separation of 2.1 Å representing weak adsorption. The intensity ratio, and the electron binding-energy difference of ~ 4 eV between the bands at lower E_B and higher E_B , both resemble the experimental γ -state spectrum. However, a side-on N_2 molecule only *weakly* interacting with the substrate (i.e., a metal- N_2 distance of $d \geq 2.1$ Å) leads to basically the same computed spectrum as the weakly interacting linear adsorbate complex,¹⁵ preventing an unambiguous identification of the γ -state bonding geometry.

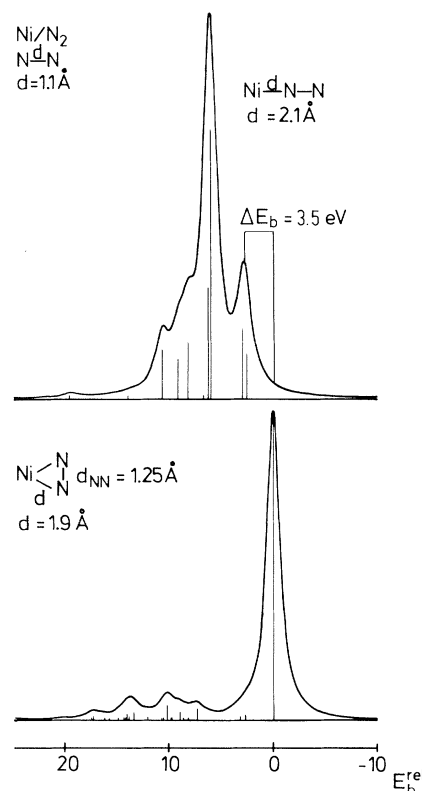


FIG. 3. Calculations of N 1s core-level spectra for a linear and triangular bonding configuration of N_2 in a Ni- N_2 cluster.

If a side-on N_2 molecule closer to the surfaces ($d = 1.9$ Å) and thus with *stronger* substrate interaction (corresponding to the α state) is ionized, only a weak satellite structure at the high-binding-energy side of the leading peak [Fig. 3(b)] results, in agreement with our α -state N 1s data. The spectrum in Fig. 3(b) was calculated for a Ni- N_2 distance of 1.9 Å and a N-N bond length of 1.25 Å. In general, it is found that with increasing N-N bond length, the core-electron spectra become more atomiclike, i.e., they exhibit less satellite intensity.¹⁵ The absolute binding-energy difference between the spectra 3(a) and 3(b) was obtained from the charge densities of the neutral and ionic species using the so-called relaxed-potential model.¹⁶ The calculated binding-energy difference between the primary hole states (lowest E_B) of end-on and side-on Ni- N_2 complexes is 3.5 eV compared with the experimental binding-energy difference of 2.2 eV.

The calculations for the N 1s core-level emission presented here and recent calculations¹⁷ by Tománek for the total-energy surface for γ - and α - N_2 on Fe(111)¹⁸ give a consistent picture of the electronic interaction of the α state with the sub-

strate. In the side-on geometry electron donation proceeds primarily through the occupied $1\pi_u$ orbital of N_2 as opposed to dominating σ donation in the linear arrangement. The $1\pi_g^*$ acceptor ability is larger in the side-on geometry than in the linear arrangement due to directed overlap between metal d functions and the in-plane component of the π orbital. Thus, charge transfer into the molecular $1\pi_g^*$ orbital lowers the activation barrier for dissociation ($E_A = 28$ kJ/mol^{5,19}). This more intense $1\pi_g^*$ coupling in the side-on as compared to the linear configuration also causes the N 1s binding energy shift in the α state to lower E_B values and reduces the satellite intensity in the side-on as compared to the linear bonding arrangement.^{15,19}

In conclusion, we observed the transition of a weakly bonded molecular γ -adsorption state into the side-on bonded α state which is the precursor for dissociation on Fe(111). The adsorbate-substrate interaction in the α state is similar to the O_2 on Pt(111) system,²⁰ where dissociation proceeds via peroxo species.²¹ However, a precursor to the peroxo states (i.e., a γ state), was not observed for O_2 on Pt(111). The open {111} plane of iron provides various side-on adsorption sites for α - N_2 , between which a distinction cannot be made from our present results. Bonding of the α state to the substrate, however, clearly involves the molecular N_2 π orbitals, and charge transfer into the antibonding $1\pi_g^*$ levels reduces the activation barrier for dissociation. Recent calculations for a hypothetical bridging dinuclear $Co_2(CO)_6(\mu-N_2)$ complex also predict this species to be stable²² and are in full agreement with the π bonding concept proposed here.

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