

**$\pi$ -Bonded N<sub>2</sub> on Fe(111): The Precursor for Dissociation**M. Grunze<sup>(a)</sup>*Fritz-Haber-Institut der Max-Planck-Gesellschaft, 1000 Berlin 33, Federal Republic of Germany*

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N<sub>2</sub> chemisorbed on Fe(111) is identified by photoelectron spectroscopy and high-resolution electron energy-loss spectroscopy as a  $\pi$ -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,<sup>1</sup> 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,<sup>2</sup> 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.<sup>3</sup>

The kinetics of dissociative nitrogen adsorption on Fe(111) have been studied in detail previously<sup>4</sup>; it was concluded that this process proceeds through a molecularly adsorbed species with a rather low activation energy. Later it was found<sup>5</sup> that this species ( $\alpha$  state) is preceded at low temperatures by a more weakly held, physisorbed  $\gamma$  state, which desorbs at about 85 K. In the present work, the  $\alpha$  state has been identified as a  $\pi$ -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 $\alpha$  radiation were performed in a Leybold Heraeus photoelectron spectrometer equipped with a rotatable cold finger.<sup>6</sup> 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.<sup>7</sup>

In Fig. 1, a sequence of N 1s spectra for the three different nitrogen bonding states on Fe(111), denoted by  $\gamma$ ,  $\alpha$  (molecular), and  $\beta$  (atomic) is displayed. The  $\gamma$  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  $\alpha$ -N<sub>2</sub>,<sup>5</sup> giving rise to the shoulder at  $\sim 399$ -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 N<sub>2</sub> pressure at  $T \geq 85$  K, since  $\gamma$ -N<sub>2</sub> is only weakly adsorbed ( $E_{ad} \leq 24$  kJ/mol).<sup>5</sup> A similar N 1s-doublet structure has been observed by Kishi and Roberts<sup>8</sup> for N<sub>2</sub> on polycrystalline iron but was interpreted incorrectly as arising from two different adsorption states of N<sub>2</sub>. After heating the predosed surface in vacuum to 97 K, all  $\gamma$ -N<sub>2</sub> is desorbed and a single species ( $\alpha$ ) ( $E_{ad} \approx 31$  kJ/mol<sup>4</sup>) characterized by a band at 399.0 eV and some intensity at higher  $E_B$  remains on the surface [Fig. 1(b)]. With

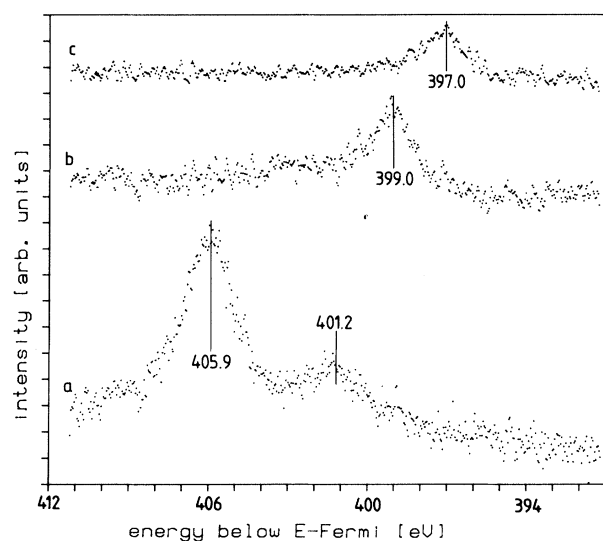


FIG. 1. N 1s core-level spectra for the three different nitrogen species on Fe(111): (a)  $\gamma$ -N<sub>2</sub>, (b)  $\alpha$ -N<sub>2</sub>, (c) atomic  $\beta$  nitrogen.

increasing substrate temperature this  $\alpha$ -state band shifts to lower binding energies, indicating a conversion of the  $\alpha$  state into the strongly bound atomic  $\beta$  state.<sup>5</sup> The characteristic N 1s spectrum of atomic  $\beta$  nitrogen is shown in Fig. 1(c). From the integrated XPS band intensities, we estimated the maximum  $\gamma$ -state and  $\alpha$ -state populations to be  $3.4 \times 10^{14}$  and  $7 \times 10^{13}$  molecules/cm<sup>2</sup>, respectively.<sup>5</sup> These values are in fair agreement with the coverage for weakly bound nitrogen on polycrystalline iron reported by Wedler<sup>9</sup> ( $\gamma$  state) and the  $\alpha$ -state nitrogen coverage on Fe(111) reported in Ref. 4.

Curve (a) in Fig. 2 displays the HREELS spectrum from the  $\alpha$  state which was obtained after exposing an Fe(111) surface at 110 K to  $150 \times 10^{-6}$  Torr-sec <sup>30</sup>N<sub>2</sub>. The band at 1490 cm<sup>-1</sup> has to be associated with the N-N stretch vibration (whose frequency is significantly lowered with respect to the 2331 cm<sup>-1</sup> value of the free molecule), while a weak shoulder at  $\sim 435$  cm<sup>-1</sup> is attributed to the M-N vibration of a small fraction of already dissociated molecules. "Off-specular" measurements show that the  $\nu_{N-N}$  band is dipole active. Subsequent warming to 170 K leads to partial desorption,<sup>4</sup> while simultaneously part of  $\alpha$ -N<sub>2ad</sub> dissociates giving rise to a band 450 cm<sup>-1</sup> [curve (b)]. These results parallel the XPS observations<sup>5</sup> and demonstrate (i) that the formation of atomic nitrogen occurs through dissociation of the molecular  $\alpha$  state, and (ii) that the N 1s levels at 399 and 397 eV indeed have to be associated with molecular ( $\alpha$ ) and atomic ( $\beta$ ) nitrogen, respectively.

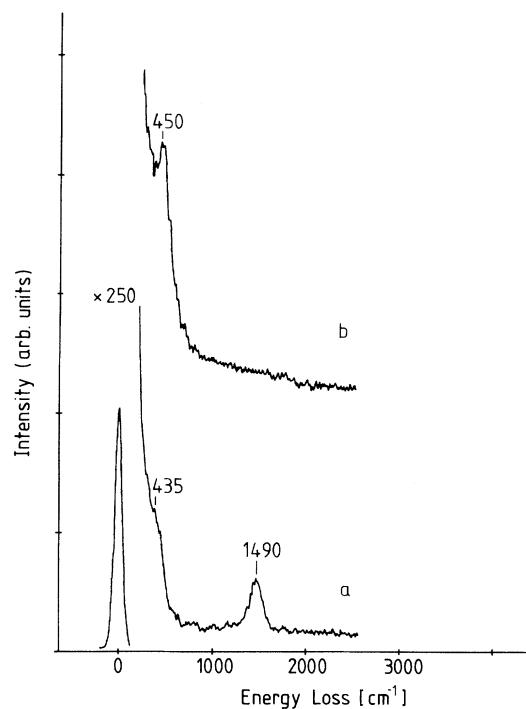


FIG. 2. HREELS data for (a)  $\alpha$ -N<sub>2</sub> and (b) atomic  $\beta$  nitrogen on Fe(111).

The observed N-N vibration for the <sup>30</sup>N<sub>2</sub>  $\alpha$  state at 1490 cm<sup>-1</sup> (which would be higher by  $\sim 30$  cm<sup>-1</sup> for <sup>28</sup>N<sub>2</sub>) is extremely low compared to the N<sub>2</sub><sup>28</sup> on Ni(110) system, for which  $\nu_{N-N} = 2194$  cm<sup>-1</sup> was determined,<sup>10</sup> and bonding to the surface in an "end-on" form could clearly be established.<sup>1</sup> Similar high  $\nu_{N-N}$  values were also reported for all dinitrogen complexes in which the ligand is attached end-on to a metal atom.<sup>11</sup> Low N-N frequencies (reaching down to 1255 cm<sup>-1</sup>) were observed for complexes in which the N<sub>2</sub> 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 N<sub>2</sub>), while in the same work it was concluded that  $\nu_{N-N}$  has to be below 1550 cm<sup>-1</sup>.<sup>12</sup> 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<sup>-1</sup> and an increased N-N bond length of 1.30 Å.<sup>13</sup> These data strongly suggest that in the present system *both* N atoms in  $\alpha$ -N<sub>2</sub> 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  $\nu_{N-N}$  for  $\alpha$ - $N_2$  on Fe(111) reflects a considerable weakening of the N-N bond by partial occupation of the antibonding  $\pi$  levels (in a manner similar to the analogous olefin or acetylene transition-metal complexes.<sup>11</sup> 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  $\alpha$ - $N_2$  is provided by the observed increase of the work function.<sup>4</sup>

A side-on bonding geometry of  $\alpha$ - $N_2$  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.<sup>14</sup> 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.<sup>14</sup> 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.<sup>14</sup> 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  $\sim 4$  eV between the bands at lower  $E_B$  and higher  $E_B$ , both resemble the experimental  $\gamma$ -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,<sup>15</sup> preventing an unambiguous identification of the  $\gamma$ -state bonding geometry.

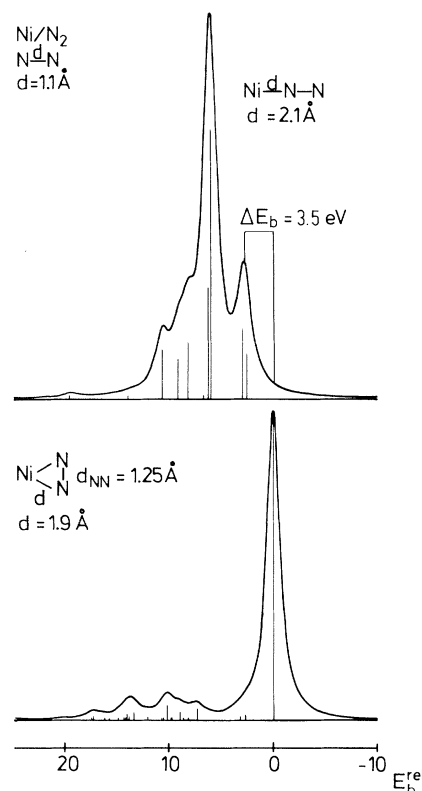


FIG. 3. Calculations of N 1s core-level spectra for a linear and triangular bonding configuration of  $N_2$  in a Ni- $N_2$  cluster.

If a side-on  $N_2$  molecule closer to the surfaces ( $d = 1.9$  Å) and thus with *stronger* substrate interaction (corresponding to the  $\alpha$  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  $\alpha$ -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.<sup>15</sup> 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.<sup>16</sup> 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 calculations<sup>17</sup> by Tománek for the total-energy surface for  $\gamma$ - and  $\alpha$ - $N_2$  on Fe(111)<sup>18</sup> give a consistent picture of the electronic interaction of the  $\alpha$  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  $\sigma$  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  $\pi$  orbital. Thus, charge transfer into the molecular  $1\pi_g^*$  orbital lowers the activation barrier for dissociation ( $E_A = 28$  kJ/mol<sup>5,19</sup>). 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  $\alpha$  state to lower  $E_B$  values and reduces the satellite intensity in the side-on as compared to the linear bonding arrangement.<sup>15,19</sup>

In conclusion, we observed the transition of a weakly bonded molecular  $\gamma$ -adsorption state into the side-on bonded  $\alpha$  state which is the precursor for dissociation on Fe(111). The adsorbate-substrate interaction in the  $\alpha$  state is similar to the  $O_2$  on Pt(111) system,<sup>20</sup> where dissociation proceeds via peroxo species.<sup>21</sup> However, a precursor to the peroxo states (i.e., a  $\gamma$  state), was not observed for  $O_2$  on Pt(111). The open {111} plane of iron provides various side-on adsorption sites for  $\alpha$ - $N_2$ , between which a distinction cannot be made from our present results. Bonding of the  $\alpha$  state to the substrate, however, clearly involves the molecular  $N_2$   $\pi$  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 stable<sup>22</sup> and are in full agreement with the  $\pi$  bonding concept proposed here.

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