

Ab initio BANDSTRUCTURE OF A LAYER OF NITROGEN MOLECULES ORIENTED IN A HERRINGBONE STRUCTURE

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Dispersion curves for nitrogen molecules physisorbed on graphite in the herringbone ($2\sqrt{3} \times \sqrt{3}$) structure are calculated and compared to recent angular resolved photoemission spectra. The calculated splitting at Γ of the $3\sigma_g$ derived molecular state and its disappearance at the Brillouin zone boundary is in good agreement with the observed spectrum. It is shown that the photoemission data for CO/Ag(1 1 1) can be also interpreted in terms of a herringbone structure.

THE STRUCTURE and orientational ordering of nitrogen molecules physisorbed on graphite have been studied by neutron diffraction [1] and low energy electron diffraction (LEED) [2, 3]. From the LEED patterns an ordered herringbone ($2\sqrt{3} \times \sqrt{3}$) structure is inferred for $T < 30$ K, where the molecular axes are parallel to the surface and the molecular centers have the commensurate ($\sqrt{3} \times \sqrt{3}$) 30° structure. Recently angular resolved photoemission was used [4] to study the electronic properties of in plane oriented N_2 and CO molecules on different substrates and to correlate the measured dispersion curves with the orientational ordering established for N_2 on graphite. For the interpretation of the experimental results semi-empirical complete neglect of differential overlap (CNDO) calculations have been employed [4].

In the present study dispersion curves are calculated for an isolated layer of N_2 molecules in the herringbone structure using *ab initio* Hartree–Fock cluster wave functions for the determination of the elements of the charge-bond-order matrix which occur in a linear combination of atomic orbitals (LCAO) ansatz briefly described below. The geometry of the N_2 overlayer used for the calculation is the one determined in the LEED studies by Diehl *et al.* [2, 3] and is shown in Fig. 1. The benzene rings in the graphite plane are indicated by hexagons. The distance a between the centers of two neighboring hexagons is 2.46 Å. The nearest-neighbor separation $|\bar{a}|$ of the centers of two N_2 molecules (center-of-mass separation) is then

$\sqrt{3}a = 4.26$ Å. Two possible unit cells for the herringbone structure are shown, both with $|\bar{a}| = 4.26$ Å. The ($2\sqrt{3} \times \sqrt{3}$) unit cell used in [4] has $|\bar{c}| = 2\sqrt{3}a = 8.52$ Å. The rectangular unit cell used in this manuscript and in [3] has $|\bar{b}| = 3a = 7.38$ Å. The overlayer contains as additional symmetry elements two glide planes (translation parallel to a plane followed by a reflection in that plane) labelled A and B which are perpendicular to each other. The angles between the molecular axes and the glide planes θ_1 and θ_2 are both 45° . The distance between the two nitrogen atoms in the N_2 molecule is assumed to be 1.0976 Å.

Figure 2 illustrates the real and reciprocal lattices with the corresponding Wigner–Seitz and Brillouin zones, respectively. The presence of two glide planes has two consequences. First this symmetry requires that the bands are degenerate on the complete Brillouin zone boundary (in the irreducible part this boundary is represented by the symmetry lines \bar{C} and \bar{D}). This was already predicted by Hund in 1936 [5] in his analysis of certain two-dimensional space groups with glide planes. Second the points in the reciprocal space indexed with crosses are absent in the LEED pattern [2, 3] which leads to a pattern expected for center-of-mass scattering. The Brillouin zone corresponding to the commensurate ($\sqrt{3} \times \sqrt{3}$) 30° hexagonal center-of-mass structure (one nitrogen molecule per unit cell) is indicated by dashed lines.

For the calculation of the band structure the following method was used. In the self-consistent LCAO

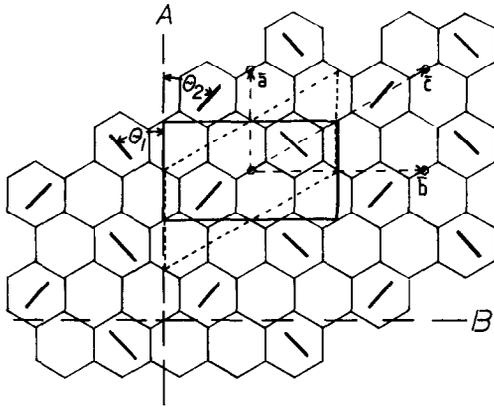


Fig. 1. The herringbone structure of N_2 molecules physisorbed on graphite. The benzene rings of the graphite plane are indicated by hexagons, the N_2 molecules as lines. Two possible unit cells are shown with $|\vec{a}| = 4.26 \text{ \AA}$, $|\vec{b}| = 7.38 \text{ \AA}$ and $|\vec{a}| = 4.26 \text{ \AA}$, $|\vec{c}| = 8.52 \text{ \AA}$, respectively. A and B label two glide planes which are perpendicular to each other. $\theta_1 = \theta_2 = 45^\circ$.

method for infinite periodic systems [6] a Bloch wave function $\psi_n(\mathbf{k}, \mathbf{r})$ is represented as

$$\psi_n(\mathbf{k}, \mathbf{r}) = \sum_i c_{in}(\mathbf{k}) \phi_i(\mathbf{k}, \mathbf{r}), \quad (1)$$

with

$$\phi_i(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mu} e^{i\mathbf{k}\mathbf{R}_{\mu}} u_i(\mathbf{r} - \mathbf{R}_{\mu}), \quad (2)$$

$u_i(\mathbf{r} - \mathbf{R}) \equiv u_i^{\mu}$ being the i th atomic orbital centered in cell μ . The energy bands and wave functions are determined from the self-consistent solution of the Hartree–Fock equations

$$F(\mathbf{k})c_n(\mathbf{k}) = E_n(\mathbf{k})S(\mathbf{k})c_n(\mathbf{k}). \quad (3)$$

In the presented work the overlap matrix elements are calculated in the first neighbors' interactions approximation. The Fock matrix elements

$$F_{ij}(\mathbf{k}) = \sum_{\mu} e^{i\mathbf{k}\mathbf{R}_{\mu}} F_{ij}^{0\mu}, \quad (4)$$

with

$$F_{ij}^{0\mu} = h_{ij}^{0\mu} + g_{ij}^{0\mu}, \quad (5)$$

are approximated in the following way. Hartree–Fock calculations were performed for two N_2 molecules in the geometry of the unit cell and for three clusters each with 6 N_2 molecules representing the unit cell and its nearest-neighbors in $\pm \vec{a}$, $\pm \vec{b}$, and $\pm \vec{c}$ direction. From the dimer and the sub-blocks of the three cluster Fock matrices, the $F^{0\mu}$ blocks in equation (4) were calculated as

$$F^{00} = F_{\vec{a}}^{00} + F_{\vec{b}}^{00} + F_{\vec{c}}^{00} - 2F_{\text{dimer}}, \quad (6a)$$

$$F^{0\vec{a}} = F_{\vec{a}}^{01}, \quad F^{0\vec{b}} = F_{\vec{b}}^{01}, \quad F^{0\vec{c}} = F_{\vec{c}}^{01}. \quad (6b)$$

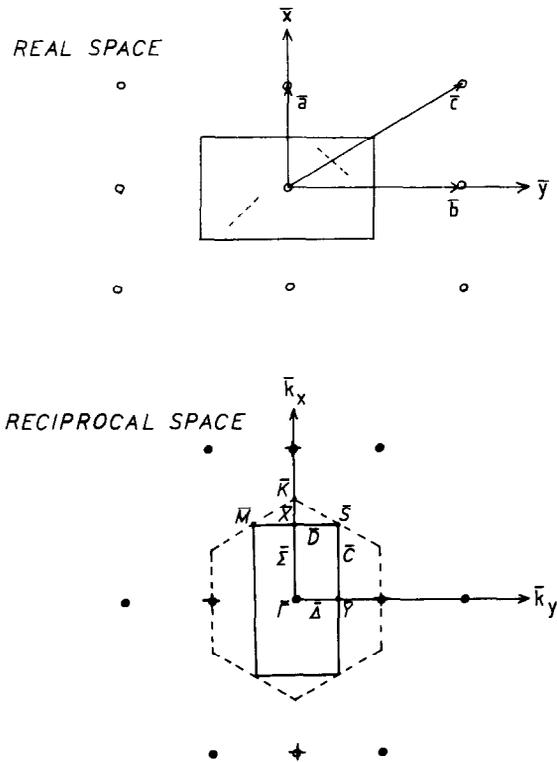


Fig. 2. Real and reciprocal lattices of the rectangular structure with corresponding Wigner–Seitz and Brillouin zone, respectively. The Brillouin zone corresponding to the hexagonal center-of-mass structure is indicated by dashed lines. \bar{K} and \bar{M} label symmetry points of the hexagonal zone. $\Gamma\bar{X} = \pi/|\vec{a}| = \pi/(\sqrt{3}a) = 0.74 \text{ \AA}^{-1}$, $\Gamma\bar{Y} = \pi/|\vec{b}| = \pi/(3a) = 0.43 \text{ \AA}^{-1}$, $\Gamma\bar{M} = \pi/(|\vec{a}| \cos 30^\circ) = 2\pi/(3a) = 0.86 \text{ \AA}^{-1}$, $\Gamma\bar{K} = \pi/(|\vec{a}| \cos^2 30^\circ) = 4\pi/(3\sqrt{3}a) = 0.98 \text{ \AA}^{-1}$.

This is equivalent to the following approximations:

(i) Only nearest-neighbors' interactions are included in the calculation of the one-electron matrix elements $h_{ij}^{0\mu}$

$$h_{ij}^{0\mu} = -\frac{1}{2} \langle u_i^0 | \Delta | u_j^{\mu} \rangle - \sum_{\nu} \sum_A \left\langle u_i^0 \left| \frac{z_A}{|\mathbf{r} - \mathbf{R}_{\nu} - \mathbf{R}_A|} \right| u_j^{\mu} \right\rangle. \quad (7)$$

(ii) In the calculation of the two-electron matrix elements

$$g_{ij}^{0\mu} = \sum_{\lambda} \sum_{\nu} \sum_l \sum_m p_{\lambda\nu}^{lm} \times \left[2 \begin{pmatrix} 0 & \mu | \lambda & \nu \\ i & j | l & m \end{pmatrix} - \begin{pmatrix} 0 & \lambda | \mu & \nu \\ i & l | j & m \end{pmatrix} \right], \quad (8)$$

integrals have been neglected (in addition to the nearest-neighbors' interactions approximation) when λ and ν denote unit cells in two different directions $\vec{a}\vec{b}$, $\vec{a}\vec{c}$, or $\vec{b}\vec{c}$ (orbitals centered in three or four different unit cells).

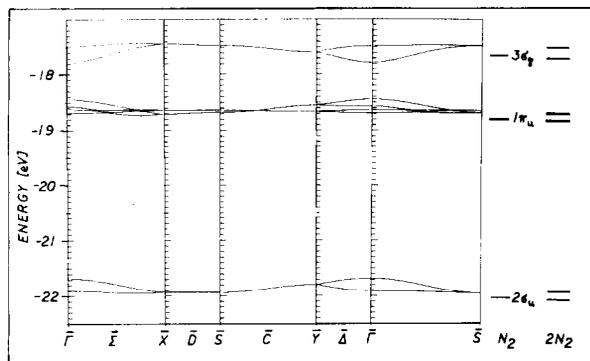


Fig. 3. Highest occupied energy levels of one N_2 molecule, of two N_2 molecules in the geometry of the unit cell, and the band structure of an N_2 layer in the herringbone structure along various symmetry lines in the irreducible part of the rectangular Brillouin zone.

(iii) The charge-bond-order matrix elements $P_{lm}^{\lambda\nu}$ are approximated by elements obtained from the self-consistent cluster calculations.

Due to the large nearest-neighbor separation of 4.26, 7.38 and 8.52 Å, respectively, it can be expected that the results obtained by using these approximations will not differ too much from a full self-consistent solution of equation (3) (which will be investigated in the future). The Clementi (7s/3p) minimal basis was used which should give a preliminary, qualitative correct picture. The results are shown in Fig. 3.

The $3\sigma_g$, $1\pi_u$, and $2\sigma_u$ molecular orbital energies split if two N_2 molecules are calculated in the unit cell geometry of the herringbone structure. The splitting amounts to 0.18 and 0.17 eV for the $3\sigma_g$ and $2\sigma_u$ level, respectively. The doubly degenerate $1\pi_u$ level splits into two pairs of almost degenerate orbital energies (0.001 and 0.01 eV individual splitting, ~ 0.15 eV total splitting). The band structure shows the following characteristic features. As a result of the presence of two molecules in the unit cell the splitting discussed before is observed at the $\bar{\Gamma}$ point ($|\bar{k}| = 0$). Due to the interaction with the surrounding molecules small crystal field shifts occur and the splitting becomes larger (0.30 and 0.23 eV for $3\sigma_g$ and $2\sigma_u$, respectively). For the $2\sigma_u$ derived state, the calculated splitting at $\bar{\Gamma}$ is about 25 per cent smaller than for the $3\sigma_g$ state due to larger 2s components in the wave functions. This can probably explain why in the experimental spectrum [4] the splitting cannot be resolved. All degeneracies are lifted for the π -orbitals. The maximum splitting at $\bar{\Gamma}$ is 0.24 eV, the individual components split only by ~ 0.1 and ~ 0.05 eV, respectively. Approaching \bar{X} ($|\bar{k}| = 0.74 \text{ \AA}^{-1}$) along $\bar{\Sigma}$ the splitting disappears and the bands become degenerate as required by symmetry [5]. The degeneracy persists along the zone boundaries (symmetry lines \bar{D} and \bar{C}).

Along $\bar{\Delta}$ the bands split again. Going from $\bar{\Gamma}$ to \bar{S} ($|\bar{k}| = 0.86 \text{ \AA}^{-1}$) dispersion curves are obtained which are very similar to the ones for the $\bar{\Sigma}$ symmetry line.

In the photoemission spectra for the N_2 /graphite system [4] a characteristic splitting of ~ 0.4 eV is observed for the $3\sigma_g$ derived state near $\bar{\Gamma}$ for low adsorption temperatures and coverages in the monolayer range. For larger values of $|\bar{k}|$ this splitting rapidly decreases and vanishes around $|\bar{k}| = 0.8 \text{ \AA}^{-1}$. Due to the presence of several domains (and due to the polycrystallinity of the substrate) [4] the differences in the dispersion in various directions of the Brillouin zone are averaged out and the zone boundaries are smeared out. Taking this into account it follows that the calculated band structure for a layer of N_2 molecules in a herringbone arrangement can explain the features of the photoemission spectrum quite well.

For CO on Ag(111) a very similar behavior was found experimentally for the dispersion of the 5σ derived states [4]. A splitting at $\bar{\Gamma}$ of about 0.5 eV is observed which disappears for larger $|\bar{k}|$ values. Around $|\bar{k}| = 0.65 \text{ \AA}^{-1}$ the two bands are already degenerate. If one assumes also a herringbone structure for the CO adsorption layer then the center-of-mass separation $|\bar{a}|$ of two neighboring CO molecules is $\sim 5 \text{ \AA}$. This yields for $\bar{\Gamma}\bar{X} = \pi/|\bar{a}| = 0.63 \text{ \AA}^{-1}$ and for $\bar{\Gamma}\bar{S} = \pi/(|\bar{a}| \cos 30^\circ) = 0.73 \text{ \AA}^{-1}$ where the bands have to be degenerate if glide plane A is a symmetry element of the overlayer. The splitting has to disappear earlier than for N_2 on graphite which is indeed observed in remarkable agreement with the theoretical values for the zone boundaries of the herringbone structure. Preliminary calculations for two CO molecules in a herringbone arrangement (with a center-of-mass separation of 5 Å) show that the largest splitting for 5σ is obtained for an OC-CO geometry (0.20 eV for OC-CO, 0.13 eV for CO-CO, 0.09 eV for CO-OC). This would indicate that glide plane A is still a symmetry element of the overlayer, but no longer glide plane B . Further calculations and experiments are necessary to confirm the interpretation that also physisorbed heteroatomic molecules form an ordered overlayer on single crystal metal surfaces.

In summary the band structure of a layer of N_2 molecules in the herringbone structure has been calculated on the *ab initio* level. An LCAO tight binding ansatz was used in which the Fock matrix blocks are approximated by corresponding blocks obtained from self-consistent cluster calculations. The good agreement of the theoretical band structure of an isolated layer with angular resolved photoemission data for the N_2 /graphite system indicates that the band structure of the physisorbed layer is very little influenced by adsorbate-substrate interactions.

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