Adsorption and Scanning-Tunneling-Microscope Imaging of Benzene on Graphite and MoS_2

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We report *ab initio* total energy and electronic structure calculations for benzene physisorbed on graphite and MoS_2. Our results constitute the first detailed *ab initio* investigation of the states through which tunneling occurs in the scanning tunneling microscope (STM) through an insulating molecule. At low voltages the density of states near the Fermi energy some way from the surface is dominated by a weak admixture of molecular states into the substrate states; the resulting STM images reflect the details of the molecule-substrate interaction. At higher voltages, images of molecular states are obtained.

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The scanning tunneling microscope (STM) [1] is now in widespread use as a real-space surface probe of atomic resolution. There has been particular interest in recent years in its use to obtain images of individual organic molecules adsorbed on surfaces. This opens the way to applications involving individual molecules [2,3]. The STM approach also promises new tools for the study of biologically important materials [4,5], including the exciting possibility of using real-space imaging to sequence nucleic acids or peptides, and has allowed the elucidation of novel types of two-dimensional ordering in systems such as smectic liquid crystals [6,7].

These organic species are generally insulating. This makes it surprising that they can be imaged with the STM, which relies on the transmission of a current. However, in the case of an adsorbed atom [8,9], resonances from atomic states lying some distance from the Fermi level can make a significant contribution to the tunneling current and render the adsorbed species clearly visible in the STM. For a molecule, however, it is not clear how the image is related to the more complex geometry. The problem is particularly pressing for complex aromatic adsorbates; this class includes many promising systems for applications. Their images depend strongly on the experimental conditions; for example, alkylcyanobiphenyl monolayers show substrate- and voltage-dependent images [7,10].

In this paper we calculate STM images for a complex aromatic molecule (benzene), while properly including the interaction with two different substrates (graphite and MoS_2). The geometry and electronic structure are calculated using a simulated quenching technique based on the first-principles molecular dynamics of Car and Parrinello [11]. We find that the STM image at low voltages, in the gap between the highest occupied (HOMO) and lowest unoccupied (LUMO) states, depends sensitively on the molecule-substrate interaction. Here the STM images a substrate state modulated by the molecule. Only at large voltages do the occupied or unoccupied states of the molecule, which are essentially unmodified by interaction with the substrate, dominate the image. We reproduce the submolecular structure experimentally resolved in low-voltage STM experiments on graphite substrates, as well as the lower resolution obtained on the MoS_2 surface.

Our calculations are based on the local density approximation (LDA) [12,13] to density functional theory. We solve the Kohn-Sham equations via the projector augmented plane-wave method [14]. This plane-wave-based technique includes explicitly the difference between the true and pseudo wave functions neglected in the pseudopotential approach. Its accuracy is comparable to that of high-quality pseudopotential calculations and of frozen-core linear augmented plane wave calculations. It allows us to treat elements such as carbon and molybdenum with a modest energy cutoff [15].

We find that the most stable site for adsorption on both substrates has the benzene centered on a site with threefold symmetry above a substrate atom. In the case of MoS_2, a sulphur atom is favored. Energies of possible high-symmetry sites differ by about 0.05 eV on graphite and 0.15 eV on MoS_2 (see Table I). Our calculated binding energy on graphite is 0.35 eV, and on MoS_2 0.36 eV. These values may still be subject to an LDA error of a few tenths of an eV, as in other weakly bonded systems, but LDA generally predicts correct equilibrium structures [16]. The agreement with the experimental binding energy of a benzene monolayer on graphite [17,18] (44 $kJ\,mol^{-1}$ or 0.45 eV per molecule) is probably fortuitous, since the latter includes molecule-molecule interactions not present in our calculation.

We find that the separation between molecule and sub-

TABLE I. Binding energies and equilibrium distances (vertical separation of the benzene carbon atoms from the uppermost surface atoms) for benzene at different high-symmetry sites on graphite and MoS_2.

Substrate	Site	Binding energy (eV)	Distance (Å)
Graphite	Atom	0.35	3.13
Graphite	Bond	0.33	3.36
Graphite	Ring center	0.29	3.38
MoS_2	Atom (Mo)	0.20	3.34
MoS_2	Atom (S)	0.36	3.06
MoS_2	Ring center	0.24	3.22

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strate exhibits a corrugation of 0.2–0.3 Å, being smallest at the sites with the lowest energy (see Table I). Rotational barriers for the isolated adsorbed molecule are very low, less than k_BT at room temperature.

Having determined the binding of the adsorbed molecules, we now turn to the resulting STM images. It is natural to think of the tunneling process in the presence of an adsorbate in terms of a double barrier model: one barrier represents the vacuum gap between tip and molecule and the other the gap between molecule and sample. The tunneling depends critically on the position of the energy levels of the well (i.e., of the molecule) relative to the Fermi energies of the tip and the substrate.

Tersoff and Hamann [19] show that, to first order in the interaction between the tip and the sample, the STM current can be written as

$$\frac{dI}{dV} = A\rho_s(\mathbf{R}, E_F - eV) , \tag{1}$$

where A is a constant proportional to the tip density of states, ρ_s is the local energy-projected density of states of the sample, $\mathbf{R}$ is the position of the tip center, and V is the tip voltage. The tip states are assumed to be s waves. This approximation, which we have tested with nonperturbative calculations [20], gives correct results for the systems studied here.

We first consider a graphite substrate. Figure 1(a) shows the Kohn-Sham eigenvalues for the benzene molecule and the Fermi energy of the surface. We find very weak mixing of molecular and substrate states. The HOMO and LUMO states are distributed symmetrically with respect to the Fermi level, as might be expected in view of the chemical similarity of the carbon ring systems. The states at the Fermi energy are predominantly derived from the substrate and lie in the middle of the HOMO-LUMO gap of the molecule.

At high voltages, when the molecular states are in resonance with the Fermi level of the tip, the calculated images are essentially charge-density maps of the molecular states and exhibit the full sixfold symmetry of the molecule [Fig. 2(a)]; the predicted corrugation reflects the carbon positions. However, the situation is quite different at the low voltages usually used in the STM. Here the molecule is essentially insulating, but the spatial extension of substrate states into the vacuum is greater above the molecule than elsewhere. The molecule "modulates" the substrate states; the image acquires atomic features of the adsorbate, but retains the symmetry of the substrate states. (In other words, the substrate induces a broadening of the molecular states into resonances which spread throughout the molecule's gap, although with very small amplitude.) This can be seen in Figs. 2(b) and 2(c); the image now has threefold, rather than sixfold, symmetry as is frequently observed in STM images of ring systems adsorbed on triply symmetric sites [7,21,22]. Note that, at the Fermi energy [Fig. 2(b)], the image is the reverse of what might be expected: the three bright spots lie over the hollow sites in the graphite sheet, not over the atoms. However, as the voltage is altered, the bright and the dark spots interchange; we discuss the origin of this energy-dependent contrast below.

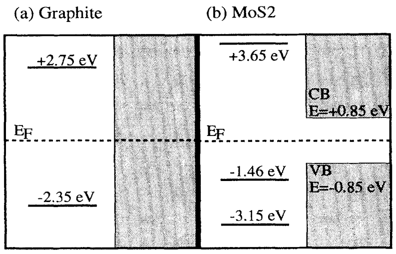

FIG. 1. Energy levels relative to the bulk bands (shaded grey) for benzene adsorbed on (a) graphite and (b) MoS_2, with the benzene in its lowest-energy positions. All energies are relative to the Fermi energy.

The STM image of bare graphite depends critically on the difference between the two inequivalent surface atoms [23,24]; this difference only appears when more than one layer of graphite is included in the calculation. We have verified explicitly that this does not affect the low-voltage image of the adsorbed benzene molecule at this site; this is because the three carbon atoms to which the benzene couples most strongly always remain equivalent.

The image of the molecule obtained at low voltages is also strongly dependent on the adsorption site: Figure 2(d) shows the image of the states at $E = E_F$ when the benzene is adsorbed on a bond-centered site.

The energy-dependent contrast can be understood on the basis of a tight-binding model of the carbon p_z states in which the molecule-surface interaction consists of a hopping matrix element between the benzene and the nearest surface atoms, plus a potential that raises the energy of those benzene orbitals above the surface atoms relative to the others. An embedded calculation [25] (equivalent to a Green's function calculation) shows an enhanced density of states near the Fermi energy on the atoms above substrate hollow sites, arising from large Green's function elements connecting neighboring atoms at midgap in the isolated molecule. (The on-site elements are suppressed by a destructive interference between the occupied and unoccupied states.) At higher energies a crossover occurs to a reversed image, in agreement with the results of the full calculation.

There are reports that bare substrates can be imaged through monolayers containing aromatic rings at low voltages [10], but our results suggest that molecules are always visible if present. This view is supported by recent experimental evidence that molecules are mechanically removed by the tip when imaging the substrate [26].

Even in pure MoS_2, interpretation of the STM image is controversial, as the S and Mo sites have the same symmetry and cannot be distinguished experimentally. One might expect that the image would be dominated by the S atoms in the top layer; however, STM studies of WTe_2 (in which the W and Te atoms have different symmetry) show that the *d* states of the subsurface W atoms appear to dominate [27]. A cluster calculation of the rate of electron tunneling out of the valence band [28] suggested a crossover from S atoms to Mo atoms as the most prominent species as the tip moves away from the surface. Our results suggest that Mo atoms are visible under different conditions: For tunneling out of the surface our charge densities clearly show that the S atoms dominate the image. However, the lowest conduction-band states exhibit node planes through the S sites, and for large distances of the tip from the sample we observe the strongest intensity over the Mo atoms; this intensity stems from the lobes of the sulphur *p* states. Such inversion of the image contrast may have been observed experimentally [29].

Figure 1(b) shows the distribution of Kohn-Sham eigenvalues for benzene on the MoS_2 substrate. The principal differences from the graphite case are the presence of a band gap in the substrate and the asymmetric positioning of the molecular levels relative to the Fermi energy. When tunneling out of the surface (positive tip voltages), resonance with the unperturbed molecular states produces an image reflecting the sixfold symmetry of the molecule [Fig. 3(a)]. The voltage dependence of the image is much weaker than on graphite, and a similar image is obtained near the top of the valence band [Fig. 3(b)]. Quantitative comparison with experiments involving liquid crystal monolayers on MoS_2 [7,30] is complicated by the surface band-bending effects arising in doped substrates. However, it is found experimentally that the images of aromatic rings are much less clear on MoS_2 than on graphite. Our theoretical images agree: in particular, we find that the depression at the ring center is much shallower on MoS_2 than on graphite (0.5 Å deep as opposed to 3.0 Å). An additional contributing effect involves the larger intermolecular spacing on MoS_2, which may allow the tip to move molecules parallel to the surface more easily, averaging a number of different images and reducing the resolution.

In conclusion, we find that electronic states derived

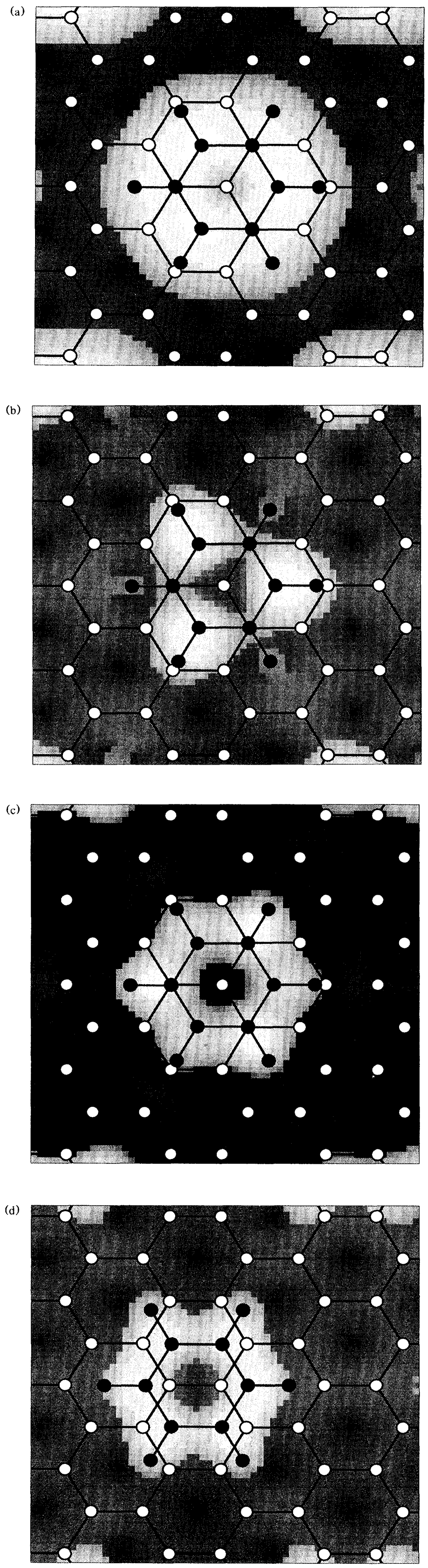

FIG. 2. Predicted STM images for benzene on graphite: (a) $E = E_F - 2.0$ eV, showing highest molecular orbital with near-perfect sixfold symmetry; (b) $E = E_F$, with strong threefold symmetry. Atoms above substrate hollows are bright; (c) $E = E_F + 1.5$ eV, with weakly threefold symmetry. Atoms above substrate atoms are bright; (d) $E = E_F$ with the benzene ring centered at a bond-centered site with twofold symmetry. The grey scale represents the tip height above the surface in constant-current mode; filled circles show molecule atoms, empty circles substrate atoms. Charge densities were obtained by convoluting a Green's function spatially with a spherical Gaussian of half-width 0.5 a.u. and in energy with a Lorentzian of half-width 0.1 eV.

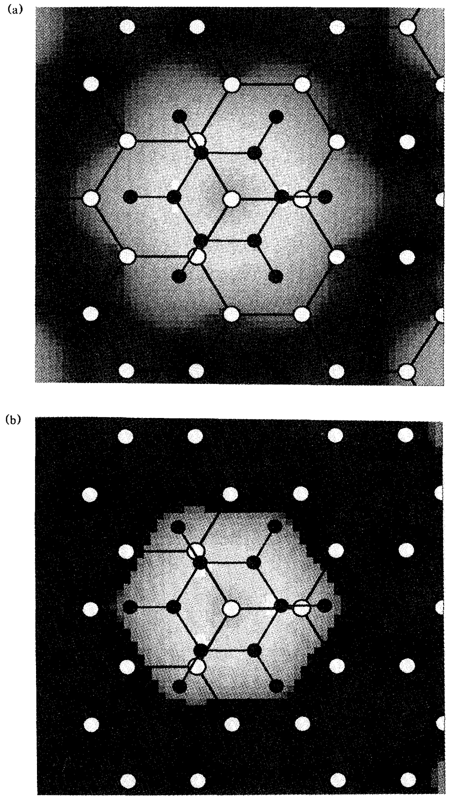

FIG. 3. Theoretical STM images for benzene adsorbed above a sulphur atom on MoS_2: (a) $E=E_F-2.0$ eV showing unperturbed molecular state, similar to that in Fig. 2(a); (b) $E=E_F-1.0$ eV, showing admixture of benzene states into the highest occupied MoS_2 level. Other details as for Fig. 2.

from *ab initio* calculations provide important information for the correct interpretation of the STM images of conjugated systems.

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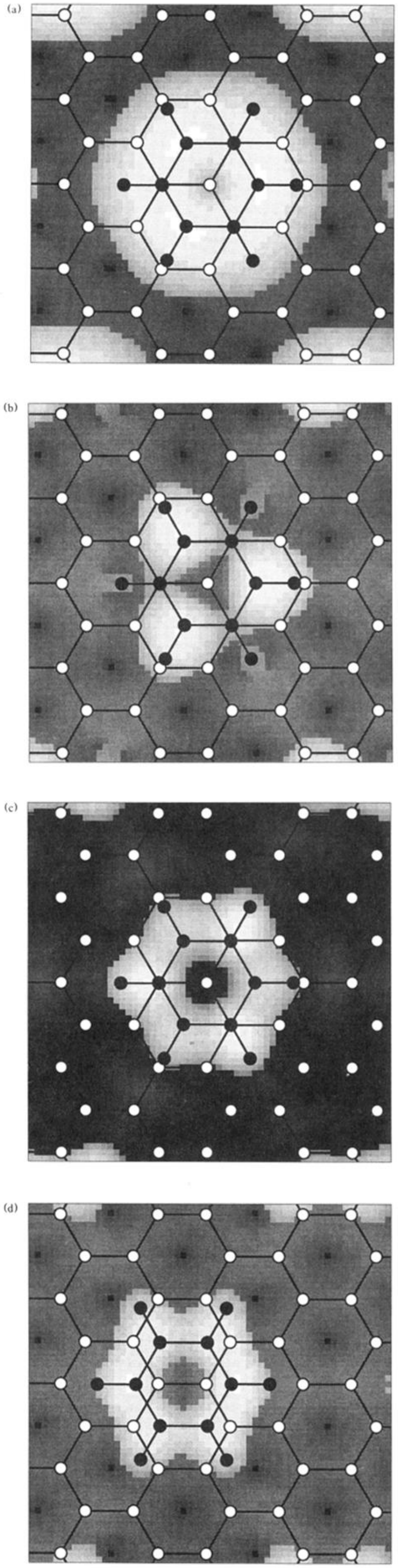

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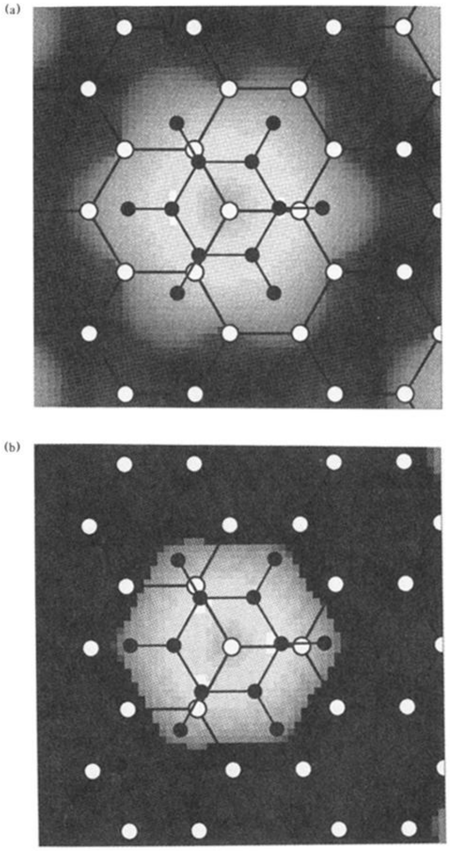

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