Light-Atom Location in Adsorbed Benzene by Experiment and Theory

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Locations of light atoms in C_6D_6 on Ru{0001} have been determined by low energy electron diffraction (LEED) and density functional theory (DFT). For the favored site/orientation in the $p(\sqrt{7} \times \sqrt{7})$-$R19°$ phase, we find alternating outward bowing of the C-D bonds of 24° and 9° via LEED, and 22° and 14° via DFT. This remarkable agreement gives important cross confirmation of the validity of these techniques in describing the subtle contributions of light atoms to adsorbate scattering and energetics. The buckling is explained as a consequence of decreased aromaticity induced by the bonding to the substrate.

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Locating the light atoms in adsorbed hydrocarbons has long presented a challenge to both experiment and theory. The low scattering factor of such atoms raises severe difficulties for surface crystallographic methods, such as low energy electron diffraction (LEED), and the shallow potential energy surfaces encountered for angular displacements of their bonds can make precise location of a theoretical energy minimum troublesome. Spectroscopic methods provide indirect information regarding bond orientations, but ultimately probe only the orbitals or vibrational modes of the system, not nuclear positions. In consequence, electron diffraction studies to date have tended to ignore the question of hydrogen atom location in hydrocarbons, and theoretical predictions of this crucial aspect of surface chemistry have largely gone untested.

A classic case is the adsorption of benzene on metal surfaces. A variety of spectroscopic and crystallographic information is available, especially for adsorption on Ru{0001} [1–8] though also for other substrates [9]. These studies were able to determine the positions of the C atoms of benzene and adsorbate-induced relaxations of the underlying substrate. The common assumption in all the diffraction studies, however, has been that the positions of the light atoms were not accessible. Information about these has only been available indirectly from near-edge x-ray absorption fine structure (NEXAFS) [6] and from theoretical studies [10,11]. Nevertheless, accurate experimental knowledge of this information is essential for a complete picture of the bonding mechanism on the surface. In this Letter we demonstrate that LEED I-V analysis *can* successfully be applied for the determination of the light-atom positions in hydrocarbons adsorbed on a metal surface. In order to place these results in context, we also report on independently performed first-principles density functional theory (DFT) calculations.

The UHV system and data acquisition procedures for the LEED experiment are described elsewhere [8,12]. Deuterated benzene (C_6D_6) was adsorbed between 170 and 270 K; as compared to hydrogen, deuterium has a lower zero point vibration amplitude and hence an increased effective scattering factor. The LEED measurements were carried out at a sample temperature of 200 K. The resulting data set for the $p(\sqrt{7} \times \sqrt{7})$-$R19°$ $(\sqrt{7})$ structure used in this work is the same as in Refs. [4] and [8]. It consists of 14 independent beams, 3 integral and 11 fractional; the curves are averaged over three data sets of independent measurements.

The LEED I-V structure search was performed using our recently developed LEED program package CLEED [13] in connection with Pendry's R_P factor [14]. LEED intensities were calculated for energies between 30 and 250 eV (see Fig. 1), leading to a total overlap between experimental and theoretical I-V curves of 1918 eV. In the present work, isotropic rms vibrational displacements of 0.10 Å for Ru and 0.15 Å for C and D were used. The values for Ru and C were optimized in the earlier structure determinations which ignored the D atoms [8]. The displacements of C and D were set equal because of their rigid interatomic bonds with C-D stretch frequencies around 2500 cm^{-1}. The other nongeometric parameters were the same as in [8], as was the procedure for calculating the error bars.

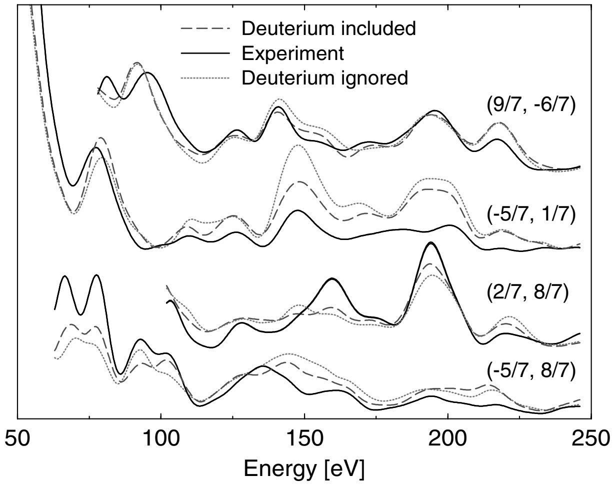

FIG. 1. Selection of experimental and calculated I-V curves for the best fit geometries.

The LEED structure search started with the adsorption geometry of the $\sqrt{7}$ phase as determined in Ref. [8]: the C_6 ring is centered over the hcp site of the substrate; the orientation (σ_v) is such that every second C atom is on top of a Ru atom and slightly elevated by 0.08 Å with respect to the other C atoms. Together with a slight buckling in the first and second Ru layers this geometry gave an R_P factor of 0.276. For the start of the search, the D atoms were added with the gas phase C-D bond lengths of 1.1 Å either at a height of 0.55 Å above the corresponding C atoms (a tilt of 30° with respect to the molecular plane) or at the same height as the C atoms. Both start positions lead to the same final result.

During the structure search the lateral and vertical parameters of the C and D atoms and the vertical parameters of the Ru atoms in the first and second layer were optimized preserving the threefold rotational symmetry. This leads to a total of 26 atoms and 19 free parameters involved in the search, which can be determined reliably with the given total energy overlap. The search led to a best fit geometry with an R_P factor of 0.252, which is outside the statistical error limit of 13% of the R_P factors achieved with the D atoms in the start positions. The geometry obtained is depicted in Fig 2, together with the results from the DFT calculations.

The DFT calculations were performed by means of the CASTEP computer code [15], using ultrasoft pseudopotentials [16] and a plane wave basis set with 300 eV kinetic energy cutoff. Exchange and correlation were included through the generalized gradient approximation [17], and the Brillouin zone of the $\sqrt{7}$ unit cell was sampled via a $2 \times 2 \times 1$ mesh [18]. The validity of the cutoff energy and mesh density was inferred from test calculations on bulk Ru, in which we obtained lattice constants of $a = 2.72$ Å and $c = 4.32$ Å, in good agreement with experimental values [19]. Similar convergence parameters were also used successfully in a recent study of benzene adsorbed on the Ni{111} surface [11]. The surface calculations were performed for a five layer Ru slab with vacuum region equivalent to eight Ru layers. Benzene was placed on one side of the slab only and allowed to relax freely, along with the top three Ru layers. The DFT structure searches for the considered hcp site/σ_v orientation were initialized in various geometries based upon the LEED results and/or adapted from previous calculations for benzene on Ni{111} [11]. We find an adsorption energy of 1.31 eV per molecule, which is greater than the value of 0.91 eV per molecule found previously for adsorption on Ni{111} [11].

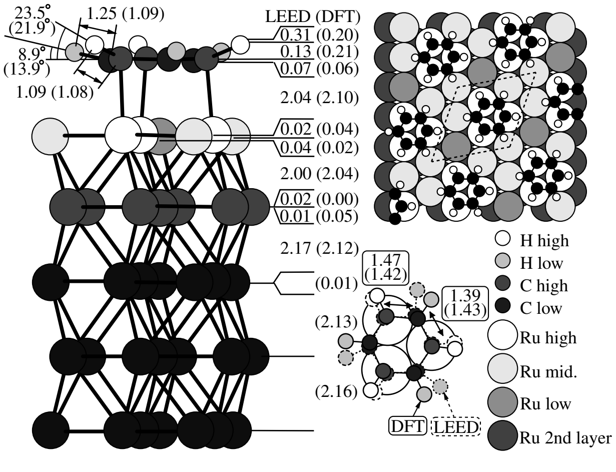

FIG. 2. Best fit LEED and DFT geometries. Lateral/vertical error bars in LEED are ±0.50 and 0.17 Å for D and ±0.10 and 0.06 Å for C; for Ru, the average vertical error bar is ±0.05 Å.

The positions of the Ru atoms in the best fit LEED structure remain the same as determined in Ref. [8], to within less than 0.02 Å. The only exception is the 2nd layer Ru atom underneath the hcp adsorption site which is now 0.04 Å higher. The vertical deviations for the C atoms are in the same range, up to 0.02 Å; laterally they are as large as 0.08 Å. These deviations are all within the statistical error limit of the new LEED structure. The same is true for the difference between LEED and DFT results for the C and Ru positions. The largest differences here are found for the vertical distance between the topmost Ru layer and the C_6 ring, which is 2.04 Å in the LEED and 2.10 Å in the DFT structure, and for the alternating C-C bond lengths, namely, 1.39 and 1.47 Å from LEED and 1.43 and 1.42 Å from DFT. The vertical distance between the two types of inequivalent C atoms is 0.07 Å (0.06 Å) in the LEED (DFT) structure.

The positions of the D atoms in the best fit geometries display the following features: (i) the same type of buckling as in the C_6 ring, but with much larger amplitude, i.e., the D atoms bonded to the upper C atoms are elevated with respect to those bonded to the lower C atoms. The vertical distance between the two inequivalent types of D atoms is 0.31 Å (0.20 Å) in the LEED (DFT) structure; (ii) the vertical distances between the D atoms and their neighboring C atoms are 0.43 and 0.19 Å (0.40 and 0.26 Å), corresponding to bond angles of 24° and 9° (22° and 14°), with respect to the molecular plane; (iii) the bond length of the upper C-D bond is 1.09 Å (1.08 Å), while the LEED and the DFT results for the lower bond differ with values of 1.25 and 1.09 Å, respectively; (iv) the most striking difference between the LEED and the DFT structure is a lateral pairing of the D atoms, which is found only in LEED. The lower D atoms are shifted by 0.66 Å away from the symmetric position towards one of their neighbors.

Since the light atoms are such weak scatterers in LEED, it is important to discuss the significance of our results. The decrease in R_P from 0.276 to 0.252 (9%) gained by including the D atoms in the model calculations may not appear large at first sight. However, a fair comparison can be made only between model structures in which the D atoms are included; if not, small unphysical shifts in the positions of the heavier atoms may be introduced during the R_P factor optimization to compensate for their missing scattering signal. The large lateral pairing shifts of the D atoms are just at the limit of significance relative to our statistical error bars ($R_P = 0.28$ without pairing). The vertical buckling of the two inequivalent types of D atoms is more significant; putting all atoms at the upper or lower height, respectively, leads to R_P factors above 0.29, which is well outside the error margin defined by Pendry's estimate of the statistical error [14]. Since this can be regarded as an upper limit and is probably too pessimistic [20], the main features of the D atom positions, the vertical buckling and the lateral pairing, can be considered significant.

In order to estimate whether molecular vibrations could account for the large difference in lateral positions of the light atoms between LEED and DFT, we have calculated a number of normal modes for the adsorbed benzene molecule (Fig. 3). The frustrated rotational mode was studied by twisting the relaxed molecule rigidly about its center of mass, while the bobbing mode was studied by displacing the molecule rigidly in the surface normal direction. Because of their large mass, Ru atoms were held fixed in their mean positions. In each case the vibrational frequency was inferred upon the assumption of simple harmonic motion. We estimate frequencies for frustrated rotation and bobbing motion of C_6H_6 as 78 and 235 cm^{-1}, respectively, which are in very good agreement with values found by He scattering for similar systems [21].

In addition, two intrinsic vibrations of the molecule were also considered: H wag modes of a_{2g} and b_{2u} symmetry (Fig. 3). Displacement patterns for these modes were obtained by solving the dynamical matrix for the free molecule, and frequencies of 1355 and 1144 cm^{-1} were deduced for the a_{2g} and b_{2u} modes, within 10 cm^{-1} of previous theoretical values [22]. For the adsorbed molecule, potential energy curves were calculated for distortion from the relaxed shape according to the same eigenvectors, and vibrational frequencies obtained by reference to the corresponding curves for the free molecule. After finally replacing H with D, we find rotational and bobbing frequencies for adsorbed C_6D_6 of 71 and 226 cm^{-1}, while the a_{2g} and b_{2u} wag modes drop to 1005 and 783 cm^{-1}, respectively (compared with free deuterated benzene values of 1047 and 813 cm^{-1}). Through a generalization of the methodology adopted in previous calculations for adsorbed benzene [11], we estimate that these frequencies imply rms lateral D displacements of around 0.04 Å in the wag modes at 200 K. The rotational mode should correspond to rms lateral D displacements of around 0.14 Å, and the bobbing mode to rms vertical molecular displacements of around 0.03 Å.

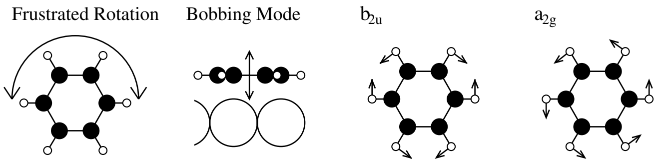

FIG. 3. Schematic diagram of selected vibrational modes.

Even allowing for some combination of all these lateral displacements, it is clear that their contribution to any apparent distortion of the molecule must be considerably smaller than the pairing observed in LEED. In consequence, we must conclude that the LEED/DFT discrepancy cannot entirely be explained as an artifact due to either single or multiple vibrational modes of the molecule. Remaining possible explanations for the disagreement include the lack of attractive van der Waals interactions within DFT, which may therefore fail to describe the intermolecular forces properly. Alternatively, the D scattering potential may be inadequately described within the LEED calculations and/or the inclusion of only isotropic vibrational displacements may induce the pairing as an artifact.

In contrast, the buckling of the light atoms appears to be a robust feature of both LEED and DFT results. Following the buckling of the C_6 ring, but with a higher amplitude, this distortion can be regarded as modifying the molecule towards the chair geometry of cyclohexane. The implied loss of aromaticity can also be seen from the calculated decrease of electronic charge in the range of the π-type orbitals in favor of an increase of charge density along the C-Ru bonds (see Fig. 4).

In a recent NEXAFS study of the saturated benzene layer on Ru{0001} it was concluded that the H atoms were bent upwards uniformly by 20°–25° [6]. This is in good agreement with our average bending of 16° (18°), especially given that the NEXAFS study did not consider the possibility of buckling. A similar bending of 21° was also found for $\mathrm{Ru_3(CO)_9}(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ by x-ray diffraction [23]. The identical Ru-C bonding of all six carbon atoms of the C_6H_6 ligand in this metal-organic complex is responsible for the uniform bending of all six H atoms without buckling. In our "$\mathrm{Ru_3}(\mu_3{:}\eta^1{:}\eta^1{:}\eta^1\text{-}C_6D_6)$" adsorption complex, benzene

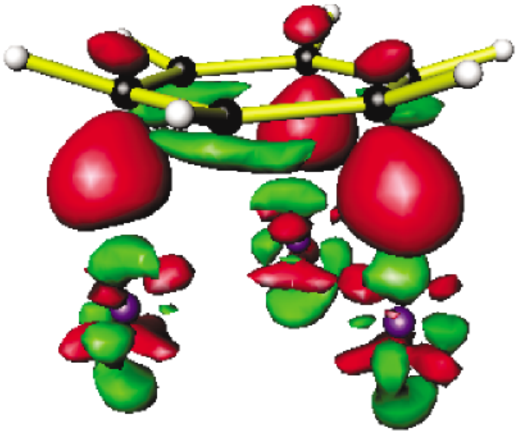

FIG. 4 (color). Charge density changes induced by adsorption: red indicates an increase and green a decrease of electron density, by $0.045e$ Å^{-3}.

has a less symmetric coordination with respect to the underlying Ru trimer, leading to the different bond angles between adjacent C and D atoms.

Finally, partitioning the calculated charge density according to a topological approach [11], we determine that the benzene molecule acquires a net negative charge of $0.37e$ [cf. values in the range $(0.44-0.49)e$ on Ni{111}]. In contrast, previous studies have often concluded that benzene must be an electron donor on transition metal surfaces: only the wholesale donation of electrons to the substrate, it has been argued, can explain the large decreases in work function that are generally observed upon benzene adsorption (up to 1.8 eV on Ru{0001} [1]). In fact, Fig. 4 rather shows that charge is transferred in both directions, from the molecule to the substrate *and* from the substrate to the molecule; moreover, it is the latter effect which clearly dominates. Notwithstanding this fact, we nevertheless calculate that the surface dipole actually *decreases* [by 0.4 D per (1×1) cell] upon adsorption of benzene. Although the net transfer of electrons from surface to molecule must tend to *increase* the surface dipole, this is more than counterbalanced by the charge redistribution within the top two substrate layers and (to a lesser extent) within the molecule itself (cf. surface-induced polarization of CO [24]). The consequent reduction in work function amounts to 2.4 eV, in excellent agreement with the experimental result.

In summary, we have determined the positions of light atoms in deuterated benzene (C_6D_6) on Ru{0001} by LEED *I*-*V* and DFT. We find an upwards bending of the C-D bonds of 16° (18°) on average. The bending is not uniform, however, but alternates between 9° (14°) and 24° (22°) for the two types of inequivalent light atoms. This strong buckling is explained in terms of a loss of aromaticity and a distortion of the molecule towards the chair geometry of cyclohexane. The atomic positions of the C atoms and of the underlying Ru atoms practically do not change with respect to an earlier LEED analysis where the light atoms were ignored.

This work demonstrates that LEED *I*-*V* analysis can successfully be applied for the determination of the light-atom positions in hydrocarbon molecules adsorbed on a metal surface, leading to an excellent agreement with theoretical predictions based on DFT calculations.

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