

Lateral Interaction in Ordered Hydrocarbon Overlayers: C-H Band Dispersion of Adsorbed Benzene.

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Abstract. – We have determined the dispersion of a C-H-derived band ($2a_{1g}$) in an ordered $(\sqrt{7} \times \sqrt{7})R 19.1^\circ$ benzene overlayer on Os(0001) via angle-resolved photoelectron spectroscopy. The maximum dispersion of about 0.4 eV can be explained on the basis of tight-binding calculations on a free unsupported benzene overlayer.

Introduction. – Lateral interactions in adsorbed molecular overlayers have been studied frequently in recent years using low-energy electron diffraction (LEED) and angle-resolved photoelectron spectroscopy (ARUPS), but have been restricted mainly to overlayers of carbon monoxide [1-4]. Even though ordering in hydrocarbon overlayers has been reported in many cases [5], and photoelectron spectroscopy have been used to study the electronic structure of these overlayers [4, 6], dispersions of adsorbate induced bands have not been reported up to now. Benzene is particularly well suited for such a study for the following reasons: well-ordered structures have been observed on many transition metal surfaces [5]. At low temperature the orientation of the carbon ring plane is parallel to the surface of hexagonal close packed surfaces. Consequently, intermolecular interaction is dominated by hydrogen-hydrogen interaction. Therefore we expect strong dispersion for those adsorbate induced bands that originate from molecular levels with predominant hydrogen character. In order to measure such dispersions the adsorbate band under consideration has to be well separated in energy from other adsorbate and substrate bands. Furthermore, strong dispersions are expected for those bands derived from totally symmetric molecular levels as will be discussed further below. We report in the present letter the observation of such strong dispersion effects for the $2a_{1g}$ derived adsorbate band of benzene adsorbed in a $(\sqrt{7} \times \sqrt{7})R 19.1^\circ$ structure on Os(0001) [6]. This result can be quantitatively explained on the basis of simple tight-binding calculations on a free unsupported benzene layer.

Experimental and theoretical results. – The experiments were performed in a standard ultra-high vacuum system (VG, ADES400) containing facilities for LEED and ARUPS. The preparation of the adsorbate was performed as reported before [6]. In previous papers we have characterized the low-temperature phase of chemisorbed benzene on Os(0001) via thermal desorption, high-resolution electron energy loss spectroscopy, LEED and ARUPS [6, 7]. Figure 1 shows angle-resolved photoelectron spectra in the energy range of 10 eV to 12.5 eV binding energy (with respect to the Fermi energy, see inset) excited with He-I radiation of the ordered low-temperature phase. In the inset we present a normal emission spectrum of the valence band region. This spectrum clearly demonstrates that benzene is molecularly adsorbed on Os(0001) as discussed earlier [6, 7].

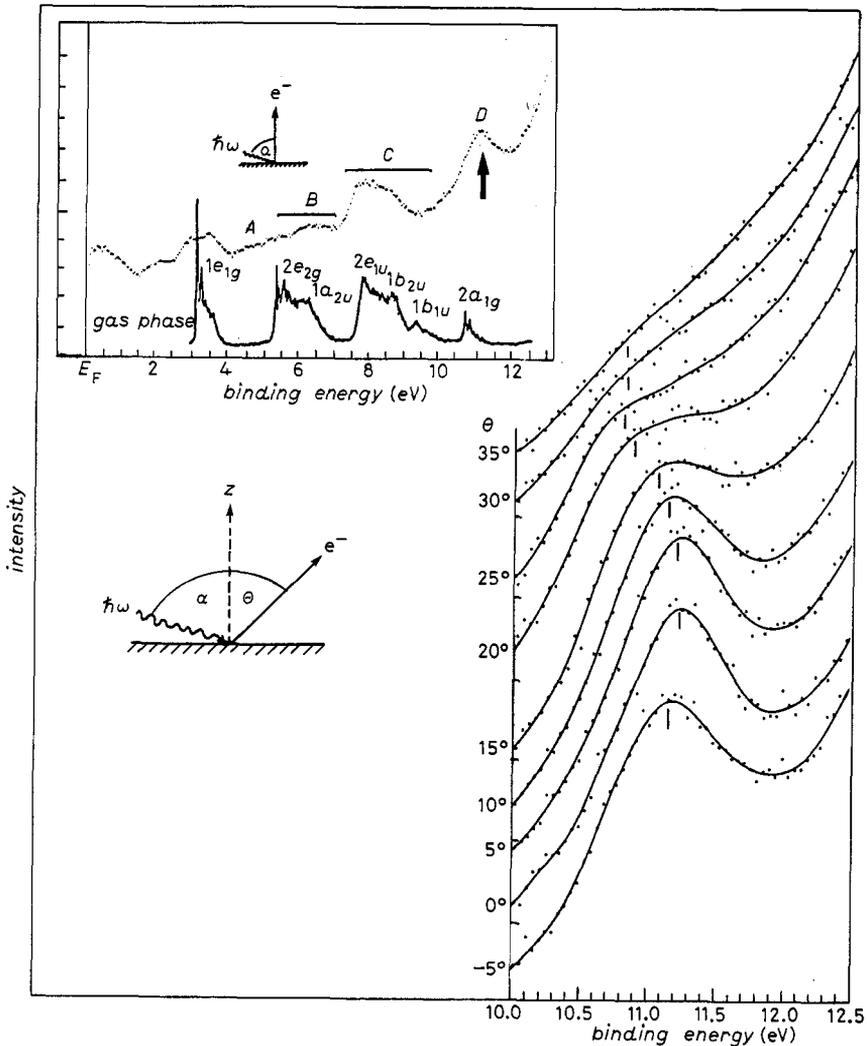


Fig. 1. – He-I photoelectron spectra of an ordered $(\sqrt{7} \times \sqrt{7})R$ 19.1° structure. The inset shows a normal emission spectrum of the valence band region (dotted line). Adsorbate bands are labelled A-D and aligned to the gas phase spectrum [8] at band D. The variation of the $2a_{1g}$ derived band (D) with emission angle θ along $\bar{\Gamma}\bar{A}$ (see fig. 3) is shown in the lower part. Binding energies are referenced to the Fermi level. $T = 260$ K, $\alpha = 72.5^\circ$, $h\nu = 21.2$ eV.

According to our assignment, the peak marked by an arrow is derived from the $2a_{1g}$ ion state of free benzene, and its polar angular dependence is plotted in the main part of the figure. The incidence angle of the light was 72.5° in order to maximize the normal emission intensity of that peak. The binding energy of the peak clearly decreases with increasing polar angle up to a maximum value at about 25° . Peak maxima in fig. 1 are determined via spline function fits after background subtraction. The dispersion as a function of k_{\parallel} derived from these data (big squares) in addition to synchrotron measurements performed at BESSY for $h\nu = 23.0$ eV (rhombs) are shown in fig. 2, and indicate a maximum value of

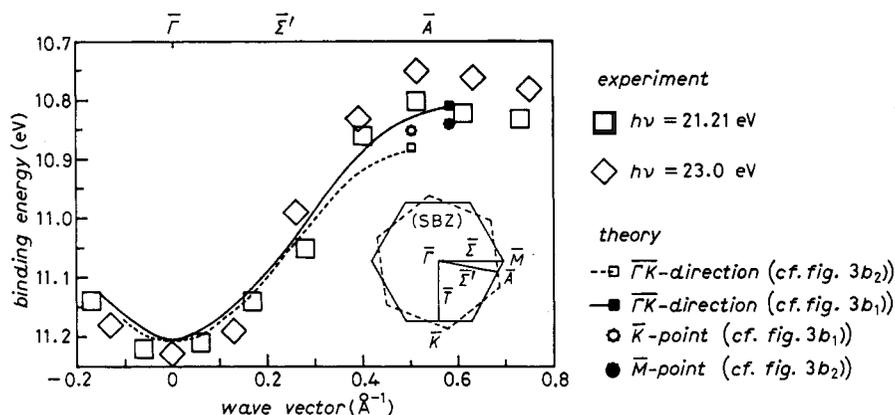


Fig. 2. - Dispersion of the a_{1g} derived band (σ_{C-H}) as a function of k_{\parallel} as deduced from the experimental data in fig. 1 (open squares). Results from tight-binding calculations are presented as full or dashed lines for the $\Gamma\bar{M}$ direction and the $\Gamma\bar{K}$ direction, respectively. The inset shows the surface Brillouin zone (SBZ) of the two overlayer domains with the common direction $\Gamma\bar{A}$. The labelling of the SBZ is compatible to ref. [10]. Additional data obtained with synchrotron radiation ($h\nu = 23$ eV) are included in the figure (rhombs).

about 0.5 eV. The adsorption of benzene on Os occurs in two domains, therefore an appropriate azimuthal direction has to be chosen. As can be seen from the two superimposed surface Brillouin zones (SBZ), depicted in the inset of fig. 2, there exists a common direction $\Gamma\bar{A}$ in both domains, along which the experiments have been performed. This corresponds to a direction towards a substrate LEED spot. The error bars are of the order of 100 meV.

We have carried out tight-binding calculations assuming nearest-neighbour interactions with semi-empirical CNDO (complete neglect of differential overlap) type wavefunctions to determine the intermolecular interaction parameters. Details of the method have been given by Greuter *et al.* [9]. The basis functions to calculate the bands are the molecular orbitals. We assume an unsupported two-dimensional benzene overlayer. The relative arrangement of the benzene molecules within the overlayer has been varied in order to simulate the probable structure shown in fig. 3a). We have chosen two extreme cases indicated in fig. 3b), *i.e.* a parallel arrangement (b_1), and an «interlocked» arrangement (b_2). Figure 3a), obviously, represents an intermediate case where the steric hinderance between interacting molecules is minimized. Figure 3c) shows a molecular orbital plot of the level considered in the present study. It belongs to the totally symmetric representation and exhibits C-H-character, prerequisites for strong intermolecular interaction as alluded to in the introduction. The calculated dispersions determined for the two different interaction geometries for the $\Gamma\bar{K}$ and the $\Gamma\bar{M}$ directions [10] are compared with experiment in fig. 2.

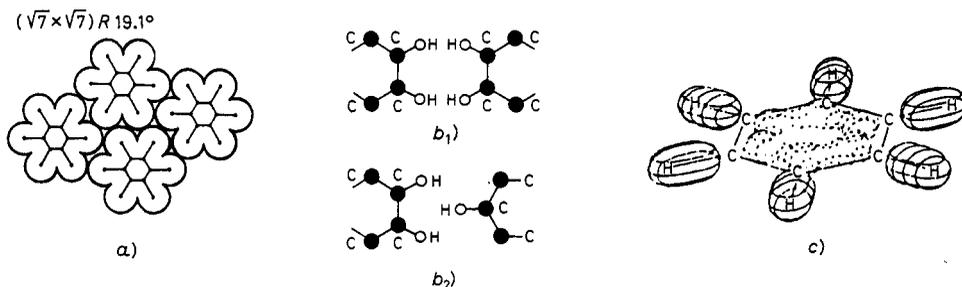


Fig. 3. - a) Proposed arrangement of the benzene molecules within the $(\sqrt{7} \times \sqrt{7}) R 19.1^\circ$ overlayer at $T < 290$ K. b) The two extreme cases of H-H interaction which are possible in a benzene overlayer: a parallel arrangement (b_1) and an «interlocked» arrangement (b_2). c) Molecular orbital plot of the $2a_{1g}$ state considered in the present study [11].

Discussion. - The essential message of the present paper is contained in fig. 2. Most of the discussion shall therefore centre on the comparison of experimentally observed and calculated dispersion. Firstly we notice that the calculated dispersions agree within the experimental error bars with the observed values. Clearly, the absolute energy of the bands have been shifted so as to minimize the average deviation between experiment and theory. Several calculated dispersion curves are included in the figure. The calculated dispersion curves correspond to two different azimuthal directions, *i.e.* $\overline{\Gamma K}$ and $\overline{\Gamma M}$, applying intermolecular interaction parameters derived from geometries b_1 , and b_2 , respectively (see fig. 3b)). The energy position of the band at the \overline{M} point is always higher than at the \overline{K} point, independent of the absolute value of the interaction parameter because the $\overline{\Gamma K}$ separation is larger in k -space than the $\overline{\Gamma M}$ separation. The absolute value of the intermolecular interaction parameter can be estimated almost quantitatively via the following procedure: we consider fig. 3b₁) where the benzene molecules are oriented parallel to each other. On both moieties we place a $2a_{1g}$ molecular benzene orbital (see fig. 3c)). The overlap between the two benzene molecules will be dominated by the overlap of the adjacent hydrogen atomic orbitals. The reason is that the overlap depends exponentially on the distance. Therefore we only need to look up these overlap values, consider the $2a_{1g}$ molecular orbital coefficients on the hydrogen atoms, and then calculate the interaction parameter. The result of such a calculation is $\beta = 0.045$ eV (β is the interaction parameter). Since the band under consideration is of σ -type, we expect a band dispersion from high binding energy at $\overline{\Gamma}$ to lower binding energy at the zone boundary. In the simplest version of the tight-binding theory the band dispersion of a σ -type band in $\overline{\Gamma M}$ and $\overline{\Gamma K}$ direction are given by 9β , and 8β , respectively. Taking the above-estimated value into account yields band dispersions in the respective directions of 0.405 eV and 0.36 eV. Those values are, very close to the dispersions plotted in fig. 2 as a result of a full calculation. A very similar crude estimate can be made for the other geometry, *i.e.* b_2) shown in fig. 3. This yields 0.36 eV and 0.32 eV, which also is not far of the value calculated via the full calculation. In conclusion we realize that the observed dispersion can be explained semi-quantitatively on the basis of very simple considerations.

The question arises, why the $2a_{1g}$ derived band shows such a dispersion while other bands seem to lack pronounced dispersion effects. (An exception may be the C ionization band (see inset fig. 1) of adsorbed benzene, but this shall be discussed in a forthcoming paper.) Only those orbitals belonging to the totally symmetric representation will exhibit significant intermolecular overlap in any intermolecular arrangement. One can see this by considering

again arrangement b_2) in fig. 3. There will be nonvanishing overlap only if the symmetry is even with respect to the mirror plane perpendicular to the ring planes. In the case of b_1) the overlap does not become zero for any possible symmetry.

Conclusions. – The observation of dispersion in the system benzene on Os(0001) is important for understanding the nature of lateral interactions in adsorbed hydrocarbon layers. In the present case the observed dispersion of the $2a_{1g}$ derived ion state of benzene appears to be dominated by through space intermolecular interactions. In order to explain the experimental dispersion data tight-binding calculations neglecting substrate interactions are fully sufficient. From the present study it is not possible to determine the azimuthal orientation of the benzene molecules on the surface.

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