

## Length Scales in Core Level Excitation: C 1s X-Ray Absorption of C<sub>60</sub>/Al

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We present evidence for atomic site-dependent excitonic effects in the x-ray absorption spectrum of an ordered chemisorbed monolayer of C<sub>60</sub>/Al(110). We observe that the broadening in the 5t<sub>1u</sub>-derived resonance and the corresponding core level resonant photoemission intensity varies with the x-ray incidence angle. This can be understood as due to changes in the strength of the interaction between the x-ray absorption final state and the substrate bands. This study provides the first direct measurement of the length scale for the localization of an excited state by the core hole. [S0031-9007(97)03909-4]

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X-ray absorption spectroscopy (XAS) is now commonly used to probe the unoccupied valence bands of solids, liquids, gases, and interfaces in order to obtain atomic site-specific information about the electronic and geometric structure of materials. However, it is not always straightforward to interpret the near-edge structure in XAS spectra. This is due in large measure to the fact that the core hole in the final state represents a strong local perturbation to the system which must in general be accounted for when analyzing the spectra [1] to obtain, e.g., a density of states (DOS). For many metals it appears [1,2] that the screening of a core hole is very efficient, occurring over a length scale of the order of the atomic radius [3]. For XAS in insulators it is often possible to describe the spectral DOS within a quasiatomic model [4], which can be related to the very weak electron transfer screening.

An intermediate case for screening in XAS appears to be that of the planar aromatic molecules. This is seen in the strong first resonance for benzene, which has been explained theoretically as an excitonic effect [5], and in similar spectral features for larger hexagon-based molecules and other aromatics [5–7]. Recent calculations of 1s XAS in C<sub>60</sub> [8] and graphite [2], which represent intermediate and large-limit cases of the hexagon series, describe the XAS profiles well, and confirm experimental studies [9,10] showing that the first major resonance at the edge is significantly localized to the core hole. XAS for these systems is shown to entail excitation of states which are well described by calculating the unoccupied DOS after replacing the core-excited C atom by N (the Z + 1 approximation). The physical extent of the orbital(s) probed is also derived from the calculations, and found to be about 5–6 bond lengths in both cases. This length therefore appears to represent a fundamental screening characteristic for two-dimensional aromatic systems.

The final state orbital extent is not possible to check via comparison with XAS data, since the theoretical transition amplitude is sensitive mainly to the part of the wave function on the core hole site and its nearest neighbors. For direct experimental access to the screening length, therefore, techniques complementary to XAS are required.

Core level resonant photoemission (RPES) has previously been applied to the study of the time scale for excited state localization in XAS of these and other systems [9–11], determining charge transfer times for adsorbates [12], and obtaining insight into electronic [13,14] and/or geometrical [15] structure of semiconductor surfaces. It has thus far not been possible to apply it to the question of the length scale of the core excitation, however, which requires a means of varying the core hole location with respect to a source of perturbation of the excited state [16].

We present angle-dependent C 1s absorption and resonant photoemission data for 1 monolayer (ML) C<sub>60</sub>/Al(111) and 1 ML C<sub>60</sub>/Al(110) which accomplish this objective for the first time. For both systems, there is a narrower LUMO-derived resonance in grazing incidence than in normal incidence, an angle dependence of the XAS which has not been reported previously for C<sub>60</sub>. As we show, by varying the angle and by using a small excitation window one can preferentially excite states at different distances from the surface. From the angle-dependent XAS shapes and energies, and RPES intensities, we obtain the magnitude of the real space charge distribution in the core-excited state, and our results strongly support the theoretical estimates [8,2] of the core hole screening length for cases of intermediate screening.

C<sub>60</sub> is a molecule which is well suited to studies of these localization effects. Its XAS spectrum is characterized, and reflects [8] the high symmetry which in the ground state gives narrow, easily identifiable molecular orbitals [17]. In addition, C<sub>60</sub> shows strong RPES when the first few XAS resonances are excited [9]. XAS and RPES can therefore be used effectively to observe perturbations, as was done, e.g., for the case of N<sub>2</sub>/Ni(100) [18]. We note that C<sub>60</sub> chemisorbs intact on Al surfaces [19,20], and the strength of the perturbation on the electronic and physical structure of the molecule varies as a function of which surface it is adsorbed upon [19]. The choice of Al substrates is also motivated by the characteristically flat valence PES background, avoiding problems encountered with, e.g., C<sub>60</sub>/Au(110) for which the Au 5d PES underlies the C<sub>60</sub> RPES [21]. In addition, the unoccupied frontier

orbitals of  $C_{60}$  which are seen in XAS are of predominantly  $\pi^*$  character [22], which allows one to emphasize excitation of atoms on different parts of the molecule by varying the angle of incidence of the incoming radiation as illustrated in Fig. 1.

All data were taken at beamline 22 of MAX-lab, using a modified SX700 monochromator and a high-efficiency electron spectrometer [23].  $C_{60}$  films were evaporated onto clean Al(111) and Al(110) substrates with pressures in the low  $10^{-10}$  mbar range, as previously described for Au(110) [21]. Ordered monolayers were produced by evaporating  $C_{60}$  while the surfaces were held at a temperature of 620 K. C 1s PES confirmed that only a monolayer was produced via a lack of extra lines, as on Au(110) [21]. XAS was measured by recording the total electron yield as a function of photon energy, with a resolution of 0.16 eV. Photon energy calibration was carried out by measuring the Al 2p direct PES with first and second order light. The Al 2p line was also used to calibrate the kinetic energy scale of the electron energy analyzer at a known photon energy. The analyzer resolution during RPES measurements was 0.3 eV, while the photon energy bandwidth was 0.16 eV as for XAS. Grazing incidence data were taken at  $75^\circ$  from normal (see Fig. 1). Unwanted angular effects in the RPES were minimized by the experimental geometry, such that grazing (normal) incidence spectra were collected at  $35^\circ$  ( $40^\circ$ )

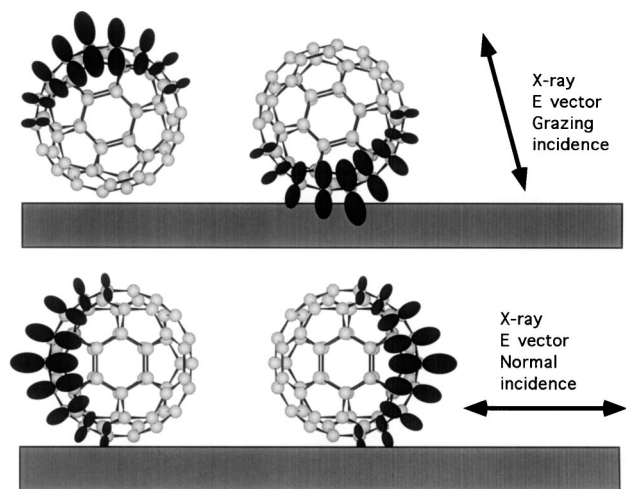


FIG. 1. Schematic of the expected angular dependence of the x-ray absorption cross section for  $C_{60}$  adsorbed on a surface. We have assumed that the direction of maximum amplitude for the  $p$  component of the core-excited  $\pi^*$  wave function is radial, consistent with a tight-binding picture [22] of the ground state. The angular dependence of the cross section is then given by  $\cos^2 \phi$ , where  $\phi$  is the angle between the electric field vector of the linearly polarized synchrotron radiation and the normal to the molecular surface at the excited atom. Grazing incidence corresponds here to  $75^\circ$  from the crystal surface normal for the Poynting vector. Since the LUMO has predominantly  $\pi^*$  character, it is clear that, in the geometry shown above, there will be a higher cross section for the core hole to be located on the sides (top and bottom) of the molecule in normal (grazing) incidence.

emission angles, and should also be greatly diminished considering the small Brillouin zone and high kinetic energy for these samples.

In Fig. 2, we present C 1s XAS data for solid  $C_{60}$ , 1 ML  $C_{60}/Al(110)$ , and 1 ML  $C_{60}/Al(111)$  in the near-edge region for the extreme incidence angles. The spectrum for solid  $C_{60}$  is not observed to be angle dependent. The lowest energy resonance in all three sets of data is due to absorption from the 1s level to the  $5t_{1u}$ -derived LUMO (lowest unoccupied molecular orbital). In the ground state of solid  $C_{60}$  this level is threefold degenerate; however, the symmetry-breaking effect of the core hole lifts this degeneracy, and the lowest-energy component dominates the cross section in XAS for each orbital [8].

We observe in Fig. 2 that for  $C_{60}/Al(110)$  and  $C_{60}/Al(111)$ , all the resonances are *broadened* compared to solid  $C_{60}$  as a result of bonding to the substrate. This broadening is most pronounced for  $C_{60}/Al(111)$ , where the perturbation on the molecular electronic structure due to the bonding interaction is stronger, as discussed in detail elsewhere [19]. For both monolayers, the width of the LUMO resonance clearly varies with incidence angle; for  $C_{60}/Al(110)$  the full width at half maximum

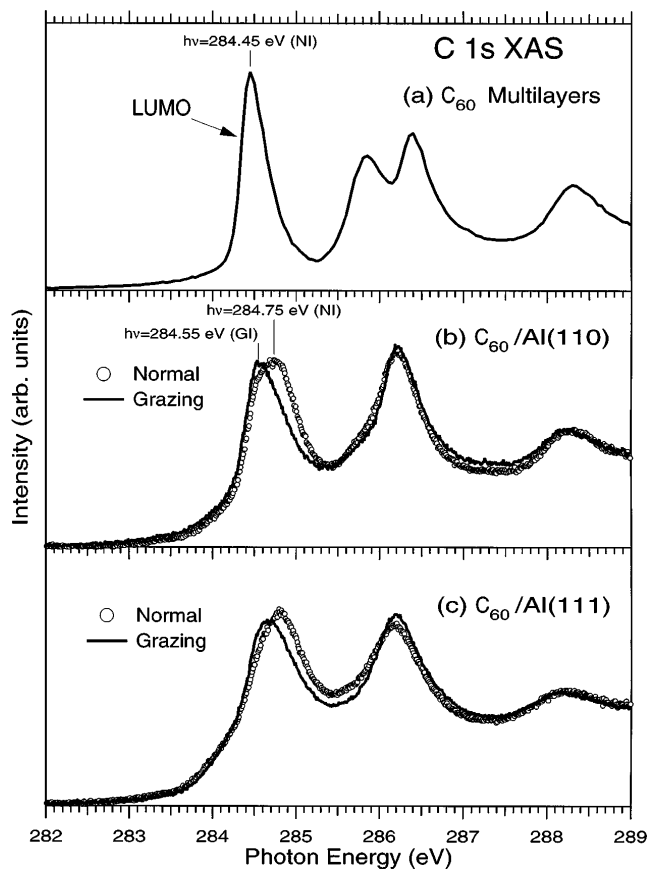


FIG. 2. XAS spectra for the samples and incidence angles indicated. The photon energies marked with arrows for solid  $C_{60}$  and 1 ML  $C_{60}/Al(110)$  spectrum for grazing incidence (GI) and normal incidence (NI) are those used during RPES measurements. The spectrum for solid  $C_{60}$  is independent of the x-ray incidence angle.

is 0.72 eV in grazing incidence, compared to 0.85 eV in normal incidence. To the extent that such broadening is regarded as reflecting the strength of the bonding interaction with the substrate bands, this implies that for the LUMO resonance the substrate interaction of the core-excited states in grazing incidence is less than for those reached in normal incidence. We therefore interpret the narrow XAS peak in grazing incidence as due to excitations away from the surface. Of course, at this angle one should also probe atoms close enough to the substrate for the excited state wave function to have a significant overlap [8], so that a portion of the spectrum should be due to these. We note that in all the ML XAS spectra there is a shoulder centered at about 284 eV, i.e., very close to the C 1s binding energy of 283.93 (283.90) for the monolayer on Al(110) [Al(111)]. This represents  $E_F$  for the unoccupied valence states, and indicates that there are carbon-derived states with metallic character. Similarly, there is a broad and strong background which has emerged throughout the entire spectrum with respect to the solid. We interpret these contributions as due to states corresponding to the direct covalent interaction between C<sub>60</sub> and Al, and the increase of these contributions for the more strongly bonded C<sub>60</sub>/Al(111) system is consistent with this assignment. This is also consistent, within the  $Z + 1$  approximation, with the finding that C<sub>59</sub>N has a strong preponderance to bind via sites very near the substituting N atom [24].

Not only the width, but the *energy* of the LUMO resonance varies with incidence angle. For solid C<sub>60</sub> the center of the resonance is at 284.45 eV; for C<sub>60</sub>/Al(110), the energy is 284.55 (284.75) in normal (grazing) incidence, and moves to 284.64 (284.80) for the more strongly bonded C<sub>60</sub>/Al(111) system. The shift of the LUMO resonance to higher energy therefore increases with the strength of the ground state substrate-C<sub>60</sub> bonding [19]. A similar energy shift is observed for polymerized C<sub>60</sub>, where the interfullerene bond is by definition covalent [25]; we thus attribute this to the mixing of  $sp^3$  character into the wave function of the  $\pi^*$ -like  $5t_{1u}$  level, which for this unoccupied, antibonding orbital should cause an upward energy shift. The fact that the energy of the LUMO resonance for grazing incidence on Al(110) is only 0.10 eV higher than for solid C<sub>60</sub>, together with the observation that the shapes of these two peaks are quite similar, supports the interpretation given above, that at this angle and energy one probes excited states which have little interaction with the surface. This implies that by selecting a narrow energy window around 284.5 eV in grazing incidence one can predominantly excite these surface-distant states.

The above model, however, contains certain assumptions: First, that the narrow part of the LUMO resonance is still derived predominantly from a single molecular orbital as for solid C<sub>60</sub> [8]; and second, that there are no additional vibrational effects due to adsorption on Al. In order to test these assumptions, we measured RPES spectra at energies corresponding to the maxima of the LUMO

at each incidence angle for both surfaces. As noted previously, e.g., [10], if the electron excited in XAS is localized to the core hole long enough to have an effect on the deexcitation process, RPES will occur (there denoted participator autoionization). The RPES deexcitation channel loses intensity if the one-electron final state orbital hybridizes with states that remove the electron from the core hole site [9,21].

We concentrate here on Al(110), because the relatively weak substrate-adsorbate interaction results in clearly defined RPES features as discussed below. RPES data for this system are compared to similar results for solid C<sub>60</sub> in Fig. 3. It is clear that the first two peaks in the spectrum for the solid correspond to RPES involving final states with electrons missing from the highest occupied MO (HOMO) and HOMO-1, whose binding energies are 1.9 and 3.1 eV, respectively, referenced to  $E_F$ . This, and the fact that the HOMO RPES represents the highest kinetic energy part of the decay spectrum, makes the identification of these features unambiguous. In order to accurately gauge the RPES intensity, the nonresonant background is also included in Fig. 3 for each spectrum. It is obvious that the HOMO RPES is stronger in grazing than in normal incidence, and numerical integration gives the values

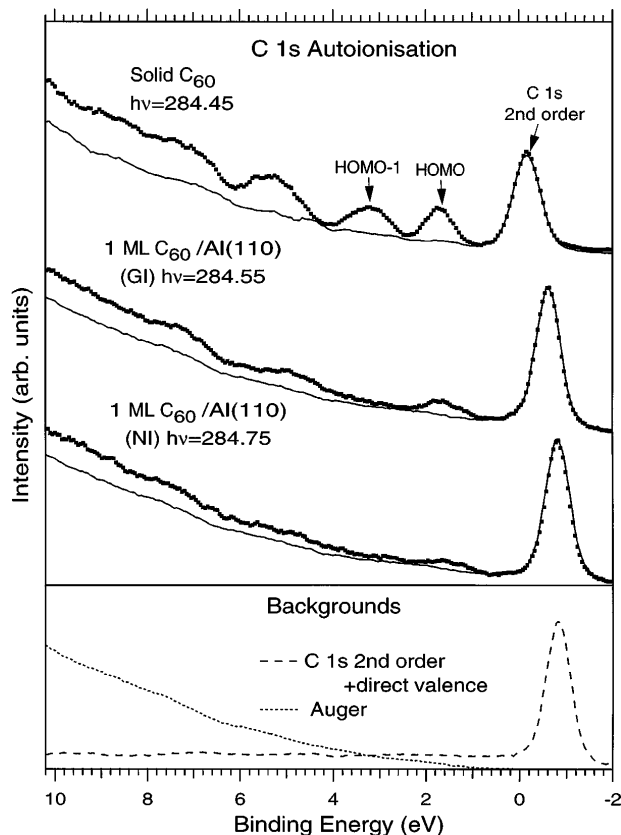


FIG. 3. RPES data for solid C<sub>60</sub>, and for 1 ML C<sub>60</sub>/Al(110) in grazing incidence (GI) and normal incidence (NI) (symbols), shown with the estimated background contribution (lines). The bottom panel illustrates the components of the background due to Auger and direct photoemission.

TABLE I. The variation in XAS cross section as measured by RPES resulting purely from the variation in incidence angle of the x rays as indicated in Fig. 1, compared to the HOMO RPES intensity when the maximum of the LUMO resonance is excited for 1 ML C<sub>60</sub>/Al(110). The fact that the HOMO RPES intensity is close to 50% is consistent with the conclusion in the text that atoms nearest to the interface contribute much less.

Incidence angle	A	B	C
	Cross section for 30 atoms near equator (% of total)	Cross section for 30 atoms at top/bottom (% of total)	Homo RPES intensity ( $h\nu = \text{LUMO}_{\text{max}}$ ) (% of thick film)
Grazing	43	57	62
Normal	68	32	36

shown in Table I. This is fully consistent with our model of the grazing incidence LUMO resonance corresponding to states with little interaction with the substrate. The fact that the HOMO RPES for C<sub>60</sub>/Al(111) (not shown) decreases drastically fully supports this interpretation in light of the stronger bonding to the substrate.

Thus RPES at  $h\nu = 284.55$  in grazing incidence corresponds to intermediate states for which the promoted electron is localized to the part of the molecule farthest away from the surface, on the assumption that the likelihood for delocalization into the substrate increases with greater proximity to the surface [26]. The extent of this geometrical variation in cross section has been estimated in a simulation based on the assumptions of Fig. 1, and this is compared to the total observed participator intensity in Table I. The agreement between columns B and C, and contraagreement between columns A and C, is strong support for the assigned localization effect. The similarity in both shape and position between the LUMO resonance for solid C<sub>60</sub> and for 1 ML C<sub>60</sub>/Al(110) in grazing incidence (Fig. 2) is thus in retrospect not remarkable. It confirms that the screening of these core-excited states is much like that in solid C<sub>60</sub>, i.e., dominated by intramolecular contributions.

We have shown that the angular dependence observed in the lowest C 1s XAS resonance for C<sub>60</sub>/Al(110) results from excitation to states for which the interaction with the states of the substrate varies. By selecting both the x-ray incidence angle and excitation energy, it is possible to selectively excite states with little overlap with the substrate. The results imply that the excitonlike state corresponding to the LUMO-derived resonance is localized to a region which is considerably smaller than the extent of the C<sub>60</sub> molecule. It must indeed be confined to within approximately seven C-C bond lengths of the core-hole site, supporting the theoretical results for C<sub>60</sub> [8] and graphite [2].

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- [1] E. Tamura, J. van Ek, M. Fröba, and J. Wong, Phys. Rev. Lett. **74**, 4899 (1995).
- [2] R. Ahuja *et al.*, Phys. Rev. B **54**, 14 396 (1996).
- [3] Ignoring many-body effects; see, e.g., E. Zaremba and K. Sturm, Phys. Rev. Lett. **66**, 2144 (1991).
- [4] See, e.g., F.M.F. de Groot, J. Electron Spectrosc. Relat. Phenom. **62**, 111 (1993).
- [5] H. Ågren, O. Vahtras, and V. Carravetta, Chem. Phys. **196**, 47 (1995), and references therein.
- [6] T. Yokoyama *et al.*, Phys. Scr. **41**, 189 (1990).
- [7] H. Oji *et al.*, J. Electron Spectrosc. Relat. Phenom. **78**, 383(1996).
- [8] B. Wästberg *et al.*, Phys. Rev. B **50**, 13 031 (1994); see S. Lunell *et al.*, Int. J. Quant. Chem. **52**, 135 (1994) for a detailed view of the relevant wave function, there denoted as 67a<sup>\*</sup>.
- [9] P.A. Brühwiler *et al.*, Phys. Rev. Lett. **71**, 3721 (1993). For C<sub>60</sub> this extends to higher resonances [8]. See also P.A. Brühwiler *et al.*, *ibid.* **73**, 2938 (1994).
- [10] P.A. Brühwiler *et al.*, Phys. Rev. Lett. **74**, 614 (1995).
- [11] D. Menzel *et al.*, J. Chem. Phys. **96**, 1724 (1992).
- [12] O. Björneholm *et al.*, Phys. Rev. Lett. **68**, 1892 (1992).
- [13] J. Faul *et al.*, Phys. Rev. B **50**, 7384 (1994).
- [14] H. Wang *et al.*, Phys. Rev. A **50**, 1359 (1994).
- [15] J.P. Long, V.M. Bermudez, and D.E. Ramaker, Phys. Rev. Lett. **76**, 991 (1996).
- [16] Such information could in principle be obtained by electron microscope-based energy loss measurements of clusters by studying the spectrum as a function of the probe position. This has not been attempted thus far to our knowledge [see, e.g., P.M. Ajayan, S. Iijima, and T. Ichihashi, Phys. Rev. B **47**, 6859 (1993), who studied carbon nanotubes, and P.E. Batson and J.R. Heath, Phys. Rev. Lett. **71**, 911 (1993), who studied Si nanoclusters], and the core hole effects could be difficult to disentangle from other dependencies in any case.
- [17] See, e.g., *Solid State Physics: Fullerenes*, H. Ehrenreich and F. Spaepen (Academic, Boston, 1994).
- [18] A. Sandell *et al.*, Phys. Rev. Lett. **70**, 2000 (1993).
- [19] A.J. Maxwell *et al.*, Phys. Rev. B **52**, R5546 (1995); (to be published).
- [20] R. Fasel *et al.*, Phys. Rev. Lett. **76**, 4733 (1996).
- [21] A.J. Maxwell *et al.*, Phys. Rev. B **49**, 10 717 (1994).
- [22] S. Satpathy *et al.*, Phys. Rev. B **46**, 1773 (1992).
- [23] J.N. Andersen *et al.*, Synchr. Rad. News **4**, 15 (1991).
- [24] K. Prassides *et al.*, Science **271**, 1833 (1996); their Fig. 4 also shows the relevant wave function.
- [25] B.S. Itchkawitz *et al.*, Chem. Phys. Lett. **243**, 211 (1995).
- [26] The fact that similar angle dependence is absent for the higher XAS resonances is consistent with the greater physical extent of the relevant orbitals; this is seen in the experimental intensities for these lines in gas phase and solid C<sub>60</sub>, and in calculations of the Z + 1 wave functions.