

PII: S0038–1098(96)00590-X

CHARGE TRANSFER AND A NEW IMAGE STATE OF C_{60} ON Cu(1 1 1) SURFACE STUDIED BY INVERSE PHOTOEMISSIONK.-D. Tsuei^a and P.D. Johnson^b^aSynchrotron Radiation Research Center and Department of Physics, National Tsin-Hua University, Tsinchu, Taiwan 300, R.O.C.^bPhysics Department, Brookhaven National Laboratory, Upton, NY 11973, USA

(Received 2 September 1996; accepted 20 September 1996 by T. Tsuzuki)

We have used inverse photoemission to study ultra-thin C_{60} films adsorbed on Cu(1 1 1) surfaces. Unlike a previous study of C_{60} adsorption on a Au film where the unoccupied states shift rigidly towards the Fermi level, the spectra here look strongly perturbed and more like those characteristic of K_3C_{60} . This indicates that the interaction of C_{60} with Cu is much stronger than with Au. Annealing at 350°C results in a well ordered (4×4) structure as seen in LEED. An additional broad peak appears below the vacuum level. This new state has a parabolic dispersion with an effective mass close to unity. We interpret this state as the image state or resonance on top of the metallized C_{60} overlayer. Copyright © 1996 Elsevier Science Ltd

Keywords: A. fullerenes, A. surfaces and interfaces, D. electronic states.

The discovery of a method for producing and purifying C_{60} in macroscopic quantities [1] has sparked a large amount of work on this molecule also known as buckminsterfullerene, fullerenes or simply buckyballs. One of the more intriguing observations in these studies is the high temperature superconductivity in the alkali doped solids [2]. The electronic structure of these compounds has been measured by photoemission, inverse photoemission and X-ray absorption spectroscopies [3, 4]. These studies indicate that with continuous K doping the lowest unoccupied molecular orbital (LUMO) of C_{60} becomes gradually filled. This observation lends strong support for the idea of complete charge transfer from the K 4s electrons to the LUMO. In particular for K_6C_{60} the LUMO band is fully occupied producing an insulating state. For K_3C_{60} the LUMO band is half-filled and it is believed to be a conductor although it has also been proposed that it is a Mott–Hubbard insulator [5]. In addition the compound K_4C_{60} was found to be an insulator, in contradiction to band theory [6].

The adsorption of C_{60} on metal surface offers a good opportunity to study the effect of dimensionality and geometry on the interaction mechanism between C_{60} and a metal and can be compared with the metal-intercalated systems. Photoemission studies of C_{60} on metal films [7]

concluded that the C_{60} molecular orbitals are aligned with the substrate Fermi levels rather than the vacuum levels. Inverse photoemission (IPES) studies of C_{60} on Au films [7] found that the C_{60} LUMO becomes a resonance and partially occupied upon chemisorption. This was interpreted as evidence of charge transfer. In this particular measurement the unoccupied molecular orbitals showed a rigid shift toward the Fermi level relative to a thick film. The authors speculated that the amount of charge transfer was small and that polarization of the molecular charge should also be small. However, a photoemission study showed very little change around the Fermi level for this system [8]. Another valence band photoemission study of adsorption on the Au(1 1 0) surface also revealed no new state [9]. This latter study of Maxwell *et al.* combined near edge X-ray absorption fine structure (NEXAFS), valence and core level photoemission. They also concluded that the C_{60} LUMO is strongly hybridized with the Au *d*-bands. More recently a similar study on Al(1 1 1) concluded that the bonding between C_{60} and the substrate is covalent [10]. The small reduction in intensity and energy shift of the LUMO in NEXAFS studies of adsorption on Cu(1 0 0) was interpreted as due to hybridization and charge transfer from the substrate to the C_{60} [11]. The observed Raman shift

of C₆₀ on noble metal films also indicates charge transfer [8].

Electron energy loss (EELS) detecting electronic transition and vibrational excitation has also been used to measure quantitatively the amount of charge transfer. It was determined that 1 ± 1 and 2 ± 1 electrons transferred to the molecule for Au(110) and Ni(110), respectively [12, 13]. While for Pt(111) the amount of charge transfer was negligible and it was concluded that the bonding is covalent instead [14]. Scanning tunneling microscopy (STM) studies have been carried out on a few metal surfaces [15–20]. In particular the study of C₆₀ on Cu(111) suggested that monolayer of C₆₀ is metallic instead of semiconducting [18].

In this communication we report on IPES study of C₆₀ adsorption on Cu(111). In agreement with the STM study we find that the monolayer is indeed metallic. Further we find through comparison with the spectrum from K₃C₆₀ that a charge transfer model best describes the observed electronic structure.

The experimental apparatus which consists of a normal incidence spectrograph and low energy electron gun has been described before [21]. The incident electron beam from a Stoffel–Johnson gun has an angular spread of $\pm 2.5^\circ$. The angular acceptance of the spectrograph was $\pm 4.5^\circ$. The fixed angle between the incident electron beam and the emitted light was 45° . The dispersion measurements were achieved by rotating the crystal. The overall energy resolution from the width of an image state characterizing the clean surface was 0.35 eV. A fixed incident energy of 15.5 eV relative to the Fermi energy was used throughout this experiment.

The C₆₀ powder of purity 99.5% was purchased commercially. It was sealed in a Ta foil rolled tube with small holes allowing the C₆₀ vapor out. A thermal couple wire was attached to the center of the tube for controlling the evaporation rate. The evaporation temperature ranged between 400° and 460°C. A low evaporation rate of approximately 13 min per monolayer (ML) was used. The source was degassed thoroughly before all measurements and little pressure rise occurred during evaporation.

LEED and Auger was used to monitor the surface ordering and cleanness. Work function changes were monitored by the retarding field method using the inverse photoemission gun.

The LEED study revealed that the C₆₀ molecules formed a (4 × 4) structure as in a previous investigation [11]. Deposition at room temperature yields only weak (4 × 4) spots which appear at a coverage as low as 0.2 ML. This is consistent with a recent STM study [18] in which it was found that C₆₀ molecules form islands with four domains of (4 × 4) structure. Annealing above 300°C leaves only a single layer on the surface.

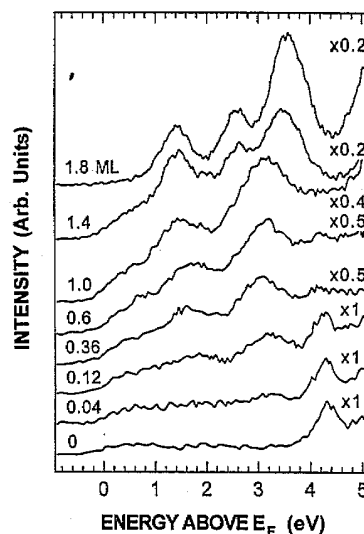


Fig. 1. Coverage dependence of the normal incidence inverse photoemission spectra from C₆₀ deposited at room temperature on Cu(111). The incident electron energy was 15.5 eV.

LEED patterns from the annealed surface showed sharp spots originating from the overlayer. The LEED intensity appeared even sharper for annealing temperatures as high as 550°C with the overlayer spots as sharp as the substrate spots. We note here that in the case of strong chemisorbed alkali systems on metal surfaces annealing to 500°C leaves less than 0.05 ML of alkali atoms on the surface. This result indicates that the bonding between C₆₀ molecules and the Cu surface is very strong. Surfaces thus prepared are extremely stable as indicated by the observation that the LEED pattern remained sharp overnight.

Figure 1 displays a series of spectra recorded at normal incidence as a function of C₆₀ coverage as indicated. The relative scale normalized to the sample current is also shown. The bottom curve was recorded from a clean surface. The peak at 4.2 eV above the Fermi energy represents the $n = 1$ image state [22]. The weak emission below the image state reflects the band gap extending from 0.9 eV below the Fermi level to 4.3 eV above. It can be seen that the image state attenuates gradually as more C₆₀ is deposited and disappears close to the saturated monolayer (ML) coverage. It should be noted that the binding energy of the image state changes very little through this coverage range. This can be understood as the image state signal originating from the clean surface area rather than the adsorbate covered region, consistent with island formation. The work function, measured by the retarding field method, did not show any change suggesting the adsorption of C₆₀ does not alter the surface potential barrier height. Two new

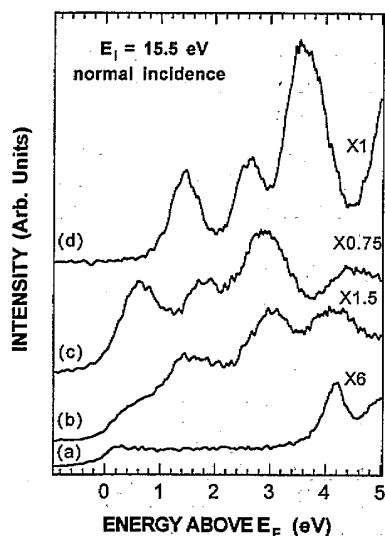


Fig. 2. Normal incidence inverse photoemission spectra from (a) a clean Cu(111) surface; (b) a 1 ML film prepared by annealing multilayers of C₆₀ off, showing sharp (4 × 4) LEED pattern; (c) a 2 ML film doped slightly with K; (d) a thick film. The relative intensity normalized to sample current is shown at right. The incident electron energy was 15.5 eV.

peaks appear in the spectra due to the C₆₀ overlayer. First at a coverage of 0.04 ML a peak shows at an energy 3.3 eV above the Fermi level. Starting at a coverage of 0.12 ML, probably because of weaker intensity another broad feature appears at about 1.7 eV above the Fermi level. These two peaks also shift towards the Fermi level by about 0.1–0.2 eV at saturation coverage. Once the second layer adsorbs on the surface the spectrum becomes very different as shown for the coverage of 1.4 ML. It looks instead rather similar to spectra observed from a multilayer.

Annealing leads to a dramatic change in the spectra. Figure 2(b) shows the spectrum from 1 ML C₆₀ after annealing off the excess layers. Compared to the unannealed 1 ML spectrum in Fig. 1 it is seen that the first peak above the Fermi level remains the same; the second peak shifts slightly downward in energy and an additional peak appears at 4.1 eV above the Fermi level. We note here that both annealed and unannealed monolayer spectra are very different from those observed in the case of C₆₀ adsorption on a Au film, in which a rigid shift of peak energies toward the Fermi level was observed [7]. It can therefore be concluded that the interaction between the C₆₀ and a Cu surface is much stronger than that between C₆₀ and a Au surface.

We have also examined the dispersion from $\bar{\Gamma}$ to \bar{M}' as shown in Figs 3 and 4. It can be seen from Fig. 3 that the first two peaks disperse very little while the additional peak disperses upwards and folds back after crossing the

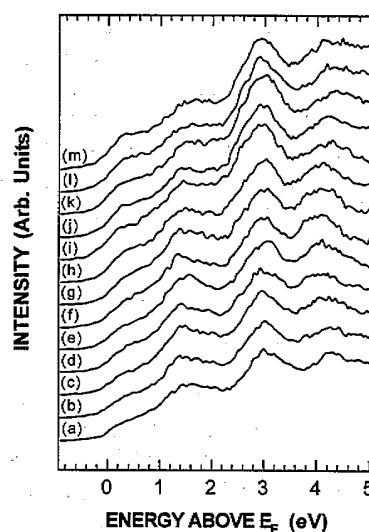


Fig. 3. Angular dependence of spectra from an annealed, well ordered (4 × 4) ML film along $\bar{\Gamma}$ to \bar{M}' direction. These spectra were taken at emission angles of (a) -9.5° ; (b) -7.5° ; (c) -5.5° ; (d) -3.5° ; (e) -1.5° ; (f) 0.5° ; (g) 2.5° ; (h) 4.5° ; (i) 6.5° ; (j) 8.5° ; (k) 10.5° ; (l) 12.5° ; (m) 14.5° . \bar{M}' of the overlayer is at about 12° off normal.

\bar{M}' point associated with the (4 × 4) overlayer (approximately 12° from normal). The binding energy of the additional peak as a function of the momentum parallel to the surface is displayed in Fig. 4. The vertical dashed line indicates the parallel momentum at the \bar{M}' point. The parabolic dotted line represents a free electron like band dispersion. It can be seen that the 4.1 eV peak disperses with an effective mass very close to unity. Measurements of the work function for the annealed films indicate no change from the clean surface either.

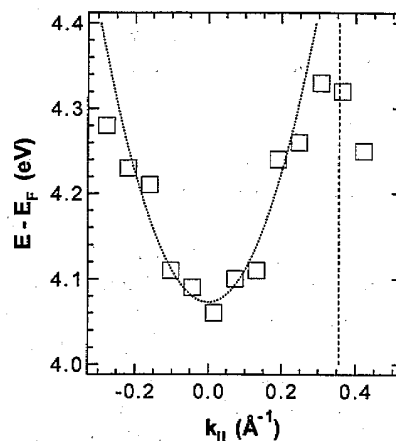


Fig. 4. The dispersion of the 4.1 eV peak as a function of momentum parallel to the surface. The vertical dashed line indicates the momentum of the \bar{M}' point. The parabolic dotted line represents a free electron like band dispersion.

For comparison the spectrum from a 2 ML C₆₀ film slightly doped with K and from a thick film are shown in Fig. 2(c) and (d) respectively. In agreement with earlier studies [3] the rigid shift of the molecular orbitals towards the Fermi energy as a result of K doping is readily seen. The unannealed spectrum looks surprisingly similar to the spectrum of K₃C₆₀ [3]. The clean spectrum at normal incidence [Fig. 2(a)] shows that the intensity in the vicinity of the Fermi energy is weak due to the presence of the band gap. The intensity at the Fermi energy from a thick film vanishes again because bulk C₆₀ is an insulator. In contrast, for a 1 ML film the Fermi level step is clearly seen. This indicates that the monolayer film is metallized in agreement with STM studies [18]. This result along with the similarity of the monolayer spectrum and the K₃C₆₀ spectrum suggests that charge transfer takes place between the substrate and the molecule. If charge transfer does occur a large dipole layer should form at the overlayer-substrate interface. However, no work function change from the clean surface was observed for all coverages, whether annealed or unannealed. This is very different from alkali adsorption on metal surfaces where a large work function decrease is generally observed. However, we note that here the C₆₀ overlayer is always in the form of islands with its local structure the same as that of a complete monolayer. Since these islands are metallized the image plane [23] must move from just outside of the clean surface to the outside of the C₆₀ overlayer. Therefore, we suggest that the interface dipole layer is screened out by the image plane. The work function measured for a monolayer is therefore purely due to the metallic overlayer and is not related to the interface.

We assign the extra peak at 4.1 eV above the Fermi level after annealing to an image state associated with the well ordered overlayer. This peak does not show up in the spectra from unannealed films indicating that it does not originate from molecular orbitals. It is noted here that the peak energy is not very different from that of the clean surface image state because the work function stays the same. Further support for this assignment is provided by the near unity effective mass for the dispersion. The image state experiences the corrugation of the (4 × 4) lattice as its dispersion is folded back at the zone boundary as shown in Fig. 4. Its width is twice the measured width of the image state observed on the clean surface indicating that its lifetime is much shorter than the latter. The image state of the clean surface lies at the top of the band gap and disperses upwards into the bulk continuum. The (4 × 4) lattice folds the clean surface Brillouin zone twice allowing new coupling to the originally forbidden bulk states. Thus the state is more appropriately described as a resonance.

In summary, we have used inverse photoemission to

probe the interaction between C₆₀ and Cu(1 1 1) surface. From the comparison with the spectrum from K₃C₆₀ film and the appearance of the Fermi level in the spectra of the adsorption system we conclude that a charge transfer model appears to provide an adequate description of our observations. A new image state or resonance associated with the well ordered C₆₀ overlayer is observed.

Acknowledgement—This work was supported in part by the Department of Energy under Contract No. DE-AC02-76CH00016.

REFERENCES

1. Kratschmer, W., Lamb, L.D., Fostiropoulos, K. and Huffman, D.R., *Nature*, **347**, 1990, 354.
2. Hebard, A.F. *et al.*, *Nature*, **350**, 1991, 600.
3. Benning, P.J., Poirier, D.M., Ohno, T.R., Chen, Y., Jost, M.B., Stepniak, F., Kroll, G.H., Weaver, J.H., Fure, J. and Smalley, R.E., *Phys. Rev.*, **B45**, 1992, 6899.
4. Chen, C.T., Tjeng, L.H., Rudolf, P., Meigs, G., Rowe, J.E., Chen, J., McCauley Jr., J.P., Smith III, A.B., McGhie, A.R., Romanaow, W.J. and Plummer, E.W., *Nature*, **352**, 1991, 603.
5. Lof, R.W., van Veenendaal, M.A., Koopmans, B., Jonkman, H.T. and Sawatzky, G.A., *Phys. Rev. Lett.*, **68**, 1992, 3924.
6. Benning, P.J., Stepniak, F., Poirier, D.M., Martins, J.L., Weaver, J.H., Chibante, L.P.F. and Smalley, R.E., *Phys. Rev.*, **B47**, 1993, 13843.
7. Ohno, T.R., Chen, Y., Harvey, S.E., Kroll, G.H., Weaver, J.H., Hauffer, R.E. and Smalley, R.E., *Phys. Rev.*, **B44**, 1991, 13747.
8. Chase, S.J., Bacsa, W.S., Mitch, M.G., Philione, L.J. and Lannin, J.S., *Phys. Rev.*, **B46**, 1992, 7873.
9. Maxwell, A.J., Bruhwiler, P.A., Nilsson, A., Martensson, N. and Rudolf, P., *Phys. Rev.*, **B49**, 1994, 10717.
10. Maxwell, A.J., Bruhwiler, P.A., Andersson, S., Arvantis, D., Hernnas, B., Karis, O., Mancini, D.C., Martensson, N., Gray, S.M., Johansson, M.K.-J. and Johansson, L.S.O., *Phys. Rev.*, **B52**, 1995, R5546.
11. Rowe, J.E., Rudolf, P., Tjeng, L.H., Malic, R.A., Meigs, G., Chen, C.T., Chen, J. and Plummer, E.W., *Int. J. Mod. Phys.*, **B6**, 1992, 3909.
12. Modesti, S., Cerasari, S. and Rudolf, P., *Phys. Rev. Lett.*, **71**, 1993, 2469.
13. Hunt, M.R.C., Modesti, S., Rudolf, P. and Palmer, R.E., *Phys. Rev.*, **B51**, 1995, 10039.
14. Cepek, C., Goldoni, A. and Modesti, S., *Phys. Rev.*, **B53**, 1996, 7466.
15. Altman, E. and Colton, R., *Surf. Sci.*, **279**, 1992, 49.
16. Howells, S., Chen, T., Gallagher, M., Sarid, D., Lichtenberger, D., Wright, L., Ray, C., Huffman, D. and Lamb, L., *Surf. Sci.*, **274**, 1992, 141.
17. Li, Y.Z., Patrin, J.C., Chandler, M., Weaver, J.H., Chibante, L.P.F. and Smalley, R.E., *Science* **252**, 1991, 547.

18. Motai, K., Hashizume, T., Shinohara, H., Saito, Y., Pickering, H., Nishina, Y. and Sakurai, T., *Japan. J. Appl. Phys.*, **32**, 1993, L450; Hashizume, T., Motai, K., Wang, X.D., Shinohara, H., Saito, Y., Maruyama, Y., Ohno, K., Kawazoe, Y., Nishina, Y., Pickering, H., Kuk, Y. and Sakurai, T., *Phys. Rev. Lett.*, **71**, 1993, 2959.
19. Gimzewski, J.K., Modesti, S. and Schlittler, R., *Phys. Rev. Lett.*, **72**, 1994, 1036.
20. Kuk, Y., Kim, D.K., Suh, Y.D., Park, K.H., Noh, H.P., Oh, S.J. and Kim, S.K., *Phys. Rev. Lett.*, **70**, 1993, 1948.
21. Johnson, P.D., Hulbert, S.L., Carrett, R.F. and Howells, M.R., *Rev. Sci. Instrum.*, **57**, 1986, 1324.
22. Hulbert, S.L., Johnson, P.D., Stoffel, N.G., Royer, W.A. and Smith, N.V., *Phys. Rev.*, **B31**, 1985, 6815.
23. Lang, N.D. and Kohn, W., *Phys. Rev.*, **B1**, 1970, 4555; **B3**, 1971, 1215.