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Field Ion Microscopy of C₆₀ Molecules*

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Field ion microscopy of C₆₀ on the tungsten substrate showed that (1) the field ion image of the C₆₀ adsorbate reflects the LUMO (lowest unoccupied molecular orbital)-induced local density of states of the C₆₀, similar to the recent STM image of the C₆₀ on the Cu(111)1x1 surface and that (2) the field evaporation occurs as a C₆₀ molecule, in glaring contrast to the recent report by Ohmae et al.

KEYWORDS: C₆₀, FIM, local density of states

Interesting contrast effects reflecting the intramolecular structures of C₆₀ molecules¹⁾ have been observed by high resolution electron microscopy²⁾ and scanning tunneling microscopy (STM).³⁻⁹⁾ Ohmae et al.¹⁰⁾ recently reported that *individual C atoms making up the C₆₀ molecule, which is adsorbed on a tungsten tip, can be observed by field ion microscopy (FIM)*. They also claimed that the *C atoms in the C₆₀ molecule evaporate individually, one by one*, in the field evaporation process. Realizing the well-known fact that the C-C interatomic bonding of C₆₀ is covalent and strong with the bonding energy of 7.4eV,¹¹⁾ exceedingly higher than the van der Waals energy between the C₆₀ molecule and the tungsten substrate, it is peculiar and even inconceivable that atoms in the C₆₀ molecule evaporate individually before the whole C₆₀ molecule is being evaporated as a unit from the substrate. Ohmae et al. also claimed that even those atoms located in the hidden side of the C₆₀ adsorbate could be observed in their FIM image. Such imaging, however, is highly unlikely, since bright spots form as a result of field ionization of imaging gas atoms at the protruding sites on the surface.

The purpose of this paper is two-fold; first to report the first true field ion micrographs of C₆₀ and secondly to show that those presented by Ohmae et al. may well be nothing more than artifacts, commonly observed during the initial imaging process. We will also discuss how the image contrast observed in the present work is related with the structures of the C₆₀ molecules, comparing with those obtained by STM.⁹⁾

As a substrate, tungsten FIM tips are used. After obtaining a hemispherical clean surface of tungsten using helium imaging gas, the imaging gas was pumped down completely to 2×10^{-8} Pa. Then the tungsten tip was transferred to a reaction chamber, in which the vacuum deposition of C₆₀ was conducted in the vacuum of 2×10^{-7} Pa. The C₆₀ molecules were deposited by sublimating the C₆₀ powder at 360°C for 5 to 15 min..⁸⁾ The tips were, then, returned to the FIM chamber and cooled down to approximately 30 K. At this temperature, it is known that C₆₀ ceases its characteristic internal rotation.¹²⁾ FIM images are observed using He imaging gas or a mixture of He and Ne.

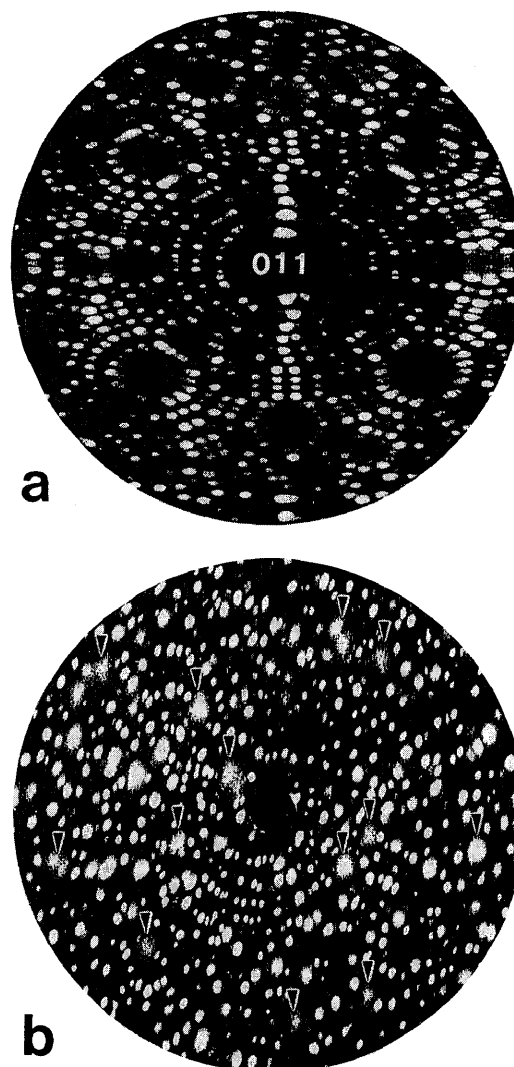


Fig. 1. FIM images for (a) the clean W surface with the (110) pole at its center and (b) the same W tip with the C₆₀ molecule adsorption. Large diffuse spots (marked by arrows in image (b)) are identified to be individual C₆₀ molecules.

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Figure 1(a) shows a typical He ion image of a clean tungsten tip. The (011) pole appears in the center, as usual for the wire drawn bcc crystal tip. The estimated tip radius from this image is approximately 210\AA . C_{60} molecules were vacuum deposited on this substrate, and imaging of C_{60} molecules were attempted starting from the low field. Initially there were only random and rather unstable bright spots, known to be the case of imaging impurity gases adsorbed on the tip surface. When the field reached at 80% of the best imaging field ($\sim 4.5\text{V/\AA}$),¹³⁾ the original orderly tungsten surface image was established, together with large and diffuse bright spots which were distributed randomly, as shown in Fig.1(b) (indicated by arrows). We note that this type of image contrast is very similar to that of carbon as reported in carbon containing ferrous alloys.^{14,15)} Furthermore, their image size is in a range of $5\text{-}15\text{\AA}$ including well-known image distortion. Therefore, we assign these diffuse and larger spots to be C_{60} molecules, although no atom-probe chemical analysis were attempted.

By changing the applied surface electric field, we found that the image contrast of C_{60} showed interesting variations. At a lower field, the contrast reflecting the intramolecular structure does not appear. However, at the field corresponding to $\sim 50\%$ ($\sim 2.3\text{V/\AA}$) of the He best imaging field, interesting features appear in the image contrast as shown in Fig. 2. The FIM image of C_{60} molecules looks like a *three-leaf clover with a center spots*. As the electrical field increases more, the contrast with a three-leaf clover shape disappears and only the center bright spots remain. With further increase of the field approaching the He best imaging field, the bright center spots become large and diffuse (Fig. 1b) and finally disappear completely. Under this situation, the image cannot be recovered even the field is reduced. When the electrical field is reduced before the single diffuse spot disappears, the three-leaf clover contrast appears again. As long as the molecule is adsorbed on the surface, the image contrast change as a function of the electrical field was very reproducible.

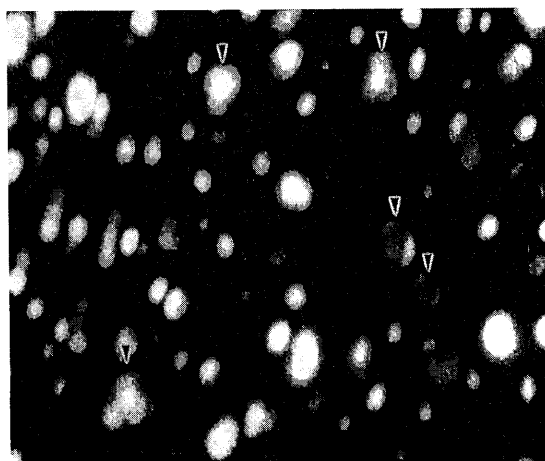


Fig. 2. An enlarged segment of a FIM image showing several C_{60} molecules in three-leaf clover shape.

We must, therefore, conclude that the C_{60} molecule adsorbate field evaporates as a unit. Figure 3 (a), (b), and (c) show this sequence following one specific C_{60} molecule located stably on the tungsten (011) terrace when the tip voltage increased from 4.0kV to 5.0kV . Figure 1(b) is essentially the same as Fig. 3(c) in the experimental conditions. The present results clearly disprove the Ohmae et al.'s claim that individual C atoms of the C_{60} molecule adsorbate field evaporate separately.

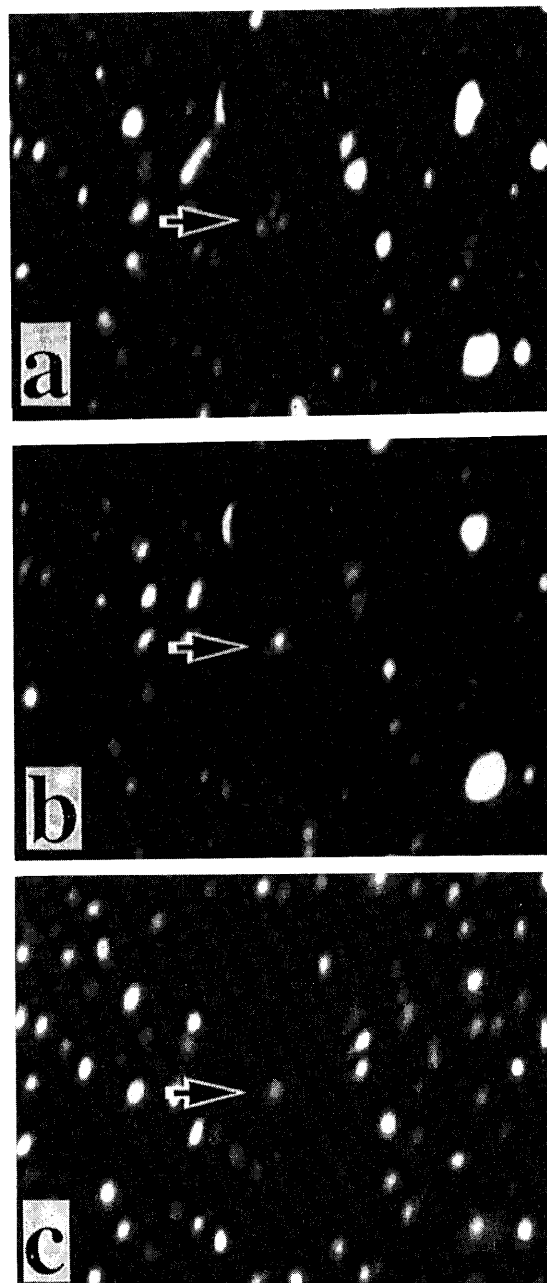


Fig. 3. A sequential FIM images showing the evolution of the image of a specific C_{60} molecule located on the (110) terrace with increasing tip voltage from 4.0kV to 5.0kV .

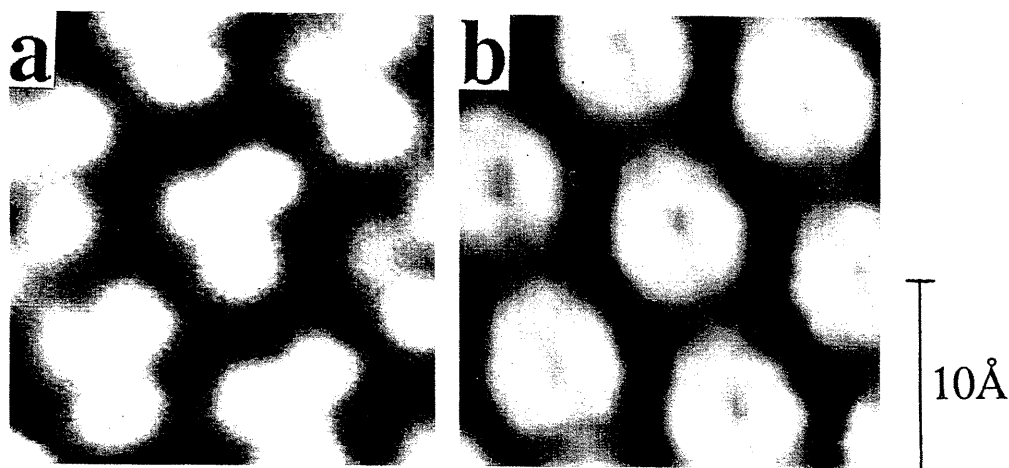


Fig. 4. Evolution of the STM images of the C_{60} molecules adsorbed on the Cu(111) surface as a function of bias potential $E_b - E_F$: (a) empty states image at $E_b - E_F = 2.0\text{eV}$, (b) filled states image at $E_b - E_F = -2.0\text{eV}$.

The field ion image is a mapping of the spatial distribution of the field ionization rate of the imaging gas atoms near the tip surface.¹⁶⁾ The field ionization rate is proportional to the product of the imaging gas atom density near a specific surface site and the electron tunneling probability of the gas atom. It is well-established, in the case of pure metal imaging where the conduction electrons are highly de-localized, that only the atoms at ledge sites and/or atoms of higher index planes are imaged, because field ionization of imaging gas atoms takes place preferentially at the locations where the electric field is the highest. The field ion image of a tungsten tip shown in Fig. 1(a) is such an example.

However, in the case of molecular adsorbates, the charge distribution of the molecule significantly influences the electron tunneling probability of the imaging gas atoms.¹⁷⁾ The image contrast cannot always be explained by the simple geometrical factor. In fact, Iwatsu et al.¹⁸⁾ reported that octacyanophthalocyanine molecules produce the FIM image having four bright spots forming a square shape pattern. Kageshima and Tsukada¹⁹⁾ simulated the FIM image using the LCAO approximation and showed that the FIM image of the molecule can be correlated with the squared amplitude of the lowest unoccupied molecular orbital (LUMO) of the adsorbed molecule. It is, thus, natural to speculate that the three-leaf clover pattern with a center bright spot for the C_{60} molecule adsorbate in the present experiment be correlated with the LUMO-induced states of the C_{60} molecule adsorbate.

STM is the ideal technique to observe and investigate the local electronic states of solid. Hashizume et al.⁹⁾ recently investigated the film growth of C_{60} adsorbate on the Cu(111)1x1 surface and reported interesting STM image contrast variations as a function of the bias voltage (Fig. 4) and interpreted them successfully in terms of the intramolecular electronic structures of the C_{60} adsorbate. The three-leaf clover like contrast (Fig. 4a), which is similar to the present FIM image, was interpreted as the LUMO-induced states, localized at pentagonal rings. The similar observation was also made by Wang et al. in the case of the C_{70} adsorbate on the Cu(111)1x1 surface.²⁰⁾ We suggest, based on this similarity in the image features, that the FIM images of the C_{60} adsorbate also reflect the

LUMO-induced states. Our interpretation appears to be in agreement with the most-recent theory by Tsukada.²¹⁾

However, we note a few significant differences between the FIM and STM images. In the FIM image, we observe an additional bright spot at the center of the three-leaf clover contrast. Also, when the bias voltage is increased, only the center bright spot is observed in FIM. These difference could well be the manifestation of the difference of the substrate material;^{8,9)} tungsten substrate for FIM and copper for STM. Taking the advantage of the hemispherical tip geometry, we can investigate the effect of the crystallographic orientation of the substrate. It does not appear, in the present case, that the contrast of the field ion image of C_{60} depends on the crystallographic orientation of the tungsten tip. The STM study of C_{60} adsorption on Cu(110) and Cu(100) are currently underway. While there are some differences between the FIM and STM images of the C_{60} adsorbate, their overall features are similar, and thus, we propose that the contrast of the FIM image reflects the LUMO-induced empty states of the C_{60} on W. The present FIM observation that the C_{60} adsorbate is stable on the W surface up to the electric field of $\sim 4.5\text{V}/\text{\AA}$ suggests that the binding energy between the C_{60} and W is rather strong due most likely to charge transfer from the W surface and additional large dipole-induced adsorption mechanism. Our STM study of the film growth of the C_{60} on the Cu(111) surface also showed that the monolayer C_{60} is strongly bound to the substrate and can be desorbed only upon heating at 600°C , while the C_{60} multiple layer film desorbs at 300°C .⁹⁾

The present FIM results can be briefly summarized as follows: 1) The C_{60} molecules can be imaged by FIM as a molecular adsorbate on tungsten tip surface, 2) At low electric fields (below the He best image field), individual molecules are imaged as large (up to 10\AA in diameter) and diffuse spots, together with the sharp and clear W ledge atom, 3) The image contrast reflects the LUMO-induced empty electronic states of the C_{60} molecule, 4) When the molecules field-evaporate, they evaporate as a molecule not atom-by-atom. These conclusions are in marked contrast with the recent claim by Ohmae et al.¹⁰⁾ that the individual C atoms making up the C_{60} molecule can be imaged and field-evaporate separately. We plan to resolve the

discrepancy between their and our FIM results using the atom-probe FIM, since we suspect that the spots observed by Ohmae et al. are artifacts.

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