

## PHOTON EMISSION FROM C<sub>60</sub> IN A NANOSCOPIC CAVITY

R. BERNDT

*Institut de Physique Expérimentale  
Université de Lausanne  
1015 Lausanne  
Switzerland*

AND

J. K. GIMZEWSKI

*IBM Research Division  
Zurich Research Laboratory  
8803 Rüschlikon  
Switzerland*

**Abstract.** We discuss properties of C<sub>60</sub> in an STM tunnel junction probed by elastic and inelastic tunneling. In particular, the interaction of the molecule with the metallic nanoscopic cavity comprised of tip and sample is considered. Molecular resolution in photon emission from C<sub>60</sub> monolayers is interpreted in these terms, and we address the extent to which photon emission from C<sub>60</sub> reflects properties of the cavity and of the molecule itself. We propose that the properties of C<sub>60</sub> in such an environment are further modified with respect to its adsorbed state on a surface.

The fascinating observation that photons are emitted from the tunnel junction region of a scanning tunneling microscope (STM) has stimulated experimental and theoretical interest [1]. Our understanding of the processes underlying emission for semiconductors is based on concepts similar to those known from conventional cathodoluminescence [2, 3]. In the case of metals, inelastic tunneling and local electromagnetic modes that are confined between tip and sample (tip-induced plasmons (TIP) modes) are involved in photon emission [1, 4, 5]. In the case of molecular systems, only recently has evidence for localized emission from individual molecules been obtained for C<sub>60</sub> measured in ultrahigh vacuum conditions at low temperatures [6, 7]. In those experiments, molecules separated by a lateral distance of  $\sim 1$  Å have been resolved. These results differ from recent reports of the observation of isolated molecules with a near-field optical microscope which resolved molecules or clusters thereof separated by large lateral dimensions [8]. More recently yet, "atomic" resolution has been observed on clean metallic surfaces using photon emission from an STM [5].

In this paper we summarize key observations which strongly suggest that in the extreme geometry of an STM tunneling junction, molecular properties are strongly modified. In particular, we propose that the enhanced electromagnetic field in the cavity of tip and sample due to TIP modes amplifies photon emission from individual molecules.

The electronic properties of C<sub>60</sub> are strongly influenced when the molecule is in close proximity to a metal surface. For C<sub>60</sub> adsorbed on Au(110), molecules in the first monolayer show a shift of their lowest occupied molecular orbitals down towards the Fermi energy  $E_F$  as shown by tunneling spectroscopy. Quite different properties have been reported for molecules in the second layer [9]. Similarly, the proximity of the STM tip above C<sub>60</sub> can also induce further shifts as well as a broadening and mixing of molecular orbitals. Consequently, it is expected that the electronic properties of a molecule in a nanoscopic metallic cavity are different from those of a free molecule or one adsorbed on a metallic surface. [6].

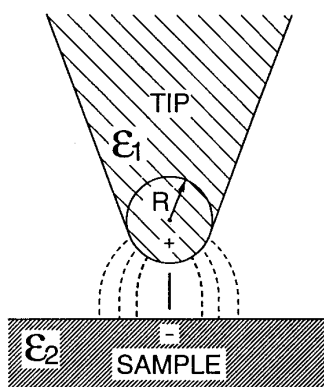
Whereas STM images predominantly reflect the elastic tunneling current, the process of photon emission in STM using metallic tips and substrates is dominated by inelastic tunneling. This inelastic tunneling is determined by the electromagnetic field strengths of the TIP modes [4, 5] as shown in Fig.1.

Conceptually, the introduction of a molecule into this cavity has several implications:

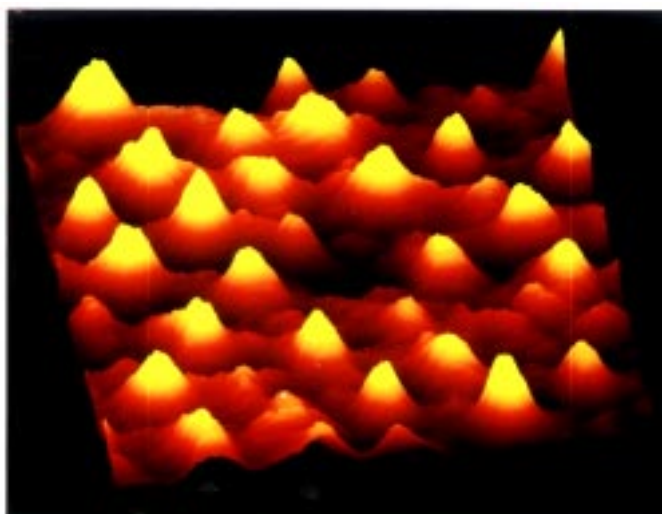
1. The electronic structure of the surface is affected.
2. The electronic structure of the molecule is strongly perturbed as discussed above.
3. The distance from the tip to the surface is increased by the presence of  $C_{60}$ .
4. The electromagnetic modes and hence the inelastic tunneling probability are modified.

Figure 2 displays a molecularly resolved photon emission map of  $C_{60}$  on Au(110). Below we address the extent to which the emission and the molecular resolution observed in Fig. 2 are related to TIP modes or to the molecules themselves.

On Au(110) surfaces,  $C_{60}$  appears as a protrusion of typically 4-5 Å, and molecular structure within these protrusions has been observed [10].



**Figure 1.** Schematic diagram of a tip-induced plasmon mode. Plus and minus signs represent a snapshot of the oscillating electron density of this approximately dipolar mode. The mode is affected by geometric parameters (distance of tip and sample, tip geometry represented by a radius) and the dielectric functions of tip and sample.



**Figure 2.** Photon intensity map of a  $C_{60}$  monolayer on a Au(110) single-crystal surface. Individual molecules separated by  $\sim 10$  Å are clearly resolved.

Calculations show that  $C_{60}$  increases the elastic tunneling by approximately six orders of magnitude compared to the equivalent junction without  $C_{60}$  [11]. This goes beyond a mere modification of the metallic density of states as predicted and observed for small adsorbates on metals [12, 13]. Hence the molecule plays an active and determining role in the elastic tunneling current. This strongly suggests that the inelastic tunneling channels are also dominated by molecular properties. The inelastic tunneling and subsequent photon emission from TIP modes on a clean Au surface is strongly distance-dependent [5]. This factor reduces emission from such a mode on  $C_{60}$ -covered areas and, similarly, hints that there is a molecular source of the photon emission. The observation that the detected emission is most intense when the STM tip is centered above a molecule provides further evidence of an active role of the molecule [6].

It is therefore unlikely that the observation of molecular resolution in photon emission from  $C_{60}$  on Au(110) shown in Fig. 2 is directly related to a tip-Au TIP mode. Instead, the emission involves the  $C_{60}$  molecules. Conventional molecular fluorescence from molecules is, however, strongly damped by their proximity to metal surfaces [14]. Little is known, however, about the properties of molecules stressed by their interactions in a nanoscopic cavity. However, one dramatic manifestation of their unusual behavior in such an environment is the surface-enhanced Raman effect (SERS) [14], in which the Raman signal from molecules in nanoscopic metallic cavities is increased by several orders of magnitude. An important contribution to this enhancement is made by the increased electromagnetic field in these cavities [14]. It should be noted that the explanation of SERS also involves charge transfer between the molecules and the surface [14]. In the present case of  $C_{60}$  on Au, charge transfer has indeed been observed [15]. We are currently investigating other organic molecular species to assess the generality of these concepts [16].

It is becoming quite clear both for elastic and inelastic tunneling that molecules exhibit radically different properties in nanoscopic cavities such as STM. This may partially explain why molecules such as hydrocarbons, which are insulators, can be imaged with STM [17]. Our observations of photon emission clearly resolved at the molecular level from  $C_{60}$  species separated by  $\sim 10$  Å provide persuasive evidence that new inelastic tunneling channels are opened, as are the elastic ones by new properties induced by the environment of the STM experiment. This has important implications. Significant changes can be induced in molecules by the proximity of a tip. As a consequence, the functionality of a molecule may be altered as well, analogous to changes in functionality by chemical modifications.

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