The Influence of surfaces and interfaces on the properties of C60 compounds
Hesper, Ronald

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Chapter 5

Image-charge screening the Coulomb interaction

Abstract

Using a combination of photoelectron and inverse photoelectron spectroscopy, we show that the band gap in a monolayer of C\textsubscript{60} on a Ag surface is strongly reduced from the solid C\textsubscript{60} surface value. We argue that this is a result of the reduction of the on-site molecular Coulomb interaction due to the influence of image charges in the metal substrate. This result suggests that the physical properties of correlated insulators and semiconductors will be strongly modified if prepared in ultra thin form on metal substrates or sandwiched between metal layers.\footnote{This chapter was published, in slightly modified form, as R. Hesper, L.H. Tjeng and G.A. Sawatzky, Strongly reduced band gap in a correlated insulator in close proximity to a metal, Europhys. Lett. 40, 177 (1997)}

5.1 Introduction

About a decade ago Duffy and Stoneham [1] predicted that the on-site Coulomb interaction, defined in an open-shell system as the ionization potential ($E_I$) minus the electron affinity ($E_A$), often referred to as the Hubbard $U$, will be strongly reduced in the proximity of a metal. This is easily understood by looking at Fig. 1, in which the creation of a positive (negative) charge is accompanied effectively by the simultaneous creation of a negative (positive) image charge in the metal which in turn reduces the ionization potential and increases the electron affinity each by $\frac{1}{2}e^2/2D$, where $D$ is the distance between the surface and the created charge. This results in a change of $U$ to $U = U_0 - e^2/2D$. It is
straightforward to infer from this that the conductivity gap in insulators or semiconductors in which the on-site Coulomb interaction plays an important role will be correspondingly reduced. For example, one could expect that the correlation gap in Mott-Hubbard systems would be strongly reduced at the insulator-metal interface, perhaps even driving the insulator into the metallic state. One can also easily see that for magnetic insulators, described by an effective half-filled band Hubbard model, the interatomic exchange interaction given in that model by $t^2/U$ will be strongly enhanced at the interface with a metal because of the reduction of $U$. This leads us to believe that the physical properties of correlated insulators could be dramatically different in close proximity to a metal.

In a concerted effort to study these effects, we have investigated the electronic structure of monolayer films of C$_{60}$ on metal surfaces and find indeed a strong reduction of the band gap. It is generally accepted that the on-site Coulomb interaction on the C$_{60}$ molecule contributes at least 1 eV to the total conductivity gap in solid C$_{60}$ [2–4]. The Coulomb interaction and the gap are smaller than in the gas phase since the free-molecule ionization potential and electron affinity are respectively reduced and enhanced due to the polarizability of the surrounding C$_{60}$ molecules, as recently worked out in detail by Rotenberg et al. [5]. Upon replacing part of the polarizable C$_{60}$ surroundings by a more strongly polarizable medium like a metal, we expect a further reduction of the ionization potential and increase of the electron affinity driving the system closer to a conventional semiconductor.

We have chosen for C$_{60}$ as a model system because of its well-understood electronic structure [6] and to forego the usual complications of, e.g., oxide films, where the interatomic distance and hence the distance to the image plane are of the order of the Fermi wavelength of the metal. For the metal substrate we use a Ag(111) surface, for the following reasons: (a) the electronic structures of the Ag metal [7, 8] is very simple, (b) hybridizational and charge transfer effects between the low density Ag sp-band and the C$_{60}$ molecular orbitals are
limited [9], (c) epitaxial growth of C\textsubscript{60} on Ag(111) is well documented [10, 11], and (d) a procedure has been found to produce exactly one single C\textsubscript{60} layer on this surface, as discussed in Chapter 3. We use photoemission (PES) and inverse photoemission (IPES) to measure the valence and conduction bands of the C\textsubscript{60} overlayer, and by comparing them to those of the surface layer of a C\textsubscript{60} solid, we can reveal the influence of the metallic screening on the properties of the C\textsubscript{60}. The properties of the overlayer and the surface layer can be easily distinguished from those of the underlying material since the experimental techniques have a probing depth of essentially not more than one C\textsubscript{60} layer, as we already saw in Chapters 3 and 4.

5.2 Experimental

The in-situ preparation of a monolayer of C\textsubscript{60} on a clean Ag(111) surface in UHV following a distillation procedure is described in detail in Chapter 3. To obtain a sample of solid C\textsubscript{60}, we have evaporated a few hundred Ångström of C\textsubscript{60} on the Ag substrate. The experiments were carried out in a combined PES/IPES spectrometer with a base pressure better than 2 × 10\textsuperscript{-10} mbar. PES spectra are taken with He-I radiation (hν = 21.2 eV), and the IPES spectra with E\textsubscript{kin} = 16.7 eV electrons vs. the Fermi level. A standard correction for the He-I satellite (1.3%) has been applied. The overall resolution is 0.1 eV and 0.5 eV respectively, and the Fermi level is calibrated using the clean Ag sample.

5.3 Results and Discussion

Figure 5.2 shows the valence band PES spectra (solid lines) and conduction band IPES spectra (dots with solid lines as guide to the eye) of a single C\textsubscript{60} monolayer on Ag(111) (upper panel) and of the surface layer of solid C\textsubscript{60} (lower panel). From the figure it can be seen that the peak-to-peak gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is 2.2 eV for the C\textsubscript{60} monolayer on Ag(111). To compare, we find 3.3 eV for the peak-to-peak gap of the surface layer of solid C\textsubscript{60}, which is in rather good agreement with earlier results (3.5 eV [2]). Apparently, a strong reduction of the band gap of a C\textsubscript{60} layer can be achieved if one replaces the underlying solid C\textsubscript{60} by a metallic substrate. This is even more remarkable if one considers also the fact that apart from a slight hybridizational broadening (and the reduced band gap), the spectra of the monolayer are identical to those of the solid surface. In other words, with the separate occupied and unoccupied C\textsubscript{60} molecular orbital structures hardly affected by the metal, we arrive at the surprising observation
Figure 5.2: Combined photoemission (solid lines) and inverse photoemission (dots with solid lines as guide to the eye) spectra of the C$_{60}$ monolayer on Ag(111) (upper panel) and the surface layer of solid C$_{60}$ (lower panel). Also included are the photoemission spectra (dashed lines) of the fully doped C$_{60}$ ("K$_6$C$_{60}$") monolayer on Ag(111) and the surface layer of solid K$_6$C$_{60}$. The on-bucky-ball Coulomb energy (U) is given by the difference between the HOMO-LUMO band gap in the undoped systems and the HOMO-LUMO molecular-orbital splitting (Δ) in the fully doped systems. The spectra show the strong reduction of the HOMO-LUMO band gap and the Coulomb energy in the presence of the metallic substrate.
5.3. Results and Discussion

that the strong band gap reduction is essentially rigid-band like.

We can try to get an understanding of this reduction of the band gap by considering the possible differences in screening mechanisms in solid C$_{60}$ and on Ag metal. It has been shown before [2,5] that the screening of excitations in solid C$_{60}$ is predominantly due to the large polarizability of the C$_{60}$ molecules themselves. As depicted in Fig. 5.3b, this causes a reduction of the ionization potential ($E_I$) and an equal increase of the electron affinity ($E_A$) relative to the gas phase because of the polarizable medium each by approximately $E_p = \frac{1}{2} ze^2 \alpha / R^4$, where $\alpha$ is the molecular polarizability, $R$ the inter-molecular distance and $z$ the coordination number. Gas-phase measurements yield $E_I = 7.6$ eV [13] and $E_A = 2.65$ eV [14], i.e., a gap value of 4.95 eV. With $z = 9$ and a gap value of 3.3 eV for the surface layer of solid C$_{60}$, we estimate that the contribution ($2E_p$) to $U$ per C$_{60}$ nearest neighbour is 0.18 eV. This compares reasonably well with the value (0.13 eV) we get with the above formula for $E_p$ if we take $\alpha = 90$ Å$^3$ [15] and $R = 10$ Å. In going to the monolayer case, three C$_{60}$ molecules are replaced by the Ag substrate, which will increase the gap by about 0.54 eV. However, apparently this can be more than compensated by the strong screening by Ag, since the observed gap is reduced from 3.3 to 2.2 eV. The contribution of the metal to the screening is therefore estimated to be 1.64 eV. Screening effects from a metal as a polarizable medium can be easily understood by using an image potential model [16] as shown in Fig. 5.3a. In this model, $E_I$ of a C$_{60}$ molecule on a metallic substrate will be reduced by $\frac{1}{2} e^2 / 2D$ and $E_A$ increased by an equal amount, so that the HOMO-LUMO gap will be reduced by $e^2 / 2D$, where $D$ is the distance between the surface and the C$_{60}$ molecule centre, which is about 5 Å. The image charge contribution to the screening is then estimated to be 1.44 eV, which is close to the experimental value of 1.64 eV mentioned above.

Figure 5.3: Photoemission and inverse photoemission processes for a monolayer of C$_{60}$ on metal (a) and for the surface of bulk C$_{60}$ (b). In both cases, the final state charges and polarizations of the bucky-balls are indicated.
To investigate the nature of the band gap of the two C\textsubscript{60} systems under study, we have also carried out a photoemission experiment in which we have doped the systems with potassium, evaporated \textit{in-situ} from a thoroughly degassed SAES getter source. Figure 5.2 shows the results for a doping concentration in which the LUMO is completely filled (dashed lines), labelled as K\textsubscript{6}C\textsubscript{60} for the solid surface and “K\textsubscript{6}C\textsubscript{60}” for the monolayer on Ag, where the quotation marks are used to indicate that, although the LUMO contains 6 electrons, the actual K concentration may deviate slightly from 6. With the LUMO now on the photoemission side of the Fermi level, we find that the HOMO-LUMO molecular orbital splitting (\Delta) is about 1.6 eV, both for the C\textsubscript{60} solid surface and the C\textsubscript{60} monolayer on Ag. It is clear that this molecular orbital splitting alone can not explain the magnitude of the band gaps of the two undoped systems. Based on previous work showing that Coulomb interactions are important in solid C\textsubscript{60} [2], we infer that these band gaps are given not only by the HOMO-LUMO molecular orbital splitting (\Delta) but also by the on-site Coulomb energy (U). From Fig. 5.2 we now can deduce that U is about 1.7 eV for the solid surface. In fact, this value corresponds very well with that obtained from Auger measurements on the solid surface of bulk K\textsubscript{6}C\textsubscript{60} (U = 1.5 ± 0.2 eV) [17], providing strong support for our assignments. For the monolayer case, one can find from Fig. 5.2 that U = 0.6 eV. With \Delta being quite insensitive to the chemical environment and also to the charge state of the C\textsubscript{60} molecule [12,18–24], we arrive at the striking result that the reduction of the band gap due to the metallic screening corresponds uniquely to the reduction of U, and that screening of charge excitations such as those which involve Coulomb interactions can be understood quantitatively using the image charge model described above.

The concept of replacing the influence of a metal on the potential of an external charge by an image charge dates back a long time [25]. It has been used to describe many instances of classical electrostatics, electron motion near interfaces, and electron phonon coupling as well. Recent examples include inverse photoemission studies which report the observation of a new type of surface states on clean metal surfaces and identify them as image potential states [26–29]. In the field of metal/metal-oxide interface research, the image charge model has been used to describe the stability of the atomic structure of the interface [30–37]. In addition we expect the electronic structure of correlated ionic insulators to be strongly modified at a metal interface because of the above mentioned screening mechanism. Besides the decreased gap there will be an increase in interactions which involve virtual charge excitations like the exchange and the superexchange. As mentioned in the introduction, modifications of U could have great influence on the physical properties of an overlayer on metal as compared to the bulk material when these properties are to some extent determined by electron correlation. One striking example may be the enhancement of the density of states
5.4 Conclusions

near the Fermi energy in an overlayer with a K$_3$C$_{60}$-like composition that we saw in Chapter 3. If the strong broadening of the bulk K$_3$C$_{60}$ features, as usually seen in photoemission, is ascribed to correlation effects, the observed narrowing of the LUMO-derived band could be caused by the screening of the metal, as spectral weight that has been pushed away from the Fermi level in bulk K$_3$C$_{60}$ is transferred back due to the diminished effective Coulomb interaction. It would be interesting to investigate the possible consequences on the transport properties and the superconducting transition temperature, if the monolayer still is a superconductor.

5.4 Conclusions

The bandgap in a monolayer C$_{60}$ on a Ag(111) surface is dramatically reduced from its C$_{60}$ solid surface value. The rigid-band like narrowing of the gap can be directly related to the weakening of the on-bucky-ball Coulomb interaction, and can be quantitatively explained using a model involving the presence of classical image charges in the Ag substrate. The success of this simple model encourages its use as an efficient method to identify key aspects determining various physical and chemical properties of metal/insulator interfaces, and may facilitate the design and engineering of novel systems in solid surface chemistry.

References

REFERENCES


