Inelastic electron tunneling spectroscopy simulations of single-molecule junctions with covalent Au-C contacts

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Abstract

Alkane chains ending with thiols or amines have been always considered a benchmark systems for studies in the field of molecular electronics [1, 2] since they can be easily functionalized and they form stable and well defined contact to gold electrodes. More recently very high conductance values have been experimentally achieved starting from trimethyl tin ($SnMe_3$)-terminated molecules [3, 4]. In general, one of the main tasks once the junction is physically realized is to verify the real compositional structure of the molecular junction. Recently Cheng et al. [4] demonstrated that trimethyl tin-functionalized alkanes, after loosing the Sn-$(CH_3)_3$ group, can form a direct Au-C bond with the metallic surface. In that condition it was possible to achieve a conductance about 100 times larger than analogous alkane based molecular junctions with other anchoring groups. Here we propose an additional way to verify experimentally the nature of metal/molecule bonding. Inelastic Electron Tunneling Spectroscopy (IETS) allows a unique compositional and structural characterization of nanojunctions since it gives the vibrational fingerprint of molecular adsorbates. So, comparing the IETS of ($SnMe_3$)-terminated chains and that one of alkane directly bonded to gold surface could allow an unambiguous characterization of metal/molecule bonding since the two molecules give qualitatively different spectra. We performed first principles calculation of the IETS of ($SnMe_2$)-terminated hexane (C6Sn) and of the same molecule but directly bonded to the gold surface through a covalent Au-C bond (C6Au) and for different electrodes separations in a regime of elastic deformation. In Fig. 1 a) and b) are shown the C6Au and C6Sn geometries respectively in the less stretched configurations. Structural relaxation of all geometries was done with the DFT code Siesta [5] while for the calculation of phonon modes and IETS the Inelastica package [6, 7] was used. For both kind of molecules the IETS present the typical peaks of alkane chains. Nevertheless, in the case of ($SnMe_2$)-terminated hexane, at low energies the CH_3 groups give a strong inelastic signal which is not present in the case of the pure hexane chain with direct Au-C bond [Fig. 1 c)]. This peak allows to easily distinguish the two types of molecule and verify the presence of a direct bond of alkane with gold surface.

References

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Figures

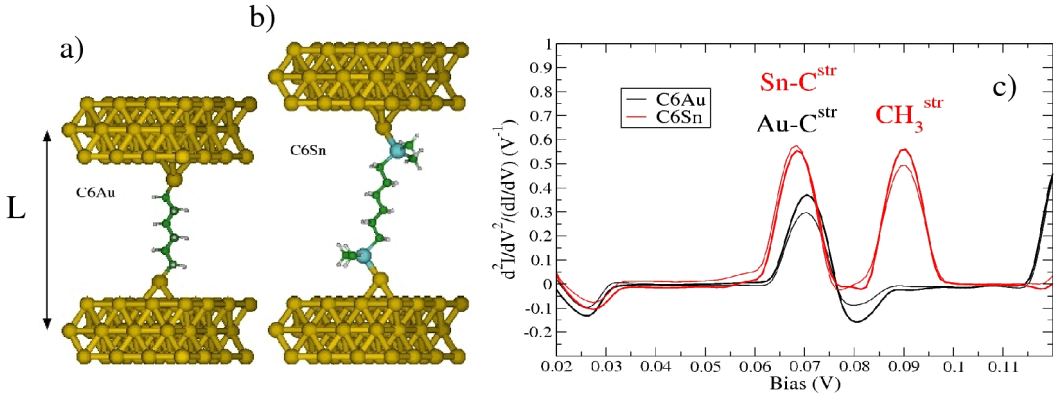

Figure 1

a) C6Au and b) C6Sn geometries in the less stretched configuration. In c) is shown the low energy part of the IETS for the two geometries. Thick line represents the signal at negative bias. At 90 meV the methyl groups give a strong signal (red curve) which is not present in the case of C6Au.