Electron-phonon couplings at C_{60} interfaces studied by doubly resonant infrared-visible sum-frequency generation spectroscopy

Y. Caudano, C. Silien, C. Humbert, L. Dreesen, A. A. Mani, A. Peremans, and P. A. Thiry
Laboratoire de Spectroscopie Moléculaire de Surface,
Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles, 61, B-5000 Namur, Belgium

The very symmetric C_{60} molecule constitutes a remarkable model system for studying electron-phonon couplings at interfaces. Indeed, despite its size, the molecule possesses a simple vibrational spectrum, that comprises only four infrared-active ($4\ T_{1u}$) and 10 Raman-active ($2\ A_g + 8\ H_g$) modes. Pure C_{60} is a semiconductor having an electronic band gap of about 2.2 eV. The lowest unoccupied molecular orbital (LUMO) can accept up to six electrons as it is of t_{1u} symmetry. In the fullerides, the LUMO is filled gradually with electrons from intercalated alkali donors (K, Rb,…). The electronic properties of these materials are strongly affected by electron-phonon couplings, and superconductivity occurs in many A_3C_{60} compounds (up to 29 K for Rb_3C_{60}). Electron transfer to C_{60} arises also from adsorption on metallic surfaces (1, 2). The interface vibrational spectrum is strongly sensitive to the fullerene charge state (2), which is tunable by alkali doping (3). Phonon couplings to the LUMO of C_{60}, in particular, can be examined specifically by surface vibrational spectroscopy (4).

Infrared-visible sum-frequency generation spectroscopy (SFG) probes selectively surfaces and interfaces of centrosymmetric media. It relies on a second-order nonlinear optical process. Two laser beams, a visible one at ω_{vis} and an infrared one at ω_{IR}, are focused at the probed interface, and a third beam generated at the sum-frequency $\omega_{SFG} = \omega_{vis} + \omega_{IR}$ is analyzed as a function of ω_{IR}. Resonant enhancement of the SFG intensity is observed when ω_{IR} matches the frequency of a vibration that is both IR and Raman active. In this respect, SFG provides a vibrational fingerprint of the interface. Two-color SFG allows to scan ω_{vis} as well, so that electronic transitions can be examined. Doubly resonant SFG (DR-SFG) occurs when the SFG signal is enhanced simultaneously by coupled vibrational and electronic transitions. In the case of materials with inversion symmetry, DR-SFG probes thus specifically interfacial electron-phonon couplings. Recently, the first studies of electronic transitions in metals and molecules by two color and DR-SFG spectroscopies were reported (5–9).

We developed a complete two-color SFG set-up with which we investigated electron-phonon couplings at C_{60}/metal interfaces and, in particular, at the C_{60}/Ag(111) interface. In principle, the symmetry of C_{60} forbids the detection of its vibrations by SFG. However, the Raman-active $A_g(2)$ pentagonal pinch mode gains large IR and SFG activities at these interfaces, due to an interfacial dynamic charge transfer resulting from the $A_g(2)$ coupling to the t_{1u} LUMO (5). Using two-color SFG, we detected a huge enhancement of the nonlinear response of the totally symmetric $A_g(2)$ vibration for sum-frequency energies above the molecular electronic gap (FIG. 1), showing the mode coupling to electronic transitions. We attribute this resonance to the coupling of the pentagonal pinch mode with the t_{1u} lowest unoccupied molecular orbital (LUMO) of C_{60}. The coupled electronic transition is in the range of 2.5 to 2.7 eV. The occurrence of DR-SFG explains the very strong intensity of the $A_g(2)$ vibration measured previously by SFG at the single visible wavelength of 532 nm, very close to the maximum of the electronic resonance.

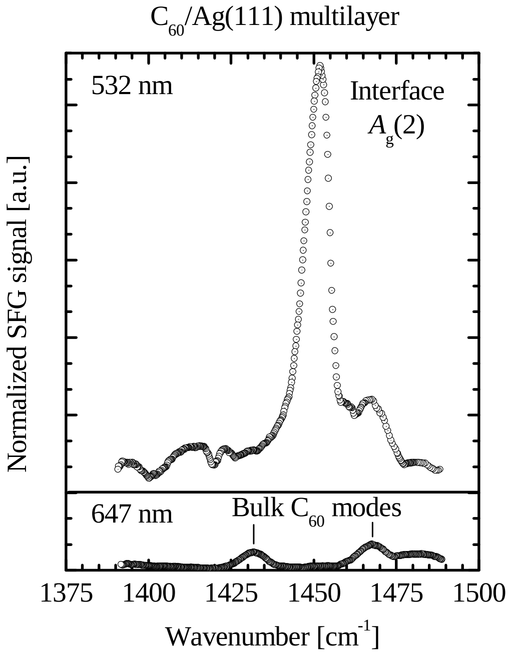

FIGURE 1: SFG spectra of a C_{60} multilayer on Ag(111) for 532 and 647 visible wavelengths, showing the occurrence of DR-SFG for the $A_g(2)$ mode at the C_{60}/Ag(111) interface.

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