Report for the Short Term Mobility of Dr. Sanja Korica

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Title: Multi-coincidence spectroscopy of Fullerenes
Proponent: Dr. P. Bolognesi (CNR-IMIP)

Since the discovery of the C_{60} molecule in 1985 many studies have been performed to investigate its fundamental properties. These properties are mainly driven by its unique molecular structure like a spherical shell.
One of the important characteristics of this molecule is the collective response of its valence electron cloud to electromagnetic radiation. This collective behavior gives rise to the occurrence of the giant dipole resonance, a surface plasmon in the absorption spectrum centered around 20 eV [1], which has been analyzed theoretically by various authors. In addition, photoionization cross-section measurements reveal a resonance near 40 eV [2], assigned as a volume plasmon analogous to observations made for C_{60} ions. Time-dependent density functional calculations confirm the collective nature of this feature as corresponding to plasmon excitation.

Another example of a physical process dominated by the electron correlations is provided by the photodouble ionization (PDI), where the absorption of a single photon results in the simultaneous ejection of two electrons from the target. The PDI of C_{60} near threshold was studied by Steger et al. [3] using single-photon ionization with synchrotron radiation and time-of-flight mass spectrometry. The ionization potential for double ionization of C_{60} has been determined to be 19.00 ± 0.03 eV from doubly charged ion yield spectra which exhibit a nearly linearly increase as function of photon energy.
The most sensitive benchmark for the various theoretical approaches to the PDI process is the study of the correlated electron emission of the two photoelectrons. However, no experiments and only one theoretical work [4] was reported so far for the study of the PDI in C_{60}.

During the two-weeks of experiments at the Gas Phase beam line of Elettra, we successfully produced a stable vapour beam of C_{60} at an operating temperature of about 470 and 510°C for the bottom and the top parts of the oven. The stability of the oven has been checked daily by measuring the photoemission spectrum of the valence bands (see figure 1).

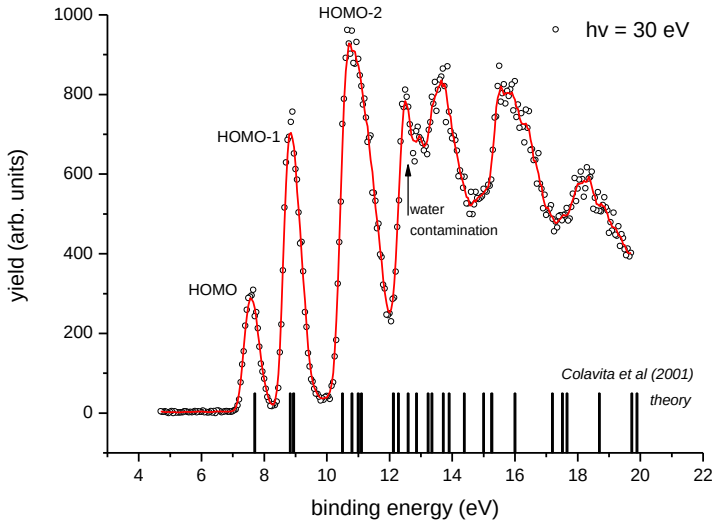

Figure 1.

The photoelectron spectrum of the valence bands of C_{60} measured at an incident photon energy of 30 eV compared to the theoretical predictions of Colavita et al. (2001) [5].

This has allowed us to perform several experiments to study both single and double photoionization of C_{60}.

1) High resolution measurements of the C_{60} photoelectron spectra in the photon energy range from 19.4 to 40 eV. Figures 2 show an example of such high resolution valence spectra recorded at the photon energy of 30 eV for the HOMO and HOMO-1 bands. The seven spectrometers of the multicoincidence set-up cover an angular range of 180°(figure 2.a) and allow for the measurement of the asymmetry parameter. Their integrated counts (figure 2.b), properly corrected by the transmission functions of the analyzers, will provide a measurement of the cross section as a function of energy.

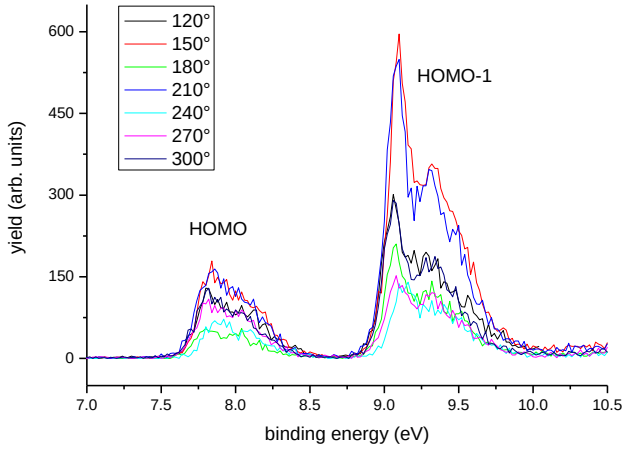

Figure 2.a. The high resolution photoelectron spectrum of the HOMO and HOMO-1 bands of C_{60} measured at 30 eV photon energy by the seven spectrometers of the multicoincidence set-up.

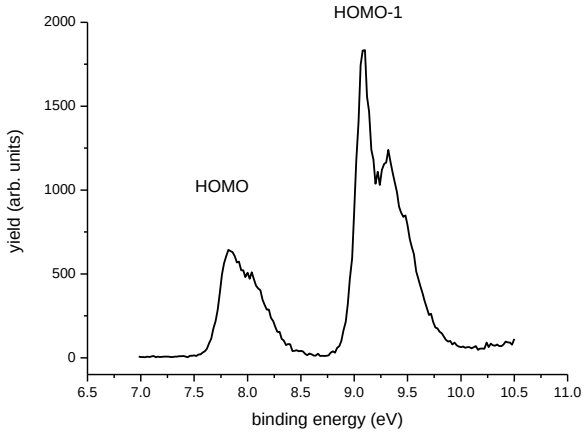

Figure 2.b. High resolution photoelectron spectrum resulting for the sum of the seven spectrometers.

The photoelectron spectrum of C_{60} (figures 1 and 2) is characterized by a number of resolved features and it is in quite satisfactory agreement with LDA calculation [5]. Besides the well-known high energy oscillations in the cross-section ratio between the two outermost bands (HOMO and HOMO-1), which will not be discussed here and can be find elsewhere [6], the most striking feature reported in the theoretical work of Colavita et al. [5] is the presence of very sharp resonances in the photoionization cross-section of different valence molecular orbitals. They are attributed to shape resonances and are related to the peculiar spherical potential well of the C_{60} cage. As a consequence, the asymmetry parameters of these states are as well very structured.

Our results of the angular integrated cross section and asymmetry parameters for the HOMO-1 and HOMO-2 states will be compared with these predictions.

2) Measurement of the triple differential cross-section (TDCS) of C_{60} via the coincident detection of the two electrons emitted in the PDI process at equal energy sharing (E_1=E_2=10.5 eV) and several angles of ejection of the fixed electron (θ_1=0, 30, 60°). The binding energy spectrum of C_{60}^{2+} measured by these photoelectron-photoelectron coincidence (PEPECO) experiments is reported in figure 3. As it can be noted, the highest intensity is achieved at binding energies far above the opening of the C_{60}^{2+} threshold, i.e. at about 30 eV binding energy. Such behavior seems to resemble the density of doubly charged ion states measured by Auger spectroscopy [7] and its full understating is still matter of investigation.

A detailed analysis of the TDCS results is in progress. It is expected that the highly symmetric structure of this molecule strongly affects the two electron correlated dynamics. Such information, that was not available from the previous measurements of Steger *et al*. [3] and Reinköster *et al*. [8], will provide the first PDI measurement in C_{60}.

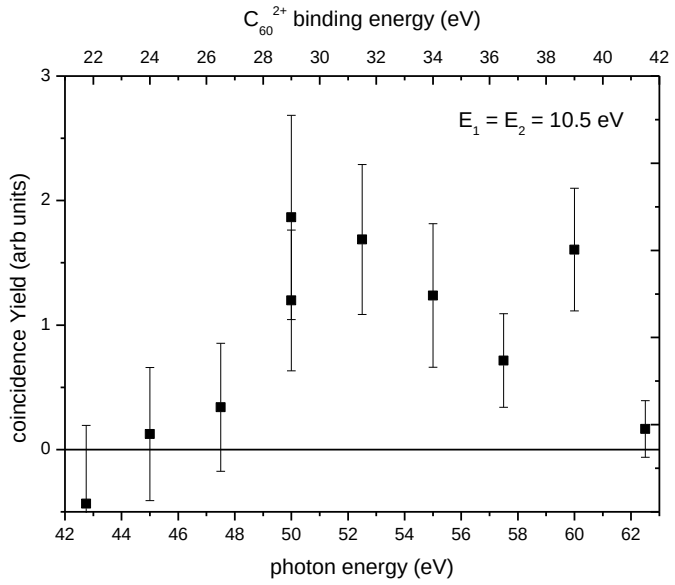

Figure 3.

C_{60}^{2+} binding energy spectrum measured by the PEPECO experiments in equal energy sharing condition. The present spectrum has been achieved by integrating over all directions of the two electrons detected by the multicoincidence set-up.

The C_{60}^{2+} binding energy scale has been calculated by the following folmula:

$$BE=h\nu-E_1-E_2$$

The spectrum shows its highest intensity at about 10 eV above the double ionization threshold, with no measurable signal (within the detection efficiency of the present spectrometer) in threshold region, i.e. towards ground state of the ion.

References

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