

PHOTOIONIZATION OF C_{60} ENDOHEDRAL ATOMS: DYNAMICAL EFFECTS OF DELOCALIZED CAGE ON THE ATOMIC PHOTOYIELD

Mohamed E. Madjet*, Himadri S. Chakraborty[†] and Jan-Michael Rost[‡]

*Freie Universitaet, Institut für Chemie (Kristallographie), Takustrasse 6, D-14195 Berlin, Germany

[†]James R. Macdonald Laboratory and Department of Physics

Kansas State University, Manhattan, Kansas 66506-2604, USA

[‡]Max Planck Institut für Physik Komplexer Systeme, Nöthnitzer Strasse 38, 01187 Dresden, Germany

One of the most intriguing properties of the the fullerene molecule is the stable hollow-cage structure, which raises the interesting possibility of preparing compounds where atoms or molecules are trapped inside forming endohedral complexes[1]. Experimentally, structures and microscopic properties of endohedral fullerenes are studied by various methods including photoelectron and electron scattering spectroscopy. Therefore, it becomes a matter of practical importance to asses the influence of electronically delocalized fullerene cage on the photodynamical behavior of the confined atom.

We consider C_{60} fullerene because of its highly symmetric nearly spherical shape, that renders the calculation relatively simple. As a prototype of alkaline-earth metallic C_{60} compounds we consider $Mg@C_{60}$, for which there is little electron transfer from the atom to the cage. We describe C_{60} by assuming four valence electrons of each carbon atom to be delocalized; the residual ionic structure is represented by a classical spherical jellium shell. Kohn-Sham equations for a system of 240 electrons *plus* a central Mg atom are then solved to obtain the ground state orbitals in the local density approximation (LDA), the dipole overlap of which with LDA continuum states provides single electron LDA photoamplitudes. However, in order to include the final-state correlation we employ a time-dependent LDA (TDLDA) methodology[2].

Strong influence of C_{60} cage through a dynamical correlation effect on the valence (3s) photoemission of Mg is discovered in the cross section from the threshold to the region of single excitation Fano resonances. To illustrate, Fig. 1 presents our result for the cross section where TDLDA calculation for $Mg@C_{60}$ (thick solid curve) shows huge enhancement over that of free Mg (thin solid) across the C_{60} plasmon region. In an interchannel coupling perspective,

this is owing to the considerable overlap of several C_{60} orbitals with the delocalized segment of atomic valence orbital. The effect is also reflected in the departure of TDLDA curve for $Mg@C_{60}$ from the corresponding single particle LDA curve (thick dashed), which *entirely* omits the correlation effect from the interchannel coupling.

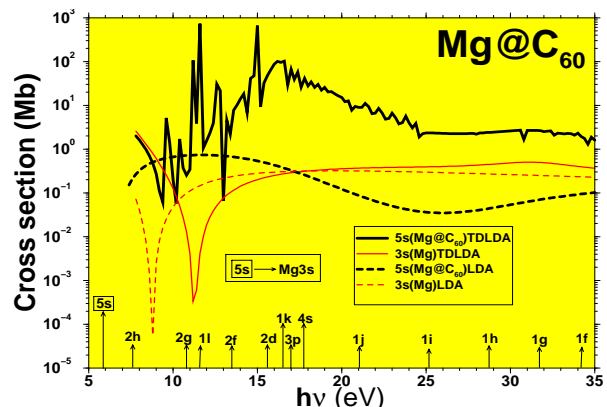


Fig. 1. Free and caged Mg valence cross section in LDA and TDLDA; the ionization thresholds are indicated.

Our most current studies on noble gas atoms $@C_{60}$ indicate similar trends, where for subshells with non-zero angular momentum the angular distribution asymmetry parameter is also found considerably influenced. We thus conclude that while the atomic structural alteration due to confinement is minimal, the dynamical effect of delocalized cage on the photoyield from the atom is rather profound.

References

- [1] J.R. Heath et al., J. Am. Chem. Soc. **107**, 7779 (1985).
- [2] P.-A. Hervieux, M.E. Madjet, and H. Benali, Phys. Rev. A **65**, 023202 (2002).