

Photoionization of open-shell halogen atoms endohedrally confined in C₆₀

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Synopsis Dipole photoionization of atomically open-shell halogen-endofullerenes Cl,Br,I@C₆₀ are calculated using time-dependent local density functional theory and a spherical potential model. Hybridization of the valence *np* orbital of the atom with a C₆₀ *p* orbital is found to strongly modify the ionization parameters.

Endofullerene molecules, formed by encapsulating atoms in fullerenes, are extremely stable form of nanoscopic matters that can exist even at room temperature. Since these entrapments have lower-cost sustenance than the laser cooling or magneto-optical trapping processes, endofullerenes are unique natural laboratories to study not only the greatly modified properties of the confined atomic system but also the confining fullerene. Notable effects include the electronic hybridization between guest-host systems [1] and strong spectral processes, such as, the plasmon excitations and quantum diffraction intrinsic to response of these molecules [2].

A number of studies have been conducted for endofullerenes involving closed shell atoms, while there have been little research on systems that confine open shell atoms. In this study, using a jellium-based local density approximation (LDA) method [1], augmented by the LB94 exchange-correlation functional [3], we model the ground state of endofullerenes encaging three halogen atoms, Cl, Br and I, which are one *np* electron shy of the shell closure. Strong atom-C₆₀ hybridization in the *np* levels is found which, however, shows a systematic weakening trend from Cl to I.

The dipole photoionization cross sections of these hybrid levels are calculated in a time-dependent LDA which includes linear response electron correlations [3]. Results for Cl@C₆₀ are presented in Figure 1. The narrow spikes in the cross sections are routine resonances from the Auger-type decay of inner-shell excitations. Comparing with the free atom *3p* result, the cross sections for the bonding and antibonding hybrid levels broadly display two energy regions: (i) plasmon-enhanced low-energy domain and (ii) broad oscillations from the coherence of cavity and confinement effects at higher energies. However, even within this generic shape, results reveal significant differences in

the details of the results between the hybrid levels. While the bonding level features stronger effects of the plasmons and a strong atomic character at higher energies, the antibonding ionization dramatically diminishes at higher energies suggesting dominant C₆₀ emission.

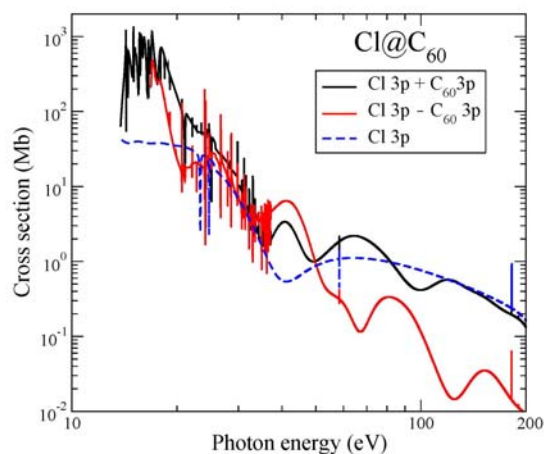


Figure 1. TDLDA cross sections of the two hybrid levels of Cl@C₆₀ and the *3p* level of free Cl.

Furthermore, detailed comparison of these results with those from Ar,Kr,Xe@C₆₀, which involve the nearby close-shell atoms in the periodic table, provides deeper insights into the role of a single shell-closing electron to noticeably influence the ionization dynamics.

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References

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