Ultrafast electronic response and charge transfer at surfaces

Fulvio Parmigiani[1], Matteo Montagnese[2], Stefania Pagliara[2], Gianluca Galimberti [2], Gabriele Ferrini[2]

[1] *Physics Department, University of Trieste and Sincrotrone Trieste (Italy)*
[2] *Department of Mathematics and Physics, Catholic University, Brescia (Italy)*

In these last decades it has been demonstrated that the optical properties of semiconductors near the electronic bandgap are dominated by excitons and their residual interactions, producing many-body effects, such as band-gap renormalization (BGR) [1], and nonlinear optical mechanisms. In particular, a deep insight has been gained on understanding the BGR in semiconductors by means of time-resolved non-linear optical spectroscopy in the femtosecond time-domain [2]. However, in semi-metallic and gap-less systems the response to strong photoexcitations is still unclear, and the studies of the dynamics and interactions of quasiparticles have been only marginal. Graphite is an interesting and intriguing material for, at least, three reasons: i) its low-dimensional, inherently inhomogeneous character; ii) its peculiar, semimetal electronic structure, constituted of optically-active π-orbital networks, characterized by a unusual topology and vanishing density of states at the Fermi surface, combined with the presence of singular points in the density of states of empty and occupied bands. iii) It is optically active in the visible and near-UV range, allowing the photoinjection of high carrier densities in the π bands. Starting from these considerations we focus our experiments on measuring, by non-linear angle resolved photoemission, the effective mass and linewidth of the IPS in highly oriented pyrolitic graphite (HOPG) sample excited by 100 fs laser pulses. By tuning the photon energy across the π-bands saddle points, located at the M point of the Brillouin Zone (BZ), i.e. the van Hove singularity (vHs), we photo-inject a high carriers density ($2 \cdot 10^{20} cm^{-3}$) in the outermost graphene layers. Here, by showing the strong correlation among the IPS electron effective mass, the IPS total fullwidth and the IPS emission intensity versus the photon energy we reveal the electron dynamics and the band renormalization effects governing the correlated interactions of the unoccupied states in graphite. On the basis of these observations we formulate a consistent self-energy model that connects by causality, via Kramers-Kronig transforms, the IPS effective mass with the IPS total fullwidth, predicting a transient bands energy renormalization mechanism consistent with the experimental observations.

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