Electron dynamics in unoccupied states of spatially aligned 7a-Graphene nanoribbons on Au(788)

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Narrow 7-armchair graphene nanoribbons (7a-GNRs) develop a band gap of up to several electron volts. Growing the nanoribbons from 10,10'-dibromo-9,9'-bianthryl precursor molecules on high-index single crystals, like Au(788), allows the preparation of spatially aligned nanoribbons with a width of about 0.74 nm and a mean length of about 23 nm. This in turn permits the study of momentum-resolved electron dynamics by angle-resolved measurements along the axes of the nanoribbons [1]. Employing UPS and IPE the bandgap was determined to about E_g ~ (2.8 ± 0.3) eV. Time-resolved photoelectron spectroscopy on such 7-aGNRs on Au(788) was carried out under ultra-high vacuum conditions utilizing a time-of-flight electron spectrometer and a multi-anode detector. The sample was excited by the frequency doubled output of a femtosecond Ti:sapphire laser amplifier at λ = 395 nm (hv = 3.1 eV). Recompressing the pulses in a quartz prism compressor yields pulse durations below 30 fs. With this set-up we identified two unoccupied states at energies of E_1 = 0.6 eV and E_2 = 3.7 eV above the Fermi energy, respectively. The energetic positions of these states are in agreement with IPE measurements we performed previously on this system [1].

From the dependence of the signal on the polarization of the incident light we found that the second state at 3.7 eV obeys a strict selection rule, indicating π-symmetry of the state. The electronic dynamics in the state can then be measured by time-resolved 3-photon photoemission spectroscopy with cross-polarized laser pulses.

Preliminary evaluation of these measurements indicates an electronic lifetime of the unoccupied state of τ ~ 70 fs. The dispersion of the involved states for $k_{||}$ = [-0.44, 0.3] $Å^{-1}$ along the ribbon axis will also be discussed as well as its influence on the electronic lifetime of the excited state.

References:
[1] S. Linden et al., Phys. Rev. Lett. **108**, 216801 (2012)