Title:	Electronic Rearrangement in Molecular Plasmons: An Electron Density and Electrostatic Potential-Based Study
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Abstract:	Plasmonic modes in single-molecule systems have been previously identified by scaling two-electron interactions in calculating excitation energies. Analysis of transition dipole moments for states of polyacenes based on configuration interaction is another method for characterising molecular plasmons. The principal features in the electronic absorption spectra of polyacenes are a low-intensity, lower-in-energy peak and a high-intensity, higher-in-energy peak. From calculations using time-dependent density functional theory with the B3LYP/cc-pVTZ basis set, both these peaks are found to result from the same set of electronic transitions, that is, HOMO−n to LUMO and HOMO to LUMO+n, where n varies as the number of fused rings increases. In this work, the excited states of polyacenes, naphthalene through pentacene, are analysed using electron densities and molecular electrostatic potential (MESP) topography. Compared to other excited states the bright and dark plasmonic states involve the least electron rearrangement. Quantitatively, the MESP topography indicates that the variance in MESP values and the displacement in MESP minima positions, calculated with respect to the ground state, are lowest for plasmonic states. The excited-state electronic density profiles and electrostatic potential topographies suggest the least electron rearrangement for the plasmonic states. Conversely, high electron rearrangement characterises a single-particle excitation. The molecular plasmon can be called an excited state most similar to the ground state in terms of one-electron properties. This is found to be true for silver (Ag6) and sodium (Na8) linear chains as well.
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