Optical Distinction and Photoinduced Phase Transition between Degenerate Ground States of Polyacene

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Polyacene oligomers, consisting of an aromatic linear array, have been attracting much interest due to their electronic multifunctionality such as field-effect transistors and light-emitting diodes. The synthesis of grapheme nanoribbons has further stimulated a renewed interest in polyacene as a basic building unit of them. Aside from such modern microelectronics, polyacene has been theoretically investigated for several decades and there lies the longstanding problem of whether and how the Peierls distortion occurs. Two types of structural instability are possible in polyacene: double bonds in a *cis* [in-phase (IP)] pattern and those in a *trans* [out-of-phase (OP)] pattern. Considerable effort has been devoted to predicting which structure is energetically preferable—*cis*-distorted, *trans*-distorted, or uniform.

In such circumstances, we first demonstrate the two Peierls-distorted states are indeed almost degenerate in their energetics but quite distinct in their optics. Calculating the polarized optical conductivity spectra within and beyond the Hartree-Fock scheme, we reveal a striking contrast between the *cis* and *trans* configurations. Second we simulate photopumping of these ground states and visualize the following lattice dynamics. Photoinduced phase transitions from the *trans* to *cis* configurations are observed but reverse transitions seem to be much less feasible (Fig. 1).

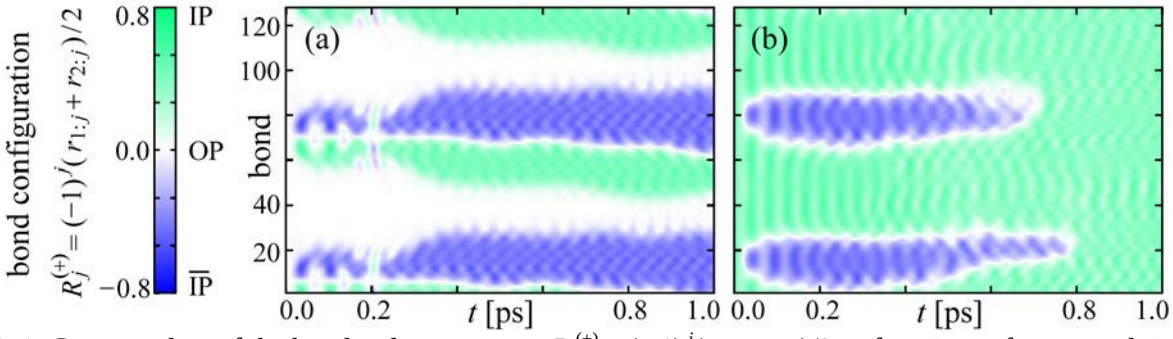

FIG. 1. Contour plots of the bond order parameter $R_j^{(+)}=(-1)^j(r_{1:j}+r_{2:j})/2$ as functions of space and time for polyacene, where $r_{l:j}$ is the distortion of the jth bond on the lth leg. At $t=0$ four electrons are pumped up against a background of the *trans* (a) and *cis* (b) configurations.