Photoinduced Structural Phase Transitions in Polyacene

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Polyacene oligomers—linear polybenzenoid hydrocarbons—have been attracting much interest due to their electronic multifunctionality such as field-effect transistors and light-emitting diodes. The synthesis of graphene 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 [2]. In contrast with the Peierls instability in polyacetylene [1], polyacene suffers from structural instability only conditionally. 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 [3].

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 (HF) scheme, we reveal a striking contrast between the *cis* and *trans* configurations [4]. Second, employing a time-dependent HF method [5], we consider photopumping these ground states and visualizing the following lattice dynamics. The *trans* configuration is easily photoconverted into the *cis* one, whereas an opposite transition, if any, is hardly completed. Domain-wall (soliton) excitations play an important role in any photoinduced phase transitions, but charged and neutral ones behave quite differently. (Figure 1).

![Figure 1: Contour plots of an trans-distortion-detectable bond variable, Rj = (-1)^j(r1j - r2j)/2, as functions of space and time for polyacene, where r1j is the distortion of the jth bond on the lth leg. At t = 0 we excite one electron (a), two electrons (b), four electrons without any spin fluctuations (c), and four electrons with local spin fluctuations (d) from the highest occupied molecular orbital(s) [HOMO(s)] to the lowest unoccupied molecular orbital(s) [LUMO(s)].](attachment:figure1.png)

References