

Infrared and Raman spectra of polyparaphenylene dimers in their aromatic and quinoidal forms for the detection of bipolarons in the charge transport of conducting polymer samples. Foerner, Wolfgang; Badawi, Hassan M.. Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia. THEOCHEM (2004), 677(1-3), 179-198.

Abstract

We have calcd. IR and Raman spectra of biphenyl, the arom. A-phase dimer and of a quinoidal B-phase dimer of polyparaphenylene at D. Functional Theory (DFT) level using a Becke-3 exchange and a Lee-Yang-Parr correlation functional (B3LYP). We found in both types of spectra features typical for the two phases, which offer the possibility to detect the presence of a quinoidal chain segment in conducting samples of the polymer. Together with more sophisticated future calcns. on longer oligomers and on higher level of calcn., it should be possible to gauge intensity ratios in the spectra theor. so that bipolarons could be found and their width be estd. spectroscopically. This is due to the fact that usually only within a bipolaron the B-phase is fully formed, which is not the case in a singly charged polaron. Calcns. on neutral model mols., while bipolarons are doubly charged, can be used for the purpose because in bipolarons the two like charges are usually quite localized in the parts of the bipolaron where the phase is changed from A to B on one side of the bipolaron or from B to A on the other side. Further, we found very interesting features useful for bipolaron detection, which are connected with mostly intra-ring motions of the atoms and thus the use of dimers, as model seems to be justified. For example, the Raman spectra of the B-phase show lines ten times more intense than the arom. phase, which are due to ring breathing and ring deformations. To obtain quant. informations about the at. motions involved in each line in the spectra, in addn. the Potential Energy Distribution of each normal mode among symmetry coordinates was calcd.