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The singlet excited states of N-acenes (N=0-5): A CASSCF/CASPT2 study of the L_a and L_b bands

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The electronic properties of polyacenes (PACs, Figure 1) are not only a very attractive for material science, but they can also serve as a model system for studying the properties of ground and excited states of extended π systems by means of theoretical methods[1].

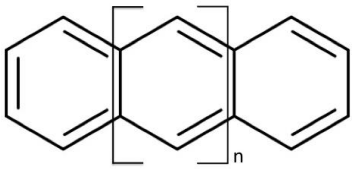

Figure 1. Structure of studied acenes (n=0-5).

In this work[1], MCSCF/CASPT2/6-31G* calculations of the polyacenes from naphthalene (n=0) to heptacene (n=5) the L_a (B_{2u} state) and L_b (B_{3u} state) bands were performed using different schemes to investigate the effect of the active space extension and the freezing of σ orbitals. Considering that acenes has D_{2h} molecular symmetry, the smaller active space consist by the CAS(8,8) which contain one virtual and one occupied orbital of each π symmetry. Larger active spaces were chosen based on the MR-AQCC occupation numbers, been the largest one CAS(14,14). Three freezing scheme were used: DOCC (all σ orbitals freeze); 2s (2s σ orbitals freeze) and 1s (1s σ orbitals freeze). A multi-configurational character of the wavefunction was found for the first excited state (B_{3u}), resulting from a linear combination of HOMO-1 → LUMO and HOMO → LUMO+1 configurations. For the second excited state (B_{2u}), the wavefunction corresponds almost exclusively to a HOMO → LUMO excitation. These investigations show quite different requirements for the two states to be described. In the valence bond formalism, the L_a state is of ionic character; it is sensitive to the

freezing scheme of the σ-orbitals but does not require an extended active space. On the other hand, the covalent L_b state requires a large active space but is not sensitive to the freezing scheme within the σ-space, i.e to the extent of dynamic correlation. To obtain a balanced description of both states, an active space containing 14 electrons in 14 orbitals and only the 1s orbitals frozen proved to be adequate to provide a balanced description of the L_a and L_b states and very good agreement with experimental absorption energies.

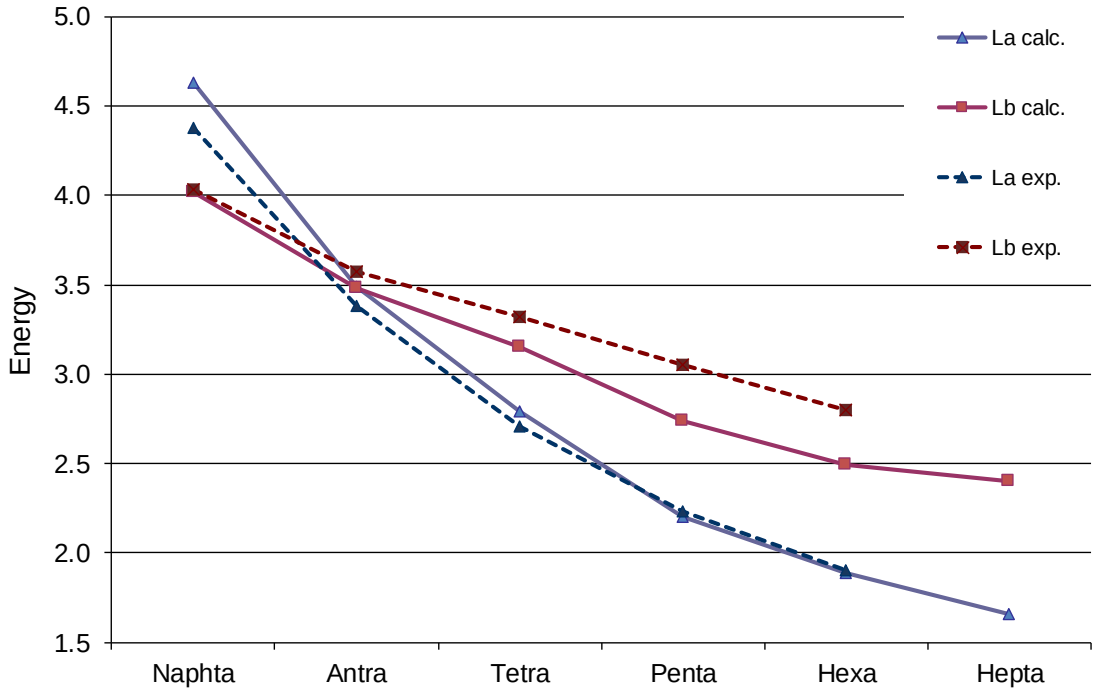

Figure 2. The CASPT2 excitation energies of L_a (1^1B_{2u}) and Lb (1^1B_{3u}) band calculated for the polyacenes series using CAS(14,14)(1s) active space and experimental[2]

Key-words: Acenes, excited states, absorption spectra, CASPT2.
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References:

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[2] Biermann, D.; Schmidt, W. Diels-Alder. *J. Am. Chem. Soc.* **1980**, *102*, 3163–3173