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 \( \pi \) systems by means of theoretical methods\(^1\).

![Figure 1. Structure of studied acenes (n=0-5).](image)

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 \( \sigma \) 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 \( \pi \) 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 \( \sigma \) orbitals freeze); 2s (2s \( \sigma \) orbitals freeze) and 1s (1s \( \sigma \) 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 $\sigma$-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 $\sigma$-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 $L_b$ (1$^1B_{3u}$) band calculated for the polyacenes series using CAS(14,14)$^{(1s)}$ active space and experimental energies.

Key-words: Acenes, excited states, absorption spectra, CASPT2.
Support: This work has been supported by CNPq, CAPES, FAPESP.
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