

# Evaluation of the Nonlinear Optical Properties for Annulenes with Hückel and Möbius Topologies

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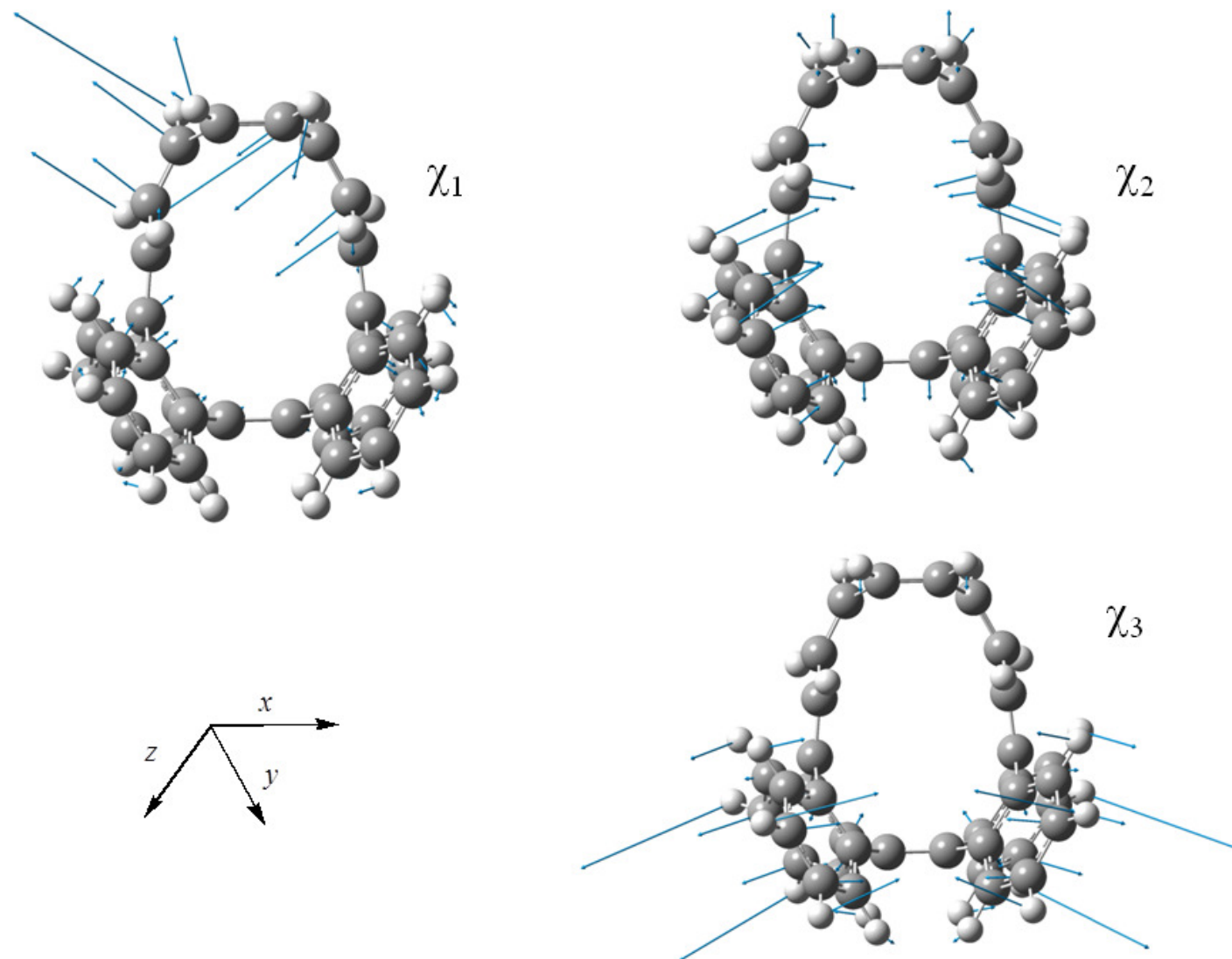
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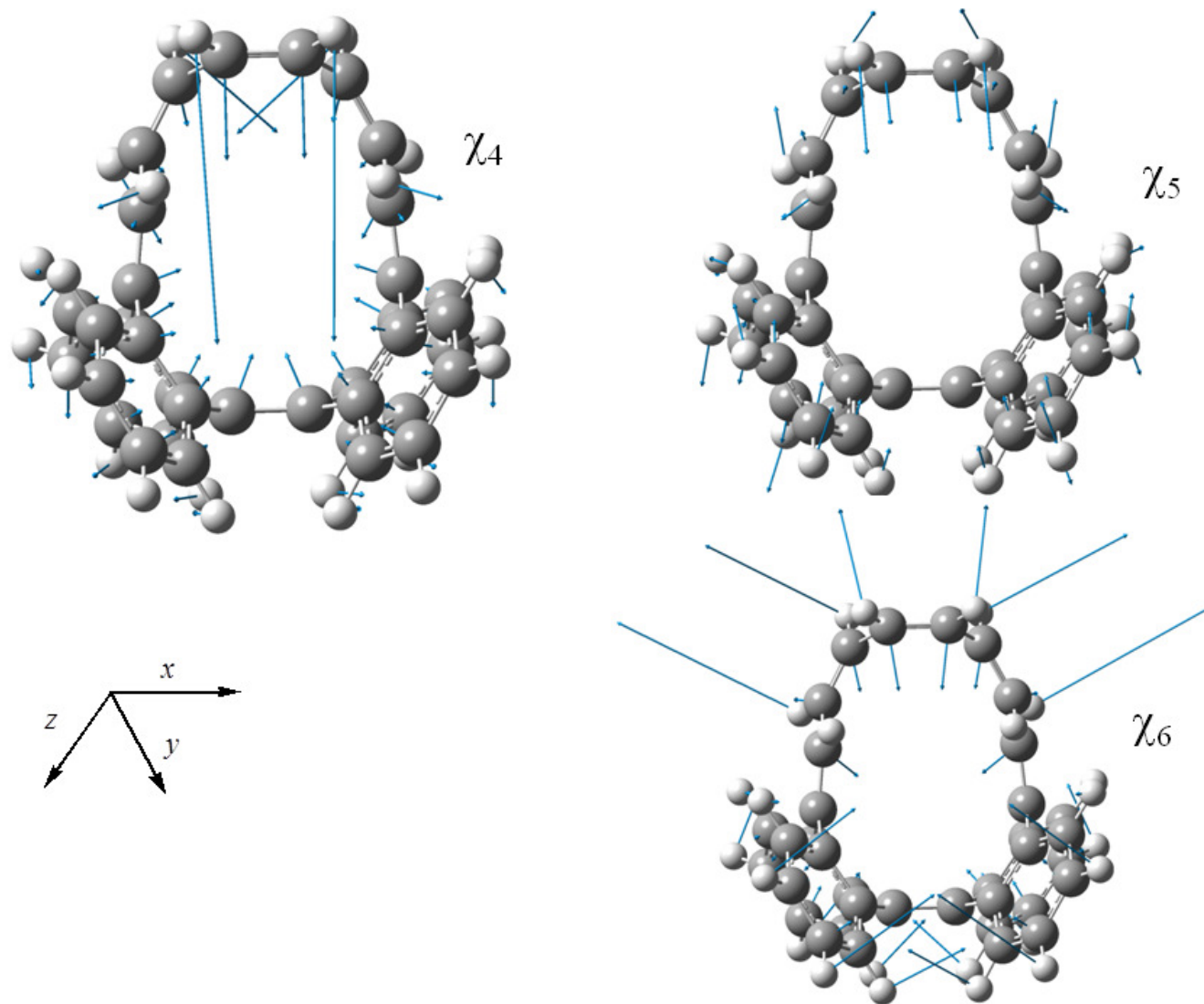
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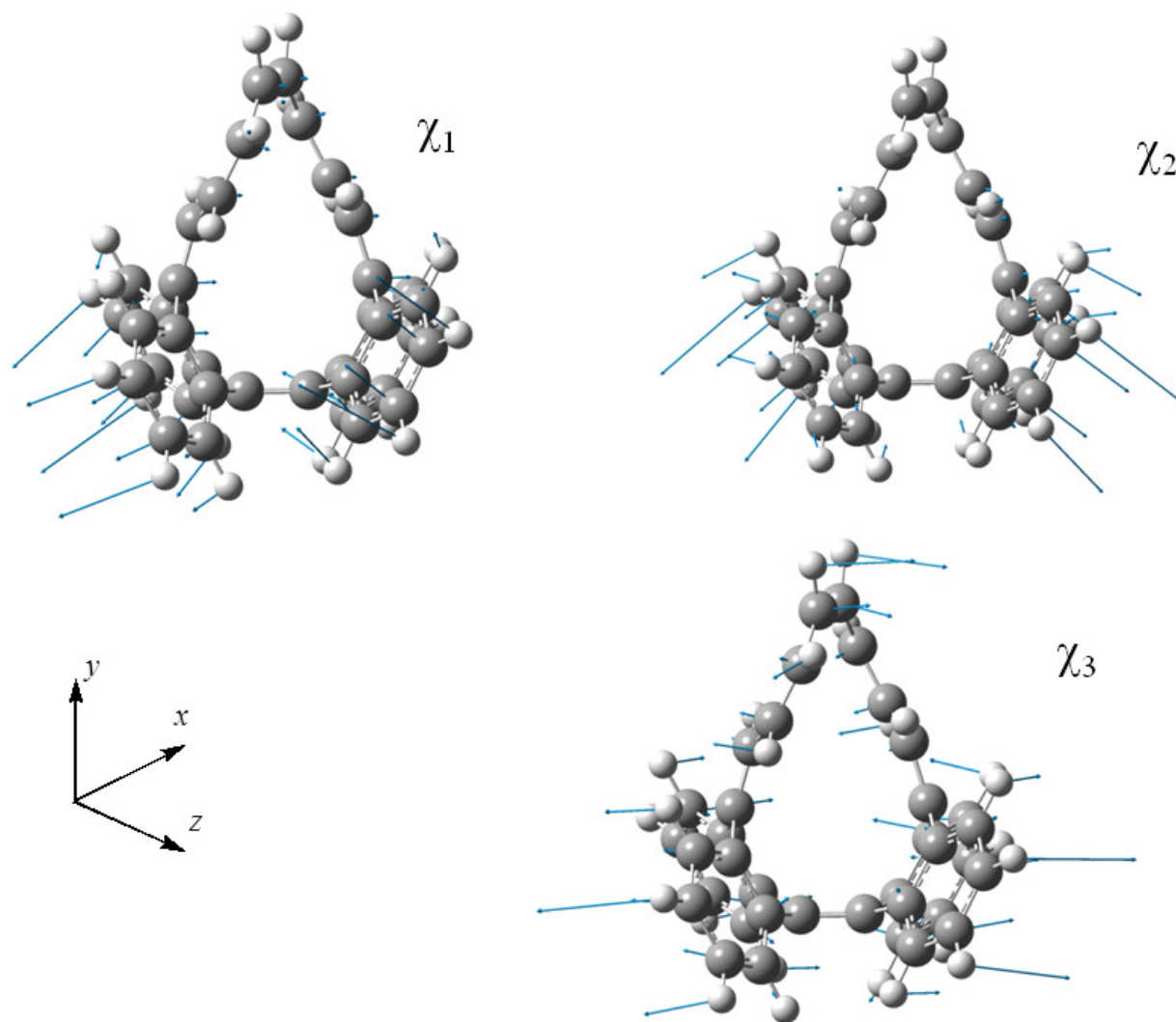
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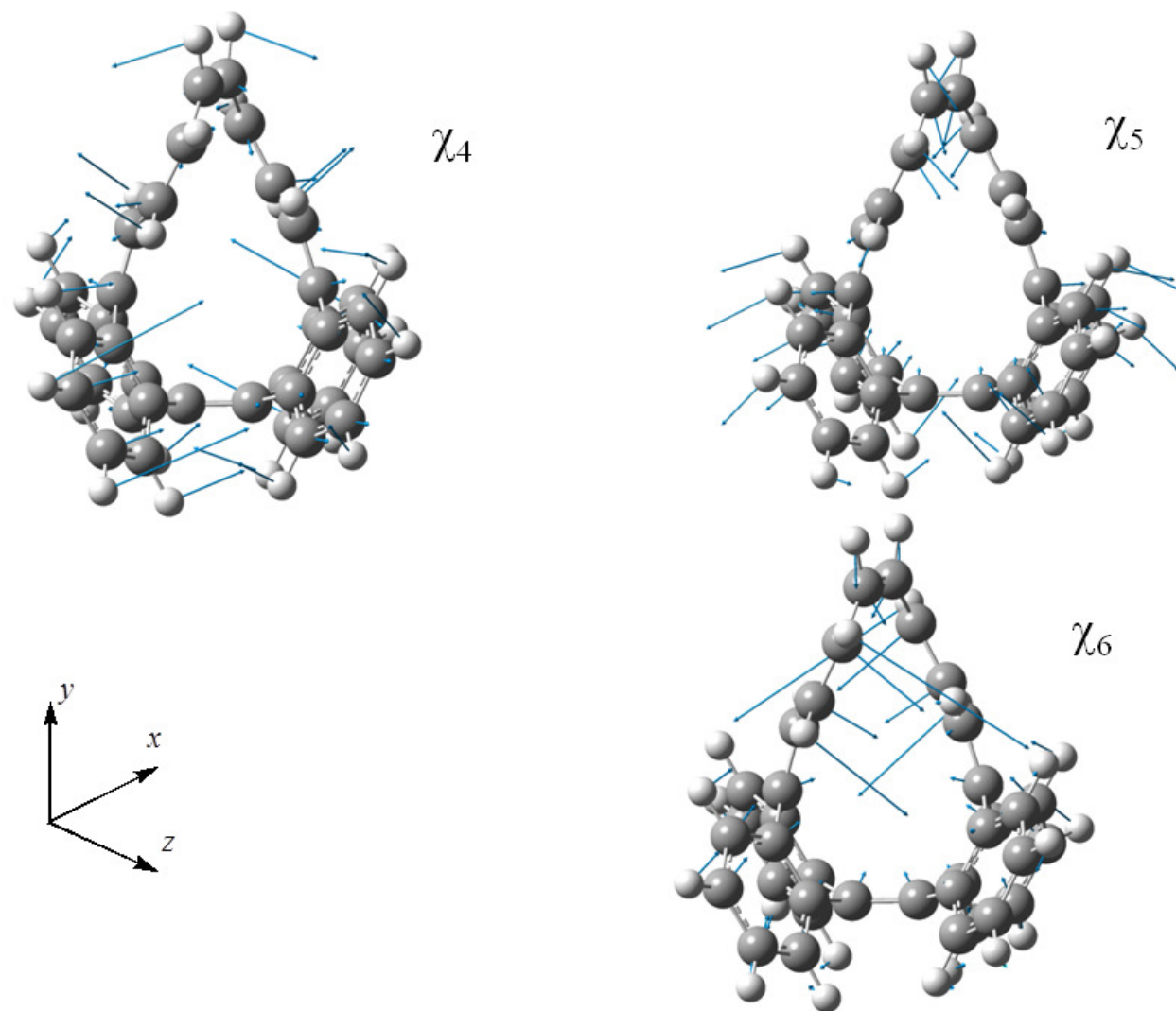
**Figure I.** Representations of the no mass-weighted orthonormal  $\chi_1$ ,  $\chi_2$ , and  $\chi_3$  of the Hückel conformation evaluated at CAM-B3LYP/6-31+G(d) level studied in this work.



**Figure II.** Representations of the no mass-weighted orthonormal  $\chi_4$ ,  $\chi_5$ , and  $\chi_6$  of the Hückel conformation evaluated at CAM-B3LYP/6-31+G(d) level studied in this work.



**Figure III.** Representations of the no mass-weighted orthonormal  $\chi_1$ ,  $\chi_2$ , and  $\chi_3$  of the Möbius conformation evaluated at CAM-B3LYP/6-31+G(d) level studied in this work.



**Figure IV.** Representations of the no mass-weighted orthonormal  $\chi_4$ ,  $\chi_5$ , and  $\chi_6$  of the Möbius conformation evaluated at CAM-B3LYP/6-31+G(d) level studied in this work.

## 1) DISCUSSION

The Figures I-IV contain the no mass-weighted orthonormal first and harmonic second-order static field-induced vibrational coordinates (FICs). The FICs are just the displacement coordinates derived from the change in the equilibrium geometry induced by a static applied field. The great advantage of the FICs is that they “concentrate” the information of the total the nuclear relaxation contribution, which contains sums over  $3N-6$  normal coordinates, in a few nuclear coordinates.

The FICs of the Hückel and Möbius conformations cannot be compared between them one by one because  $\chi_1, \chi_2, \chi_3, \chi_4, \chi_5,$  and  $\chi_6$  are the result of an orthogonalization process. However, analyzing the whole sets one can see that both sets of 6 vectors show some similarities and differences that can be discussed. For instance, the FICS plotted in the Figures 1-4 can be divided in two groups: a) displacements which imply the movement of atoms from the [16] annulene; b) displacements which mainly imply the movement of atoms of the benzenes attached to the annulene structure. In the Hückel conformation only  $\chi_3$  matches to the group b), whereas  $\chi_1, \chi_2, \chi_4, \chi_5,$  and  $\chi_6$  can be considered from the group a). In the Möbius topology  $\chi_3, \chi_4, \chi_5,$  and  $\chi_6$  can be considered from the group a), while  $\chi_1$  and  $\chi_2$  match to the group b). Then, the movement of the [16] annulene has a more important role in the nuclear relaxation contribution for the Hückel conformation than its counterpart for the Möbius structure. On the contrary, the FICS of the Möbius topology give more relevance to the movement of the attached benzenes. As a whole these differences lead to a set of FICs that causes a major *flexibility* of the Hückel than the Mobius ring, which could explain than the values of IOF approximation for NR Kerr and IDRI effects are larger for the Hückel conformation than the Möbius one.