Revisiting Cyclobutadiene: Insights from Valence Bond Theory under the Quantum Interference Perspective

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INTRODUCTION

Cyclobutadiene is one of the most intriguing systems in chemistry. For many decades it has been the focus of a great diversity of experimental and theoretical studies. Despite its apparently simple electronic structure, interesting and unexpected features were identified since the early works. Although it is widely accepted that the majority of its peculiar properties are due to a combination between electronic (antiaromaticity?) and structural (high angular strain) effects, their relative contributions and origin are still subjects of research.[1]

METHODS

The Generalized Product Function Energy Partitioning (GPF-EP) method[2-6] has been applied for the description of the cyclobutadiene molecule. The influence of quasi-classical and quantum interference contributions on each chemical bond of the system were analyzed along the automerization reaction coordinate for the lowest singlet and triplet states. In the GPF-EP ansatz, the total energy of the system can be separated as follows:

$$E[tot] = E[ref] + E[x] + E[I] + E[II] \qquad (1)$$

where E[ref] is the total reference energy, E[I] and E[II] are the first and second-order interference energies respectively, and E[x] is the total intergroup exchange energy, which arises from the antisymmetrization of the GPF wave function.

RESULTS AND DISCUSSION

The results show that the interference effect reduces the electronic energy of the singlet cyclobutadiene relative to the second-order Jahn-Teller distortion, which takes the molecule from a D_{4h} to a D_{2h} structure. Our results also suggest that the π space of the $^1B_{1g}$ state of the square cyclobutadiene is composed of a weak 4c-4e bond, while the $^3A_{2g}$ state has a 4c-2e π bond (Figure 1). Finally, we also show that, although strain effects are non-negligible, the thermodynamics of the main decomposition pathway of cyclobutadiene in the gas-phase is dominated by the π space interference.

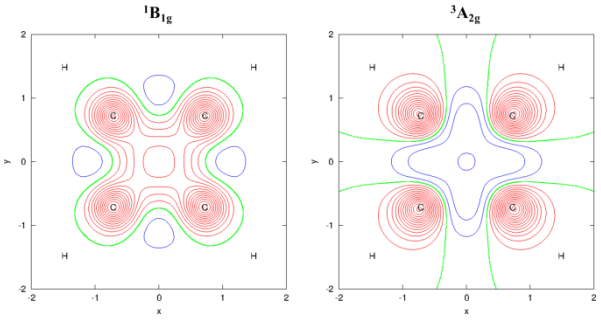

Figure 1.Interference density profile of the π space of singlet and triplet cyclobutadiene.

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