



Photophysics of barrelene: The Jahn-Teller and pseudo-Jahn-Teller effects



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ABSTRACT

The static and dynamic aspects of Jahn-Teller(JT) and pseudo-Jahn-Teller(PJT) interactions between ground (\tilde{X}^2A_2) and first three excited electronic states (\tilde{A}^2E' , \tilde{B}^2E'' and \tilde{C}^2A_1) of bicyclo-[2,2,2]-octa-2,5,7-triene (barrelene) radical cation (BI^+) are theoretically investigated here. This belongs to the $(E + E) \otimes e$ and $(E + A) \otimes e$ JT-PJT class of compounds as described by the symmetry of the electronic states and the molecular point group. The complex vibronic dynamics on the coupled electronic states of the cation is simulated by both time-independent and time-dependent wave packet propagation method using multi configuration time-dependent Hartree scheme. The JT effects in the \tilde{A} and \tilde{B} electronic states and the PJT coupling between the \tilde{B} and \tilde{C} electronic states of BI^+ are found very strong. The final theoretical results are compared with the experimental results.

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1. Introduction

Barrelene (bicyclo-[2,2,2]-octa-2,5,7-triene) (BI) is an archetypal Möbius and strained organic hydrocarbon [1]. It has three concentric and non-conjugated π – bonds which are localized on three vinylic moieties and interact through space and through bonds [2–4]. It has been a fascinating system with intriguing photochemical and photophysical properties [5–7]. This contains the required structural moiety to undergo a di- π methane rearrangement to cyclooctatetraene [8]. Repulsions among these π – orbitals result into a large strain in this molecule which is reflected in the low value of its ionization potential [9] and low value of the heat of hydrogenation [10]. Photoelectron spectroscopy has been used as an indigenous tool to understand the special electronic effects associated with the π – orbitals in BI and related compounds [11]. It was found that the s character of the σ – frame increases linearly with the increasing number of π – bonds in the system [11]. As a result the onset of the σ bond shifts to the higher energy and the lowest bands in the photoelectron spectrum are formed by π – orbitals [11]. The molecular orbital (MO) sequence of the BI molecule (calculated at the second-order Møller-Plesset perturbation (MP2)/cc-pVDZ level of theory) at its D_{3h} equilibrium symmetry configuration reads ... $(6a'_1)^2(3e'')^4(5e')^4(1a'_2)^2$. The nature of these MOs are shown schematically in Fig. 1. The highest

occupied MO (HOMO(−0.29245 a.u)) is a'_2 which is of π – type. This is a single MO of its kind in BI in which the interactions between the π – orbitals of the adjacent C atoms are of bonding type and results into three double bond formation. The pairwise interactions between the π – orbitals of three double bonds are antibonding type giving rise to strain in the molecule. The next MO (HOMO-1(−0.36464 a.u)) of e' symmetry is also π type (cf., Fig. 1) and doubly degenerate. HOMO-2(−0.46233) is also a degenerate MO of e' symmetry but is of σ – type. The next MO (HOMO-3(−0.47431 a.u)) is also σ – type and a nondegenerate MO of a'_1 symmetry.

One electron ionization from each of the above MOs (in the order discussed above) yields barrelene radical cation (BI^+) in its electronic ground \tilde{X}^2A_2 and excited \tilde{A}^2E' , \tilde{B}^2E'' and \tilde{C}^2A_1 (here after will be designated as \tilde{X} , \tilde{A} , \tilde{B} and \tilde{C}) states. Vibronic structures of these electronic states have been studied in a photoelectron spectroscopy experiment [11]. The vibronic bands span over ~ 8–13 eV ionization energy range reveal both resolved and broad features. The best resolved feature of the first band (in the ionization energy range 8–9 eV) is attributed to the \tilde{X} state of BI^+ has been assigned to be formed by a symmetric vibrational (~ 570 cm^{-1}) mode. In particular, structure of this band has been discussed in detail (aided by the best theoretical calculations possible in those days) in connection with “through space” interaction of the π – MOs leading to strain in BI as indicated in the other experiments [10] stated above. An overall contraction of the molecular cage from \tilde{X}^1A_1 state of BI to the \tilde{X} state of BI^+ is estimated. This contraction implies a reduced antibonding interactions between the π – MOs of

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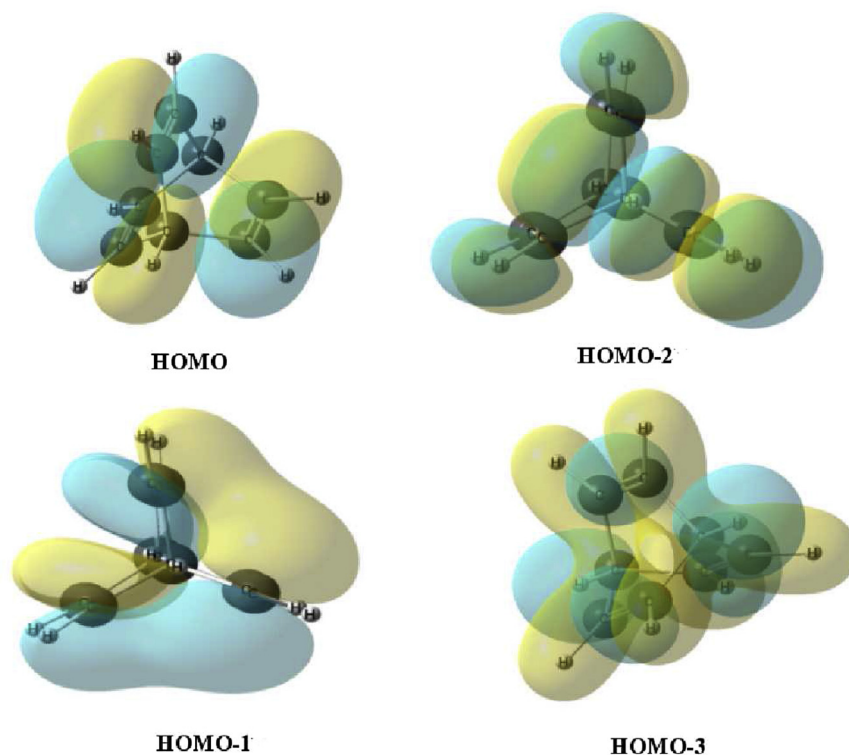


Fig. 1. The schematic diagram of the valence canonical molecular orbitals of barrelene molecule.

Bl^+ and provides an evidence that Bl is a strained system. While the first band of Bl^+ is qualitatively understood to some extent, the next two bands originating from the degenerate e' and e'' MOs, respectively, lack such understanding. Dominant progressions of a $\sim 420 \text{ cm}^{-1}$ vibrational mode is estimated for the \tilde{A} band originating from the e' MO of Bl. This band reveals a bimodal intensity profile which is reminiscent of similar systems prone to Jahn-Teller (JT) distortions [11–16]. Both the \tilde{A} and \tilde{B} states of Bl^+ belong to this category and the interpretation of their spectral features requires to take account of the JT interactions [12–16] within the degenerate electronic states. Apart from this the involvement of the nondegenerate electronic states \tilde{X} and \tilde{C} may also trigger a pseudo-Jahn-Teller type of interaction with the degenerate \tilde{A} and \tilde{B} states, provided it is permitted by the symmetry rules and there exists a coupling vibrational mode of appropriate symmetry.

Let us therefore examine the symmetry rules as applicable in this specific case. The 42 vibrational modes of Bl decompose into $6a'_1 + a'_2 + 7e' + 2a''_1 + 5a''_2 + 7e''$ irreducible representations (IRREPs) of the D_{3h} symmetry point group (The symmetry representations of the electronic states and the vibrational modes are given in the upper-, lower-case symbols, respectively, throughout this paper). The symmetrized direct product of two E' or E'' representations in the D_{3h} point group in first-order yields [17],

$$(E')^2 = (E'')^2 = a'_1 + e'. \quad (1)$$

Similarly, the direct products of the electronic states of different symmetry in the D_{3h} symmetry point group yields

$$\begin{aligned} A'_2 \otimes E' &= e' \\ A'_2 \otimes E'' &= e'' \\ E' \otimes A'_1 &= e' \\ E'' \otimes A'_1 &= e'' \\ E' \otimes E'' &= a''_1 + a''_2 + e'' \end{aligned} \quad (2)$$

The symmetry selection rules stated above reveal that the degenerate e' vibrational modes can split the degeneracy of the E' and E'' electronic manifold (in first-order) and can lead to $(E \otimes e)$ -JT effects. The same vibrational modes can also cause PJT coupling between the \tilde{X} – \tilde{A} and \tilde{A} – \tilde{C} electronic states. The e'' vibrational modes are the PJT active modes between the \tilde{X} – \tilde{B} , \tilde{A} – \tilde{B} and \tilde{B} – \tilde{C} electronic states. The a'_2 , a''_1 and a''_2 vibrational modes can be PJT active modes between the \tilde{A} – \tilde{B} electronic states. The totally symmetric a'_1 vibrational modes are condon active in all the electronic states.

In order to look into the specific details of the recorded photoionization bands (three lowest) of Bl we attempt a detail theoretical study here by performing electronic structure calculations and the simulation of nuclear dynamics. As well-known the involvement of the excited electronic states of polyatomic molecules lead to curve-crossings and conical intersections (CIs) of different types [18–20] which finally decide the fate of the nuclear motion on these electronic states. A diabatic electronic basis has always been useful to avoid the singular nature of the nonadiabatic coupling terms of the adiabatic electronic basis [21–25]. Because the divergent derivative coupling terms of the adiabatic electronic basis are a headache for the computational treatment of the nuclear dynamics, on the exact or near degeneracy of electronic PESs. An alternative electronic representation, the so called diabatic (or quasi-diabatic) representation, which avoids singular coupling elements present in the adiabatic electronic basis. The diabatic electronic states are obtained by a unitary transformation of the adiabatic electronic states within an affordable subspace. This transformation is picked to deliver the electronic states in the relevant subspace smoothly varying as a function of the nuclear coordinates, such that the derivative coupling term are sufficiently small to be neglected. In this representation, the electronic Hamiltonian becomes non diagonal. Therefore, in the following we resort to a diabatic electronic representation [21–25]. First we construct a vibronic Hamiltonian

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