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“Towards experimental determination of conical intersection properties: Twin State model and Comparison with bound excited states”

Appendices

Appendix A: A resumé of the frequency "exaltation" effect

(This is a brief summary of the effect. The interested reader is referred to previous papers.)

The purpose of the model, called the Kekulé'-crossing model, is to provide a logical physical basis for the apparently unusual behavior of Kekulé'-type vibrational modes in the 1^1B_{2u} excited state of benzene (the frequency exaltation), discovered by two-photon spectroscopy¹ and subsequently observed in many other aromatic hydrocarbons². It was considered for years as a spectroscopic “anomaly”, as in most molecules, and also in other benzene modes of the 1^1B_{2u} state, the frequencies of electronic excited states tend to be smaller than in the ground state due to weaker bonding.. The model is based on the idea that the electronic ground state (1^1A_{1g}) and the first 1^1B_{2u} excited state may be considered to a realistic approximation as twin states, arising from in- and out-of-phase combinations of the same two Kekulé structures³. The Kekulé crossing model is used to account for other ground state properties of these systems, and the observed spectroscopic “anomaly” in fact provides the first direct experimental proof of the dominance of these structures in determining the physical and chemical properties of the ground state of benzene and other aromatic molecules.

The frequency up-shift (also termed exaltation) is well documented and appears to be a general phenomenon. For instance, the frequency of the skeletal mode **1** in the 1^1B_{2u} state of benzene (the ν_{14} mode, 1570 cm^{-1}) is 261 cm^{-1} higher than that of the same mode in the ground 1^1A_{1g} state.¹ It is interesting to note that the assignment of this mode presented unexpected difficulties in the early days of the vibrational spectroscopy of benzene. Extensive valence bond (VB) calculations following the pioneering study of Da Silva et al⁴ show that these two structures give a good quantitative description of the states around the D_{6h} geometry.

¹ L. Wunsch, H.J. Neusser, E.W. Schlag, *Chem. Phys. Lett.*, 1975, **31**, 433.

² S. Shaik, S. Zilberg and Y. Haas, *Acc. Chem. Res.*, 1996, **29**, 211.

³ Y. Haas and S. Zilberg, *J. Amer. Chem. Soc.*, 1995, **117**, 5387.

⁴ E.C. DaSilva, J. Gerratt, D.L. Cooper and M. Raimondi, *J. Chem. Phys.*, 1994, **101**, 3866.

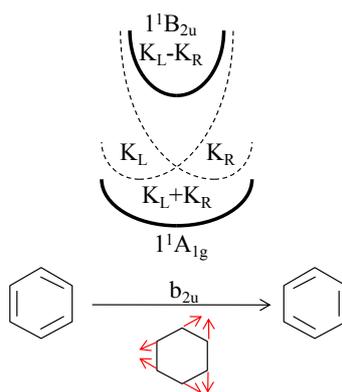


Figure 1. A schematic description of the intended crossing of the potential curves of the two Kekule' structures (K_L and K_R) of benzene along the b_{2u} coordinate alternating these structures, and of the state curves (shown in heavy print) resulting from their avoided crossing.

At the center, D_{6h} symmetry, the avoided crossing results in the ground electronic state 1^1A_{1g} and the 1^1B_{2u} state. Inspection of Figure 1 shows that the potential energy curves of these states may be viewed as consisting of two parts coalescing at the symmetric middle configuration. In the ground state the right hand side is dominated by the K_L structure and the left hand side by the K_R structure. Motion along the b_{2u} coordinate, either to the right or to the left, is accompanied by shortening of the double bonds and lengthening of the single bonds. Thus, the ground state b_{2u} mode acts in harmony with the bonding preference of the Kekule' forms. In contrast, the right hand side of the potential curve of the excited state is dominated by the strained form of K_R , and its left limb by the strained K_L . Consequently, motion along the b_{2u} coordinate starting from the excited D_{6h} structure, must take place in mismatch with the bonding features of the Kekule' structures, since such motion leads to stretching of the double bonds while simultaneously compressing the single bonds. Physically, this situation is manifested in Figure 1 by the steeper slope of the $1B_{2u}$ potential curve as compared to the shallow slope of the $1A_{1g}$ curve. This is the physical reason for a larger force constant as well as for the frequency exaltation of the Kekule'-type b_{2u} mode in the excited state relative to the ground state. Since b_{2u} is the *only* coordinate along which the two Kekule' structures interconvert, the mode selectivity is readily accounted for. Furthermore, the $1B_{2u}$ state is the only excited state formed by the out-of-phase combination of the two Kekule' structures, hence the *state* selectivity.

Appendix B: VB interpretation of Acepentalene PES explaining why the degenerate twin is the ground state

The symmetric 3-fold domain of acepentalene PES is based on three equivalent isomeric structures (the global minimum) – A,B and C.

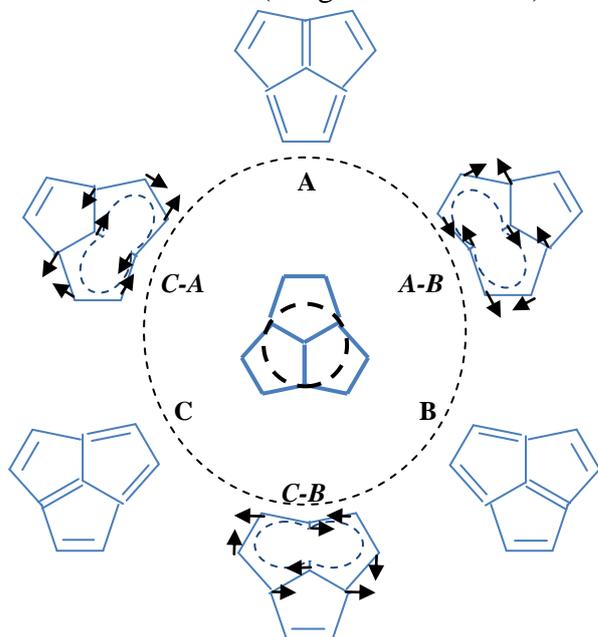


Figure 1. Schematic representation of the ground state PES of acepentalene (**I**) with three equivalent minima A, B and C, three equivalent TS between two minima with corresponding reaction coordinate (marked by black arrows) and a central high symmetry structure. A Longuet - Higgins loop (dashed cycle) is also shown, see text for details.

The global minimum is a conjugated C_s structure with alternated C=C double and C-C single bonds (Figure Ia and IIa, article). Let us assume for the moment that the covalent Kekulé structures are the dominant contributions to the electronic wave functions (WF) of the corresponding minimum – A, B or C. This means that all points incorporated in the domain are describable by the combination of these basic VB structures. The borders of the domain are the reaction coordinates between every reactant- product pair: (A,B), (B,C) and (A,C). The transition state WF is an anti-combination of two Kekule structures: (A-B), (C-B) and (C-A), because it includes the even number of electron pairs in resonance between two covalent structures⁵. The CAS results fully supported these conclusion and show that the TS is an open-shell electronic WF $1^1A''$ – antisymmetric with respect to the symmetry plane σ_h , which converts the reactant to the product. This is clear evidence that the covalent Kekule structures are the dominant contributions, as assumed, and the proposed model based on the three Kekule VB structures is a well founded approximation.

⁵ S. Zilberg and Y. Haas, *J. Phys. Chem., A.*, **1999**, *102*,10843-1850.

A closed loop through the three minima and the three transition states combining them: $A \rightarrow (A-B) \rightarrow -B \rightarrow (-B+C) \rightarrow C \rightarrow (C-A) \rightarrow -A$ changes its sign, since the transition state is constructed from the out-of-phase combination of the reactant and product. The loop is therefore a phase inverting Longuet-Higgins⁶ one, and according to the Longuet-Higgins theorem⁷ contains an electronic degeneracy. .

Consider the C_{3V} configuration - for the case of acepentalene, where the all three VB structures A,B and C are degenerate: $E_A = E_B = E_C = \alpha$. Also the pair interactions between them are equivalent: $E_{AB} = E_{BC} = E_{CA} = \beta$. The matrix describing the three-state system at the symmetric configuration:

$$\begin{vmatrix} \alpha-E & \beta & \beta \\ \beta & \alpha-E & \beta \\ \beta & \beta & \alpha-E \end{vmatrix}$$

This matrix diagonalizes to yield:

$$\begin{vmatrix} \alpha-\beta-E & 0 & 0 \\ 0 & \alpha-\beta-E & 0 \\ 0 & 0 & \alpha+2\beta-E \end{vmatrix}$$

Thus, the 3-state system⁸ splits to two electronic energy levels at the symmetric configuration. The energy separation between these levels is 3β . The non-degenerate ($\alpha+2\beta-E$) level is described by the symmetric combination (A+B+C) of the three Kekule structures. The degenerate ($\alpha-\beta-E$) level is described by a two component electronic WF (a degenerate singlet 1E state in the C_{3V} configuration). Of course, the order of these states depends on the β and it can be estimated by VB calculation. But we can use instead the topological Longuet-Higgins theorem. The ground state Longuet-Higgins loop is a phase-inverting in this case. Consequently this loop encircles a S_0/S_1 degeneracy and therefore the third state of the 3-state system is a non-degenerate excited state.

The splitting of the 3-state system at the symmetric configuration is an avoided crossing along 2 coordinates. The non-degenerate state is a twin state to degenerate one and both are constructed by different combinations of the same basic

⁶ S. Zilberg and Y. Haas, *Eur. J. Chem.*, **1999**, 5, 1755-1765.

⁷ a) G. Herzberg and H.C. Longuet-Higgins, *Discuss. Faraday Soc.*, **1963**, 35, 77-82;

b) H.C. Longuet-Higgins, *Proc. Roy.Soc London A.*, **1975**, 344, 147-156

⁸ S. Zilberg and Y. Haas, *J. Phys. Chem., A.*, **2003**, 107, 1222-1227.

three Kekule structures. The twin state is thus the excited state S_2 , which is a non-degenerate 1A_1 state (C_{3v}).