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Origins of the Exalted b_{2u} Frequency in the First Excited State of Benzene

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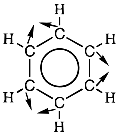
Abstract: A mechanism for the frequency exaltation of the b_{2u} mode in the $^1B_{2u}$ excited state of benzene is presented and supported by quantitative modeling (by means of both full π-CI as well as ab initio VB calculations of benzene). It is shown that the two Kekulé structures of benzene undergo avoided crossing along the b_{2u} coordinate. The memory of the avoided crossing of the π-Kekulé forms dictates that the b_{2u} mode of the ground state would undergo shortening of the double bonds and lengthening of the single bonds, while at the same time the b_{2u} mode of the excited state would stretch the double bonds and shorten the single bonds. As such, the Kekulé-avoided crossing model provides a single mechanism that accounts for the origins of the low skeletal b_{2u} frequency in the ground state, its mode mixing (Duschinsky mixing) with the hydrogen b_{2u} rocking vibration, its frequency exaltation in the $^1B_{2u}$ excited state, and the state selectivity of this exaltation. The Kekulé-avoided crossing model is suggested as a general mechanism for frequency exaltation of the localizing modes in those excited states of delocalized molecules that are the out-of-phase counterparts of the corresponding ground states.

Introduction

Haas and Zilberg (HAZ)[1] have recently discussed the intriguing experimental frequency shift in the first excited state of benzene (the $^1B_{2u}$ state). In agreement with pioneering assignments,[2,3] the most striking feature in the vibrational frequency data is the Kekulé b_{2u} mode, **1**, which undergoes an upward shift of 257−261 cm^{-1} in comparison with the highest in-plane b_{2u} vibration of the ground state (1309 cm^{-1}).



1 **b_{2u} (C)**

As noted by HAZ, as well as by most workers in the area, all other vibrational modes[1,4] behave "normally" and undergo frequency reduction in the excited state. This frequency reduction is expected from the decrease in π-bonding that attends the excitation of an electron from a π- to a π^*-orbital. Since the Kekulé mode is the localizing mode for the resonating π-electrons in the ground state, its exaltation in the excited state is all the more intriguing; how is it possible that disruption of "aromaticity" which must accompany the excitation ends up stiffening, from all the available modes, only the *localizing mode*, **1**?

Noting this nature of **1**, HAZ[1] interpreted the frequency shift in terms of the Shaik, Hiberty, Lefour, and Ohanessian (SHLAO) characterization of the delocalized π-electrons of benzene as a distortive species which is locked into a D_{6h} symmetry by the σ-frame.[5] The HAZ[1] articulation of the SHLAO[5] model has shown for the first time that the decade old debate about the electronic structure behavior of benzene[5,6] is not purely theoretical, but that the debate is linked to experimental facts that can be interpreted reasonably if the distortive nature of the π-electrons is at least postulated. Thus, according to the HAZ interpretation, the $\pi-\pi^*$ excitation disrupts the delocalization of the π-electrons and weakens thereby the π-distortive propensity. This weakening should in turn reveal "more clearly the influence of the σ-potential on the b_{2u} mode"[1] and lead to a frequency exaltation of this vibrational mode.

Clearly, while the HAZ interpretation breathes life into the π-electronic problem of benzene, the explanation nevertheless

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(4) ν_2 and ν_7 undergo very slight upward shifts which may be ascribed possibly to the slight shortening of the C−H bonds in the $^1B_{2u}$ excited state. See, e.g., **4** and **5** in the text.

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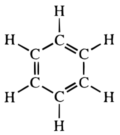
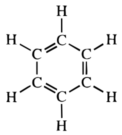
does not provide a clear physical mechanism for the effect. For example, this explanation does not account for the state specificity of the frequency exaltation. Moreover, the phenomenon has been reported by HAZ[7] for other derivatives of benzene (e.g., in styrene and indene) in the excited state that corresponds to the $^1B_{2u}$ state of benzene, as well as for the $^1B_{2u}$ excited state of anthracene[8] (using Mulliken's convention). A similar observation has been made by Mikami and Ito[9] and Swiderek et al.[3g] for the $^1B_{2u}$ excited state of naphthalene. *Thus, what might have looked initially as an isolated finding may turn out to be a ubiquitous phenomenon characteristic of delocalized systems*. It is required then to formulate a lucid physical mechanism which projects the origins of the excited state's phenomenon, the extent of its state- and mode-selectivity, and its seemingly counterintuitive relationship to the behavior of the π-electrons in the ground state. This is the goal of the present paper which provides a mechanism of the phenomenon supported by quantitative modeling following the SHLAO model[5] and the recent definitive SCVB assignment of the covalent nature of the $^1B_{2u}$ state by da Silva et al.[10] As will be shown, the two Kekulé structures **2** and **3** of benzene undergo avoided crossing along the b_{2u} coordinate, and as such provide a single mechanism that accounts for the origins of the, once controversial, low skeletal b_{2u} frequency in the ground state,[11] its mode mixing (Duschinsky mixing[3a,c,d−f]) with the hydrogen b_{2u} rocking vibration, its frequency exaltation in the $^1B_{2u}$ excited state, and the state selectivity of this exaltation.



2 (*K_l*)



3 (*K_r*)

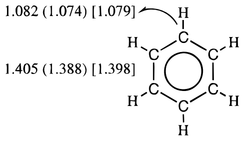
Methods and Means of Modeling

Right at the outset we emphasize that our focus in this paper is not to reproduce accurately the frequencies or their force constants. This has been done very well by the pioneering efforts of the active groups in the area,[3] who have also pointed out that the phenomenon is well described within the adiabatic approximation with no need to evoke a nonadiabatic origin.[3g,h] Thus, we shall focus here on the modeling of the phenomenon, in terms of the potential energy of the ground and excited states, with an attempt to derive its qualitative physical essence, albeit by reasonable quantitative means.

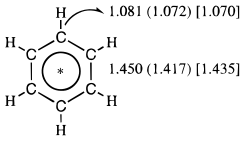
MO and CI calculations were carried out by use of GAMESS-94.[12] Benzene was optimized in the ground and its $^1B_{2u}$ states at different levels, using RHF for the ground state and CIS for the excited state with the 6-31G and STO-3G basis sets, as well as by use of full π-CI with the STO-3G basis set for the two states. All levels show the b_{2u} frequency exaltation, in agreement with previous results which span a range of computational sophistication.[1,3d,g,h,i] The full π-CI/STO-3G level was consequently deemed sufficient for the elucidation of the mechanism of the frequency exaltation.

The full π-CI option itself is necessary because it allows us to obtain all the roots corresponding to the possible $\pi-\pi^*$ excitations and to ensure that the modeling of the π-avoided crossing will always involve the correct state in terms of its energy and symmetry along the distortion coordinate. In addition, as was shown by da Silva, Gerratt, Cooper, and Raimondi (SGCAR)[10] in their SCVB study of benzene, both the ground and the $^1B_{2u}$ excited states are essentially covalent. This conclusion is further supported by the recent extensive CASCF/CI and CASPT2 studies by Roos et al.[13] which are to date the most extensive calculations of the ground and excited states of benzene. These calculations show that unlike the ionic excited states which require extensive dynamic correlation correction, the ground and first excited states are essentially covalent and can be calculated in a satisfactory manner at the CASSCF level. Thus, the full π-CI/STO-3G calculation also is expected to provide a semiquantitatively correct description for these two states. Indeed, the studies by Swiderek et al.[3g] show that STO-3G provides reasonable $^1A_{1g}-^1B_{2u}$ excitation energy, reasonable excited state geometry, and correct, albeit exaggerated, trends in the behavior of the b_{2u} frequencies. This qualitatively reasonable performance will carry over to the modeling of the problem in terms of the corresponding π- and σ-energetic behavior along the b_{2u} mode (Figure 2). It is worthy to emphasize, however, that higher excited states of benzene and especially the ionic ones[10,13] cannot be treated at the level used in our studies.

The skeletal geometries for the $^1A_{1g}$ and the $^1B_{2u}$ states of benzene are shown in **4** and **5**. The full π-CI/STO-3G calculations are shown out of parentheses and the RHF/6-31G or CIS/6-31G results are shown in parentheses (CIS/STO-3G gives comparable results for $^1B_{2u}$, with $R_{CC} = 1.4197$ Å). The values in the square brackets are the experimental data.[14] It is seen that the benzene nucleus in the $^1B_{2u}$ excited state expands relative to the ground state, while conserving the D_{6h} symmetry in accord with all experimental and previous computational findings.[2a,3g,10,14b] The vertical excitation energy at the full π-CI/STO-3G level is 5.3 eV, in reasonable agreement with the experimental value (4.9 eV).[2a,14b]



4 (**$^1A_{1g}$**)



5 (**$^1B_{2u}$**)

VB Calculations. The VB calculations were carried out with the Utrecht package TURTLE,[15] coauthored by Verbeck, Langenberg, Byrman, and van Lenthe, as a development of the VBSCF method of van Lenthe and Balint-Kurti.[16] This is a general multiconfiguration method that allows the use of nonorthogonal orbitals of a desired shape. Both the coefficients of the VB structures and their orbitals are optimized simultaneously, starting from a given initial guess. The orbital optimization procedure was carried out with a super-CI algorithm based on the generalized Brillouin theorem[17] and double-checked by the approximate Newton−Raphson method and different acceleration procedures to ensure convergence to the same final solution.

The main purpose of the VB calculations is to provide a qualitative physical model for the full π-CI/STO-3G calculations. Accordingly, the VB calculations utilized the STO-3G basis set, along with test calculations with the 6-31G basis set.[18,19] In all the calculations, the σ-electrons were kept in 18 doubly occupied orbitals taken from a

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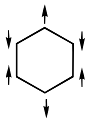
corresponding SCF calculation of benzene for the appropriate geometry. These orbitals were kept frozen during the VB procedure in accord with the SGCAR[10] study, which finds only small effects of the repolarization of the σ-frame, and with the CASPT2 study of Roos et al.,[13b] which shows that the $\sigma-\pi$ correlation in the two states is virtually identical. This is in agreement with the covalent nature of the two states, which as such are expected to share the same σ-frame and to affect it to a small extent.

At the simplest and most basic level the VB calculations included only the two Kekulé structures, **2** and **3**, with strictly localized AO's (see later, Figure 1). To test whether the STO-3G basis set retrieves the two-Kekulé picture that emerged in the SGCAR[10] high-level study, the calculations were carried out with the two Kekulé structures, **2** and **3**, but now allowing the AO's to optimize freely.[10,20] As a result, the orbitals become slightly delocalized, in a symmetric fashion, and mimic thereby some of the missing ionic and other structures.[21,22] It is noted that the distorted optimized AO's keep the correct symmetry of the molecule as is often emphasized by the authors of the SCVB method.[23] The resulting total VB energies at the D_{6h} geometry (R_{CC} = 1.40 Å) are in excellent agreement with full π-CI data; the ground state is ca. 4.8 kcal/mol higher while the $^1B_{2u}$ state is ca. 1.3 kcal/mol higher. The resulting vertical excitation energy is 5.2 eV in comparison with the 4.9 eV experimental value,[2a,14b] 5.29 eV for the full π-CI result, and 5.3 eV in the more sophisticated SGCAR[10] study as well as with 5.1 eV at the VB/6-31G level in our own study. The calculated resonance energy of 22.5 kcal/mol is likewise in good agreement with the corresponding SCVB value[24] of 21.03 kcal/mol, using much better basis sets, and with 19.7 kcal/mol at our VB/6-31G calculation.

The effect of the three Dewar structures[23] was found to be quantitatively very small. Thus, upon inclusion of the three Dewars, the ground state energy was lowered by 0.4 kcal/mol while the excited state energy remained unchanged as might be expected from symmetry consideration of the Dewar structures.[10] Furthermore, adding the 24 ortho-ionic structures has very little effect on the two states. Thus, the two-Kekulé picture is an excellent approximation for the ground and the $^1B_{2u}$ excited states, at the uniform D_{6h} structure. At the distorted D_{3h} geometries, the VB energy for the ground state is still very good, in comparison with the full π-CI, but the excited state VB energy is significantly steeper. Addition of the ortho-ionic structures tempers the rise of the excited state's energy at the distorted geometries. However, the basic feature—the relative steepness of the two states that sets in at the simplest two-Kekulé level (Figure 1)—remains unaffected by all the additional VB structures. These results, as well as extensive tests on the isoelectronic H_6 problem, led to the conclusion that the two Kekulé structures, **2** and **3**, capture the qualitative physical essence of the $^1A_{1g}-^1B_{2u}$ state-pair behavior. It was decided therefore to restrict further discussion of the modeling to the behavior of the two Kekulé structures, **2** and **3**, along the b_{2u} mode, **1**.

Modeling of the π-Avoided Crossing. The modeling of π-energies followed our recent analysis[6a] in terms of the quasiclassical state (QC), **6**, which was calculated at each geometry along the b_{2u} mode and served as a model for the σ-frame (note that the QC state is defined for pure AO's without delocalization tails). It is apparent from **6** that this QC state is the π-type spin-alternant determinant (also called Neél or antiferromagnetic state[25]) that involves six unpaired and spin-uncoupled p_π electrons. As was shown previously[6a] the interaction of these p_π electrons along the b_{2u} mode is virtually nonbonding over a significant geometric variation. It follows that the energy change of the QC state represents the energy change of the σ-frame in the field of six noninteracting p_π electrons.



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The π-bonding energy is obtained therefore by subtracting the energy of the QC state from the VB or full π-CI energies, eq 1. Tracing this

$$E(\pi) = E(\text{full}) - E_{QC}(\sigma);\quad E(\text{full}) = E(\text{VB}) \text{ and/or } E(\text{full } \pi\text{-CI}) \tag{1}$$

energy difference along the b_{2u} mode will represent in turn the behavior of the π-bonding energies associated with the $^1A_{1g}$ and $^1B_{2u}$ states along the Kekulé b_{2u} coordinate. As a benchmark of the QC state analysis of bonding energies, the modeling was repeated also for the VB and full CI calculations of the ground and $^1B_2$ states of the isoelectronic system, H_6, providing precisely the same physical mechanism of avoided crossing (as shown later in Figure 1b). The CIS results for H_6 and benzene were tested too, and failed to model their full CI counterparts, and therefore the CIS method was abandoned for further modeling of the problem (see ref 13b for reasons why CIS may not be appropriate for excited states). It is perhaps interesting to note that simple extended Hückel theory[26] does reproduce the correct behavior. All the test calculations are not reported in this paper in order not to dilute the main message. Instead we focus on the two-Kekulé VB/STO-3G calculation with localized AO's and the full π-CI/STO-3G results.

In the following section we first present the VB analysis and the corresponding π-energies of the two Kekulé structures and their in-phase and out-of-phase combinations, the $^1A_{1g}$ and $^1B_{2u}$ states. The resulting π-energies will provide in a following analysis the requisite insight for the π-CI behavior. Subsequently, a physical mechanism will be proposed for the frequency exaltation of the Kekulé b_{2u} mode (**1**) and the other associated phenomena. A link will be drawn then between the excited state and ground state behavior of the π-electrons.

Results and Discussion

VB-Avoided Crossing. Following SGCAR[10] as well as Fox and Matsen,[27] symmetry assignment of VB wave functions is straightforward. Consider the consequences of applying the symmetry elements of the D_{6h} point group on the left-hand and right-hand Kekulé structures shown above in **2** and **3**. It is apparent that the σ_v plane, the in-plane C_2, and the inversion (i) symmetry operations all transform K_1 to K_r and vice versa. These VB forms constitute therefore inversion, rotation, and mirror-images of each other. Therefore, the positive linear combination of the Kekulé structures will behave as the totally symmetric *gerade* state, $^1A_{1g}$, while the corresponding negative linear combination will behave as the *ungerade* $^1B_{2u}$ state, as given in eqs 2a and 2b:

$$\Psi_1(^1A_{1g}) = N(K_1 + K_r) \tag{2a}$$

$$\Psi_2(^1B_{2u}) = N(K_1 - K_r) \tag{2b}$$

Thus, the $^1A_{1g}$ and $^1B_{2u}$ states of benzene correspond to the in-phase and out-of-phase states made of the two Kekulé forms.[5a,10,27] Along the b_{2u} distortion mode, away from the D_{6h} origins, the linear combinations will not involve equal amounts

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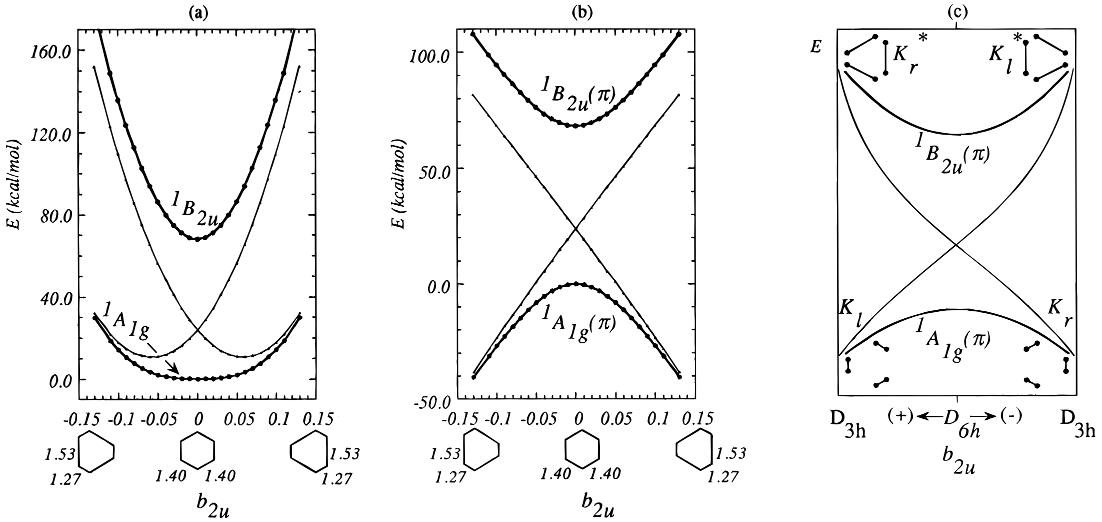


Figure 1. VB calculated ground and $^1B_{2u}$ excited states of benzene along the skeletal b_{2u} coordinate using the Kekulé structures **2** and **3** with localized AO's. The b_{2u} coordinate is defined as half of the difference, in Å, between the lengths of two neighboring C−C bonds. The energies of the individual structures are shown in regular lines, while the state curves are drawn with bold lines. The zero of the energy scale is the ground state at the D_{6h} regular geometry. (a) The total (σ and π) energy curves. (b) The π-curves only, calculated by use of eq 1. (c) A qualitative avoided crossing diagram of the π-electrons after ref 5a. The electrons are drawn as dots and singlet pairs are connected by lines. The D_{3h} extremes refer to one short bond and one infinitely long bond.

of the two structures; the ground state will be dominated by the most stable Kekulé structure and the excited state by the less stable one.

Figure 1a shows the behavior of the total energies of the two Kekulé structures and the corresponding states, computed with the VB method. It is apparent that the two Kekulé structures interchange along the skeletal b_{2u} coordinate and by mixing the crossing is being avoided, leading thereby to the two state curves in the bold lines. As a result of the avoided crossing, the ground state energy becomes relatively flat along the b_{2u} mode while the excited state's energy becomes very steep in the same mode. While the above behaviors of the Kekulé's may already account for the frequency exaltation of the b_{2u} mode in the excited state, what still remains unclear is the electronic mechanism of this avoided crossing.

To elucidate the electronic mechanism we present Figure 1b which traces only the π-energy along the same b_{2u} mode. The result is a π-avoided crossing diagram with two π-curves that intersect and avoid the crossing to generate the corresponding π-states. This is in precise accord with the qualitative model in Figure 1c which was proposed in the SHLAO[5a] treatment of the π-electronic behavior of benzene. Here the p_π electrons are indicated as dots and their singlet pairings by lines that connect the dots. According to this model, π-resonance at the $^1A_{1g}(D_{6h})$ state is achieved by avoided crossing which requires initially destabilization of the two π-only Kekulé structures that have to be brought into resonance from their natural bond-alternated D_{3h} geometries. At these extreme D_{3h} points of the b_{2u} coordinate, one Kekulé structure is a ground state while the other is an excited state and hence designated by an asterisk. The excited Kekulé structures are related to the ground structure by unpairing the short π-bonds of the ground structure and pairing anew these electrons across the long C−C bonds in the excited structure. As such, each excited Kekulé at the extremes of the b_{2u} coordinate serves as a "prepared state" that allows the reorganization of the electrons from one Kekulé structure to the other in the ground state. Thus, along the b_{2u} coordinate, which interchanges the identity of the short and long C−C linkages, the Kekulé structures swap their ground−excited state roles and cross one another, while their mixing causes avoidance of the crossing and generates the final π-states.

The shape of the final π-curves has been predicted[5a] to depend on the promotion energy gap between the ground Kekulé structure and its excited structure at the D_{3h} extremes. These energy gaps have been estimated in the original treatment[5] to be large, and indeed the VB computed promotion energies in Figure 1b are seen to be significant (129 kcal/mol) even for a finite D_{3h} distortion. With such a large excitation energy SHLAO[5] have predicted that the avoided crossing will feature a distortive π-curve in the ground state, with the $^1A_{1g}(\pi)$ species occupying the top of the barrier at the D_{6h} geometry, while, in contrast, the excited state π-curve has been predicted to possess a minimum occupied by the $^1B_{2u}(\pi)$ species and to rise steeply with deviations from the D_{6h} symmetry. This is indeed born out perfectly by the VB computed curves in Figure 1b, which shows how the distortive−attractive behavior of the π-curves is the origin of the flatness of the ground state total energy curve and the steepness of the excited state's curve in part a of Figure 1.

***π*-Avoided Crossing in the CI Calculations.** To demonstrate that this simple VB model carries over to the full π-CI calculations we present the latter results in Figure 2. Part a of the figure shows the total energy curves for the ground and the excited states, while part b shows the corresponding π-curves as well as the common σ-curve (given by $E_{QC}(\sigma)$). It is seen from Figure 2b that here too, the ground state π-curve is distortive while the excited state curve (curve 1) is attractive, much the same as the VB curves of the two Kekulé structures in Figure 1b. Furthermore, curve 2 in Figure 2b ascertains that the behavior is not dependent on the initial C−C bond length of the D_{6h} structure and the distortive−attractive behavior of the π-curves recurs for R_{CC} = 1.45 Å; the latter corresponding to the optimized distance of the $^1B_{2u}$ excited state (see **5**). This repulsive−attractive behavior of the π-curves is the root cause of the shallow ground state curve as opposed to a steep excited state curve in Figure 2a.

The VB model is seen therefore to provide a basis for the full π-CI results, and to shed insight not only into the ground state's behavior, but also into the nature of the $^1B_{2u}$ excited state. These two states are seen to be twin-states which exhibit virtually mirror-image behaviors in accord with their genesis from the avoided crossing of the two Kekulé structures.

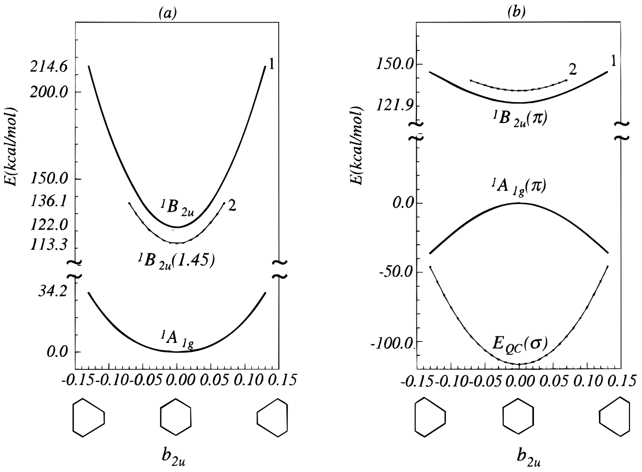


Figure 2. Full π-CI/STO-3G curves for the ground and $^1B_{2u}$ excited states of benzene along the skeletal b_{2u} coordinate. Excited state curve #1 refers to the same D_{6h} geometry as in the ground state ($R_{CC} = 1.40$ Å), while curve #2 refers to the optimized geometry of the excited state ($R_{CC} = 1.45$ Å). State energies are arranged as in Figure 1. (a) The total energy curves (σ and π). (b) The π-curves, and the common σ-curve (given by E_{QC}). To fit E_{QC} into the figure, the minimum of the curve is placed arbitrarily at -116 kcal/mol.

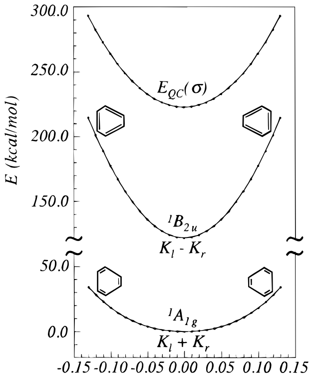


Figure 3. The full π-CI state curves (the minima of the two states at the D_{6h} origins refer to $R_{CC} = 1.40$ Å) and the σ-curve, along the b_{2u} coordinate. Drawn are the Kekulé structures and their electron pairing modes that dominate the energy behavior of the curves that emanate from the D_{6h} origins. Note that the ground Kekulé structures correlate diagonally to the excited structures as shown in Figure 1c.

π-Avoided Crossing: A Physical Mechanism for the Exalted b_{2u} Frequency and Its Mode Mixing Patterns. Figure 3 summarizes the essential insight needed to discuss the spectral shift and its various ramifications. The behavior of the total energy curves is further elucidated in the figure pictorially by the resonance structures that dominate the various branches of the curves based on the discussion of the curve crossing in Figure 1c. Thus, owing to the π-avoided crossing, the ground state branches that emanate from the $^1A_{1g}(D_{6h})$ origins are dominated by the Kekulé structures with π-bond pairing across the C$-$C linkages that are en route to be shortened. The resulting b_{2u} potential is then quite soft because the mode is assisted by the stabilization of the Kekulé structure that is allowed to distort in-phase with its bonding preference. In contrast, the excited state branches that emanate from the $^1B_{2u}(D_{6h})$ origins are dominated by the Kekulé structures with π-bond pairing across those C$-$C linkages that undergo the lengthening during the b_{2u} distortion. The resulting b_{2u} potential is then very stiff because it is resisted by the destabilization of the Kekulé structures that distort in mis-match with their intrinsic bonding preferences. *Thus, it is the memory of the avoided crossing of the π-Kekulé forms which dictates that the b_{2u} mode of the ground state would undergo shortening of the double bonds and lengthening of the single bonds, while at the same time the b_{2u} mode of the excited state would stretch the double bonds and shorten the single bonds.*

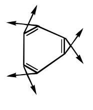
Having elucidated the electronic mechanism, we may now express the total force constant for the skeletal b_{2u}(C) mode for the two states as the sum and differences of the σ- and π-force constants, eqs 3a and 3b:

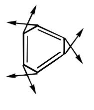
$$k(^1A_{1g}) = k_\sigma - |k_\pi(^1A_{1g})| \tag{3a}$$

$$k(^1B_{2u}) = k_\sigma + k_\pi(^1B_{2u}) \tag{3b}$$

$$k(^1B_{2u})/k(^1A_{1g}) > 1; \quad \omega(^1B_{2u})/\omega(^1A_{1g}) > 1 \tag{3c}$$

From the preceding discussion it is apparent that the contributing π-terms in eqs 3a and 3b are Kekuléan, and that the sign inversion of the π-contribution is related to the switched location of the double bond from the short C$-$C linkage in the ground state to the long one in the excited state, as depicted in **7** and **8**. Thus, the "Kekulé term", **7** for the ground state, and its complementary "anti-Kekulé term", **8** for the excited state, provide a vivid pictorial description of eq 3c that expresses the force constant and frequency exaltation of the skeletal b_{2u} frequency upon excitation to the $^1B_{2u}$ state.


7 $b_{2u}(^1A_{1g})$


8 $b_{2u}(^1B_{2u})$

These conclusions are in accord with the findings of HAZ[1] for the frequencies and force constants of the hexadeutrated benzene. Furthermore, the suggestion of Scherer and Overend[11d] and its adaptation by Robey and Schlag[3c] and by Goodman and co-workers,[3b] that the force field of benzene must include a "Kekulé term" rather than delocalization terms, finds now a physical justification by the avoided crossing mechanism. It is by avoided crossing that the ground state b_{2u}(C) mode becomes associated with the Kekulé term, **7**, and the excited state mode with the anti-Kekulé term, **8**.

Let us discuss now the origins of the Duschinsky effects[28] observed for the b_{2u} vibration.[1,3a,c,d$-$f] It was originally observed by Metz et al.[3a] that the ground state b_{2u} frequencies possess mixed Kekulé and H-rocking modes, while in the excited state the two modes separate and constitute almost pure Kekulé (b_{2u}(C)) and H-rocking (b_{2u}(H)) vibrations. This separation of the modes in the excited state has been discussed in terms of the mixing of the original ground state b_{2u} modes (Duschinsky rotation[28]), and while the precise extent of the mixing is still unsettled,[3b,c,d$-$f] it is agreed by all researchers that the excited state modes are largely, albeit not completely, uni-atomic in nature as opposed to the mixed nature of the ground state modes.

These effects can be discussed qualitatively with reference to Figure 4, which is a heuristic mixing diagram between the symmetry adapted skeletal and hydrogenic modes, which are designated respectively as b_{2u}(C) and b_{2u}(H). Of course the mode mixing is quantitatively complex and depends on three different force constants and effective masses,[3b] and hence Figure 4 should be considered primarily as a simplified qualitative conceptual aid of the problem. The relative energy levels of the pure atomic modes are indicated in the figure by the horizontal lines of the energy scale, while the mixing is

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(28) Duschinski, F. *Acta Spectrochim. U.R.S.S.* **1937**, *7*, 551.

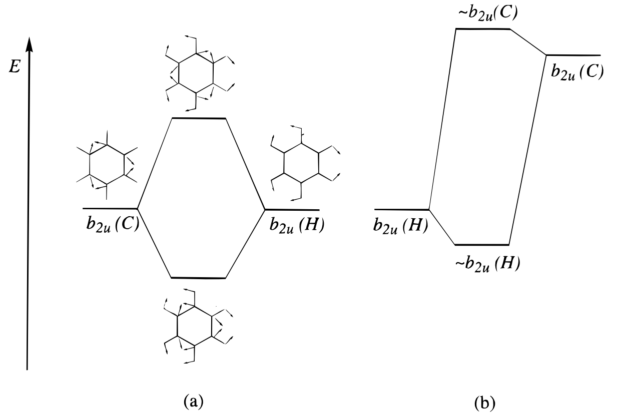

Figure 4. Mode mixing diagram showing the mixing of the b_{2u}(C) and b_{2u}(H) modes to the final observed modes. Part a describes the situation for the ground state modes. The carbon-centered and hydrogen-centered modes are approximately degenerate and mix to give in-phase and out-of-phase combination modes. Part b describes the situation for the modes in the $^1B_{2u}$ excited state. Here the carbon-centered and hydrogen-centered modes are well separated and mix to a small extent. The resulting modes involve almost pure uni-atomic motions.

indicated in the same manner as done for orbital mixing.[29] Thus, in the ground state in Figure 4a, the Kekulé term, **7**, softens the b_{2u}(C) mode and lowers its energy, and as a result it approaches the energy of the hydrogen rocking mode, b_{2u}(H). The two almost degenerate modes mix and generate the in-phase and out-of-phase b_{2u} combinations observed in the experimental[3a,b,c,d−f] and computed spectrum.[1,3g,i] In the excited state in Figure 4b, the "anti-Kekulé" term, **8**, stiffens the b_{2u}(C) mode and its energy increases. This increase creates a significant energy gap between the skeletal b_{2u}(C) mode and the hydrogen rocking mode b_{2u}(H). Consequently, the modes mix only to a small extent and remain as almost pure C and H modes.

***π*-Avoided Crossing: Origins of the Mode and State Selectivity of the Frequency Exaltation.** The avoided crossing mechanism is also the root cause of the state and mode selectivity of the phenomenon. Thus, as shown in eqs 2a and 2b only the $^1A_{1g}$ state and *the first* $^1B_{2u}$ state can be made from linear combinations of the Kekulé structures. All other excited states have been shown by SGCAR[10] to be either ionic (e.g., $^1B_{1u}$, $^1E_{1u}$) or Dewar benzene types ($^1E_{2g}$). Similarly, a higher lying $^1B_{2u}$ state can be made from a linear combination of the ortho-ionic structures.[10] It follows therefore that the avoided crossing mechanism connects the ground state with one and only one excited state, the covalent $^1B_{2u}$ state. Furthermore, since the two Kekulé structures avoid the crossing only along the skeletal b_{2u} coordinate, and not along any other, the only exalted mode will be b_{2u}(C) and not any other. In fact, all other in-plane modes will be reduced in the ground state and will reflect thereby the usual effect expected from the reduction in overall π-bonding attending the excitation of an electron from a bonding π-MO to an antibonding π^*-MO. Thus, the mode and state selectivity of the spectral shift is a probe of the avoided crossing mechanism, and vice versa; the avoided crossing is the physical mechanism responsible for the selectivity of the frequency exaltation observed in the $^1A_{1g}-{}^1B_{2u}$ state pair. There may be other frequency shifts that are related to the HAZ[1] explanation (disruption of the ground state π-distortivity by electronic excitation), or to a general vibronic coupling mechanism, but these effects are not expected to be as spectacular, or quite as selective as the avoided crossing driven effect, described here.

Concluding Remarks: The Spectral Shift and π-Electronic Behavior

This paper shows that the π-avoided crossing contributes a distortive π-energy to the ground state b_{2u}(C) mode and a strongly restoring π-energy to the excited state mode. As such, the avoided crossing constitutes a common mechanism that is responsible simultaneously for the low ground state b_{2u} frequency and the exalted b_{2u} frequency in the $^1B_{2u}$ excited state. In the sense that the mechanism describes the key features of the spectral shift of the b_{2u}(C) mode, in this same sense the observation of the spectral shift comes as close as possible to an experimental probe for the π-distortivity in the ground state of benzene. Thus, on the background of the thunderous evidence of "aromaticity" there is a spectroscopic whisper suggestive yet of the distortive nature of the π-electrons of ground state benzene.

The ground state π-distortivity has been implicated already in 1959 by Longuet-Higgins and Salem,[30] who used Hückel theory with the variable β parameter to discuss bond alternation in annulenes. Subsequently, Berry[11e] accounted for the controversially low b_{2u} frequency in the ground state using basically the same Hückel-type approach. Scherer and Overend[11d] argued that the b_{2u} frequency is low, in accord with Mair and Hornig's[11b] and contrary to Ingold's[11a] assignment, and can be accounted for by adding a Kekulé-stabilizing term to the pristine Urey−Bradely force field. The exalted excited state b_{2u} frequency has been explained by a vibronic coupling mechanism.[9] Nevertheless, each issue appeared either puzzling or altogether controversial, and in the whole the benzene puzzle remained fragmentary with separate ground state and excited state pieces which require unification. It is through the Kekulé avoided crossing model[5] that the ground and excited state phenomena are seen to be coupled-observables derived from a single origin. This unification of the ground and excited state treatments provides the benzene problem[5,6a] a new and fundamental significance.

It was the HAZ[1] paper that made the connection between the excited state finding and the SHLAO[5] theoretical model about the ground state, and in this sense the HAZ paper constitutes a significant articulation of the avoided crossing model. Beyond this single story of benzene, this articulation opens a window for further experimental investigation of the avoided crossing mechanism. Indeed, *a variety of molecules with delocalized electrons (i.e., conjugated aromatic and antiaromatic systems, allylic systems, delocalized clusters, and hypercoordinated species) can be described in terms of the Kekulé-crossing model* and would pose therefore an opportunity to investigate the frequency exaltation of the localizing mode in the excited state that corresponds to the out-of-phase counterpart of the ground state. All the more, the frequency exaltation phenomenon may well carry over to other state pairs that are mutually related by avoided crossing along a given normal mode. As such, the analysis that is presented in this paper for a single molecule is in fact a prototype for a ubiquitous phenomenon and may serve thereby as a basis for further research to explore the range of its applicability.

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[29] See for example: Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

[30] Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London* **1959**, *A251*, 172.