A Kekulé-Crossing Model for the "Anomalous" Behavior of the \(b_{2u}\) Modes of Aromatic Hydrocarbons in the Lowest Excited \(1^B_{2u}\) State

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I. Introduction

This Account presents a model that provides a lucid physical basis for the apparently unusual behavior of Kekulé-type vibrational modes in the \(1^B_{2u}\) excited state of benzene and other aromatic hydrocarbons. The model, called the Kekulé-crossing model, is based on the idea that the electronic ground state \((1^A_{1g})\) and the first \(1^B_{2u}\) excited state may be considered to a reasonable approximation as twin states, arising from in- and out-of-phase combinations of the same Kekulé structures. The Kekulé-crossing model is used to account for other properties of these systems, and the observed spectroscopic "anomaly" in fact provides the first experimental proof of the dominance of these structures in determining the physical and chemical properties of benzene and other aromatic molecules.

As shall be shown the model is general enough and can form a basis for thinking about delocalized ground states and their twin excited states made of the out-of-phase combination of the same set of Kekulé structures.

The frequency up-shift of the Kekulé-type \(b_{2u}\) modes in the \(1^B_{2u}\) electronically excited state of several aromatic hydrocarbons (benzene, naphthalene, anthracene, and some of their derivatives\(^2\)–\(^4\)) is well documented and appears to be a general phenomenon. For instance, the frequency of the skeletal mode \(1\) in the \(1^B_{2u}\) state of benzene (the \(ν_{14}\) mode, 1570 cm\(^{-1}\)) is 261 cm\(^{-1}\) higher than that of the same mode in the ground \(1^A_{1g}\) state.\(^2\) How is it possible that the mode that disrupts the ground state’s aromaticity possesses a higher frequency in the excited state? It is interesting to note that the assignment of this mode presented unexpected difficulties in the early days of the vibrational spectroscopy of benzene. A straightforward force field (Urey–Bradley type) predicted that the ground state mode should have a frequency of about 1600 cm\(^{-1}\),\(^3\) and after the firm establishment of the lower value (1309 cm\(^{-1}\)), it was necessary to add a special "Kekulé term" to the force field\(^6\) in order to reproduce the low experimental frequency value. The

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In this Account we show that the Kekulé-crossing model may be applied to other polyaromatic hydrocarbons, and that this generalization allows the prediction of the expected behavior of the Kekulé-type modes for all the acene series.

II. Kekulé-Crossing Model

The model, applied to benzene, was discussed in detail elsewhere, so only a brief survey of the main assumptions and results follows. It is easily shown, on the basis of symmetry transformations of the Kekulé structures, that the ground electronic state of benzene and the excited state may both be considered as combinations of the two Kekulé structures, and that these two structures give a good quantitative description of the states around the ground and excited state potentials is still determined by the two Kekulé structures. Consequently, presentation of the physical origins of the phenomenon requires only the Kekulé structures. This is the main goal of our treatment which seeks a qualitative physical insight rather than an accurate calculation of the frequencies.

Figure 1 shows a schematic representation of the modes for the case of benzene. It is based on the VB-calculated energy of the two Kekulé structures as a function of motion along the $b_{2u}$ coordinate and that changes the two Kekulé structures. The energy of $K_1$ is seen to be minimal at the geometry in which the three double and three single bonds have their standard equilibrium values. Stretching of the double bonds and simultaneously contracting the single bonds, by motion along the $b_{2u}$ coordinate, increases the energy of $K_1$ which becomes a highly strained excited structure. The same situation holds for $K_r$ for reverse motion along the same coordinate. These two diabatic energy curves would have intersected at the symmetric perfect hexagonal structure, but since they can mix with each other, they avoid the crossing and generate the two symmetry-adapted states which are the in- and out-of-phase combinations ($A_{1g}$ and $B_{2u}$). The resulting two adiabatic potential surfaces, shown as $B_{2u}$. Extensive valence bond (VB) calculations following the pioneering study of Da Silva et al., show that these two structures give a good quantitative description of the states around the $D_{6h}$ geometry. At distorted $D_{3h}$ geometries, one needs ionic structures. However, the relative steepness of the ground and excited state potentials is still determined by the two Kekulé structures.

According to this Kekulé-crossing model, the benzene case can be explained by the avoided crossing mechanism of Shaik and Hiberty, assuming that the ground $A_{1g}$ and first excited $B_{2u}$ states of the molecules may be described as arising primarily from the two Kekulé structures. As such, their avoided crossing along the $b_{2u}$ coordinate leads to softening of the ground state potential, and a stiffening of the excited state potential.
in heavy type in the figure, represent the behavior of the \(1^1A_{1g}\) and \(1^1B_{2u}\) states upon motion along the \(b_{2u}\) coordinate.

Inspection of Figure 1 shows that the potential energy curves of the \(1^1A_{1g}\) and \(1^1B_{2u}\) 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 \(K_i\) 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 Kekulé 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 \(K_i\). 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 Kekulé 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 \(1^1B_{2u}\) potential curve as compared to the shallow slope of the \(1^1A_{1g}\) curve. This is the physical reason for a larger force constant as well as for the frequency exaltation of the Kekulé-type \(b_{2u}\) mode in the excited state relative to the ground state. Since \(b_{2u}\) is the only coordinate along which the two Kekulé structures interconvert, the mode selectivity is readily accounted for. Furthermore, the \(1^1B_{2u}\) state is the only excited state formed by the out-of-phase combination of the two Kekulé structures, hence the state selectivity. Scheme 1 illustrates the above mechanism: the \(b_{2u}\) mode interchanges the Kekulé structures which are the constituents of the ground and excited states. In the ground state, the shallow potential due to the in-phase \(K_i + K_r\) combination leads to a low frequency, while in the excited state, the strained out-of-phase \(K_i - K_r\) potential due to the combination leads to the exalted frequency.

III. Effect of Substitution on the Benzene Ring

Substitution reduces the \(D_{6h}\) symmetry of benzene and might be expected to lead to diminution of the effect. However, calculations on styrene, trans-\( \beta \)-methylstyrene,\(^{14}\) and indene\(^{15,16}\) show that in the first excited state the benzene nucleus is nearly a uniform hexagon, and the frequency of the \(b_{2u}\)-like vibration increases by about 350 cm\(^{-1}\), in comparison with the respective ground states of these molecules. This is explained by the fact that this vibration remains largely localized in the benzene portion of the molecule, and that the much steeper slope of the upper state for motion along this coordinate is not affected much by substitution (Scheme 2). We may therefore infer that the Kekulé-crossing model makes correct predictions even for strongly perturbing ring substitution.

This may be explained by assuming that the ground state and the first excited state of styrene (and other substituted molecules) are also well represented as twin states formed from Kekulé-type structures, by analogy to Figure 1. The “pseudo-A\(^{11}\)g” and “pseudo-B\(^{2u}\)” characters of these states are supported by the fact that the oscillator strength of the transition between these states is very small (0.00217), as if the \(D_{6h}\) symmetry rules apply to the styrenes as well. A quantum chemical calculation of the form of the exalted mode in styrene and in indene shows that indeed it involves mostly a Kekulé-type motion in the benzene ring.\(^{16}\)

IV. Naphthalene and Anthracene

The arguments presented in the case of benzene can be extended to other acenes, provided the excited state

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Figure 1. A schematic description of the intended crossing of the potential curves of the two Kekulé structures (\(K_i\) 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.

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and the ground state may be described as Kekulé pairs, along a suitable coordinate. In the case of naphthalene, a SCVB computation\(^{(18)}\) showed that the ground state is very well represented by the three Kekulé structures. In higher acenes the computations become tedious, but it turns out that predictions based on the Kekulé model hold not only for naphthalene but also for anthracene. We therefore adopt the working hypothesis that the set of Kekulé forms of an acene-type molecule provide the basis for analyzing the behavior of the Kekulé-type \(b_{2u}\) modes in the ground and the first excited \(B_{2u}\) state. Using Scheme 1, we may generalize as follows:

Any pair of Kekulé forms that are interchangeable by a suitable vibrational mode (which is necessarily a \(b_{2u}\)-type for the acene series) will give rise to in-phase and out-of-phase combination states, the former being the ground state and the latter the \(1B_{2u}\) state (albeit not necessarily the first excited state). The frequency of the interchanging mode in the excited state will be exalted with respect to that of the ground state.

Let us then apply this generalization to naphthalene and anthracene, and compare its predictions with experiment and calculations.

### IV.a. Naphthalene

The three classical Kekulé structures of naphthalene are shown in 9–11. The subscripts \(c\), \(l\), and \(r\) indicate the location of the vertically oriented double bond in the center in \(N_c\), and on the left and right, respectively, in \(N_l\) and \(N_r\).

\[ N_c \quad N_l \quad N_r \]

\(N_c\) has the full symmetry of the \(D_{2h}\) group and transforms as the totally symmetric irreducible representation \(A_g\). The \(N_l\) and \(N_r\) forms are mutually interchangeable by the \(i\), \(c_2\), and \(\sigma_v\) symmetry operations, much as in the case of benzene. An in-phase combination leads to an \(A_g\) state, and an out-of-phase combination to a \(B_{2u}\) state. These symmetry-adapted wave functions can now be mixed with the \(N_c\) form to yield the final states as shown schematically in Figure 2. Part a shows the in-phase and out-of-phase states formed from \(N_l\) and \(N_r\), and part b depicts the combination of these states with \(N_c\) to yield the final states. Due to symmetry match, \(N_c\) can mix only with the in-phase combination, leading to the ground state \(S_0(1A_g)\) and a high energy state of \(1A_g\) symmetry (not shown). The out-of-phase combination \(N_l - N_r\) which has no symmetry match remains as is and becomes the first excited \(1B_{2u}\) state.

Figure 2. A schematic description of the energy level diagram for naphthalene, showing the formation of the \(^1A_g\) and \(^1B_{2u}\) states from the three Kekulé structures. See the text for details.

### IV.b. Anthracene

There are four classical Kekulé structures for anthracene (12–15); two (12 and 13) involve bond alternation around the central ring, as in benzene, and are designated as \(B_i\) and \(B_r\). The other two (\(A_i\) and \(A_r\)) are annulenic and involve bond alternation along the periphery of the molecule. These \(A_i\) and \(B_i\) couples are pairwise interchangeable by the \(D_{2h}\) symmetry elements \(i\), \(c_2\), and \(\sigma_v\); the positive (in-phase) and negative (out-of-phase) combinations of these pairs are therefore symmetry adapted and transform as \(A_g\) and \(B_{2u}\), respectively, as shown in Figure 3a. Extending the Kekulé-crossing model to this case shows that each \(A_g-B_{2u}\) pair is related by an avoided crossing along a suitable \(b_{2u}\) coordinate.

\[ B_i \quad B_r \]

\[ A_i \quad A_r \]


Scheme 4 depicts these $b_{2u}$ modes that interchange the Kekulé pairs.

The state diagram is obtained by considering the interaction between the symmetry-adapted wave functions, as shown in Figure 3b. The lowest excited state that can be constructed from the Kekulé forms is the bonding combination of the two $B_{2u}$ configurations. This excited state turns out to be $S_2$, and has been recently studied by two-photon spectroscopy\(^8\) and by ab initio calculations.\(^9\) The $S_3$ state of anthracene is of $B_{1u}$ symmetry, and has a predominantly ionic character in the VB representation.

The wave functions of the ground state $S_0(1A_g)$ and the $S_2(1^1B_{2u})$ state can be expressed as a linear combination of the Kekulé structures (Scheme 4), as follows:

\[
\Psi(S_0) = c_1(A_1 + A_r) + c_2(B_1 + B_r) \quad (1)
\]
\[
\Psi(S_2) = c_1'(A_1 - A_r) + c_2'(B_1 - B_r) \quad (2)
\]

The $S_0$ and the $S_2$ states are constructed of in- and out-of-phase combinations of the Kekulé forms, and are therefore related by avoided crossings of the $A_1/A_r$ and $B_1/B_r$ types in the two dimensions defined by the interchanging modes in Scheme 4. The vibrations associated with these modes are thereby expected to have a higher frequency in the $S_2$ state than in the $S_0$ state. This prediction was verified recently computationally\(^9,10\) and appears to be confirmed experimentally for the $B_1/B_r$ pair switching mode. The $A_1/A_r$ one has not yet been definitely assigned.

**IV.c. A Frequency Gauge Index.** The foregoing analysis shows that one can predict the frequency change of the $b_{2u}$ vibrational modes between the ground state and the covalent $1^1B_{2u}$ state of many aromatic hydrocarbons. A lucid way of presenting the vibrational data for the ground state and the various excited states is by using a frequency gauge index ($I_k$) defined as

\[
I_k = \prod_k \left[ \omega_k(S_0) / \omega_k(S_2) \right]
\]

where the multiplication is carried over all vibrational frequencies $\omega_k$ of a given symmetry type $k$.

Figure 4 is a plot of $I_k$ for the computed frequency data for benzene, naphthalene, and anthracene for the lowest $B_{2u}$ and $B_{1u}$ electronically excited states. It is apparent that $I_k$ is smaller than unity for all symmetry types, except for the case of $b_{2u}$ symmetry for the $B_{2u}$
state. Thus, this index provides a concise way of demonstrating the mode and state selectivity of the frequency exaltation phenomenon, for the molecules discussed so far.

V. Atomic Motions in the Exalted Frequency Modes

The b2u modes of ground state benzene, naphthalene, and anthracene involve motion of both carbon and hydrogen atoms. As has been noted by many researchers,2,20 the two b2u modes in the 11B2u state of benzene exhibit a different nature: the frequency exalted mode involves only carbon atom motion, while the other mode only hydrogen atom movement, and the latter mode's frequency is lower than in S0. A similar trend was calculated for two b2u modes of naphthalene, as can be seen in Chart 1, and for anthracene, as shown in refs 9 and 10.

The Kekulé model, as outlined above, considered essentially only the heavy atom (carbon) motion. Symmetry arguments require that the hydrogen atoms also perform a similar b2u-type motion, and the observed trend can be accounted for using the schematic mode mixing diagram of Figure 5. Consider the overall vibrational motion as consisting of a combination of a carbon atom mode (ω(C)) and a hydrogen atom mode (ω(H)), both being symmetry adapted. The hydrogen mode is considered to be common for the ground and excited states, and is shown therefore in the middle of the diagram, labeled for short as ω(H). The carbon modes for the ground and excited states are drawn on the left- and right-hand sides of the diagram (ω(C) and ω(C*), respectively). It is seen that ω(C*) is placed higher than ω(C), in accord with our analysis of the exalted frequency of this mode in the excited state. Also shown in the middle part of the diagram is ω(D), the corresponding deuterium mode.

It is useful to consider first the case of deuterated benzene, in which the frequencies of the heavy and light atoms are significantly different. The large energy difference between ω(D) and either ω(C) or ω(C*) results in weak interactions, and the b2u vibrations in either the ground or the excited state remain therefore approximately pure atomic modes. Consequently, the frequency exaltation effect in the 1B2u state of C6D6 represents essentially the effect of the “pure” carbon atom mode. In C6H6, ω(H) happens to have a frequency similar to that of the carbon atom mode (ω(C)) of the ground state, and consequently the two mix and form in-phase and out-of-phase combination modes (e.g., for benzene see Figure 2 in ref 4), of somewhat different frequencies than the pure atomic motions. In the 1B2u state, however, the ω(C*) mode's frequency is much higher due to the stiffening of the Kekulé-dominated potential, and therefore mixing between the two modes is much less efficient, resulting in a separated pure atomic motions.

It is instructive to compare the foregoing qualitative arguments with the experimental conclusions derived by Goodman and co-workers20 based on measurements of the two-photon absorption cross-section (δ) for the two b2u modes (denoted spectroscopically as modes 14 and 15, ν14 being the higher frequency). As was discussed by Goodman et al.20 the cross-section δ increases with the increase of the skeletal (as opposed to hydrogenic) contribution to the normal mode. It was found that the ratio δ(1501)/δ(1401) is about 0.25 in C6H6, while for C6D6 the same drops to 0.042. For the same modes in the B2u excited state, the ratio is found to be very small for both isotopomers of benzene; i.e., δ(15C6)/δ(14C6) = 0.0035 for C6H6 and 0.001 for C6D6. In contrast, for 13C6H6 the cross-section ratio for the excited state modes increases. These findings provide direct experimental support for the mode mixing diagram (Figure 5) which derives from the Kekulé model.

VI. Generalization to Larger Linear Acenes

The foregoing discussion shows that the modes that undergo frequency up-shift in the covalent 1B2u excited state may be identified by enumerating the classical Kekulé structures and finding pairs that are interchangeable by skeletal modes (e.g., Scheme 4). The switching mode is necessarily of b2u symmetry, a property that carries over to the whole acene series. Therefore, a generalization suggests itself: in all the acene compounds, a frequency exaltation of at least one b2u mode is expected in the lowest lying (the covalent) 1B2u state.


Figure 5. Construction of the observed b2u vibrational modes of benzene from carbon atom and hydrogen atom modes. See the text for details.

Chart 1

1B2u (S1)  
1Ae (S0)

ω(C)  1587 cm⁻¹
V=1587 cm⁻¹

ω(D)  1103 cm⁻¹
V=1103 cm⁻¹

ω(C*)  1236 cm⁻¹
V=1236 cm⁻¹

ω(D*)  1333 cm⁻¹
V=1333 cm⁻¹
The enumeration of the Kekulé modes can be systematized following Cyvin and Gutman’s monograph. Pairing the Kekulé structures that cross one another is done by applying the symmetry operations \( i, C_2 \), and \( \sigma_v \): two structures that are interchanged by these operations will undergo avoided crossing along the switching coordinate mode. The switching mode is expected to exhibit a considerable frequency exaltation. On the basis of the analysis of anthracene, one mode seems to be more strongly affected than others, and this is likely to be the benzene-like (inner ring exchanging) mode in acenes containing an odd number of rings.

Table 1 summarizes this generalization, and provides an overview of the expected behavior. The first column of numbers gives the total number of classical Kekulé structures of the acene. The next column notes the number of interchangeable Kekulé pairs. One of them (the last entry) is always an annulenic pair in which bonds shift to-and-fro around the periphery of the molecule. Other pairs are localized in segments of the acene as specified by the ring identity in parentheses. The last column lists the number and placement of the \( b_{2u} \) modes that switch the Kekulé pairs and that are therefore expected to undergo frequency exaltation. As an illustration, structures 16 and 17 depict the two expected modes for tetracene; one central naphthalenic and the other annulenic. In a similar fashion, three modes are expected for pentacene—benzenic, anthracenic, and annulenic—the second being identical to the annulenic mode of anthracene, operating on the three central rings.


The Kekulé-crossing model presented in this paper shows that the frequency exaltation observed for certain \( b_{2u} \) modes in the \( 1^1B_{2u} \) states of aromatic hydrocarbons is a necessary result of the fact that these states are primarily covalent in nature, in the sense that they may be considered as linear combinations of the classical Kekulé structures. Thus, the ground and the \( 1^1B_{2u} \) states are very closely described by the states generated simultaneously (at the uniform geometry, \( D_0 \), or \( D_2 \)) by an avoided crossing between appropriate pairs of Kekulé-type structures along switching \( b_{2u} \) coordinates. The modes that undergo the frequency exaltation are the same ones that interchange the Kekulé pairs.**
The fact that the exalted mode is calculated to be a purely carbon atom motion, whereas in the ground state the same mode possesses mixed motion of carbon and hydrogen atoms, is also in line with the model. The exalted frequency observed for this mode in the $^3B_{2u}$ state ($\sim 1550 \text{ cm}^{-1}$) is typical for such motion, and arises due to the mismatch between the nuclear motion and the bonding features of the constituent Kekulé structures. This theory provides therefore a physical basis for the introduction of the special Kekulé term that had to be added to the standard Urey–Bradley force field in order to account for the apparently too low frequency of the $b_{2u}$ mode of benzene in the ground state: it is a reflection of the fact that, in the ground state, the $\pi$ electrons tend to distort the molecule to an alternating Kekulé structure, making the potential for motion along the $b_{2u}$ coordinate more shallow than the standard force fields predict. The mode and state selectivity of the frequency exaltation phenomenon is therefore a natural result of the model.

While this Account is concerned mainly with linear acenes and with the discussion of the Kekulé-crossing model, it should be added that frequency up-shifts were measured also for other systems and discussed by means of the vibronic coupling (VC) mechanism. For instance, excitation of polyenes to the $^2A_g$ state ($S_1$) is often (but not always) accompanied by a frequency increase of one of the $\alpha$ modes ("C=C" stretch). This phenomenon, as well as the frequency exaltation of the $\gamma_4$ mode in benzene, has been accounted for using the VC mechanism. In the VC model, one starts with diabatic states of a given symmetry which are eigenfunctions of the electronic Hamiltonian in a given geometry and symmetry. The introduction of linear coupling between these diabatic states, via a specific vibrational motion, results in the decrease of the frequency of the coupling mode in the ground state, and under certain conditions may lead to a frequency increase in the excited state. To effectively use the VC model, one has to define the appropriate diabatic electronic wave functions and then calculate through quantum-chemical methods all the quantities involved. By comparison, the Kekulé-crossing model starts from the diabatic Kekulé structures, which by themselves are not proper symmetry-adapted eigenfunctions of the electronic Hamiltonian. By mixing the Kekulé structures along an interchanging coordinate, one obtains the appropriate symmetry eigenfunctions of the electronic Hamiltonian, and in so doing identifies the nature of the electronic states. This reveals the interrelations between the two states in question, and simultaneously distinguishes the up-shifted vibrational mode as oscillating along the interchanging coordinate. As such, the Kekulé crossing constitutes a qualitatively transparent and physically vivid model for the origins of the frequency upshift, as well as for its mode and state selectivities. Furthermore, using the Kekulé structures as the initial diabatic set makes lucid predictions possible also in cases where symmetry is too low to facilitate specific assignments. Thus, for example, the successful predictions of the Kekulé-crossing model for non-symmetric molecules like styrene and indene show that the frequency exaltation of the localizing mode is not associated with the symmetry of the states, but rather with their constitution as avoided crossing "twin pairs" of the Kekulé forms.

Finally, it is shown that the model is easily extended to larger molecules of the acene series, and similar extensions to other systems are also expected. In fact, avoided crossings of Kekulé forms have been invoked in as diverse systems as metal clusters and hypercoordinated radicals and molecules. Frequency exaltation may turn out to be a ubiquitous phenomenon in chemistry, for delocalized systems that are describable as twin pairs of covalent VB structures, and presumably also for state pairs of general nature which maintain between them an avoided crossing relationship.

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