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A Kekulé-Crossing Model for the "Anomalous" Behavior of the b_{2u} Modes of Aromatic Hydrocarbons in the Lowest Excited $^1B_{2u}$ 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 1^1B_{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 (1^1A_{1g}) and the first $^1B_{2u}$ 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.

Sason Shaik received his B.Sc. and M.Sc. from Bar-Ilan University and his Ph.D. from the University of Washington, where he was a Fulbright Scholar (1974–1978). After spending one postdoctoral year at Cornell, he joined the staff of the Ben Gurion University in 1980, and in 1992 moved to the Hebrew University. He is an applied quantum chemist interested in the construction of unified concepts for problems of bonding, structure, and reactivity. Current interests include organic electron transfer reactivity, the role of electronic delocalization in ground and excited states, two-state reactivity patterns of transition metal catalysis, and examination of the perfectly resonating state as a model for the transition state.

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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 1^1B_{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 1^1B_{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.[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},[5] 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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(2) (a) Hochstrasser, R. M.; Wesel, J. E. *Chem. Phys. Lett.* **1974**, *24*, 1. (b) Wunsch, L.; Metz, F.; Neusser, H. J.; Schlag, E. W. J. *Chem. Phys.* **1976**, *66*, 386. (c) Friedrich, D. M.; McClain, W. M. *Chem. Phys. Lett.* **1975**, *32*, 541.

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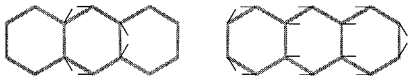
physical nature of this term was left unexplained, but turns out to arise naturally from the proposed model. It should be noted that this mode's frequency poses serious difficulties, even to the very sophisticated quantum mechanical calculations.[7]

1 **2**

In naphthalene, the Kekulé-type mode **2** is annulenic in type and undergoes a frequency exaltation of 189 cm^{-1} in the 1^1B_{2u} state relative to the ground state.[3a] In anthracene there exist two Kekulé-type modes, one (**3**) in which the benzene-like vibration is localized in the central ring and has been shown recently to undergo an up-shift of 231 cm^{-1}.[8–10] The b_{2u} modes in the B_{2u} states can be observed only by two-photon absorption, making their observation somewhat difficult; the second anthracene mode (**4**) has not been definitely assigned yet. It is calculated to be exalted by 96 cm^{-1}.[10]



3 **4**

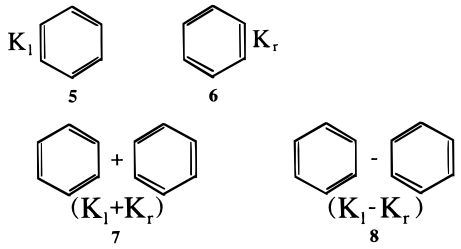
This phenomenon of frequency up-shift of the b_{2u} modes is in contrast with the usual pattern of frequency *decrease* which is observed upon electronic excitation. The weakening of π bonding which attends an excitation of an electron from a bonding to an antibonding orbital is intuitively expected to reduce the force constant of the associated normal modes and thereby, provided the reduced masses remain unchanged, to lead to smaller vibrational frequencies. Indeed, this expected trend is the observed behavior in many aromatic molecules (see ref 10 and references therein). Furthermore, the frequency up-shift is specific to the 1^1B_{2u} state and, to the best of our knowledge, is not observed in other excited singlet states of benzene, naphthalene, and anthracene. We are thus dealing here with a mode- and state- selective phenomenon. As discussed in a recent ab initio modeling,[11] the phenomenon originates in the simultaneous genesis of the 1^1A_{1g} and 1^1B_{2u} electronic states from the avoided crossing of the Kekulé structures along the b_{2u} coordinate, hereafter referred to as the Kekulé-crossing model.

According to this Kekulé-crossing model, the benzene case can be explained by the avoided crossing mechanism of Shaik and Hiberty,[11] assuming that the ground 1^1A_{1g} and first excited $^1B_{2u}$ 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 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,[11,12] 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 $^1A_{1g}$ ground electronic state of benzene and the 1^1B_{2u} excited state may both be considered as combinations of the two Kekulé structures K_l (**5**) and K_r (**6**). Thus, since the D_{6h} point group symmetry operations, inversion (i), 180° rotation (c_2), and reflection through a plane perpendicular to the molecular plane (σ_v), interconvert K_l and K_r, it follows that their positive combination **7** transforms as the totally symmetric representation of the group (A_{1g}), while their negative combination **8** transforms



as B_{2u}. Extensive valence bond (VB) calculations following the pioneering study of Da Silva et al.[13] show that these two structures give a good quantitative description of the states around the D_{6h} geometry.[11] 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. 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[11] energy of the two Kekulé structures as a function of motion along the b_{2u} coordinate that interchanges the two Kekulé structures. The energy of K_l 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_l 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

(7) Handy, N. C.; Maslen, P. E.; Amos, R. D.; Andrews, J. S.; Murray, C. W.; Laming, G. J. *Chem. Phys. Lett.* **1992**, *197*, 506.
(8) Wolf, J.; Hohlneicher, G. *Chem. Phys.* **1994**, *181*, 185.
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(13) da Silva, E. C.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *J. Chem. Phys.* **1994**, *101*, 3866.

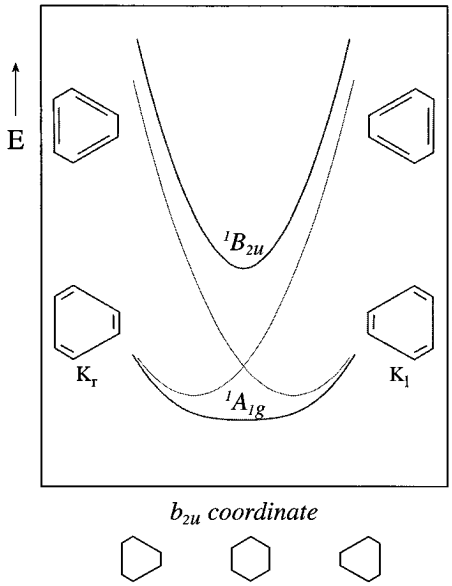
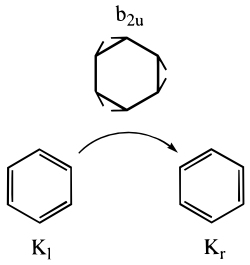


Figure 1. A schematic description of the intended crossing of the potential curves of the two Kekulé structures (K_l and K_r) of benzene along the b_{2u} coordinate alternating these structures, and of the state curves (shown in heavy print) resulting from their avoided crossing. At the center, D_{6h} symmetry, the avoided crossing results in the ground electronic state 1^1A_{1g} and the 1^1B_{2u} state.

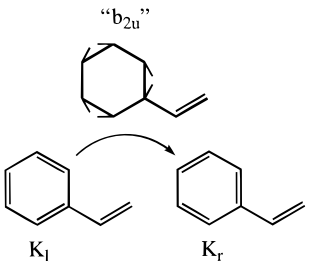
in heavy type in the figure, represent the behavior of the 1^1A_{1g} and 1^1B_{2u} states upon motion along the b_{2u} coordinate.

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_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 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_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 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 $^1B_{2u}$ 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 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 $^1B_{2u}$ 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 $K_l + K_r$ combination leads to a low frequency, while in the excited state, the strained out-of-phase

Scheme 1



Scheme 2



$K_l - K_r$ 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*-β-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_{1g}" 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 (0.002[17]), 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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(15) Kendler, S.; Zilberg, S.; Haas, Y. *Chem. Phys. Lett.* **1995**, *242*, 139.
(16) Zilberg, S.; Kendler, S.; Haas, Y. *J. Phys. Chem.*, in press.
(17) Hemley, R. J.; Dinur, U.; Vaida, V.; Karplus, M. *J. Am. Chem. Soc.* **1985**, *107*, 836.

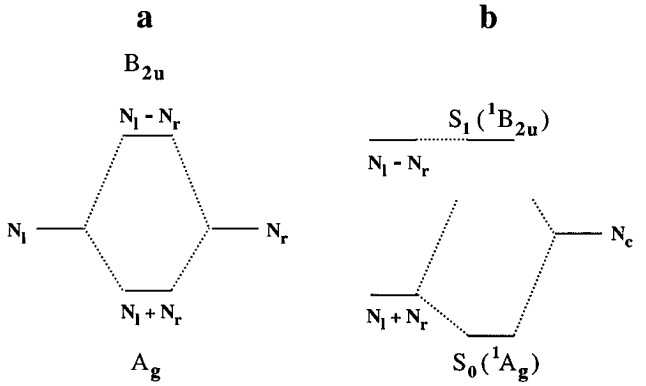


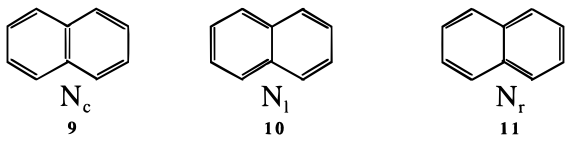
Figure 2. A schematic description of the energy level diagram for naphthalene, showing the formation of the ^1A_g and $^1B_{2u}$ states from the three Kekulé structures. See the text for details.

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 1^1B_{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.

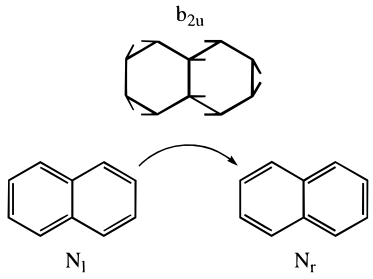
Let us then apply this generalization to naphthalene and anthracene, and compare its predictions with experiment and calculations.

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.



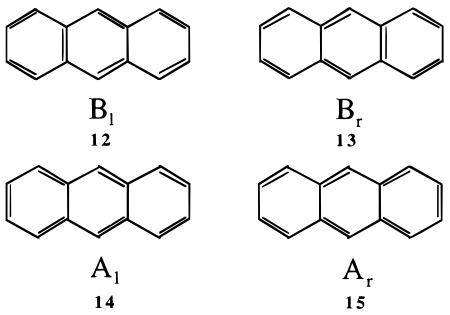
N_c has the full symmetry of the D_{2h} group and transforms as the totally symmetric irreducible representation A_g. The N_l and N_r forms are mutually interchangeable by the i, c_2, and σ_v symmetry operations, much as in the case of benzene. An in-phase combination leads to an A_g state, and an out-of-phase 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 1^1B_{2u} state.

Scheme 3



Scheme 3 shows that a b_{2u}-type vibration interchanges the N_l and N_r structures, by alternating the lengths of the C−C bonds, much as in the case of benzene (Scheme 1). According to our model, this vibration is expected to have a higher force constant (and thus frequency) in the 1^1B_{2u} excited state. This assumes that the contribution of the N_c state to the ground state wave function has a negligible effect on the motion along the b_{2u} coordinate. The fact that frequency exaltation is experimentally observed[3] appears to justify this assumption. This reasoning predicts also that the π electrons tend to distort the ground state molecule to a Kekulé-type molecule, in line with a recent detailed computational analysis,[19] based on ab initio modeling of the π energy. Finally, we note that the ab initio computed mode whose frequency is exalted in the 1^1B_{2u} state is *annulenic*, not involving motion along the central bond, precisely as predicted by the Kekulé-crossing model.

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_l and B_r. The



other two (A_l and A_r)are annulenic and involve bond alternation along the periphery of the molecule. These $A_{l,r}$ and $B_{l,r}$ couples are pairwise interchangeable by the D_{2h} symmetry elements i, c_2, and σ_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.

(18) Sironi, M.; Cooper, D. L.; Gerratt, J.; Raimondi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 675.

(19) Hiberty, P. C.; Danovich, D.; Shurki, A.; Shaik, S. *J. Am. Chem. Soc.* **1995**, *117*, 7760.

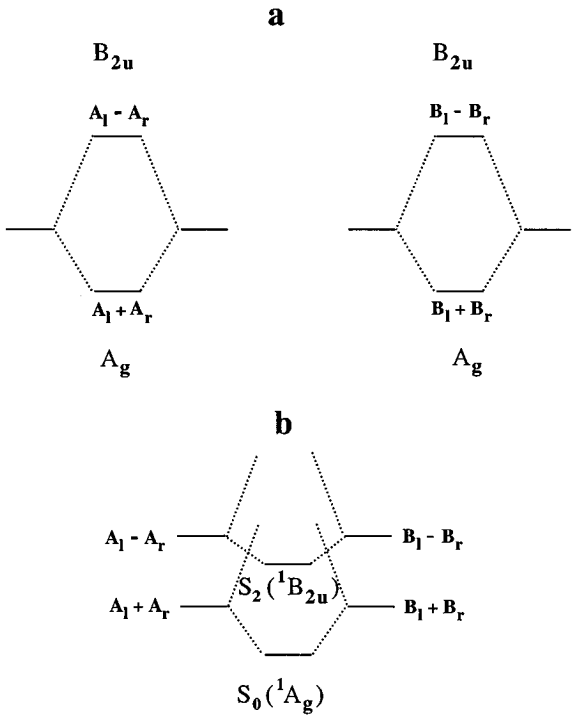
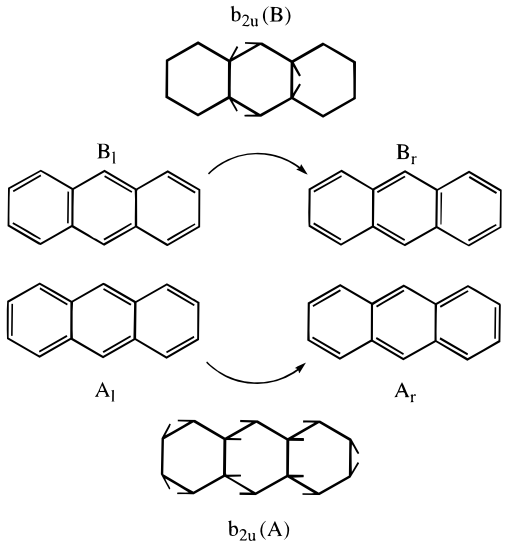


Figure 3. A schematic description of the (a) symmetry-adapted combinations of the four Kekulé structures of anthracene and (b) state diagram of the low lying electronic states of anthracene, constructed from these symmetry-adapted combinations. The A and B combinations are assumed to have the same energies.

Scheme 4



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_1 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:

$$\Psi(S_0) = c_1(A_l + A_r) + c_2(B_l + B_r) \quad (1)$$

$$\Psi(S_2) = c'_1(A_l - A_r) + c'_2(B_l - B_r) \quad (2)$$

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_l/A_r and B_l/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_l/B_r pair switching mode. The A_l/A_r one has not yet been definitely assigned.

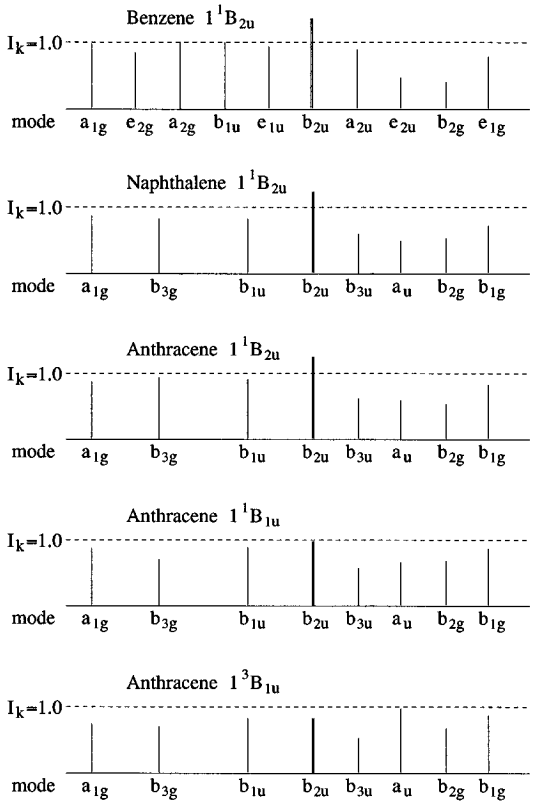


Figure 4. Frequency gauge index I_k (eq 3) for some electronic states of benzene, naphthalene and anthracene. The index exceeds 1 only for the b_{2u} symmetry modes of the 1^1B_{2u} states.

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 $^1B_{2u}$ 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

$$I_k = \prod_k [(\omega_k)_{S_i}/(\omega_k)_{S_0}] \quad (3)$$

where the multiplication is carried over all vibrational frequencies ω_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}

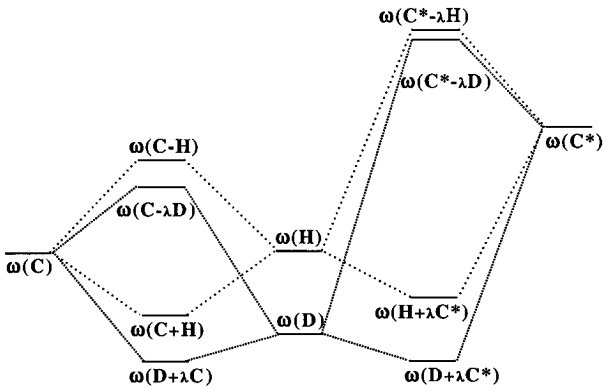


Figure 5. Construction of the observed b_{2u} vibrational modes of benzene from carbon atom and hydrogen atom modes. See the text for details.

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.

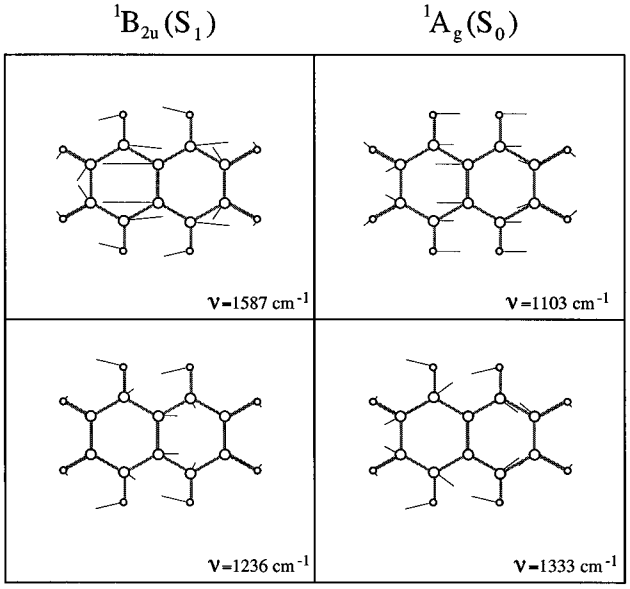
V. Atomic Motions in the Exalted Frequency Modes

The b_{2u} 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 b_{2u} modes in the 1^1B_{2u} 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 S_0. A similar trend was calculated for two b_{2u} 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 b_{2u}-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 (b_{2u}(C)) and a hydrogen atom mode (b_{2u}(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 b_{2u} vibrations in either the ground or the excited state remain therefore approximately pure atomic modes. Consequently, the frequency exaltation effect in the 1^1B_{2u} state of C_6D_6 represents essentially the effect of the "pure" carbon atom mode. In C_6H_6, 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 1^1B_{2u} 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.

Chart 1



It is instructive to compare the foregoing qualitative arguments with the experimental conclusions derived by Goodman and co-workers[20] based on measurements of the two-photon absorption cross-section (δ) for the two b_{2u} modes (denoted spectroscopically as modes 14 and 15, ν_{14} 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 $\delta(15_0^1)/\delta(14_0^1)$ is about 0.25 in C_6H_6, while for C_6D_6 the same drops to 0.042. For the same modes in the B_{2u} excited state, the ratio is found to be very small for both isotopomers of benzene; i.e., $\delta(15_0^1)/\delta(14_0^1) = 0.0035$ for C_6H_6 and 0.001 for C_6D_6. In contrast, for $^{13}C_6H_6$ 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 $^1B_{2u}$ 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 b_{2u} 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 b_{2u} mode is expected in the lowest lying (the covalent) $^1B_{2u}$ state.*

(20) Goodman, L.; Berman, J. M.; Ozkabak, A. G. *J. Chem. Phys.* **1989**, *90*, 2544. Ozkabak, A. G.; Goodman, L.; Berman, J. M. *Chem. Phys. Lett.* **1990**, *168*, 253.

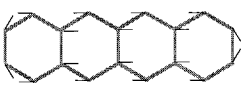
Table 1. The Kekulé Structures and the Predicted b_{2u} Modes Which Undergo Frequency Exaltation in the 1^1B_{2u} Excited State of Acenes

acene	no. of Kekulé structures	no. of interchangeable Kekulé pairs[a]	no. of exalted b_{2u} modes[b]
A	2	1 (A)	1 (A)
A B	3	1 (A, B)	1 (A, B)
A B C	4	1 (B), 1 (A−C)	1 (B), 1 (A−C)
A B C D	5	1 (B, C); 1 (A−D)	1 (B, C); 1 (A−D)
A B C D E	6	1 (C); 1 (B−D); 1(A−E)	1 (C); 1 (B−D); 1 (A−E)
$2n + 1$	$2n + 2$	1; B + $2m$ (m = 1, 2, ..., n)[c]	1; B + $2m$ (m = 1, 2, ..., n)
$2n + 2$	$2n + 3$	1; N + $2m$ (m = 1, 2, ..., n)[d]	1; N + $2m$ (m = 1, 2, ..., n)

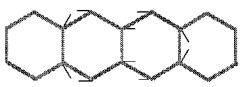
[a] The letters in parentheses signify the rings over which the interchanging Kekulé pair undergoes bond shift (resonance). [b] The placement of the b_{2u} mode matches precisely the resonance regions of the corresponding interchangeable Kekulé pairs described in footnote *a*. [c] Consult structure **18**. The single pair corresponds to the resonance in the central benzenic (B) moiety. The other pairs indicated by B + $2m$ correspond to resonance over segments composed of the central benzene moiety (B) flanked by pairs of benzene moieties whose number is given by $2m$. [d] Consult structure **19**. The single pair corresponds to the resonance in the central naphthalenic (N) moiety. The other pairs indicated by N + $2m$ correspond to resonance over segments composed of the central naphthalene moiety (N) flanked by pairs of benzene moieties whose number is given by $2m$.

The enumeration of the Kekulé modes can be systemized following Cyvin and Gutman's monograph.[21] Pairing the Kekulé structures that cross one another is done by applying the symmetry operations i, c_2, and σ_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



16

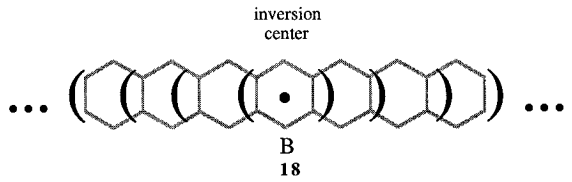


17

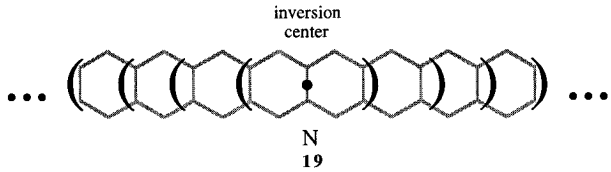
for tetracene; one central naphthalenic and the other annulenic. In a similar fashion, three modes are expected for pentacene—benzenic, anthracenic, and annulenic—the second being identical to the annulenic mode of anthracene, operating on the three central rings.

(21) Cyvin, S. J.; Gutman, I. *Kekulé structures in benzenoid hydrocarbons*; Lecture Notes in Chemistry, Vol. 46; Springer-Verlag: Heidelberg, 1988.

Structures **18** and **19** depict the general case of the even and odd acenes, respectively. Generalizing, the most localized mode in each class occurs around the inversion center and is either benzenic (**18**) or naphthalenic (**19**), depending on whether the acene is odd- or even-membered. The other modes extend by successively adding to the central mode two more flanking rings. It is apparent that further application of the Kekulé-crossing model is straightforward and can be used as a guide for designing and interpreting experiments on other systems.[28]



B
18



N
19

VII. Summary

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_{6h} or D_{2h}) 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.[10]

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 $^1B_{2u}$ state ($\sim$1550 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 π electrons tend to distort the molecule to an alternating Kekulé structure,[12] 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.[22] For instance, excitation of polyenes to the 2^1A_g state (S_1) is often (but not always) accompanied by a frequency increase of one of the a_g modes ("C═C" stretch[22]). This phenomenon, as well as the frequency exaltation of the ν_{14} mode in benzene,[23] has been accounted for using the VC mechanism.[22] 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.[22,24] 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 up-shift, 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[14,16] 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.[25−27] 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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(28) Note added in proof: A Kekulé-crossing model was used to explain similar findings in ethano-bridged [14]annulene. See: Klingensmith, K. A.; Dewey, H. J.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 1539.