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## The Calculation of Franck-Condon Factors for the Electronic Transitions of the Polyacenes

By

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Progressional intensities have been calculated for the  ${}^1L_a$  band of the polyacenes which give good agreement with experiment. The Franck-Condon factors are calculated on the assumption that the frequencies and normal modes in the ground and excited states are identical. Our results, based on a simple force field, also show that the assumption (by McCoy and Ross) that the C-C stretching frequencies are degenerate is satisfactory as far as the calculation of the shape of the overall vibrational envelope is concerned.

Wir berechneten die Intensitäten der  ${}^1L_a$ -Progressionen von Acenen, in guter Übereinstimmung mit dem Experiment. Die Franck-Condon-Faktoren werden unter der Annahme bestimmt, daß Frequenzen und Normalschwingungen im Grund- und angeregten Zustand gleich sind. Unsere mit einem einfachen Kraftansatz erhaltenen Ergebnisse zeigen weiter, daß die Annahme (von McCoy und Ross) entarteter C-C-Valenzschwingungen ausreicht, um die allgemeine Schwingungsstruktur der Bandenveloppe zu berechnen.

Nous avons calculé les intensités de progression de la bande  ${}^1L_a$  des acènes, en bon accord avec l'expérience. Les facteurs de Franck-Condon sont déterminés, en admettant des fréquences et vibrations normales identiques pour les états fondamental et excité. Nos résultats, sur base d'un champ de force simple, montrent de plus que l'hypothèse (de McCoy et Ross) des vibrations de valence C-C dégénérées est satisfaisant pour le calcul de la forme générale de l'enveloppe vibrationnelle des bandes.

McCoy and Ross [5] have given a method for the calculation of the intensities of the vibrational components of the electronic bands of aromatic hydrocarbons which gives results in reasonable agreement with experiment. Their calculations are based on the assumption that only one vibrational mode, or a set of degenerate modes, contributes to the vibrational progression; an assumption which was suggested by the fact that solution spectra often show only a single vibrational progression (e. g. the dominant  $1400\text{ cm}^{-1}$  progression that appears in the  ${}^1L_a$  bands of the aromatic hydrocarbons). However, the higher resolution spectra obtained from a vapour or low temperature crystal show that there may be several vibrational modes appearing quite strongly as progressions.

The great advantage in working with the assumption of McCoy and Ross is that one can calculate Franck-Condon factors\*\* without any knowledge of the normal modes of the molecule. However, it is an interesting problem in itself why

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\*\* The Franck-Condon factors are squares of the overlap integrals between the vibrational wave functions of the ground state and those of the excited electronic state. Within the Born-Oppenheimer approximation and the assumption that the electronic transition moment is a slowly varying function of the nuclear co-ordinates, the intensities of the vibronic bands are proportional to their Franck-Condon factors.

only one progression is observed, and in this paper we present calculations of progression intensities without making the McCoy and Ross assumption. In this way, we shall attempt to explain why there appears to be only one dominant vibrational progression in the  ${}^1L_a$  band of the polyacenes and why this frequency is usually close to  $1400\text{ cm}^{-1}$ .

The calculation falls into three sections:

- a) The calculation of approximate normal modes.
- b) The calculation of changes in bond length on electronic excitation.
- c) From a) and b) above the Franck-Condon factors are calculated.

#### a) The Normal Co-ordinates

There have been several detailed normal co-ordinate studies of benzene and naphthalene, but there has been no general treatment of the higher members of the series. The object of this earlier work was to obtain a good fit with infra-red and Raman frequencies of the molecules. Our object is to obtain a set of normal co-ordinates which are sufficiently accurate to calculate reliable vibrational overlap integrals for the whole series of molecules. Clearly we are unable to adopt such a sophisticated force field for the series as those which have been used for benzene and naphthalene.

There is no reason to expect, and no evidence for, a change in symmetry of these molecules when they are excited to the  ${}^1L_a$  state. It follows that only the totally symmetric modes can occur in a vibrational progression, and these will be in-plane vibrations. The spectral region around  $1400\text{ cm}^{-1}$  is generally associated with the C-C stretching modes, which may be mixed with some C-H bending. However, McCoy and Ross have shown that deuteration of anthracene gives no significant change in the overall vibrational pattern, and following them, we have therefore assumed that the observed progression is dominated by C-C skeletal stretching frequencies.

Our normal modes have been calculated on the basis of a single parameter force field consisting of the C-C stretching constant  $k$ . Initially, an interaction constant  $k'$  was included for the stretching of neighbouring C-C bonds. For small  $k'$  this parameter exerts a first order perturbation so that the energies are linear functions, and the normal modes are almost independent, of  $k'$ . Further, the best fit was obtained with  $k' = 0.02\text{ md}/\text{\AA}$  ( $k = 5.7\text{ md}/\text{\AA}$ ) which did not appreciably improve the results compared with  $k' = 0$  ( $k = 5.6$ ). For these reasons  $k'$  has been neglected as being unimportant for our purpose. We have also assumed the ring structure to be perfectly hexagonal.

The force field is not sufficiently sophisticated to give accurate normal co-ordinates and frequencies. However, it gives a reasonably good fit with the experimental, totally symmetric, carbon skeletal frequencies of benzene and naph-

Table 1. *Comparison of Calculated and Observed Frequencies (cm<sup>-1</sup>)*  
(Totally symmetric C-C stretch only)

	Benzene	Naphthalene			
Observed [4]	992	762	1025	1379	1579
Calculated	985	675	1049	1431	1550

thalene. The calculated and observed frequencies, evaluated with  $k = 5.6 \text{ md}/\text{\AA}$ , are compared in Tab. 1.

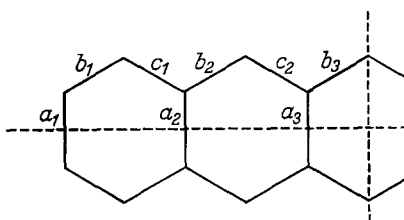
The calculated frequencies given by the one parameter force field are shown in Tab. 3, it is seen in all cases that there are a number of vibrational frequencies between about  $1300$  and  $1600 \text{ cm}^{-1}$ . It is now necessary to establish whether just one of these gives rise to a strong progression or whether they are sufficiently close in energy to be considered degenerate for the calculation of Franck-Condon factors.

### b) The Calculation of Bond Order Changes on Excitation

Like McCoy and Ross, we have assumed a linear correlation between bond length and bond orders derived from molecular orbital calculations. A number of expressions relating the ground state bond lengths  $R$  ( $\text{\AA}$ ) to the Hückel Bond Order  $P$  have been proposed for the aromatic hydrocarbons. These all show a

Table 2. Bond Order Changes for Excitation to the  ${}^1L_a$  State

	$a_1$	$a_2$	$a_3$	$b_1$	$b_2$	$b_3$	$c_1$	$c_2$
Naphthalene	0.138 <i>0.129</i>	0 <i>-0.054</i>		-0.224 <i>-0.228</i>			0 <i>0.0156</i>	
Anthracene	0.096 <i>0.112</i>	0.002 <i>-0.001</i>		-0.136 <i>-0.148</i>	-0.080 <i>-0.140</i>		0.056 <i>0.090</i>	
Tetracene	0.067	0.025	0	-0.087	-0.087		0.053	0
Pentacene	0.048	0.025	0.003	-0.058	-0.073	-0.031	0.042	0.027



nearly linear relation between the two,  $\delta R$  ( $\text{\AA}$ ) =  $-\kappa \delta P$ , with  $\kappa$  being between 0.15 and 0.20. The uncertainty in the experimental bond lengths does not really allow  $\kappa$  to be more precisely fixed. However, it is by no means certain that the same relation should hold for excited states because an electron in an antibonding orbital may have a larger effect on bond lengths than one in a bonding orbital. The increase in bond length associated with the benzene  $2600 \text{ \AA}$  ( $B_{2u} \leftarrow A_{1g}$ ) transition has been determined accurately by DUNN\* to be  $0.038 \text{ \AA}$ . As the appropriate bond order change is  $1/6$ , then these data are fitted by the expression:

$$\delta R$$
 ( $\text{\AA}$ ) =  $-0.228 \delta P$ .

We have adopted this expression for the calculation of bond length changes for the whole polyacene series.

The simplest interpretation of the  ${}^1L_a$  band is that it is associated with an electron transfer from the highest occupied to the lowest unoccupied molecular

\* Private communication.

Table 3. *Components of the Molecular Distortion along the Direction of the Normal Coordinates*

Naphthalene		Anthracene		Tetracene		Pentacene	
Calculated Frequency (cm <sup>-1</sup> )	<i>D</i> . Q (Å)	Calculated Frequency (cm <sup>-1</sup> )	<i>D</i> . Q (Å)	Calculated Frequency (cm <sup>-1</sup> )	<i>D</i> . Q (Å)	Calculated Frequency (cm <sup>-1</sup> )	<i>D</i> . Q (Å)
1550	0.0874	1550	0.0753	1550	0.0545	1550	0.0556
1431	-0.0840	1437	-0.0556	1550	0.0346	1550	0.0001
1049	0.0262	1324	0.0191	1440	-0.0391	1442	-0.0185
675	0.0149	1002	0.0081	1367	-0.0144	1391	0.0105
		617	0.0082	1023	0.0034	1292	-0.0010
				815	-0.0010	1015	0.0017
				592	0.0052	746	0.0004
						580	0.0035

orbital. On this interpretation, the change in bond order on excitation is given by  $-2 c_{1\mu} c_{1\nu}$ , where  $c_{1\mu}$  is the coefficient of atom  $\mu$  in the highest occupied orbital. This follows from the pairing property of the orbitals of an alternant hydrocarbon in a zero-overlap scheme. The bond order changes calculated from Hückel orbitals are shown in Tab. 2.

More elaborate calculations, including configuration interaction, for naphthalene and anthracene give rather higher bond order changes than those obtained from Hückel theory and these are shown in italics in Tab. 2. We shall confine ourselves to Hückel calculations for the whole series — but the configuration interaction calculations suggest that we may be slightly underestimating the true bond length changes.

The predicted bond length changes for each molecule may be regarded as an  $n$ -dimensional vector  $\mathbf{D}$  in the space spanned by the  $n$  normal coordinates. Tab. 3 shows the components of  $\mathbf{D}$  along each normal co-ordinate  $Q_i$ .

From Tab. 3 it is evident that as the molecular size increases the magnitude of the components decreases and becomes concentrated more within the modes of frequencies around 1500 cm<sup>-1</sup>. In terms of the progressional envelope this means that the progression length should be reduced and the structure be more regular for the higher members. This is in general agreement with experiment.

### e) The Calculation of Progressional Intensities

The Franck-Condon factors have been calculated from the data of Tab. 3 with the further assumptions that the vibrational frequencies and the normal modes in the ground and excited electronic states are the same. This means in effect that the shape of the potential energy surface in the two electronic states is the same and only the equilibrium positions of the nuclei are changed. From tables of vibrational overlap integrals which have been evaluated for simple molecules it is clear that the intensity of a vibrational progression depends much more on changes in bond length than on changes in force constant. A typical result shows that if the equilibrium distance is changed by an amount equal to the zero point vibrational amplitude, then a further change of 20% in the force constant will only change the Franck-Condon factors for the first few members of the progression by 10% or less.

We assume that in the ground electronic state only the lowest vibrational state is occupied whose vibrational wave function is:

$$\Psi_{(0)} = \prod_{i=1}^n \vartheta_0(Q_i). \quad (1)$$

The vibrational wave functions in the excited electronic state are then given by:

$$\Psi'_{(j)} = \prod_{i=1}^n \vartheta_{m_i}(Q'_i) \quad (2)$$

where  $Q'_i = Q_i + \delta Q_i$  and  $m_i$  is the vibrational quantum number of the  $i$ 'th mode.

If electronic excitation results in a vibronic change from the states described by (1) to (2) above, then the associated intensity relative to the  $\Psi'_{(0)} \leftarrow \Psi_{(0)}$  vibronic transition is:

$$\frac{I_{j \leftarrow 0}}{I_{0 \leftarrow 0}} \simeq \frac{\langle \Psi_{(0)} | \Psi'_{(j)} \rangle^2}{\langle \Psi_{(0)} | \Psi'_{(0)} \rangle^2} = \prod_{i=1}^n \left( \frac{\langle \vartheta_0(Q_i) | \vartheta_{m_i}(Q'_i) \rangle^2}{\langle \vartheta_0(Q_i) | \vartheta_0(Q'_i) \rangle^2} \right). \quad (3)$$

A typical product term in this expression is:

$$\frac{\langle \vartheta_0(Q_k) | \vartheta_{m_k}(Q'_k) \rangle^2}{\langle \vartheta_0(Q_k) | \vartheta_0(Q'_k) \rangle^2} = \frac{S_{0m_k}^2}{S_{00}^2} \quad (4)$$

which is the ratio of the Franck-Condon factors corresponding to the  $m \leftarrow 0$  and the  $0 \leftarrow 0$  transition in the  $k$ th mode. Further it may be shown that [6]

$$\frac{S_{0m_k}^2}{S_{00}^2} = \frac{a_k^2 m_k}{2^{m_k} (m_k!)} \quad (5)$$

where

$$a_k = \frac{\delta Q_k}{Q_k^0} = \frac{\mathbf{D} \cdot \mathbf{Q}_k}{|Q_k|} / Q_k^0 \quad (6)$$

and  $Q_k^0$  is the zero point vibrational amplitude in the  $k$ th mode given by

$$Q_k^0 = \frac{1}{2\pi} \left( \frac{2\hbar}{m\nu_k} \right)^{\frac{1}{2}}. \quad (7)$$

From equations (3) to (7) above we have calculated the intensities of the most important fundamental, overtone and combination bands.

### Results and Discussion

The calculated intensities are compared with experiment in Fig. 1. The lines represent the position and relative intensities of the vibrational progressions (the  $0 \leftarrow 0$  band is fitted to experiment) and the dotted line is a spectrum synthesised from gaussian vibrational components with a half-band width of  $170 \text{ cm}^{-1}$ . There is generally good agreement between the observed and synthesised peak height although there appears to be a tendency to underestimate the intensity of the higher vibrational components for the larger molecules in the series. Our calculations also overestimate slightly the spacing of the principal vibrational maxima.

Low temperature fluorescence and absorption of single mixed crystals of anthracene and tetracene suggest that the  $1 \leftarrow 0$  transition involving the vibration of about  $1400 \text{ cm}^{-1}$  should be more intense than the corresponding  $1550 \text{ cm}^{-1}$  vibration. This is contrary to our results. Further for naphthalene our normal co-ordinate corresponding to  $1550 \text{ cm}^{-1}$  is very similar to that corresponding to

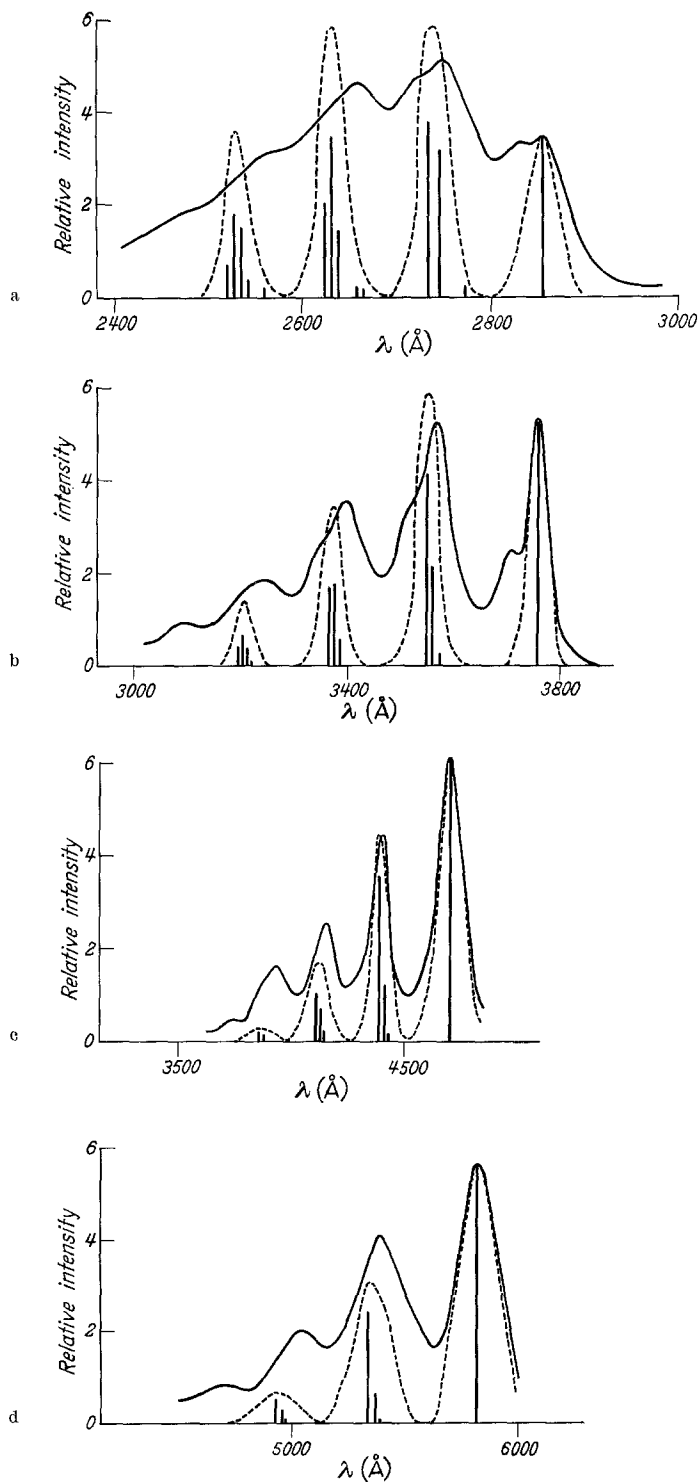


Fig. 1. Comparison of calculated and experimentally observed intensities for the  $^1L_a$  band of the polyacenes. a) Naphthalene (in iso-octane, 26° C) [1], b) Anthracene (in iso-octane, 25° C) [2], c) Tetracene (in alcohol) (Replot from ref. [3]), d) Pentacene (in trichlorobenzene) (Replot from ref. [3])

a frequency of  $1375\text{ cm}^{-1}$  calculated from a more sophisticated force field. We have examined various force fields including one in which the C-C stretching constant is taken to be proportional to the C-C bond lengths but have concluded that no force field which takes into account only C-C stretching co-ordinates will give agreement with experiment in this respect. The inversion of the intensity ratio for these two frequencies is probably due to the neglect of bending co-ordinates, however more accurate experimental intensity data are required to ascertain just how serious is this omission.

Our calculations show more pronounced differences between the maxima and minima in the spectra than is observed. This is because we have neglected all the bending co-ordinates in our normal modes and also ignored the contribution from excited vibrational levels in the ground state (hot bands).

In conclusion, the assumption made by McCoy and Ross that all the C-C stretching frequencies can be treated as degenerate is, for the  ${}^1L_a$  bands of these compounds, a good one, because the only vibrations which contribute intensity to the progression have a frequency close to  $1400\text{ cm}^{-1}$ . However, if one calculates spectra using the assumption of degeneracy then the intensity of the maxima are increased substantially for naphthalene and anthracene. McCoy and Ross avoided this difficulty by using a smaller value of  $\nu$ , and obtained results for anthracene which are comparable to ours.

Finally one can draw one important assertion from our results which is that on excitation, at least to the  ${}^1L_a$  state there is not an overall increase in bond length in the molecule. If this were the case, one would expect to see strong progressions in the lower frequency, totally symmetric, vibrations, and this is not the case.

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