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Franck-Condon Factors for Large Aromatic Molecules

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In an earlier paper [1] (referred to as I), we calculated the relative intensities of vibrational components appearing in the ^1L_a band of the linear polyacenes and showed that these were in good agreement with experiment. We have since found that the components of the vector (in terms of normal co-ordinates) representing the change in equilibrium configuration on electronic excitation, were calculated by an incorrect procedure. Although the formulae given in the paper are correct, in our calculations we confused the transpose with the inverse of the $\boldsymbol{L}$ matrix*. Because in our calculation the reduced mass was factored out of the $\boldsymbol{G}$ matrix, $\boldsymbol{L}$ was nearly orthogonal, and hence $\boldsymbol{L}^{-1}$ was nearly the same as $\boldsymbol{L}^{\dagger}$. The results we presented in I are therefore not grossly in error.

The corrected envelopes are included for the polyacenes in Fig. 1. The calculated positions and relative intensities of the more important fundamentals are included in the table.

The dotted envelopes are calculated on the basis of a bond order-bond length relation $R = \varkappa P$ with $\varkappa$ chosen to fit the known bond length changes associated with the benzene $^1B_{2u} \leftarrow {}^1A_{1g}$ transition, as described in I. It is seen that for the polyacenes the progressional intensity is rather less than that observed experimentally. If the value of $\varkappa$ is increased from 0.228 to 0.300 the calculated envelopes (shown in Fig. 1 by broken lines) are in much better agreement. By comparing the dotted and dashed envelopes one can see that $\varkappa$ is a very sensitive parameter in the theory.

Similar calculations have been carried out for the ^1L_a bands of perylene and pyrene. For perylene, once again better agreement is obtained using $\varkappa = 0.3$ rather than 0.228, as may be seen from Fig. 1. Pyrene, on the other hand, is an exception to the general trend in that the reverse is true. With $\varkappa = 0.3$ the intensities are considerably overestimated and the corresponding broken line has not

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* We use the nomenclature of Wilson, Decius and Cross [2]. If $\boldsymbol{d}$ is the column vector giving the change in equilibrium configuration in the terms of internal co-ordinates, then the change in terms of normal co-ordinates is $\boldsymbol{Q} = \boldsymbol{L}^{-1}\boldsymbol{d}$, where $\boldsymbol{S} = \boldsymbol{L}\boldsymbol{Q}$ and the elements of $\boldsymbol{L}$ are normalised to the $\boldsymbol{G}$ matrix such that $\boldsymbol{G} = \boldsymbol{L}\boldsymbol{L}^{\dagger}$. Our error amounted to writing $\boldsymbol{Q} = \boldsymbol{L}^{\dagger}\boldsymbol{d}$.

Two misprints appear in Paper I. The entry under benzene calculated in table (of I) should be 892 cm^{-1} and the entry under anthracene (a_2) in table should be 0.016 rather than 0.002.

A detailed general theory of Franck-Condon factors for polyatomics taking into account changes in normal coordinates on excitation has been given by Sharp and Rosenstock [3], but previously applied only to small molecules.

Table. *Calculated Vibrational Fundamental Frequencies* (ν in cm^{-1}) *and Intensities* (I) *Relative to the* 0—0 *Band for some Aromatic Hydrocarbons*

Naphthalene[a]		Anthracene[a]		Tetracene[a]		Pentacene[a]		Pyrene[a]		Perylene[a]		Phenanthrene[b]	
ν	I	ν	I	ν	I	ν	I	ν	I	ν	I	ν	I
675	0.164	617	0.065	593	0.029	580	0.014	523	0.044	478	0.029	586	0.108
1048	0.135	1002	0.015	815	0.000	745	0.000	987	0.077	858	0.003	937	0.033
1431	0.548	1324	0.036	1023	0.002	1015	0.001	1058	0.004	1044	0.030	1003	0.007
1550	0.467	1437	0.237	1367	0.019	1292	0.000	1323	0.000	1315	0.007	1152	0.008
		1550	0.346	1440	0.116	1391	0.009	1513	0.508	1374	0.000	1331	0.102
				1550	0.073	1442	0.062	1550	0.185	1527	0.339	1402	0.078
				1550	0.181	1550	0.000			1550	0.190	1521	0.039
						1550	0.189					1550	0.189
												1550	0.006

The intensities in this table are calculated using $\varkappa = 0.228$. For $\varkappa = 0.300$ they must be multiplied by a factor of 1.731. The overtones and combinations require multiplication by different factors. [a] ^1L_a excited state; [b] ^1L_b excited state.

been plotted. This suggests that $\varkappa$ may be better treated as an empirical parameter which is adjusted for different series of aromatic compounds.

With reference to the table, the calculated intensities in the case of anthracene and tetracene for the vibrational component around 1500 cm^{-1} is more intense than that around 1400 cm^{-1}. As pointed out in I the reverse is experimentally observed (see also the measurements of BREE et al. [*4*]). We have now found that this discrepancy can be removed by including angle bending co-ordinates into the vibrational problem. For anthracene we repeated the calculation using a force field consisting of a diagonal C–C-stretching force constant F (with the same value as used earlier)*, $F_{\alpha\alpha}$, the C–C–C angle bending force constant and $F'_{\alpha\alpha}$ an interaction force constant between the neighbouring angle bends. The values for $F_{\alpha\alpha}$ and $F'_{\alpha\alpha}$ were taken from DUINKER's benzene force field [*5*]; namely $F_{\alpha\alpha} = 0.563$ and $F'_{\alpha\alpha} = 0.316$ md/Å. An additional problem is now that the changes in bond order do not completely specify the changes in geometry because there are some angular degrees of freedom remaining. These degrees of freedom were determined by minimising the energy of the distorted molecule using the same force field. Using $\varkappa = 0.228$ this calculation gave the two highest stretching fundamental frequencies as 1593 and 1496 cm^{-1} with intensities relative to the 0—0 transition of 0.119 and 0.413 respectively. Although the frequency fit is not as good as with our single force field (it could presumably be improved by adjusting the parameters F, $F_{\alpha\alpha}$ and $F'_{\alpha\alpha}$) the ratio of the intensity of the high-

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* The exact value of F is 5.630 md/Å.

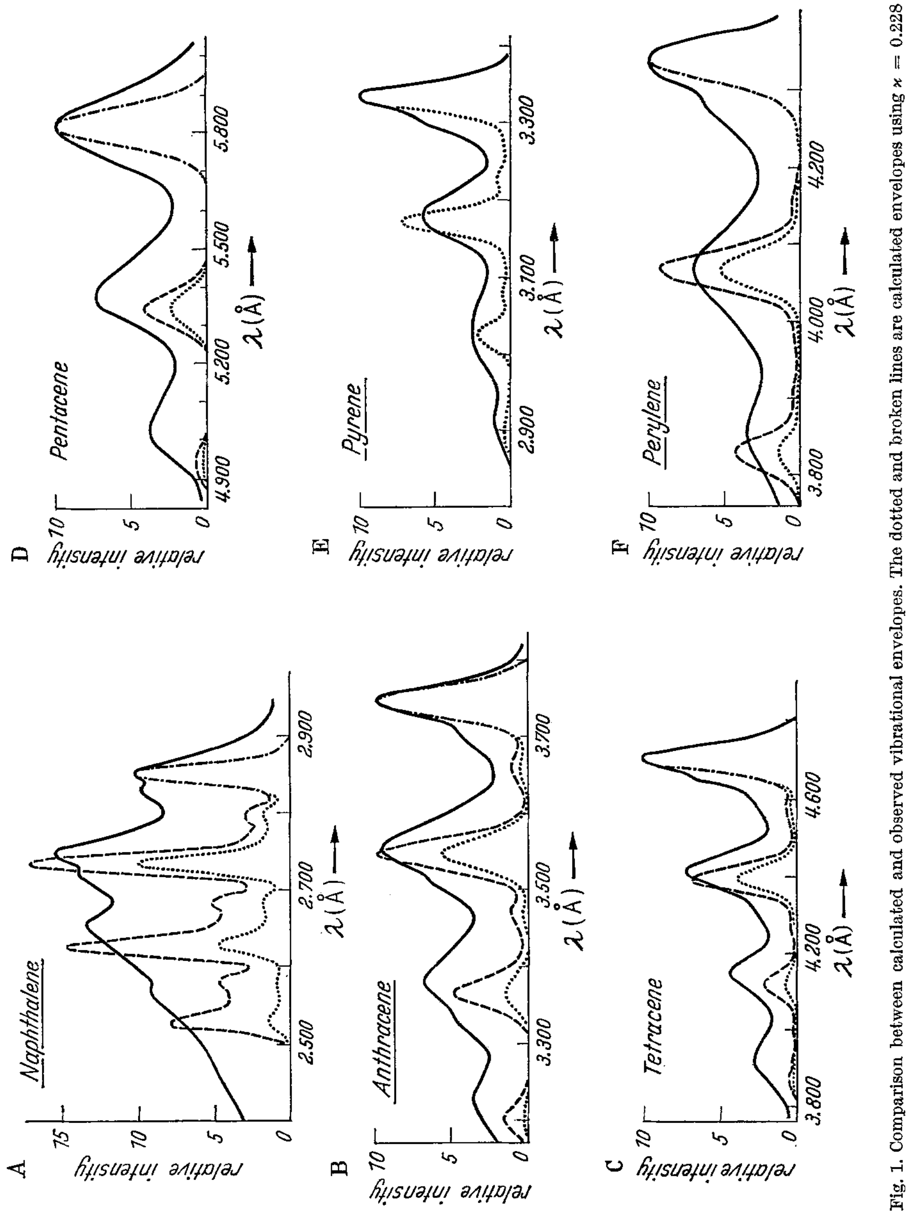

Fig. 1. Comparison between calculated and observed vibrational envelopes. The dotted and broken lines are calculated envelopes using $\varkappa = 0.228$ and 0.300 respectively. The continuous lines are replots of the solution spectra obtained by Clar [6].

est two stretching vibrations is now in agreement with experiment. We therefore deduce that the incorrect order in the progressional intensities of the progressions having a frequency close to 1450 cm^{-1} was due to our simplified normal co-ordinates.

For phenanthrene the ^1L_a band underlies to a large extent the more intense ^1L_b band and accurate progressional intensities cannot be determined experimentally. However, the ^1L_b band at longer wavelength is interesting because two progressions are observed, one with a frequency of 670 cm^{-1}, the other, which is stronger, of about 1378 cm^{-1} [6]. Calculations based on our simple model (considering C–C-stretches co-ordinates only and bond order changes calculated from Hückel theory) indicate that four vibrational modes are predominantly excited (as shown in the table). The frequencies of three of them fall in the region of 1330 to 1550 cm^{-1}, and in a solution spectrum would appear as one progression. The fourth corresponds to the lowest frequency C–C-stretching vibration (with calculated frequency of 586 cm^{-1}). This low frequency progression is more intense than the corresponding low frequency progressions of the polyacenes. It is reasonable to suppose that the higher group of frequencies would appear as a single progression in the solution spectra and that our calculated frequency of 586 cm^{-1} corresponds to the 780 cm^{-1} fundamental observed. The calculations are therefore in qualitative agreement with experiment although with $\varkappa = 0.228$ we again underestimate the intensities of the progression.

From these results, we conclude that changes in bond length calculated from simple excited state wave-functions and the linear bond order-bond length relationship, coupled with a simple normal co-ordinate analysis of the skeletal vibrations, gives progressional intensities qualitatively in good agreement with experiment. The agreement is improved if the parameter $\varkappa$ is optimised for each series of hydrocarbons, and further if a more sophisticated force field is chosen. Our assumption that the force fields in the ground and excited states are the same probably does not lead to any serious error.

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