Molecular Deformation and Vibrational Structure of the First U.V. Band in Linear Polyenes

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We try to reproduce the vibrational structure of the first U.V. band of linear polyenes, using the simple model proposed by McCoy and Ross. The Hückel orbitals give satisfactory results for the first terms of the series but a bad asymptotic behaviour when the dimension of the system increases. Bond alternation improves slightly the agreement with experimental spectra, but a discrepancy remains: we discuss its possible origin.

Nous essayons de rendre compte de l'intensité des bandes vibrationnelles de la première transition U.V. des polyenes linéaires, à l'aide du modèle simple de McCoy et Ross. La méthode de Hückel donne des résultats satisfaisants pour les premiers composés de la série, mais un mauvais comportement asymptotique quand la dimension du systeme augmente. L'alternance des liaisons améliore légèrement les résultats mais laisse subsister une divergence pour les chaînes longues: nous discutons l'origine possible de cette divergence.

Es wird versucht, die Schwingungsstruktur der ersten UV-Bande der linearen Polyene mit Hilfe des Modells von McCoy und Ross wiederzugeben. Die Hückel-Orbitale geben zufrieden-stellende Resultate nur für die ersten Glieder der Serie, aber schlechtes asymptotisches Ver-halten für große n. Bindungsalternierung verbessert die Übereinstimmung geringfügig. Der Ursprung der Diskrepanz wird zu erklären versucht.

Introduction

The vibrational structure of U.V. bands of conjugated systems may be correlated with the deformation of the nuclear skeleton of the molecule in the excited state. McCoy and Ross [6] were able to reproduce the shape of the spectra of several polyacenes, assuming a change in the excited bond lengths propor-tional to the change of the bond orders and using a very simplified calculation of Franck-Condon factors. Later on, Miller and Murrell [8] refined these previous calculations, using normal modes of the molecule, but found no significant im-provement of the theoretical shape. They noticed that increasing the dimension of the delocalized system, one gets an increase in the relative intensity of the $0 \leftarrow 0$ band.

In a recent paper [5], one of us had proposed an empirical method to calculate the stabilization energy of excited and ionized states of conjugated systems, which arises from the change of the molecular shape. This method was applied in the very crude approximation of Hückel theory, to the series of linear even poly-enes. Assuming all the bonds to be equivalent (same value of the non-diagonal Hamiltonian element β and same force constant k), we got an explicit expression

of the stabilization energy for the $k \leftarrow j$ transition, as a function of the number of carbon atoms in the molecule:

$$\Delta E = \frac{4}{k} \left(\frac{\partial \beta}{\partial l}\right)^2 \frac{1}{n+1} \left[2 - \cos \frac{k-j}{n+1} \pi\right].$$ (1)

For the lowest energy transition ($^1A \leftarrow {}^1B$ transition) Eq. (1) becomes:

$$\Delta E = \frac{4}{k} \left(\frac{\partial \beta}{\partial l}\right)^2 \frac{1}{n+1} \left[2 - \cos \frac{\pi}{n+1}\right].$$ (2)

This law, which indicates a decrease of the stabilization energy, when n increases, seemed astonishing. We thought that the evolution of the vibrational structure of the U.V. band could be correlated with this result. In fact it is well known for a long time [1] that in the experimental spectra the relative intensity of the $0 \leftarrow 0$ band increases with n, which is in agreement with our result. We decided thus to give an approximate but quantitative treatment of this phenomenon, using the method proposed by McCoy and Ross [6].

Method

These authors applied formulas valid for diatomic molecules to several aromatic hydrocarbons, assuming that only one normal coordinate is needed to describe the vibrations of the molecule: in our case this hypothesis is sufficient to reproduce the general shape of the experimental spectrum in benzol, composed by three appearent maximas, always separated by approximately $40 \cdot 10^{+12}$ sec^{-1}. (A more complicated structure appears in the absorption spectrum in Ether-Alcool at -196 °C [1].)

McCoy and Ross [6] use the relationship:

$$I_p/I_0 = \frac{\nu_p}{\nu_0} (x^{2p}/p!)$$ (3)

which gives the ratio between the intensities of $p \leftarrow 0$ and $0 \leftarrow 0$ bands. The quantities ν_p and ν_0 are the frequencies of the two bands and x is given by

$$x = \sqrt{\frac{k}{2h\nu}} R$$

where k is the unique force constant, ν the frequency of the vibration and R the bond length change. For polyatomic molecules R is the length of the vector in the space of bond length displacement coordinates, if all bonds are assumed to represent normal equivalent coordinates. We thus may write

$$R^2 = \sum_{rs} \Delta l_{rs}^2$$ (5)

l_{rs} representing the length of the chemical rs bond. We had demonstrated that, within the same hypothesis:

$$R^2 = 2 \frac{\Delta E}{k}$$ (6)

where ΔE is the stabilization energy.

Thus, x^2 in Eq. (3) is easily expressed as a function of ΔE.

$$I_p/I_0 = \frac{\nu_p}{\nu_0} \left(\frac{\Delta E}{h\nu}\right)^p /p!.$$ (7)

As ΔE given by Eq. [2] is a function of the number of Carbon atoms, I_p/I_0 may be expressed as an explicit function of n. And for instance:

$$I_1/I_0 = \frac{v_p}{v_0} \frac{C}{n+1} \left[2 - \cos \frac{\pi}{n+1} \right] \qquad (8)$$

where C is a constant involving k, $\left(\dfrac{\partial \beta}{\partial l}\right)$ and v.

Results and Discussion

We applied this formula from $n = 6$ to $n = 20$ and compared the results with the experimental spectra reported by WOODS et al. [11], A. D. MEBANE [7] and SONDHEIMER et al. [9]. The quantity C in Eq. (8) was always adjusted to fit the
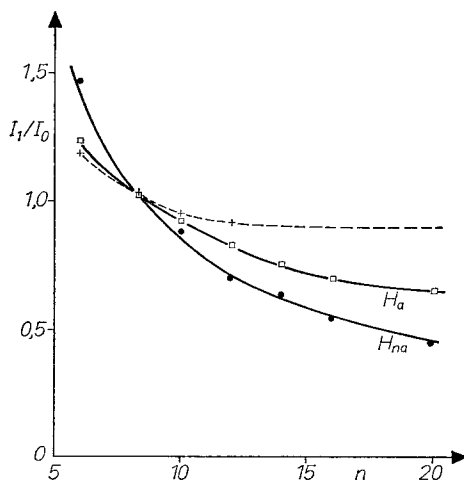

Fig. 1. Theoretical and experimental evolution of I_1/I_0 as a function of n; — — — Experimental curve, ———— Theoretical curves H_a with bond alternation, H_{na} without bond alternation

I_1/I_0 ratio for $n = 8$. The results of Eq. (8) are reported in the 2nd and 7th column of the Table. The agreement is quite nice for the first three members of the series, but does not lead to a non zero limit, while experiments indicate that I_1/I_0 tends to a finite limit. We must notice however that for large n the purity of the sample is not well defined [9] which has a certain influence on the value of the ratio I_1/I_0.

This bad asymptotic behaviour of the simplest Hückel theory for polyenes is not exceptionnal: it is well known that in that scheme the first transition energy tends to zero as $B/(n+1)$ when n increases while experimental transition energies tend to a limit. It is also well known that one may find a limit of this transition energy by introducing the bond length alternation hypothesis [3]. This was formaly demonstrated by W. KUTZELNIGG [4], using a perturbation development. We thus performed again our calculations using $\beta_{C=C} = 1.3\, \beta_{aromatic}$ and $\beta_{C-C} = 0.7\, \beta$. The results are reported in column 4.5 and 8.9 of the Table. In columns 4 and 8 we used the same value of the force constant k for both bonds, and the results in columns 5 and 9 are obtained assuming $k_{C=C} = 2k_{C-C}$ [which is a reasonable assumption (see for instance [2])]. The results are very parallel.

Table. *Intensities ratio of the $0 \leftarrow 0$, $0 \leftarrow 1$, and $0 \leftarrow 2$ bands of the first UV transition of linear polyenes*

number of carbon atoms	I_1/I_0 exp.	calculated			I_2/I_0 exp.	calculated		
		non alt.	alt.[d]	alt.[e]		non alt.	alt.[d]	alt.[e]
$n = 6$	1.18[a]	1.46	1.23	1.23	0.84	1.07	0.75	0.83
$n = 8$	1.05[a]	(1.05)	(1.05)	(1.05)	0.64	0.55	0.55	0.55
$n = 10$	0.95[b]	0.89	0.93	0.92	0.55	0.39	0.43	0.42
$n = 12$	0.92[c]	0.71	0.82	0.78	0.57	0.24	0.30	0.29
$n = 14$	~0.9[b]	0.63	0.73	0.69	~0.5	0.20	0.26	0.24
$n = 16$	~0.9[c]	0.55	0.70	0.67	~0.5	0.16	0.24	0.22
$n = 20$	~0.9[c]	0.45	0.65	0.63	~0.5	0.11	0.21	0.20

[a] Ref. [11]; [b] Ref. [7]; [c] Ref. [9]; [d] all k equivalents; [e] different values of k for double and simple bonds.

We see easily from the Table and Fig. 1, that bond alternation gives a better agreement with experiment for the first members of the series and lowers the decrease of I_1/I_0 for large n. We are not able from the behaviour to $n = 30$ to deduce if I_1/I_0 tends to a non zero limit in the case of bond alternation: to deduce this rigourously, we must perform a double perturbation expansion combining the perturbations developped in papers [4] and [5]. But, any way, we may say that bond alternation alone cannot give a satisfactory agreement with the observed limit of I_1/I_0 about 0.9: for $n = 30$ this ratio lies about 0.43. To get a good behaviour it would be necessary to assume an enormous difference between $\beta_{C=C}$ and β_{C-C}. Our perturbation is already much greater than usual: Streitwieser [10] for instance proposes $\beta_{C=C} = 1.1\,\beta$ and $\beta_{C-C} = 0.9\,\beta$. We think thus that another explanation is required. Since McCoy-Ross and Miller-Murrell results are so close, we do not think that a more sophisticated model of the vibrational properties of the molecule would change the situation. On another hand canonical self-consistant Molecular Orbitals do not differ significantly from Hückel orbital and their use would not improve the results.

The bad asymptotic behaviour is due to the complete delocalization of the Molecular Orbitals involved in the transition: indeed there are $3n - 6$ normal coordinates ($n - 1$ bonds here), and the coefficients on each atom are about $\frac{1}{\sqrt{n+1}}$. For each bond the variation in bond length is thus proportionnal to $1/n$, and the change in energy proportionnal to $\frac{1}{n^2}$. Thus for the whole molecule the stabilization energy is proportionnal to $1/n$. To get a good asymptotic behaviour one must invoke a phenomenon limitating the delocalization. One could first imagine that a certain flexibility of such a long chain in solution could prevent a complete delocalization. But Miller and Murrell's results [8] show strikingly an analogous situation in the series of linear polyacenes, which are certainly planar: going from naphtalene to pentacene it appears that the calculated ratio I_1/I_0 decreases much more fastly than the experimental one. As a last explanation it is possible that,

for the study of the excited states, the best self-consistent Molecular Orbitals are more localized than the canonical Molecular Orbitals provided by the diagonalization of the self-consistent Hamiltonian.

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