COMMENTS

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Comment on "Some Considerations on the Electronic Spectra of Cyclic Polyenes"[1)]

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Whatever the merit of the combined application of a FE-treatment and the hole/particle formalism, proposed by Basu[1)] for the calculation of the electronic spectra of all-*cis* cyclic polyenes containing n π-electrons in a perimeter system of at least D_{nh} symmetry, the experimental results known to date do *not* constitute proof that the predicted convergence limit for the $^1L_b \leftarrow {}^1A$ transition does exist. In fact they agree much better with the assumption that for $n\to\infty$ the difference $\Delta E = E(^1L_b) - E(^1A)$ does not differ much from zero. The limit of ΔE for $n\to\infty$ is definitely much smaller than suggested by Fig. 1 of Ref. 1, which is based on wrong or inadequate data.[2)]

Many-electron SCF treatments including configuration interaction[2,3)] indicate that ΔE for the longwave $^1L_b \leftarrow {}^1A$ transition of all-*cis* cyclopolyenes satisfying Hückel's rule should depend on n according to $\Delta E \propto \sin(\pi/n)$. Using the data given in Ref. 2 for cyclic π-systems with $n=6$, 10, 14, 18 we find

$$\Delta E = [(-1.47\pm1.93) + (85.99\pm6.57)\sin(\pi/n)]\times 10^3\ \mathrm{cm}^{-1}$$

a regression line which does not miss the origin $\sin(\pi/\infty)=0$ significantly. (Predicted 90% security confidence limits for $n=22$: 8.8 to $12.8\times10^3\ \mathrm{cm}^{-1}$; $n=26$: 6.7 to $11.1\times10^3\ \mathrm{cm}^{-1}$; $n=30$: 5.1 to $9.9\times10^3\ \mathrm{cm}^{-1}$). Of course linear extrapolation beyond $n\approx30$ is dangerous, because of higher order terms which are not accounted for, if one uses the transformation of the independent variable n into the new variable $\sin(\pi/n)$. However, the analysis clearly indicates that the value of the upper limit of ΔE for $n\to\infty$ must be at best of the order of $5\times10^3\ \mathrm{cm}^{-1}$, especially if the lack of planarity of some of the reference systems is taken into account. This value is close to the highest frequency vibrational modes and thus "zero" for all practical purposes.

References

1) S. Basu, This Bulletin, **48**, 368 (1975).

2) H. R. Blattmann, E. Heilbronner, and G. Wagnière, *J. Amer. Chem. Soc.*, **90**, 4786 (1968); and references given therein.

3) W. Moffit, *J. Chem. Phys.*, **22**, 320 (1954); H. C. Longuet-Higgins, and L. Salem, *Proc. Roy. Soc.*, **A251**, 172 (1959), **A255**, 435 (1960); **A257**, 445 (1960); E. Heilbronner and J. N. Murrell, *Mol. Phys.*, **6**, 1 (1963).