Theoret. chim. Acta (Berl.) 14, 250—252 (1969)

Relationes

Configuration Interaction Calculations on the Dinegative Ion of Coronene

ANNEMARIE HAUPT
Laboratory for Physical Chemistry, University of Amsterdam, Amsterdam, The Netherlands

G. J. HOYTINK
Department of Chemistry, The University, Sheffield S3 7HF, U.K.

Received April 16, 1969

Configuration interaction calculations using different sets of parameter values were performed to investigate the separation of the $^3A_{2g}$- and $^1A_{1g}$-levels of the dinegative ions of coronene and annulene. In both cases the separation remains less than 0.1 eV for all four different sets of γ-values.

Experimental investigations on the ground state of the coronene dinegative ion have shown that this state can be either singlet or triplet depending on the extent of interaction with the counter ions [1, 2, 3]. Since the first antibonding π-electronic level of coronene is two fold degenerate, a first approximation leads to the expectation that the ground state of the coronene dianion is triplet (Hund's rule). Jesse [4] has carried out a restricted configuration interaction calculation which led to a drastic change of the configurational energy level scheme. This is shown in parts *A* and *B* of Fig. 1. We see that configuration interaction gives rise to a considerable lowering of the energy of the $^1A_{1g}$ configuration. We have now extended the configuration interaction including all configurations for which the quotient $\langle H_{ij}\rangle^2/\Delta E \geq 0.001$ eV and using again the Pariser-Parr set of γ-values. The results of these calculations are shown in part *C* of Fig. 1. It is apparent that the calculation by Jesse [4] accounts for the greater part of the correction in the wavefunction. The extension of the number of configurations included in the configuration interaction calculation has a

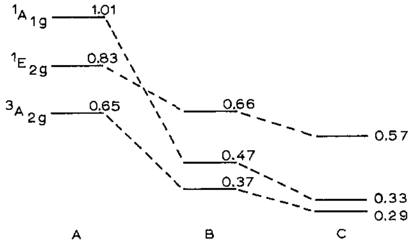

Fig. 1. Lower part of the term scheme of the coronene dianion. Parameters after [4]. *A* before CI. *B* limited CI [1]. *C* extended CI

comparitively smaller effect as a result. The earlier conclusion that the two lowest energy levels are close together, remains unaltered.

In view of the crude approximations involved in the semi-empirical method of calculation, one cannot expect to make a more precise location of the states when they are separated by an amount of energy of the order of 0.1 eV. However, it is still an open question whether by the choice of a different set of γ-values in the Pariser-Parr treatment, the separation between the two states would not change drastically. In order to settle this question we have carried out the same configuration interaction treatment using the set of γ-values introduced by Mataga [6], Longuet-Higgins and Salem [7] and the γ-set based on theoretical values [8] (Table 1). The results of these calculations have been listed in Table 2 for the dinegative ions of annulene and coronene. The schematic illustration of these results has been given in Fig. 2. In both cases the four different approaches lead to a separation of the singlet A_{1g} and the triplet A_{2g} energy levels that does not exceed 0.1 eV (except in the case of coronene with parameters according to Ref. [7]). This is in a very good agreement with the experimental observations for coronene which indicates that the free ion has a triplet ground state with a lowest singlet state separated from the ground state by less than 0.1 eV [3].

Table 1. *Values of integrals (eV)*

	Pariser/Parr [5]	Mataga [6]	Longuet-Higgins and Salem [7]	theoretical [8]
$-\beta_C$	2.39	2.388	2.236	2.734
γ_{00}	10.53	10.840	8.025	17.618
γ_{01}	7.30	5.298	1.425	8.924
γ_{02}	5.46	3.855	0	5.574
γ_{03}	4.90	3.505	0	4.876

Table 2. *Energy levels (eV)*

	Symmetry	Pariser/Parr [5]	Mataga [6]	Longuet-Higgins and Salem [7]	theoretical [8]
Coronene	$^1E_{2g}$	$+0.57$	-1.73	-5.81	-3.74
	$^1A_{1g}$	$+0.33$	-1.95	-5.90	-4.26
	$^3A_{2g}$	$+0.29$	-1.97	-6.07	-4.17
Annulene	$^1E_{2g}$	-1.12	-2.97	-4.60	-6.27
	$^1A_{1g}$	-1.68	-3.46	-4.92	-7.31
	$^3A_{2g}$	-1.69	-3.50	-4.93	-7.24

The energies are given with respect to the energy $(M_C + 2\alpha_C)$ where M_C refers to the energy of the closed shell ground state $|1\bar{1}2\bar{2}....n\bar{n}|$ ($n = 18$, 24 resp.) of the molecule.

In a recent article it is suggested that vibronic mixing will also contribute to the energy separation between the two states [9]. According to these authors who assumed the singlet A_{1g}- and the singlet E_{2g} levels to be degenerate, a relative lowering of 1.000 cm^{-1} ($\cong 0.124$ eV) in the energy of the $^1A_{1g}$ level with respect to the $^3A_{2g}$ level is calculated. Using the same method but taking into account the energy difference between the $^1A_{1g}$- and $^1E_{2g}$-levels, the relative lowering in the energy of the $^1A_{1g}$-level turns out to be 0.04 eV for the annulene and 0.07 eV for the coronene dianion (parameters according to Ref. [5]). It is seen that this effect is of the same order of magnitude as the calculated energy difference between the $^3A_{2g}$- and $^1A_{1g}$-levels of the dianions discussed.

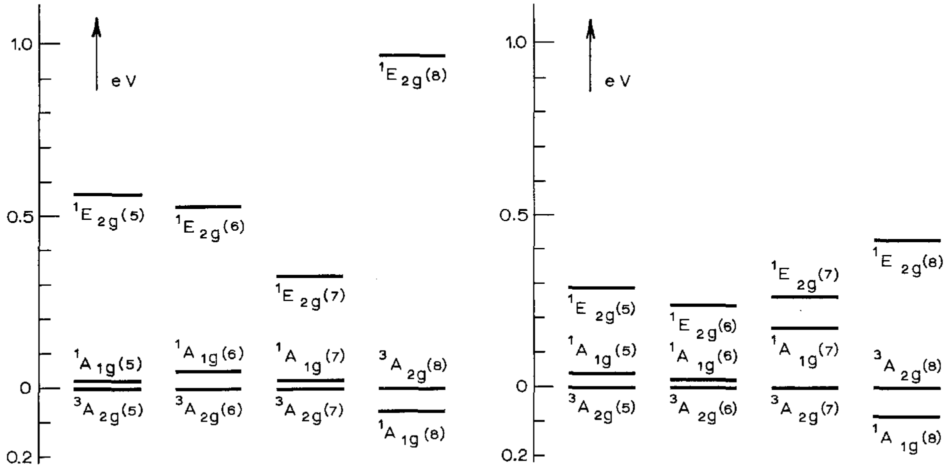

Fig. 2. Lower part of the term schemes of the dinegative ions of annulene (L.H.S.) and coronene (R.H.S.). Parameters according to [5], [6], [7], and [8], as indicated in the figures

It would go too far to add these data for the vibronic mixing to the data listed in Table 2, since then we would put too much confidence in the reliability of the approximation methods used. Nevertheless, it is interesting that in spite of the crude approximations one obtains such a close correspondence between the calculations and the experimental findings.

Acknowledgements. Annemarie Haupt wishes to thank the South African Council for Scientific and Industrial Research for a research grant, the Dutch Government for a bursary awarded under the auspices of the Netherlands-South African Cultural Agreement and to express her appreciation to the members of the Physical Chemistry Department of the University of Amsterdam for their hospitality.

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Professor G. J. Hoytink
Department of Chemistry
The University
Sheffield S3 7HF, England