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Conjugated Radicals

VI.* Semiempirical Open-Shell PPP-Like Calculation with Doubly Excited Configurations on the Naphthalene Radical Anion

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The naphthalene radical anion was calculated by the open-shell SCF method due to Roothaan combined with a configuration interaction treatment. The effect of the doubly excited configurations on the calculated transition energies was found to be unimportant in view of the interpretation of its electronic spectrum.

Introduction

The electronic spectra of polyacene radical anions have been the subject of several theoretical studies [1–4]. The observed transition energies were well explained by open-shell calculations, but, the agreement of the calculated excitation energies with the observed ones became poorer for the higher energy transitions. Ishitani and Nagakura believe that [3] "in order to decrease this discrepancy, we must take the electron configurations with higher energy like doubly excited configurations". The result of such a calculation, which takes doubly excited configurations into account, is reported in the present paper for the naphthalene radical anion.

Description of Calculations

The open-shell SCF procedure due to Roothaan [5] was used with the approximations [4–6] commonly accepted for closed-shell PPP calculations. Two centre Coulomb repulsion integrals were evaluated by the method due to Mataga and Nishimoto [7]. For the ionization potential and electron affinity of the carbon atoms the values 11.22 eV and 0.69 eV were used. The core resonance integral β_{CC} was taken to be -2.318 eV. An idealized geometry with all bond distances equal to 1.40 Å was considered. Using this SCF procedure the following two calculations were carried out:

1. In the first one, the singly excited configurations of the types A, B, C_α, and C_β, as shown in Fig. 1, were constructed from the SCF molecular orbitals (MO's), and together with the ground state function included in the configuration interaction calculation. All configurations corresponding to one-electron transitions

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* Part V: Collect. Czechoslov. Chem. Commun. **35**, 892 (1970).

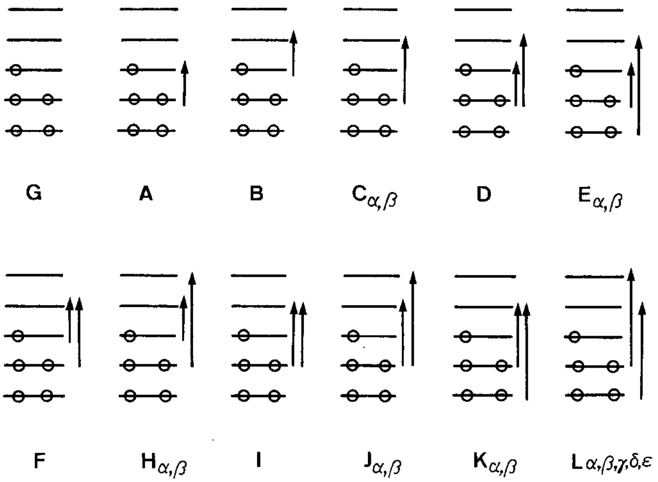

Fig. 1. Types of the singly and doubly excited configurations. *G* means the ground state, Greek symbols denote the different spin functions of the mutually orthogonal states

from one of the four highest doubly occupied MO's or the singly occupied MO to one of the unoccupied MO's were considered, and thus a secular determinant of order 41 was solved.

2. The second calculation was performed in the same way, but with a different set of states used in the configuration interaction calculation. Besides all the possible singly excited states A, B, C_α, and C_β, the configurations of types $D-L$, shown in Fig. 1 which arise formally from the transitions of two electrons, were also taken into account. Due to the limitations set by the computer storage, it was only possible to solve a secular problem of at most order 53. Therefore, the configurations were divided into four groups according to their symmetry, viz. to the B_{2g}, B_{1g}, B_{3u}, and A_u states, and the corresponding secular problems were treated separately. As the ground state has B_{2g} symmetry and as the $B_{2g} \rightarrow B_{1g}$ transitions are forbidden, the B_{1g} states were not taken into consideration. From all the remaining doubly excited states of the $D-K$ types, having other than B_{1g} symmetry, we excluded both the configurations having the highest virtual MO doubly occupied and configurations where the excitation took place from the two lowest bonding MO's. Only ten L-type configurations were taken into account: $L_{\alpha,\beta,\gamma,\delta,\varepsilon}(4\rightarrow 7, 5\rightarrow 8)$ having B_{3u} symmetry and $L_{\alpha,\beta,\gamma,\delta,\varepsilon}(4\rightarrow 7, 5\rightarrow 9)$ having B_{2g} symmetry. Altogether 50 configurations with B_{2g} symmetry, 52 with B_{3u} symmetry and 52 with A_u symmetry were considered. In this way, namely by factorizing the CI matrix into the separate secular problems according to symmetry we were able to use only a single-configurational function for the ground state in the evaluation of the transition moments. However, the calculated transition moments are believed not to differ considerably from the accurate values, which would be obtained by using the CI ground state function.

The calculations were performed on an EL–X8 computer in the Computing Centre of the University of Würzburg (Germany).

Table. *Results of configuration interaction calculations (Only allowed transitions are presented)*

Transition	E(eV)	$\tilde{\nu}$(cm^{-1}) $\times 10^{-3}$	f[a]	$\log f$	Symmetry of the excited state	Weights
			40 singly excited configurations			
1	1.81	14.57	0.093	−1.036	B_{3u}	B (6→7) 92.3
2	2.36	19.03	0.016	−1.791	A_u	B (6→9) 67.6
3	2.90	23.42	0.107	−0.970	A_u	A (5→6) 58.0
4	4.21	33.95	0.200	−0.698	B_{3u}	C_α(5→8) 50.7, A (4→6) 30.3
5	4.66	37.58	0.473	−0.325	B_{3u}	C_β(5→8) 45.2, A (4→6) 44.8
6	5.52	44.54	0.091	−1.042	A_u	C_β(4→8) 69.6
7	6.08	49.03	0.917	−0.038	B_{3u}	C_α(5→8) 40.7, C_β(5→8) 35.9, A (4→6) 18.5
			Doubly excited configurations included			
1	1.86	15.06	0.074	−1.129	B_{3u}	B (6→7) 88.2
2	2.54	20.55	0.007	−2.148	A_u	B (6→9) 60.5
3	2.99	24.13	0.105	−0.978	A_u	A (5→6) 48.9
4	4.17	33.66	0.164	−0.785	B_{3u}	C_α(5→8) 66.5, A (4→6) 15.5
5	4.63	37.41	0.199	−0.702	B_{3u}	A (4→6) 51.5, C_β(5→8) 27.9
6	5.24	42.30	0.003	−2.548	A_u	C_β(4→8) 59.1
7	5.99	48.31	0.738	−0.133	B_{3u}	C_β(5→8) 39.9, A (4→6) 18.8, C_α(5→8) 14.5

[a] f stands for the oscillator strength.

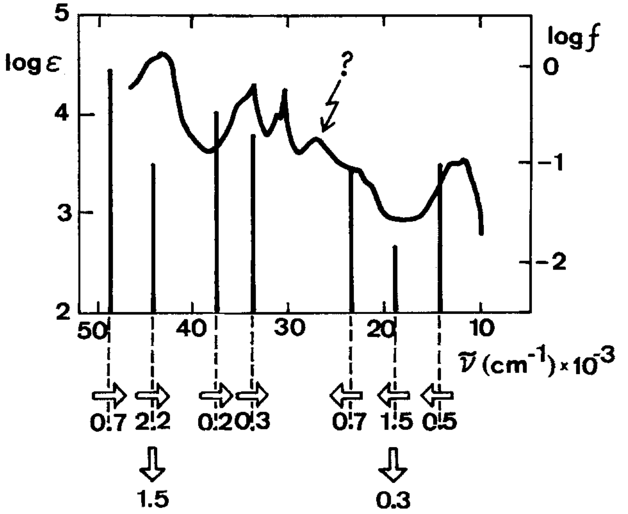

Fig. 2. Results of configuration interaction calculations. Vertical lines represent the allowed transitions as obtained from the calculation including 40 singly excited configurations. The effect of inclusion of doubly excited states in the configuration interaction is indicated by arrows below the figure: the horizontal arrows (⇒) indicate the changes in transition energies, the vertical (⇓) denote the changes in log$f$. The absorption curve was taken from Brandes, K. K., and Gerdes, R. J.: J. physic. Chem. 71, 508 (1967), the band denoted by the question mark is due to absorption of other species than the naphthalene anion radical as reported by Hoijtink, G. J., Velthorst, N. H., and Zandstra, P. J.: Molecular Physics 3, 533 (1960)

Results and Discussion

The results obtained are given in the Table and presented in Fig. 2. The desired improvement in the agreement of calculated transition energies with the observed ones was not achieved by including doubly excited states in the configuration interaction calculation; in fact their effect was rather unimportant. On the other hand, this failure indicates, that singly excited configurations represent a reasonable set of states for open-shell CI calculations. Moreover, the semiempirical parameters adjusted in closed-shell PPP calculations for the set of singly excited states seem to be suitable also for open-shell calculations with a similar extent of configuration interaction.

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