

## SEMIEMPIRICAL MO CALCULATIONS ON THE ELECTRONIC SPECTRA OF CONJUGATED HYDROCARBON RADICALS HAVING DEGENERATE GROUND STATES\*

J. KUHN\*\*, P. ČÁRSKY and R. ZAHRADNÍK

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, 121 38 Prague 2*

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Results of semiempirical MO calculations are presented for 10 hydrocarbon radicals having a doubly degenerate molecular orbital occupied in the ground state by one or three electrons. The configuration interaction treatment is based on the "half-electron" SCF theory which accounts explicitly for the presence of degenerate molecular orbitals constituting the open shell. The calculations, performed within the framework of the PPP and CNDO approximations, give a good interpretation of the electronic spectra.

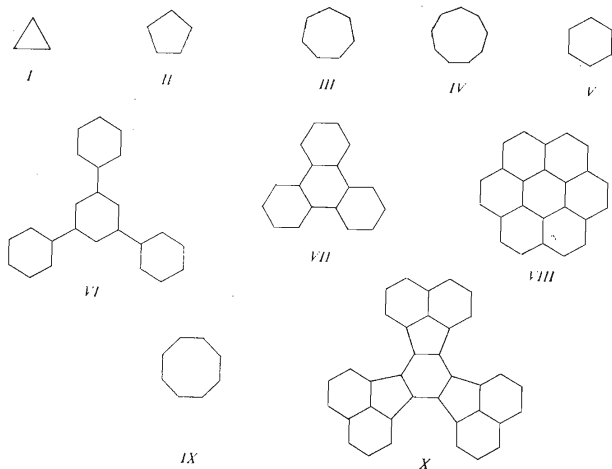
Preceding papers of this series have been restricted to treatments of radicals with nondegenerate ground states, *i.e.* to systems having a single nondegenerate open shell molecular orbital. Recently we have extended<sup>1</sup> this SCF-CI computational scheme to accommodate radicals which have degenerate ground states such as those with a doubly degenerate molecular orbital occupied by one or three electrons. In the present paper we apply this procedure to conjugated radicals  $I-X$  (their skeletons are outlined below) with the goal of interpreting their electronic spectra.

Several theoretical studies devoted to this topic have already been reported. Hoijtink<sup>2</sup> used a simple version of the method of Pariser and Parr based on the HMO orbital energies and applied it to mononegative ions of benzene and coronene. Ishitani and coworkers<sup>3</sup> and Gardner<sup>4</sup> have performed calculations of the same type on the benzene anion. Odd cyclic radicals  $I-III$  were calculated by Longuet-Higgins and McEwen<sup>5</sup> in the single transition approximation. In recent SCF-CI calculations of Shida and Iwata<sup>6</sup>, the radical anions of  $V$  and  $VII-IX$  were treated as having nondegenerate ground states. Brugman and coworkers<sup>7</sup> have studied the decacyclene ( $X$ ) anion by the "molecules in molecules" method. We think that the calculations presented in this paper represent further progress in the theoretical MO approach because they are free of some of the approximations involved in the MO calculations just mentioned. To our knowledge there are only three calculations that are of a comparable level of sophistication to ours: Kimmel and Strauss<sup>8</sup> calculated the cyclooctatetraene radical anion for several molecular geometries of differing symmetry; Karwowski<sup>9</sup> studied the effect of the configuration interaction basis on the

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\*\* Postdoctoral Fellow of the Swiss National Foundation.

transition energies in benzene ions within the framework of the PPP method; and Nakayama and I'Haya<sup>10</sup> studied the electronic spectra of benzene ions and their Jahn-Teller distortions in the PPP approximation with variable  $\beta$ .



### CALCULATIONS

We distinguish two cases, hereafter referred to as the case  $n = 1$  and  $n = 3$ , according to the number of electrons occupying the doubly degenerate open shell molecular orbitals. In both we have used the SCF "half-electron" method in its generalized form<sup>11</sup> which accounts explicitly for degenerate molecular orbitals forming the open shells. From molecular orbitals so determined we constructed wave functions for ground and singly excited states and subjected them to configuration interaction. We considered all types of configurations, designated as  $A-E$  (for definitions see ref.<sup>1</sup> and Appendices  $A-C$ ), which correspond formally to one-electron promotions from the ground state. The explicit formulas for CI matrix elements are listed in the Appendices  $D-F$ . The calculations were of a standard PPP type using the following parameters:  $I_C(\text{VSIP}, 2p) = 11.22 \text{ eV}$ ;  $\beta_{CC} = -2.318 \text{ eV}$ ;  $\gamma_{CC} = 10.53 \text{ eV}$ ; two-center repulsion integrals were evaluated by the Mataga-Nishimoto formula. Standard geometries of regular polygons with all C—C bond lengths being  $1.40 \text{ \AA}$  were used throughout. In  $X$  the rings were slightly distorted to preserve the planar geometry. For smaller systems,  $I-III$  and  $V$ , we also performed the CNDO calculations. We followed closely the original version of the CNDO/S method of Del Bene and Jaffé<sup>12</sup>, with a modification suggested later<sup>13</sup>, i.e., using the Mataga-Nishimoto approximation for repulsion integrals. For the C—H bond lengths we assume a standard value of  $1.1 \text{ \AA}$ . In systems with up to ten atomic orbitals, we performed a complete configuration interaction calculation for

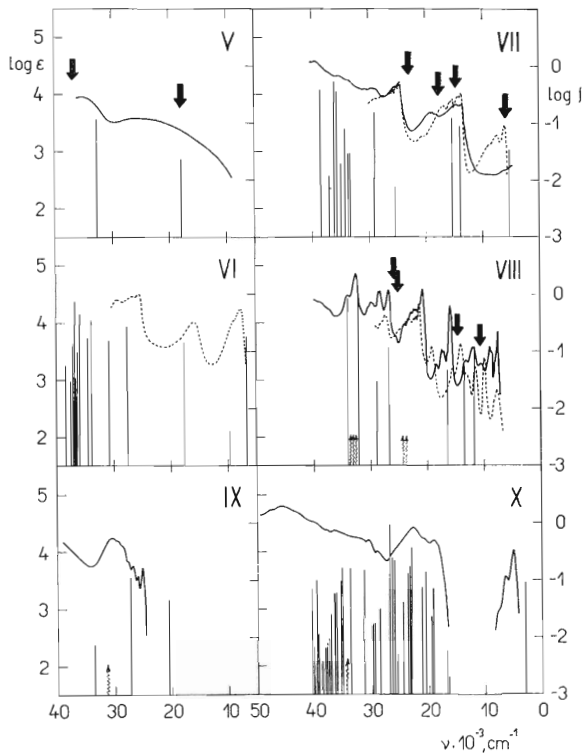


FIG. 1

Electronic Spectra of the Radical Ions of Hydrocarbons *V*–*X* and Results of the Open Shell PPP-Like Calculations

Solid curves radical anions; dashed lines radical cations; thick arrows indicate transition energies in radical cations inferred from the photoelectron spectra; for radical cations of *VI*–*VIII* the left side scales in arbitrary units ( $\log \epsilon + C$ ); for references and additional details see text.

all singly excited configurations. In larger  $\pi$ -systems, we performed a CI-calculation with the 45 lowest singly excited configurations (doubly occurring configurations of types  $C_\alpha$ ,  $C_\beta$ ,  $A'$  and  $B'$  are counted only once). In the CNDO calculations we did the same amount of configuration interaction for each of the symmetries with subscript u or g, or superscript ' or ". In the quartet calculations, we included only those configurations that were also taken into account in the doublet calculations.

#### SOURCE OF EXPERIMENTAL DATA

Electronic spectra of some of the radicals under study were recorded in more than one laboratory and thus several absorption curves are available for them. We preferred those published most recently and covering the largest spectral region; they have mostly been taken from the papers of Shida and Iwata<sup>6</sup> (anions of *V* and *IX*, cations of *VI* (ref.<sup>14</sup>), *VII* and *VIII*) and Hoijtink and his coworkers (anions of *VII* (ref.<sup>2</sup>) and *X* (ref.<sup>15</sup>)). Spectrum of the coronene anion originates from ref.<sup>61</sup>. The absorption curves in the original papers were redrawn in Fig. 1 using the  $\log \epsilon$  and  $\nu$  ( $10^{-3} \text{ cm}^{-1}$ ) scales, their ratio being 1 : 10 as used in collections of spectral data. The allowed electronic transitions, predicted by the LCI-SCF calculations, have been entered in Fig. 1 as vertical lines. Using the empirical relationship  $\log \epsilon = \log f + 4.5$ , the heights of the lines represent the predicted intensities ( $f$  means the predicted oscillator strength). Predicted forbidden transitions are indicated by wavy lines with arrows. For radical cations we also made use of photoelectron spectral data, assuming the transition energies in radical cations as differences between the first and higher ionization potentials of the parent hydrocarbons (for details on such a treatment see ref.<sup>17</sup>); we found data in the literature for benzene<sup>18</sup>, triphenylene<sup>19</sup>, and coronene<sup>20</sup>.

#### RESULTS AND DISCUSSION

We shall first deal with the assumption that the ground states of the radicals under study are degenerate. This is implied by performing calculations for highly symmetric molecular geometries which brings about the degeneracy of frontier molecular orbitals. The real molecules, however, tend to depart from these highly symmetric conformations owing to the Jahn-Teller effect; this has been established for radicals by the MO calculations<sup>21-23</sup>. Our theoretical approach may therefore appear to be questionable. In our opinion, however, it is still justifiable for two reasons. Firstly, we think that the Jahn-Teller distortion brings about small changes in transition energies; the calculated transition energies (*vide infra*) which closely match the experimental data support this. Secondly, a "standard" LCI-SCF treatment based on a nondegenerate ground state of lower symmetry should allow for low-lying multiply excited states corresponding to electron promotions from and to the degenerate frontier orbital split by the Jahn-Teller distortion; this circumstance would complicate the calculation considerably. The only systems where the theoretical model is less substantiated are the strained rings *IV* and *IX*. Here the calculations performed for planar structures may poorly describe the electronic structure of *IV* and the anion of *IX* (*vide infra*).

We present the results of our calculations in Table I and II and discuss the individual systems *I-X* separately in the following text.

TABLE I

## Predicted Doublet-Doublet Electronic Transitions in Odd Cyclopolyenylys

Transition <sup>a</sup>	Transition energy <sup>b</sup> and oscillator strength		
	PPP		CNDO
Cyclopropenyl			
$A'_2(\sigma^* \leftarrow \pi^0)$	—		26.7 0.000
$E'(\sigma^* \leftarrow \pi^0)$	—		30.2 0.040
$E'(\pi^0 \leftarrow \sigma)$	—		44.0 0.004
$A'_1(\sigma^* \leftarrow \pi^0)$	—		46.5 0.000
$E'(\pi^0 \leftarrow \sigma)$	—		53.7 0.000
$E''(\pi^0 \leftarrow \pi)$	63.0	0.278	57.4 0.054
$A''_1(\pi^0 \leftarrow \pi)$	73.9	0.371	56.9 0.070
Cyclopentadienyl			
$A''_2(\pi \leftarrow \pi)$	24.2	0.015	29.8 0.001
$E''_1(\pi^* \leftarrow \pi^0)$	44.8	0.000	39.9 0.000
$E''_2(\pi^0 \leftarrow \sigma)$	—		41.4 0.000
$E''_1(\pi^0 \leftarrow \sigma)$	—		42.6 0.004
$A''_1(\pi^* \leftarrow \pi^0)$	50.7	0.190	44.7 0.138
$E''_2(\pi^* \leftarrow \pi^0)$	51.8	0.010	47.0 0.002
$E''_2(\sigma^* \leftarrow \pi^0)$	—		53.3 0.000
$E''_2(\pi^* \leftarrow \pi^0)$	59.3	0.564	53.9 0.574
Tropyl			
$E''_3(\pi \leftarrow \pi)$	24.0	0.006	21.4 0.014
$E''_2(\pi^0 \leftarrow \pi)$	34.3	0.000	37.4 0.000
$E''_1(\pi^0 \leftarrow \pi)$	39.8	0.006	43.1 0.008
$E''_3(\sigma^* \leftarrow \pi^0)$	—		44.3 0.000
$E''_2(\pi^0 \leftarrow \sigma)$	—		48.1 0.002
$E''_3(\pi^0 \leftarrow \pi)$	46.2	0.570	49.7 0.700
$E''_2(\pi^0 \leftarrow \sigma)$	—		52.2 0.002
$E''_1(\pi^0 \leftarrow \pi)$	49.8	0.792	52.8 0.706
Cyclononatetraenyl			
$E''_1(\pi \leftarrow \pi)$	21.4	0.000	—
$E''_2(\pi^* \leftarrow \pi^0)$	27.8	0.000	—
$A''_2(\pi \leftarrow \pi)$	29.6	0.000	—
$E''_3(\pi^* \leftarrow \pi^0)$	32.5	0.006	—
$E''_1(\pi^* \leftarrow \pi^0)$	41.5	0.812	—
$E''_3(\pi^* \leftarrow \pi^0)$	43.6	1.014	—
$E''_4(\pi \leftarrow \pi)$	48.0	0.000	—
$A''_1(\pi \leftarrow \pi)$	49.4	0.000	—
$E''_1(\pi \leftarrow \pi)$	53.1	0.548	—

<sup>a</sup> Only upper states are indicated; the ground states of radicals I—IV are  $E''$ ,  $E''_1$ ,  $E''_2$ ,  $E''_2$ ; with electronic transitions to upper states which are not significantly mixed with other excited states we designated open shell and virtual orbitals by circles and asterisks, resp.; <sup>b</sup> in  $\text{cm}^{-1} \cdot 10^{-3}$ .

TABLE II  
 Predicted Doublet-Doublet  $\pi$ -Electronic Transitions in Radical Anions Derived from  $V-X$

Transition	Transition energy <sup>a</sup>	$f^b$	$\log f$
Benzene radical anion			
$B_{2g} \leftarrow E_{2u}$	18.1	0.024	-1.620
$E_{1g} \leftarrow E_{2u}$	32.6	0.124	-0.907
$B_{1g} \leftarrow E_{2u}$	46.8	0.288	-0.551
$E_{1g} \leftarrow E_{2u}$	47.1	0.040	-1.398
$B_{2g} \leftarrow E_{2u}$	55.8	0.483	-0.316
Triphenylbenzene radical anion			
$A_2'' \leftarrow E''$	6.6	0.184	-0.735
$E'' \leftarrow E''$	9.4	0.000	—
$A_1'' \leftarrow E''$	9.4	0.004	-2.398
$E'' \leftarrow E''$	17.5	0.149	-0.827
$E'' \leftarrow E''$	27.5	0.279	-0.554
$A_1'' \leftarrow E''$	30.9	0.159	-0.799
$A_2'' \leftarrow E''$	33.8	0.354	-0.451
Triphenylene radical anion			
$A_2'' \leftarrow E''$	5.2	0.036	-1.444
$E'' \leftarrow E''$	14.1	0.090	-1.046
$A_1'' \leftarrow E''$	15.3	0.121	-0.917
$E'' \leftarrow E''$	25.2	0.006	-2.222
$E'' \leftarrow E''$	29.1	0.152	-0.818
$E'' \leftarrow E''$	33.5	0.030	-1.523
Coronene radical anion			
$A_{1u} \leftarrow E_{1g}$	11.8	0.130	-0.886
$E_{2u} \leftarrow E_{1g}$	13.0	0.062	-1.208
$A_{2u} \leftarrow E_{1g}$	16.5	0.041	-1.387
$B_{2g} \leftarrow E_{1g}$	23.7	0.000	—
$E_{1g} \leftarrow E_{1g}$	24.3	0.000	—
$E_{2u} \leftarrow E_{1g}$	26.7	0.116	-0.936
$E_{2u} \leftarrow E_{1g}$	28.6	0.030	-1.523
$A_{2u} \leftarrow E_{1g}$	31.8	0.768	-0.115
$B_{1g} \leftarrow E_{1g}$	32.8	0.000	—
$B_{2g} \leftarrow E_{1g}$	33.2	0.000	—
$E_{1g} \leftarrow E_{1g}$	33.7	0.000	—
$A_{1u} \leftarrow E_{1g}$	34.0	1.054	0.023

TABLE II  
(Continued)

Transition	Transition energy <sup>a</sup>	$f^b$	$\log f$
Cyclooctatetraene radical anion			
$E_{1g} \leftarrow E_{2u}$	20.5	0.044	-1.357
$E_{1g} \leftarrow E_{2u}$	26.9	0.110	-0.959
$A_{2u} \leftarrow E_{2u}$	31.4	0.000	—
$E_{3g} \leftarrow E_{2u}$	33.6	0.008	-2.097
$E_{3g} \leftarrow E_{2u}$	44.5	1.082	0.034
Decacyclene radical anion			
$A_1'' \leftarrow E''$	2.6	0.096	-1.036

<sup>a</sup> In  $\text{cm}^{-1} \cdot 10^{-3}$ ; <sup>b</sup> oscillator strength.

*Odd cyclopolyenylys.* The only experimental data available are those reported for the cyclopentadienyl and tropyli radicals. Our results for the former agree with those calculated previously<sup>5</sup>. They predict only one  ${}^2A_2'' \leftarrow {}^2E_1''$  transition in the visible region of the spectrum and give a good interpretation of the absorption observed<sup>24,25</sup> at  $30000 \text{ cm}^{-1}$ . The absorption of the tropyli radical observed at 38450, 43654, and  $45991 \text{ cm}^{-1}$  has been attributed to three members of a Rydberg series<sup>26</sup>. Our calculations give four valence-shell electronic transitions falling into this range but the assignment to a Rydberg series cannot be ruled out on intensity grounds since two of the predicted transitions are forbidden and two weakly allowed. The theory suggests, however, that a medium strong  ${}^2E_3'' \leftarrow {}^2E_2''$  transition has been overlooked in a longer-wavelength region. A strong absorption is predicted at a border between the ultraviolet and vacuum ultraviolet regions. The results of the calculation for the cyclononatetraenyl radical (IV) are somewhat uncertain because of its unknown structure. The only guide here is the experimental evidence available for its anion: the latter appears to be aromatic<sup>27</sup> but Staley and Pearl suggested<sup>28,29</sup> it may be nonplanar concluding this from the conformation of the cyclononatrienyl anion.

*Radical ions of alternant hydrocarbons V–VIII.* These systems being alternant hydrocarbons, the PPP-like calculations give the same results for their cation and anion radicals as would be expected on the basis of pairing properties of molecular orbitals in alternant hydrocarbons. Hence the results presented in Fig. 1 and Table II refer to both monopositive and mononegative ions. For the benzene ions we have also performed CNDO calculations; the results are remarkable because of the break-

down of the pairing properties of MOs (*cf.* Table III) but the overall agreement with experiment is inferior to that given by the  $\pi$ -electron calculation. The direct spectral data available for the benzene radical cation (first band at  $20800\text{ cm}^{-1}$  (ref.<sup>30</sup>) and  $18000\text{ cm}^{-1}$  (ref.<sup>31</sup>), second band<sup>32</sup> at  $31200\text{ cm}^{-1}$ ) suggest that the CNDO approach overestimates the differences between monopositive and mononegative ions. Next

TABLE III

CNDO Doublet-Doublet Electronic Transitions in Benzene Ions

Transition <sup>a</sup>	Transition energy <sup>b</sup>	Oscillator strength
Benzene cation		
$E_{2g} \leftarrow E_{1g}(\pi^{\circ} \leftarrow \sigma)$	23.6	0.000
$A_{2u} \leftarrow E_{1g}(\pi \leftarrow \pi)$	25.2	0.026
$E_{2u} \leftarrow E_{1g}(\pi^* \leftarrow \pi^{\circ})$	31.9	0.096
$E_{1u} \leftarrow E_{1g}(\pi^{\circ} \leftarrow \sigma)$	46.2	0.002
$A_{1u} \leftarrow E_{1g}(\pi^* \leftarrow \pi^{\circ})$	46.5	0.213
$E_{2u} \leftarrow E_{1g}(\pi^* \leftarrow \pi^{\circ})$	47.4	0.016
$B_{2u} \leftarrow E_{1g}(\pi^{\circ} \leftarrow \sigma)$	49.0	0.000
$E_{1u} \leftarrow E_{1g}(\pi^* \leftarrow \sigma)$	49.4	0.000
$E_{1u} \leftarrow E_{1g}(\pi^* \leftarrow \sigma)$	56.6	0.000
$E_{1u} \leftarrow E_{1g}(\pi^* \leftarrow \sigma)$	56.6	0.000
$E_{1g} \leftarrow E_{1g}(\pi^* \leftarrow \pi^{\circ})$	57.2	0.000
$A_{2u} \leftarrow E_{1g}(\pi \leftarrow \pi)$	59.5	0.734
Benzene anion		
$B_{2g} \leftarrow E_{2u}(\pi \leftarrow \pi)$	14.0	0.032
$B_{1u} \leftarrow E_{2u}(\sigma^* \leftarrow \pi^{\circ})$	30.8	0.000
$E_{1g} \leftarrow E_{2u}(\pi^{\circ} \leftarrow \pi)$	32.1	0.096
$E_{2g} \leftarrow E_{2u}(\sigma^* \leftarrow \pi^{\circ})$	36.5	0.050
$A_{1g} \leftarrow E_{2u}(\sigma^* \leftarrow \pi^{\circ})$	43.6	0.000
$B_{1g} \leftarrow E_{2u}(\pi^{\circ} \leftarrow \pi)$	46.8	0.212
$E_{1u} \leftarrow E_{2u}(\sigma^* \leftarrow \pi^{\circ})$	46.8	0.000
$E_{1g} \leftarrow E_{2u}(\pi^{\circ} \leftarrow \pi)$	47.6	0.016
$E_{2g} \leftarrow E_{2u}(\pi^{\circ} \leftarrow \sigma)$	50.5	0.000
$B_{2g} \leftarrow E_{2u}(\pi \leftarrow \pi)$	55.3	0.586
$A_{1u} \leftarrow E_{2u}(\pi^* \leftarrow \pi)$	56.5	0.000
$A_{2g} \leftarrow E_{2u}(\pi^{\circ} \leftarrow \sigma)$	58.0	0.000

<sup>a</sup> With electronic transitions to upper states which are not significantly mixed with other excited states we designated open shell and virtual orbitals by circles and asterisks, respectively; <sup>b</sup> in  $\text{cm}^{-1} \cdot 10^{-3}$ .



TABLE IV

The Lowest-Energy Doublet-Quartet and Quartet-Quartet Electronic Transitions Given by the PPP Calculations

Transition <sup>a</sup>	Transition energy <sup>b,c</sup>
Cyclopropenyl	
D <sub>1</sub> ← D <sub>0</sub> ${}^2E'' \leftarrow {}^2E''$	63.0 (57.4) <sup>d</sup>
D <sub>2</sub> ← D <sub>0</sub> ${}^2A_1'' \leftarrow {}^2E''$	73.9 (56.9)
Q <sub>1</sub> ← D <sub>0</sub> ${}^4A_1'' \leftarrow {}^2E''$	30.9 (33.9)
Cyclopentadienyl	
D <sub>1</sub> ← D <sub>0</sub> ${}^2A_2'' \leftarrow {}^2E_1''$	24.2 (29.8)
Q <sub>1</sub> ← D <sub>0</sub> ${}^4E_2'' \leftarrow {}^2E_1''$	26.9 (20.9)
Q <sub>2</sub> ← Q <sub>1</sub> ${}^4E_1'' \leftarrow {}^4E_2''$	30.4 (44.5) <sup>e</sup>
Q <sub>3</sub> ← Q <sub>1</sub> ${}^4E_2'' \leftarrow {}^4E_2''$	35.0 (48.1)
Tropyl	
D <sub>1</sub> ← D <sub>0</sub> ${}^2E_3'' \leftarrow {}^2E_2''$	24.0 (21.4)
Q <sub>1</sub> ← D <sub>0</sub> ${}^4E_1'' \leftarrow {}^2E_2''$	21.7 (23.3)
Q <sub>2</sub> ← Q <sub>1</sub> ${}^4A_1'' \leftarrow {}^4E_1''$	12.7 (15.6)
Q <sub>3</sub> ← Q <sub>1</sub> ${}^4E_2'' \leftarrow {}^4E_1''$	29.0 (26.5)
Cyclononatetraenyl	
D <sub>1</sub> ← D <sub>0</sub> ${}^2E_1'' \leftarrow {}^2E_2''$	21.4 —
Q <sub>1</sub> ← D <sub>0</sub> ${}^4E_3'' \leftarrow {}^2E_2''$	18.0 —
Q <sub>2</sub> ← Q <sub>1</sub> ${}^4E_4'' \leftarrow {}^4E_3''$	15.5 —
Q <sub>3</sub> ← Q <sub>1</sub> ${}^4E_3'' \leftarrow {}^4E_3''$	25.3 —
Benzene cation <sup>f</sup>	
D <sub>1</sub> ← D <sub>0</sub> ${}^2A_{2u} \leftarrow {}^2E_{1g}$	18.1 (25.2)
Q <sub>1</sub> ← D <sub>0</sub> ${}^4E_{2u} \leftarrow {}^2E_{1g}$	25.8 (24.4)
Q <sub>2</sub> ← Q <sub>1</sub> ${}^4B_{1g} \leftarrow {}^4E_{2u}$	11.1 (11.4)
Q <sub>3</sub> ← Q <sub>1</sub> ${}^4B_{2g} \leftarrow {}^4E_{2u}$	14.9 (25.8)
Triphenylbenzene anion	
D <sub>1</sub> ← D <sub>0</sub> ${}^2A_2'' \leftarrow {}^2E''$	6.6 —
Q <sub>1</sub> ← D <sub>0</sub> ${}^4E'' \leftarrow {}^2E''$	23.2 —
Q <sub>2</sub> ← Q <sub>1</sub> ${}^4A_2'' \leftarrow {}^4E''$	4.3 —
Q <sub>3</sub> ← Q <sub>1</sub> ${}^4A_1'' \leftarrow {}^4E''$	5.2 —

TABLE IV  
(Continued)

Transition <sup>a</sup>		Transition energy <sup>b,c</sup>	
Triphenylene anion			
D <sub>1</sub> ← D <sub>0</sub>	<sup>2</sup> A <sub>2</sub> ' ← <sup>2</sup> E''	5.2	—
Q <sub>1</sub> ← D <sub>0</sub>	<sup>4</sup> E'' ← <sup>2</sup> E''	25.2	—
Q <sub>2</sub> ← Q <sub>1</sub>	<sup>4</sup> A <sub>2</sub> ' ← <sup>4</sup> E''	1.2	—
Q <sub>3</sub> ← Q <sub>1</sub>	<sup>4</sup> A <sub>1</sub> ' ← <sup>4</sup> E''	3.0	—
Coronene anion			
D <sub>1</sub> ← D <sub>0</sub>	<sup>2</sup> A <sub>1u</sub> ← <sup>2</sup> E <sub>1g</sub>	11.8	—
Q <sub>1</sub> ← D <sub>0</sub>	<sup>4</sup> E <sub>2u</sub> ← <sup>2</sup> E <sub>1g</sub>	23.0	—
Q <sub>2</sub> ← Q <sub>1</sub>	<sup>4</sup> B <sub>2g</sub> ← <sup>4</sup> E <sub>2u</sub>	4.1	—
Q <sub>3</sub> ← Q <sub>1</sub>	<sup>4</sup> B <sub>1g</sub> ← <sup>4</sup> E <sub>2u</sub>	5.7	—
Cyclooctatetraene anion			
D <sub>1</sub> ← D <sub>0</sub>	<sup>2</sup> E <sub>1g</sub> ← <sup>2</sup> E <sub>2u</sub>	20.5	—
Q <sub>1</sub> ← D <sub>0</sub>	<sup>4</sup> E <sub>3g</sub> ← <sup>2</sup> E <sub>2u</sub>	17.9	—
Q <sub>2</sub> ← Q <sub>1</sub>	<sup>4</sup> B <sub>1u</sub> ← <sup>4</sup> E <sub>3g</sub>	10.4	—
Q <sub>3</sub> ← Q <sub>1</sub>	<sup>4</sup> E <sub>2u</sub> ← <sup>4</sup> E <sub>3g</sub>	21.1	—
Decacyclene anion			
D <sub>1</sub> ← D <sub>0</sub>	<sup>2</sup> A <sub>1</sub> ' ← <sup>2</sup> E''	2.6	—
Q <sub>1</sub> ← D <sub>0</sub>	<sup>4</sup> E'' ← <sup>2</sup> E''	16.3	—
Q <sub>2</sub> ← Q <sub>1</sub>	<sup>4</sup> A <sub>2</sub> ' ← <sup>4</sup> E''	0.1	—
Q <sub>3</sub> ← Q <sub>1</sub>	<sup>4</sup> A <sub>1</sub> ' ← <sup>4</sup> E''	0.3	—

<sup>a</sup> The lowest-energy doublet-doublet transitions are added for the sake of comparison. <sup>b</sup> In  $\text{cm}^{-1} \cdot 10^{-3}$ ; the CNDO results for systems I–III and V are given in parentheses. <sup>c</sup> With alternant systems the entries apply to cations, too. <sup>d</sup> CNDO predicts  $5 \pi \leftarrow \sigma$  and  $\sigma \leftarrow \pi$  doublet-doublet transitions in the region 26000–54000  $\text{cm}^{-1}$ . <sup>e</sup> CNDO predicts  $7 \pi \leftarrow \sigma$  and  $\sigma \leftarrow \pi$  quartet-quartet transitions in the region 32000–48000  $\text{cm}^{-1}$ . <sup>f</sup> CNDO also predicts low-energy  $\pi \rightarrow \sigma$  transitions in the cation:  ${}^2\text{E}_{2g} \leftarrow {}^2\text{E}_{1g}$  at 23600  $\text{cm}^{-1}$  and  ${}^4\text{E}_{1u} \leftarrow {}^4\text{E}_{2u}$  at 24900  $\text{cm}^{-1}$ ; CNDO results for the anion:  ${}^2\text{E}_{2g} \leftarrow {}^2\text{E}_{2u}$  14000;  ${}^4\text{E}_{1g} \leftarrow {}^2\text{E}_{2u}$  24700;  ${}^4\text{A}_{2u} \leftarrow {}^4\text{E}_{1g}$  9400;  ${}^4\text{A}_{1u} \leftarrow {}^4\text{E}_{1g}$  12300  $\text{cm}^{-1}$ .

let us consider the systems VI–VIII. While with triphenylene and triphenylbenzene the agreement between theory and experiment is excellent, the situation with coronene is less clear-cut. The poor agreement may in this case be due to deficiencies in our

theoretical approach, but there are two points in favour of the open shell theory. Firstly, the complexity and dissimilarity of the spectra of the two coronene ions in the long-wavelength region make it difficult to assign electronic transitions unambiguously to absorption maxima and, secondly, the transition energies given by the photoelectron spectral data are in reasonable agreement with the calculation. The second band in the photoelectron spectrum of coronene<sup>20</sup> exhibits two maxima at 8.64 and 9.15 eV, which implies the transition energies in the coronene cation at 10500 and 14600  $\text{cm}^{-1}$ , respectively. It has been claimed<sup>20</sup>, however, that this band "can confidently be attributed to ionization from the  $\pi$  levels  $2e_{1g}$ ,  $1b_{1g}$ , and  $1b_{2g}$ " which would imply three electronic transitions in the coronene cation in the long-wavelength region; our calculation supports this assignment giving the first three transitions as almost pure  $2e_{1g} \rightarrow 2e_{2u}$ ,  $1b_{1g} \rightarrow 2e_{2u}$ , and  $1b_{2g} \rightarrow 2e_{2u}$  electron promotions.

*Cyclooctatetraene radical anion.* We only consider the mononegative ion of IX, since the electronic spectrum of the monopositive ion gives evidence<sup>6</sup> that it retains the same olefinic structure as the neutral tube-shaped molecule. The predicted transition energies in the anion of IX are seen in Fig. 1 to be underestimated by about 2000–5000  $\text{cm}^{-1}$ . It is tempting to ascribe this discrepancy to the nonplanar structure of the anion predicted by the MINDO/2 calculations<sup>29</sup>, but otherwise all the available evidence is consistent with the assumption of a structure of a regular or slightly distorted octagon (see papers cited in refs<sup>6,8</sup>).

*Decacyclene radical anion.* For this radical the theory gives a good account of the observed absorption. Typically as with other radical ions of large nonalternant hydrocarbons<sup>33</sup>, the theory predicts a large number of allowed transitions covering the whole visible and ultraviolet regions. This feature, however, prevents any more detailed analysis of the spectrum.

*Quartet states.* In Table IV we present the predictions for the lowest-energy doublet-quartet transition and the two lowest-energy quartet-quartet transitions. In analogy with the triplet states<sup>34</sup> it is likely that no quantitative treatment of quartet states is possible unless a modification is made in the parameter set. Nevertheless we think that the data presented may be of use to experimentalists as a qualitative guidance. Experimentally the observation of the quartet-doublet phosphorescence or even quartet-quartet spectra is a difficult task. The drawback in the former is due to the circumstance that the lowest quartet state is located above one or more doublet excited states<sup>35,36</sup>. On the basis of the HMO orbital level schemes, the radicals having degenerate ground states represent the only conceivable type of the electronic structure, where the lowest-energy transition might lead to a quartet state. Indeed, the entries in Table IV suggest that this could possibly be the case with systems II, III, IV and IX. Nevertheless the differences between  $D_1 \leftarrow D_0$  and  $Q_1 \leftarrow D_0$  energies

are very small and CNDO does not predict the order of  $Q_1$  and  $D_1$  states consistently with the  $\pi$ -electron calculations. Hence, it is only possible to conclude that the lowest quartet states in *II*, *III*, *IV* and *IX* are to be expected very close to the lowest excited doublet states. The lowest quartet state in *I* is due to a  $\pi \leftarrow \pi$  transition; CNDO predicts however several  $\sigma \leftarrow \pi$  and  $\pi \leftarrow \sigma$  doublet-doublet transitions of lower energy. The order of  $Q_1$  and  $D_1$  states in the benzene cation radical given by CNDO is most probably unrealistic because of overestimated differing features between the two benzene ions. With the other systems, anions of *VI*, *VII*, *VIII* and *X*, the lowest excited states can confidently be assigned to doublet states. The only experimental evidence about the location of a quartet state is available for the decacyclene anion; the quartet-doublet phosphorescence observed<sup>37</sup> at  $14500 \text{ cm}^{-1}$  is in agreement with our calculation which predicts four quartet states in the region  $16300$  to  $18500 \text{ cm}^{-1}$ .

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## Appendix

A. Doublet Configurations for the Case  $n = 1$ 

Designation	Occupation of		Wave function
	$\varphi_m$	$\varphi_{m'}$	
$G^1$	1	0	$ \dots \varphi_m\rangle$
$G^2$	0	1	$ \dots \varphi_{m'}\rangle$
$A^1(i \rightarrow m)$	2	0	$ \dots \varphi_i \bar{\varphi}_m \dots \varphi_m\rangle$
$A^2(i \rightarrow m')$	0	2	$ \dots \varphi_i \bar{\varphi}_{m'} \dots \varphi_{m'}\rangle$
$C_a^1(i \rightarrow k)$	1	0	$(1/2)^{1/2} [ \dots \varphi_i \bar{\varphi}_k \dots \varphi_m\rangle +  \dots \varphi_k \bar{\varphi}_i \dots \varphi_m\rangle]$
$C_a^2(i \rightarrow k)$	0	1	$(1/2)^{1/2} [ \dots \varphi_i \bar{\varphi}_k \dots \varphi_{m'}\rangle +  \dots \varphi_k \bar{\varphi}_i \dots \varphi_{m'}\rangle]$
$C_b^1(i \rightarrow k)$	1	0	$(1/6)^{1/2} [ \dots \varphi_i \bar{\varphi}_k \dots \varphi_m\rangle -  \dots \varphi_k \bar{\varphi}_i \dots \varphi_m\rangle + 2 \dots \varphi_i \bar{\varphi}_m \dots \varphi_k\rangle]$
$C_b^2(i \rightarrow k)$	0	1	$(1/6)^{1/2} [ \dots \varphi_i \bar{\varphi}_k \dots \varphi_{m'}\rangle -  \dots \varphi_k \bar{\varphi}_i \dots \varphi_{m'}\rangle + 2 \dots \varphi_i \bar{\varphi}_{m'} \dots \varphi_k\rangle]$
$B^3(m, m' \rightarrow k)$	0	0	$ \dots \varphi_k\rangle$
$D_a(i \rightarrow m, m')$	1	1	$(1/2)^{1/2} [ \dots \varphi_i \bar{\varphi}_m \dots \varphi_{m'}\rangle +  \dots \varphi_i \bar{\varphi}_m \dots \varphi_{m'}\rangle]$
$D_b(i \rightarrow m, m')$	1	1	$(1/6)^{1/2} [ \dots \varphi_i \bar{\varphi}_m \dots \varphi_m\rangle -  \dots \varphi_i \bar{\varphi}_m \dots \varphi_{m'}\rangle + 2 \dots \varphi_m \bar{\varphi}_i \dots \varphi_m\rangle]$

B. Doublet Configurations for the Case  $n = 3$ 

Designation	Occupation of		Wave function
	$\varphi_m$	$\varphi_{m'}$	
$G^1$	1	2	$ \dots \varphi_m, \bar{\varphi}_m, \varphi_m $
$G^2$	2	1	$ \dots \varphi_m, \bar{\varphi}_m, \varphi_{m'} $
$B^1(m \rightarrow k)$	0	2	$ \dots \varphi_m, \bar{\varphi}_m, \varphi_k $
$B^2(m' \rightarrow k)$	2	0	$ \dots \varphi_m, \bar{\varphi}_m, \varphi_k $
$C_a^1(i \rightarrow k)$	1	2	$(1/2)^{1/2} [ \dots \varphi_i, \bar{\varphi}_k, \dots \varphi_m, \bar{\varphi}_m, \varphi_m  +  \dots \varphi_k, \bar{\varphi}_i, \dots \varphi_m, \bar{\varphi}_m, \varphi_m ]$
$C_a^2(i \rightarrow k)$	2	1	$(1/2)^{1/2} [ \dots \varphi_i, \bar{\varphi}_k, \dots \varphi_m, \bar{\varphi}_m, \varphi_{m'}  +  \dots \varphi_k, \bar{\varphi}_i, \dots \varphi_m, \bar{\varphi}_m, \varphi_{m'} ]$
$C_b^1(i \rightarrow k)$	1	2	$(1/6)^{1/2} [ \dots \varphi_i, \bar{\varphi}_k, \dots \varphi_m, \bar{\varphi}_m, \varphi_m  -  \dots \varphi_k, \bar{\varphi}_i, \dots \varphi_m, \bar{\varphi}_m, \varphi_m  + 2 \dots \varphi_i, \bar{\varphi}_m, \dots \varphi_m, \bar{\varphi}_m, \varphi_k ]$
$C_b^2(i \rightarrow k)$	2	1	$(1/6)^{1/2} [ \dots \varphi_i, \bar{\varphi}_k, \dots \varphi_m, \bar{\varphi}_m, \varphi_{m'}  -  \dots \varphi_k, \bar{\varphi}_i, \dots \varphi_m, \bar{\varphi}_m, \varphi_{m'}  + 2 \dots \varphi_i, \bar{\varphi}_{m'}, \dots \varphi_m, \bar{\varphi}_m, \varphi_k ]$
$A^3(i \rightarrow m, m')$	2	2	$ \dots \varphi_i, \bar{\varphi}_m, \dots \varphi_m, \bar{\varphi}_{m'}, \varphi_{m'} $
$E_g(m, m' \rightarrow k)$	1	1	$(1/2)^{1/2} [ \dots \varphi_k, \bar{\varphi}_m, \varphi_{m'}  +  \dots \varphi_k, \bar{\varphi}_{m'}, \varphi_m ]$
$E_g(m, m' \rightarrow k)$	1	1	$(1/6)^{1/2} [ \dots \varphi_k, \bar{\varphi}_m, \varphi_{m'}  -  \dots \varphi_k, \bar{\varphi}_{m'}, \varphi_m  + 2 \dots \varphi_m, \bar{\varphi}_k, \varphi_{m'} ]$

## C. Quartet Configurations

Designation	Occupation of		Wave function
	$\varphi_m$	$\varphi_{m'}$	
The case $n = 1$			
$C^1(i \rightarrow k)$	1	0	$(1/3)^{1/2}( \dots \bar{\varphi}_k \dots \varphi_m  -  \dots \bar{\varphi}_k \bar{\varphi}_i \dots \varphi_m  -  \dots \bar{\varphi}_i \bar{\varphi}_m \dots \varphi_k )$
$C^2(i \rightarrow k)$	0	1	$(1/3)^{1/2}( \dots \varphi_i \bar{\varphi}_k \dots \varphi_{m'}  -  \dots \varphi_k \bar{\varphi}_i \dots \varphi_{m'}  -  \dots \varphi_i \bar{\varphi}_m \dots \varphi_k )$
$D(i \rightarrow m, m')$	1	1	$(1/3)^{1/2}( \dots \varphi_i \bar{\varphi}_{m'} \dots \varphi_m  -  \dots \varphi_m \bar{\varphi}_i \dots \varphi_m  -  \dots \varphi_i \bar{\varphi}_m \dots \varphi_{m'} )$
The case $n = 3$			
$C^1(i \rightarrow k)$	1	2	$(1/3)^{1/2}( \dots \varphi_i \bar{\varphi}_k \dots \varphi_m \bar{\varphi}_m \bar{\varphi}_m \varphi_m  -  \dots \varphi_k \bar{\varphi}_i \dots \varphi_m \bar{\varphi}_m \bar{\varphi}_m \varphi_m  -  \dots \varphi_i \bar{\varphi}_m \dots \varphi_m \bar{\varphi}_m \varphi_k )$
$C^2(i \rightarrow k)$	2	1	$(1/3)^{1/2}( \dots \varphi_i \bar{\varphi}_k \dots \varphi_m \bar{\varphi}_m \varphi_{m'}  -  \dots \varphi_k \bar{\varphi}_i \dots \varphi_m \bar{\varphi}_m \varphi_{m'}  -  \dots \varphi_i \bar{\varphi}_{m'} \dots \varphi_m \bar{\varphi}_m \varphi_k )$
$E(m, m' \rightarrow k)$	1	1	$(1/3)^{1/2}( \dots \varphi_k \bar{\varphi}_m \varphi_{m'}  -  \dots \varphi_k \bar{\varphi}_m \varphi_m  -  \dots \varphi_m \bar{\varphi}_k \varphi_{m'} )$

D. CI Doublet-Doublet Matrix Elements for the Case  $n = 1$ 

In the following tables we present the general formulas for the CI doublet-doublet matrix elements based on the SCF molecular orbitals given by the half-electron method for the case  $n = 1$ . ( $\epsilon_{ij}$  stand for the orbital energies, the molecular repulsion integrals are defined as  $\langle ij | kl \rangle = \iint \varphi_i^*(1) \varphi_j^*(2) e^2 / r_{12} \varphi_k(1) \varphi_l(2) \text{ d}\tau$ , the transition moments between configurations are expressed in terms of  $r_{xy} = \int \varphi_x^* r \varphi_y \text{ d}\tau$ .)

## Diagonal elements

Type (X)	$\langle X   \hat{H}   X \rangle - \langle G^1   \hat{H}   G^1 \rangle$ elements <sup>a</sup>	Comment <sup>b</sup> for the case $n = 3$
$A^1(i \rightarrow m)$	$\epsilon_m - \epsilon_i + 3/4 \langle mm   mm \rangle - 1/2 \langle mm'   mm' \rangle + 1/4 \langle mm'   m'm \rangle - 3/2 \langle im   im \rangle + 1/2 \langle im'   im' \rangle + 3/4 \langle im   mi \rangle - 1/4 \langle im'   m'i \rangle$	$\epsilon, (ik)$
$C_\alpha^1(i \rightarrow k)$	$\epsilon_k - \epsilon_i + 1/2 \langle km   km \rangle - 1/2 \langle km'   km' \rangle - 1/4 \langle km   mk \rangle + 1/4 \langle km'   m'k \rangle - 1/2 \langle im   im \rangle + 1/2 \langle im'   im' \rangle + 1/4 \langle im   mi \rangle - 1/4 \langle im'   m'i \rangle - \langle ik   ik \rangle + 2 \langle ik   ki \rangle$	$(ik)$
$C_\beta^1(i \rightarrow k)$	$\epsilon_k - \epsilon_i + 1/2 \langle km   km \rangle - 1/2 \langle km'   km' \rangle + 3/4 \langle km   mk \rangle + 1/4 \langle km'   m'k \rangle - 1/2 \langle im   im \rangle + 1/2 \langle im'   im' \rangle + 5/4 \langle im   mi \rangle - 1/4 \langle im'   m'i \rangle - \langle ik   ik \rangle$	$(ik)$
$B^3(m, m' \rightarrow k)$	$\epsilon_k - \epsilon_m - 1/2 \langle km   km \rangle - 1/2 \langle km'   km' \rangle + 1/4 \langle km   mk \rangle + 1/4 \langle km'   m'k \rangle + 1/4 \langle mm   mm \rangle + 1/2 \langle mm'   mm' \rangle - 1/4 \langle mm'   m'm \rangle$	$\epsilon, (ik)$
$D_\alpha^3(i \rightarrow m, m')$	$\epsilon_m - \epsilon_i - 1/2 \langle im   im \rangle - 1/2 \langle im'   im' \rangle + 1/4 \langle im   mi \rangle + 1/4 \langle im'   m'i \rangle - 1/4 \langle mm   mm \rangle + 1/2 \langle mm'   mm' \rangle + 5/4 \langle mm'   m'm \rangle$	$\epsilon, (ik)$
$D_\beta^3(i \rightarrow m, m')$	$\epsilon_m - \epsilon_i - 1/2 \langle im   im \rangle - 1/2 \langle im'   im' \rangle + 5/4 \langle im   mi \rangle + 5/4 \langle im'   m'i \rangle - 1/4 \langle mm   mm \rangle + 1/2 \langle mm'   mm' \rangle - 3/4 \langle mm'   m'm \rangle$	$\epsilon, (ik)$

<sup>a</sup> The formulas for the  $\langle X | \hat{H} | X \rangle - \langle G^2 | \hat{H} | G^2 \rangle$  elements for  $X = A^2, C_\alpha^2$ , and  $C_\beta^2$  can be obtained by interchanging  $m$  and  $m'$  in the corresponding tabulated expressions; for  $X = B^3, D_\alpha^3$ , and  $D_\beta^3$  they are equal to the corresponding tabulated expressions because of  $\epsilon_m' = \epsilon_m$  and  $\langle mm | mm \rangle = \langle m'm' | m'm' \rangle$ . <sup>b</sup> See Appendix F.



## Off-diagonal elements

Type	$\langle X^1   \hat{H}   Y^1 \rangle$ elements <sup>a</sup>	Transition moment <sup>a</sup>	Comment <sup>b</sup> for the case $n=3$
$A^1(i \rightarrow m) - G^1$	$3/4 \langle mm   mi \rangle - 1/2 \langle m'm   m'i \rangle + 1/4 \langle m'm   im' \rangle$	$r_{mi}$	(ik) (-1)
$A^1(i \rightarrow m) - A^1(h \rightarrow m)$	$-3/2 \langle mi   mh \rangle + 3/4 \langle mi   hm \rangle + 1/2 \langle m'i   m'h \rangle - 1/4 \langle m'i   hm' \rangle$	$-r_{hi}$	(hk) (il)*
$C_g^1(i \rightarrow k) - G^1$	$(1/2)^{1/2} [\langle mk   mi \rangle - 1/2 \langle mk   im \rangle - \langle m'k   m'i \rangle + 1/2 \langle m'k   im' \rangle]$	$\sqrt{(2)} r_{ki}$	(-1)
$C_g^1(i \rightarrow k) - A^1(h \rightarrow m)$	$\sqrt{(2)} [\langle im   kh \rangle - 1/2 \langle im   hk \rangle]$	0	(ik) (hl)
$C_g^1(i \rightarrow k) - A^1(i \rightarrow m)$	$(1/2)^{1/2} [3/4 \langle mm   mk \rangle - 1/2 \langle m'm   m'k \rangle + 1/4 \langle m'm   km' \rangle + 2 \langle im   ki \rangle - \langle im   ik \rangle]$	$(1/2)^{1/2} r_{km}$	(ik)
$C_g^1(i \rightarrow k) - C_g^1(h \rightarrow l)$	$2 \langle hk   li \rangle - \langle hk   il \rangle$	0	†
$C_g^1(i \rightarrow k) - C_g^1(i \rightarrow l)$	$1/2 \langle mk   ml \rangle - 1/4 \langle mk   lm \rangle - 1/2 \langle m'k   m'l \rangle + 1/4 \langle m'k   lm' \rangle + 2 \langle ik   li \rangle - \langle ik   il \rangle$	$r_{ki}$	
$C_g^1(i \rightarrow k) - C_g^1(h \rightarrow k)$	$-1/2 \langle mh   mi \rangle + 1/4 \langle mh   im \rangle + 1/2 \langle m'h   m'i \rangle - 1/4 \langle m'h   im' \rangle + 2 \langle kh   ik \rangle - \langle kh   ki \rangle$	$-r_{hi}$	
$C_\beta^1(i \rightarrow k) - G^1$	$\sqrt{(6)/2} \langle mk   im \rangle$	0	†
$C_\beta^1(i \rightarrow k) - A^1(h \rightarrow m)$	$-\sqrt{(6)/2} \langle mi   kh \rangle$	0	(ik) (hl) (-1)
$C_\beta^1(i \rightarrow k) - A^1(i \rightarrow m)$	$\sqrt{(6)/2} [3/4 \langle mm   mk \rangle - 1/2 \langle m'm   m'k \rangle + 1/4 \langle m'm   km' \rangle - \langle im   ik \rangle]$	$\sqrt{(6)/2} r_{km}$	(ik) (-1)
$C_\beta^1(i \rightarrow k) - C_g^1(h \rightarrow l)$	0	0	†
$C_\beta^1(i \rightarrow k) - C_g^1(i \rightarrow l)$	$\sqrt{(3)/2} \langle mk   im \rangle$	0	†
$C_\beta^1(i \rightarrow k) - C_g^1(h \rightarrow k)$	$-\sqrt{(3)/2} \langle mh   im \rangle$	0	†
$C_\beta^1(i \rightarrow k) - C_g^1(i \rightarrow k)$	$\sqrt{(3)/2} [\langle mk   km \rangle - \langle mi   im \rangle]$	0	†

## Appendix D (continued)

Type	$\langle X^1   \hat{H}   Y^1 \rangle$ elements <sup>a</sup>	Transition moment <sup>a</sup>	Comment <sup>b</sup> for the case $n = 3$
$C_{\beta}^1(i \rightarrow k) - C_{\beta}^1(h \rightarrow l)$	$-\langle hk   il \rangle$	0	†
$C_{\beta}^1(i \rightarrow k) - C_{\beta}^1(i \rightarrow l)$	$1/2\langle mk   ml \rangle + 3/4\langle mk   lm \rangle - 1/2\langle m'k   m'l \rangle + 1/4\langle m'k   lm' \rangle - \langle ik   il \rangle$	$r_{ki}$	
$C_{\beta}^1(i \rightarrow k) - C_{\beta}^1(h \rightarrow k)$	$-1/2\langle mh   m'i \rangle + 5/4\langle mh   im \rangle + 1/2\langle m'h   m'i \rangle - 1/4\langle m'h   im' \rangle - \langle kh   ki \rangle$	$-r_{hi}$	

<sup>a</sup> The formulas for the  $X^2 - Y^2$  elements can be obtained by interchanging  $m$  and  $m'$  in the tabulated expressions. <sup>b</sup> See Appendix F.

Type	$\langle X^2   \hat{H}   Y^1 \rangle$ elements <sup>a</sup>	Transition moment <sup>a</sup>	Comment <sup>b</sup> for the case $n = 3$
$G^2 - G^1$	0	0	†
$A^2(i \rightarrow m') - G^1$	$\langle m'm'   im \rangle$	0	$(ik)(-l) *$
$A^2(h \rightarrow m') - A^1(i \rightarrow m)$	0	0	†
$A^2(i \rightarrow m') - A^1(i \rightarrow m)$	$\langle m'm'   mm \rangle$	0	*
$C_{\alpha}^2(i \rightarrow k) - G^1$	$(1/2)^{1/2} [2\langle km'   im \rangle - \langle kmv'   mi \rangle]$	0	$(mm')(-l)$
$C_{\alpha}^2(h \rightarrow k) - A^1(i \rightarrow m)$	0	0	†
$C_{\alpha}^2(i \rightarrow k) - A^1(i \rightarrow m)$	$(1/2)^{1/2} \langle km'   mm \rangle$	0	$(ik) *$
$C_{\alpha}^2(i \rightarrow k) - C_{\alpha}^1(h \rightarrow l)$	0	0	†

## Appendix D (continued)

Type	$\langle X^2   \hat{H}   Y^1 \rangle$ elements <sup>a</sup>	Transition moment <sup>a</sup>	Comment <sup>b</sup> for the case $n=3$
$C_2^2(i \rightarrow k) - C_2^1(i \rightarrow l)$	$\langle km'   lm \rangle - 1/2 \langle km'   ml \rangle$	0	(mm') (-1)
$C_2^2(i \rightarrow k) - C_2^1(h \rightarrow k)$	$-\langle hm'   im \rangle + 1/2 \langle hm'   mi \rangle$	0	(mm') (-1)
$C_2^2(i \rightarrow k) - C_2^1(i \rightarrow k)$	$-\langle im'   im \rangle + 1/2 \langle im'   mi \rangle + \langle km'   km \rangle - 1/2 \langle km'   mk \rangle$	0	(mm') (ik)
$C_2^2(i \rightarrow k) - G^1$	$\sqrt{(6)/2} \langle m'k   im \rangle$	0	(mm')
$C_2^2(h \rightarrow k) - A^1(i \rightarrow m)$	0	0	†
$C_2^2(i \rightarrow k) - A^1(i \rightarrow m)$	$\sqrt{(6)/2} \langle m'k   mm \rangle$	0	(ik) (-1) *
$C_2^2(i \rightarrow k) - C_2^1(h \rightarrow l)$	0	0	†
$C_2^2(i \rightarrow k) - C_2^1(i \rightarrow l)$	$\sqrt{(3)/2} \langle m'k   lm \rangle$	0	(mm')
$C_2^2(i \rightarrow k) - C_2^1(h \rightarrow k)$	$-\sqrt{(3)/2} \langle m'h   im \rangle$	0	(mm')
$C_2^2(i \rightarrow k) - C_2^1(i \rightarrow k)$	$\sqrt{(3)/2} [\langle m'k   km \rangle - \langle m'i   im \rangle]$	0	(mm')
$C_2^2(i \rightarrow k) - C_2^1(h \rightarrow l)$	0	0	†
$C_2^2(i \rightarrow k) - C_2^1(i \rightarrow l)$	$\langle km'   lm \rangle + 1/2 \langle km'   ml \rangle$	0	
$C_2^2(i \rightarrow k) - C_2^1(h \rightarrow k)$	$3/2 \langle hm'   mi \rangle - \langle hm'   im \rangle$	0	
$C_2^2(i \rightarrow k) - C_2^1(i \rightarrow k)$	$-\langle im'   im \rangle + 3/2 \langle im'   mi \rangle + \langle km'   km \rangle + 1/2 \langle km'   mk \rangle$	0	(mm') (ik)

<sup>a</sup> The formulas for the  $X^1 - Y^2$  elements can be obtained by interchanging  $m$  and  $m'$  in the tabulated expressions. <sup>b</sup> See Appendix F.

## Appendix D (continued)

Type	$\langle X   \hat{H}   X \rangle$ elements, $X = B^3$ or $D$	Transition moment	Comment <sup>a</sup> for the case $n = 3$
$B^3(m, m' \rightarrow k) - B^3(m, m' \rightarrow l) - 1/2 \langle mk   ml \rangle + 1/4 \langle mk   lm \rangle - 1/2 \langle m'k   m'l \rangle + 1/4 \langle m'k   lm' \rangle$		$r_{ki}$	(hk) (il)
$D_2(i \rightarrow m, m') - B^3(m, m' \rightarrow k) (1/2)^{1/2} [\langle mm'   ik \rangle + \langle mm'   ki \rangle]$		0	*
$D_2(i \rightarrow m, m') - D_2(h \rightarrow m, m') - 1/2 \langle mh   mi \rangle + 1/4 \langle mh   im \rangle - 1/2 \langle m'h   m'i \rangle + 1/4 \langle m'h   im' \rangle$		$-r_{hi}$	(hk) (il)
$D_\beta(i \rightarrow m, m') - B^3(m, m' \rightarrow k) \sqrt{(6)/2} [\langle mm'   ki \rangle - \langle mm'   ik \rangle]$		0	*
$D_\beta(i \rightarrow m, m') - D_2(h \rightarrow m, m') \sqrt{(3)/2} [\langle m'h   im' \rangle - \langle mh   im \rangle]$		0	(hk) (il) (-1)
$D_\beta(i \rightarrow m, m') - D_2(i \rightarrow m, m') \sqrt{(3)/2} [\langle im'   m'i \rangle - \langle im   mi \rangle]$		0	(ik) (-1)
$D_\beta(i \rightarrow m, m') - D_\beta(h \rightarrow m, m') - 1/2 \langle mh   mi \rangle + 5/4 \langle mh   im \rangle - 1/2 \langle m'h   m'i \rangle + 5/4 \langle m'h   im' \rangle$		$-r_{hi}$	(hk) (il)

<sup>a</sup> See Appendix F.

Type	$\langle X   \hat{H}   Y^1 \rangle$ elements <sup>a</sup> , $X = B^3$ or $D$	Transition moment <sup>a</sup>	Comment <sup>b</sup> for the case $n = 3$
$B^3(m, m' \rightarrow k) - G^1$	$-1/4 \langle mk   mm \rangle - 1/2 \langle m'k   m'm \rangle + 1/4 \langle m'k   mm' \rangle$	$r_{km}$	(ik) (-1) *
$B^3(m, m' \rightarrow k) - A^1(i \rightarrow m)$	$\langle ik   mm \rangle$	0	*
$B^3(m, m' \rightarrow k) - C_2^1(h \rightarrow l)$	$(1/2)^{1/2} [2 \langle hk   lm \rangle - \langle hk   ml \rangle]$	0	(ik) (hl) *
$B^3(m, m' \rightarrow k) - C_2^1(i \rightarrow k)$	$(1/2)^{1/2} [1/4 \langle mi   mm \rangle + 1/2 \langle m'i   m'm \rangle - 1/4 \langle m'i   mm' \rangle - \langle ki   km \rangle + -(1/2)^{1/2} r_{im}]$ $+ 2 \langle ki   mk \rangle]$		(ik) *
$B^3(m, m' \rightarrow k) - C_\beta^1(h \rightarrow l)$	$\sqrt{(6)/2} \langle hk   ml \rangle$	0	(ik) (hl) (-1) *

## Appendix D (continued)

Type	$\langle X   \hat{H}   Y^1 \rangle$ elements, <sup>a</sup> $X = B^3$ or $D$	Transition moment <sup>a</sup>	Comment <sup>b</sup> for the case $n = 3$
$B^3(m, m' \rightarrow k) - C_{\beta}^1(i \rightarrow k)$	$\sqrt{(6)/2}[-1/4\langle mi   mn \rangle - 1/2\langle m'i   m'm \rangle + 1/4\langle m'i   mm' \rangle + \langle ki   km \rangle]$	$\sqrt{(6)/2}r_{im}$	(ik) (-1) *
$D_{\alpha}(i \rightarrow m, m') - G^1$	$(1/2)^{1/2}[1/2\langle m'm   im \rangle + 5/4\langle m'm   mi \rangle - 1/4\langle m'm'   im' \rangle]$	$(1/2)^{1/2}r_{m'i}$	(ik) (-1) *
$D_{\alpha}(i \rightarrow m, m') - A^1(h \rightarrow m)$	$(1/2)^{1/2}[-2\langle m'h   mi \rangle + \langle m'h   im \rangle]$	0	(ik) (hl) *
$D_{\alpha}(i \rightarrow m, m') - A^1(i \rightarrow m)$	$(1/2)^{1/2}[-2\langle m'i   mi \rangle + \langle m'i   im \rangle]$	0	(ik) *
$D_{\alpha}(i \rightarrow m, m') - C_{\alpha}^1(h \rightarrow l)$	$\langle hm'   li \rangle - 1/2\langle hm'   il \rangle$	0	(ik) (hl) *
$D_{\alpha}(i \rightarrow m, m') - C_{\alpha}^1(i \rightarrow k)$	$1/2[-1/4\langle m'm'   m'k \rangle + 1/2\langle mm'   mk \rangle + 5/4\langle mm'   km \rangle + 2\langle im'   ki \rangle - \langle im'   ik \rangle]$	$1/2r_{m'k}$	(ik) *
$D_{\alpha}(i \rightarrow m, m') - C_{\beta}^1(h \rightarrow l)$	$-\sqrt{(3)/2}\langle hm'   il \rangle$	0	(ik) (hl) (-1) *
$D_{\alpha}(i \rightarrow m, m') - C_{\beta}^1(i \rightarrow k)$	$\sqrt{(3)/2}[-1/4\langle m'm'   m'k \rangle + 1/2\langle mm'   mk \rangle + 5/4\langle mm'   km \rangle - \langle im'   ik \rangle]$	$\sqrt{(3)/2}r_{m'k}$	(ik) (-1) *
$D_{\beta}(i \rightarrow m, m') - G^1$	$-\sqrt{(6)/2}[1/4\langle m'm'   m'i \rangle - 1/2\langle mm'   mi \rangle + 3/4\langle mm'   im \rangle]$	$\sqrt{(6)/2}r_{m'i}$	(ik) *
$D_{\beta}(i \rightarrow m, m') - A^1(h \rightarrow m)$	$\sqrt{(6)/2}\langle hm'   mi \rangle$	0	(ik) (hl) (-1) *
$D_{\beta}(i \rightarrow m, m') - A^1(i \rightarrow m)$	$\sqrt{(6)/2}\langle im'   mi \rangle$	0	(ik) (-1) *
$D_{\beta}(i \rightarrow m, m') - C_{\alpha}^1(h \rightarrow l)$	$\sqrt{(3)/2}[2\langle hm'   li \rangle - \langle hm'   il \rangle]$	0	(ik) (hl) (-1) *
$D_{\beta}(i \rightarrow m, m') - C_{\alpha}^1(i \rightarrow k)$	$-\sqrt{(3)/2}[1/4\langle m'm'   m'k \rangle - 1/2\langle mm'   mk \rangle + 3/4\langle mm'   km \rangle - 2\langle im'   ki \rangle + \langle im'   ik \rangle]$	$\sqrt{(3)/2}r_{m'k}$	(ik) (-1) *
$D_{\beta}(i \rightarrow m, m') - C_{\beta}^1(h \rightarrow l)$	$1/2\langle hm'   il \rangle$	0	(ik) (hl) *
$D_{\beta}(i \rightarrow m, m') - C_{\beta}^1(i \rightarrow k)$	$1/2[1/4\langle m'm'   m'k \rangle - 1/2\langle mm'   mk \rangle + 3/4\langle mm'   km \rangle + \langle im'   ik \rangle]$	$-1/2r_{m'k}$	(ik) *

<sup>a</sup> The formulas for the  $X \cdot Y^2$  elements can be obtained by interchanging  $m$  and  $m'$  in the tabulated expressions, if  $X = D_{\beta}$  they must be multiplied moreover by  $-1$ . <sup>b</sup> See Appendix F.

E. CI Quartet-Quartet Matrix Elements for the Case  $n = 1$ 

The following general formulas for the CI matrix quartet-quartet elements are based on the SCF molecular orbitals given by the half-electron method for the case  $n = 1$ . ( $\epsilon_y$  stands for the orbital energies, the molecular repulsion integrals are defined as  $\langle ij | k \rangle = \iint \varphi_i^*(1)\varphi_j^*(2) e^2 / r_{12} \cdot \varphi_k(1)\varphi_l(2) d\tau$ .)

Type	Electronic interaction elements <sup>a</sup>	Comment <sup>b</sup> for the case $n = 3$
	Diagonal $\langle X   \hat{H}   X \rangle - \langle G^1   \hat{H}   G^1 \rangle$ elements	
$C^1(i \rightarrow k)$	$\epsilon_k - \epsilon_i + 1/2\langle mk   mk \rangle - 3/4\langle mk   km \rangle - 1/2\langle m'k   m'k \rangle + 1/4\langle m'k   km' \rangle -$ $- 1/2\langle mi   mi \rangle - 1/4\langle mi   im \rangle + 1/2\langle m'i   m'i \rangle - 1/4\langle m'i   im' \rangle - \langle ik   ik \rangle$	(ik)
$D(j \rightarrow m, m')$	$\epsilon_m - \epsilon_j - 1/4\langle mm   mm \rangle + 1/2\langle mm'   mm' \rangle - 3/4\langle mm'   m'm \rangle -$ $- 1/2\langle mi   mi \rangle - 1/4\langle mi   im \rangle - 1/2\langle m'i   m'i \rangle - 1/4\langle m'i   im' \rangle$	$\epsilon_i$ , (ik)
	Off-diagonal elements	
$C^1(i \rightarrow k) - C^1(h \rightarrow l)$	$-\langle hk   il \rangle$	†
$C^1(i \rightarrow k) - C^1(j \rightarrow l)$	$1/2\langle mk   ml \rangle - 3/4\langle mk   lm \rangle - 1/2\langle m'k   m'l \rangle + 1/4\langle m'k   lm' \rangle - \langle ik   il \rangle$	
$C^1(i \rightarrow k) - C^1(h \rightarrow k)$	$-1/2\langle mh   mi \rangle - 1/4\langle mh   im \rangle + 1/2\langle m'h   m'i \rangle - 1/4\langle m'h   im' \rangle - \langle kb   ki \rangle$	
$C^2(i \rightarrow k) - C^1(h \rightarrow l)$	0	
$C^2(i \rightarrow k) - C^1(j \rightarrow l)$	$\langle km'   lm \rangle - \langle km'   ml \rangle$	
$C^2(i \rightarrow k) - C^1(h \rightarrow k)$	$-\langle hm'   im \rangle$	
$C^2(i \rightarrow k) - C^1(i \rightarrow k)$	$-\langle im'   im \rangle + \langle km'   km \rangle - \langle km'   mk \rangle$	(mm') (ik)
$D(j \rightarrow m, m') - D(h \rightarrow m, m')$	$-1/2\langle mh   mi \rangle - 1/4\langle mh   im \rangle - 1/2\langle m'h   m'i \rangle - 1/4\langle m'h   im' \rangle$	(hk) (il)
$D(j \rightarrow m, m') - C^1(h \rightarrow l)$	$-\langle hm'   il \rangle$	(ik) (hl) *
$D(j \rightarrow m, m') - C^1(i \rightarrow k)$	$1/2\langle mm'   mk \rangle - 3/4\langle mm'   km \rangle - 1/4\langle m'm'   m'k \rangle - \langle im'   ik \rangle$	(ik) *

<sup>a</sup> By interchanging  $m$  and  $m'$  in the tabulated expressions one can arrive at the formulas for the following elements:  $\langle C^2 | \hat{H} | C^2 \rangle - \langle G^2 | \hat{H} | G^2 \rangle$  (from  $\langle C^1 | \hat{H} | C^1 \rangle - \langle G^1 | \hat{H} | G^1 \rangle$ );  $\langle X^2 | \hat{H} | Y^2 \rangle$  (from  $\langle X^1 | \hat{H} | Y^1 \rangle$ );  $\langle X^2 | \hat{H} | Y^1 \rangle$  (from  $\langle X^1 | \hat{H} | Y^2 \rangle$ );  $\langle D | \hat{H} | C^1 \rangle$ ; in this last expression moreover the sign of the element must be changed). <sup>b</sup> See Appendix F.

F. CI Matrix Elements for the Case  $n = 3$ 

The majority of the elements can be simply inferred from those for the case  $n = 1$  by performing the instructions indicated by symbols in the last columns of tables in Appendices D and E. The meaning of the symbols is as follows: † leave the matrix elements unchanged; (—) multiply by —1;  $\epsilon$  replace  $(\epsilon_m - \epsilon_l)$  by  $(\epsilon_k - \epsilon_m)$  and *vice versa*; (ab) interchange a and b wherever appearing in the repulsion integrals and transition moments. Then, take conjugate complex transition moments; \* take the conjugate complex repulsion integral, i.e., for  $\langle ab | cd \rangle$  write  $\langle cd | ab \rangle$ .

Furthermore the A, B, and D configurations have to be replaced by the B, A, and E configurations, respectively; excitations ( $i \rightarrow m$ ) by ( $m \rightarrow k$ ), ( $h \rightarrow m$ ) by ( $m \rightarrow l$ ), ( $i \rightarrow m, m'$ ) by ( $m, m' \rightarrow k$ ), ( $h \rightarrow m, m'$ ) by ( $m, m' \rightarrow l$ ), ( $m, m' \rightarrow k$ ) and ( $m, m' \rightarrow l$ ) by ( $h \rightarrow m, m'$ ). All transition moments must moreover be multiplied by —1.

The elements which cannot be inferred in this way are listed below (the molecular repulsion integrals are defined as  $\langle ij | kl \rangle = \iint \phi_i^* \phi_j \phi_k \phi_l$ ,  $\phi_i^*(2) e^2 / r_{12} \phi_k(1) \phi_l(2) dt$ , transition moments between configurations are expressed in terms of  $r_{xy} = \int \phi_x^* r \phi_y dt$ ).

## Doublet-doublet matrix elements

Type	$\langle X   \hat{H}   Y \rangle$ elements <sup>a</sup>	Transition moment
$C_2^1(i \rightarrow k) - C_2^1(h \rightarrow k)$	$1/2 \langle mh   mi \rangle - 1/4 \langle mh   im \rangle - 1/2 \langle m'h   m'i \rangle + 1/4 \langle m'h   im' \rangle + 2 \langle kh   ik \rangle - \langle kh   ki \rangle$	$-r_{hi}$
$C_2^1(i \rightarrow k) - C_2^1(i \rightarrow l)$	$-1/2 \langle mk   ml \rangle + 1/4 \langle mk   lm \rangle + 1/2 \langle m'k   m'l \rangle - 1/4 \langle m'k   lm' \rangle + 2 \langle ik   li \rangle - \langle ik   il \rangle$	$r_{kl}$
$C_\beta^1(i \rightarrow k) - C_\beta^1(h \rightarrow k)$	$1/2 \langle mh   mi \rangle + 3/4 \langle mh   im \rangle - 1/2 \langle m'h   m'i \rangle + 1/4 \langle m'h   im' \rangle - \langle kh   ki \rangle$	$-r_{hi}$
$C_\beta^1(i \rightarrow k) - C_\beta^1(i \rightarrow l)$	$-1/2 \langle mk   ml \rangle + 5/4 \langle mk   lm \rangle + 1/2 \langle m'k   m'l \rangle - 1/4 \langle m'k   lm' \rangle - \langle ik   il \rangle$	$r_{kl}$
$C_\beta^2(i \rightarrow k) - C_\beta^2(h \rightarrow k)$	$\langle hm   im' \rangle + 1/2 \langle hm   m'i \rangle$	0
$C_\beta^2(i \rightarrow k) - C_\beta^2(i \rightarrow l)$	$3/2 \langle mk   lm' \rangle - \langle mk   m'l \rangle$	0

<sup>a</sup> By interchanging m and m' in the tabulated expressions one can arrive at the  $X^2 - Y^2$  elements from  $X^1 - Y^1$  and  $X^1 - Y^2$  from  $X^2 - Y^1$ .

## Quartet-quartet matrix elements

Type <sup>a</sup>	$\langle X   \hat{H}   Y \rangle$ elements <sup>a</sup>
$C^1(i \rightarrow k) - C^1(i \rightarrow l)$	$-1/2 \langle mk   ml \rangle - 1/4 \langle mk   lm \rangle + 1/2 \langle m'k   m'l \rangle - 1/4 \langle m'k   lm' \rangle - \langle ik   il \rangle$
$C^1(i \rightarrow k) - C^1(h \rightarrow k)$	$1/2 \langle mh   mi \rangle - 3/4 \langle mh   im \rangle - 1/2 \langle m'h   m'i \rangle + 1/4 \langle m'h   im' \rangle - \langle kh   ki \rangle$
$C^2(i \rightarrow k) - C^1(h \rightarrow k)$	$\langle hm   im' \rangle - \langle hm   m'i \rangle$
$C^2(i \rightarrow k) - C^1(i \rightarrow l)$	$-\langle km   lm' \rangle$

<sup>a</sup> By interchanging  $m$  and  $m'$  in the formulas for the  $C^1 - C^1$  elements one can arrive at the  $C^2 - C^2$  elements.



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