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USE OF SEMIEMPIRICAL MODELS FOR CALCULATION OF B TERMS IN MCD SPECTRA—III[a]

PARISER-PARR-POPLE (PPP) PREDICTIONS FOR DICATIONS AND DIANIONS OF PENTALENE AND HEPTALENE

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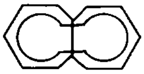
Abstract—The PPP model is used to predict the MCD spectra of the doubly-charged ions of pentalene and heptalene. The excited states of the 10 π-electron ions are both related to those of naphthalene and exhibit interesting configuration pairing similar to that found in alternant hydrocarbons. Certain aspects of the results are very sensitive to the choice of parameters and to inclusion of doubly excited configurations in the PPP model. Comparison with the so far non-existent experimental data would probably be useful for testing the various proposed versions of the model.

We have shown recently[1] that the simple PPP model accounts well for the signs of the several lowest B terms[2] in the magnetic circular dichroic (MCD) spectra of numerous uncharged non-alternant hydrocarbons. Application of MCD spectroscopy to organic compounds is of relatively recent origin and in spite of present lively interest[2,3] only a rather limited number of spectra have been published, compared, say, with ordinary UV spectroscopy. Thus, an opportunity presents itself to predict MCD spectra of selected groups of interesting π-electron molecules before these have actually been measured.

One such group of considerable current interest are the double ions of pentalene 1 and heptalene 2. While the dianions have already been prepared,[4,5] the dications remain unknown. In addition to the general significance of these ions for the theory of aromaticity, several additional points may be of significance. First, it has been pointed out recently[6] that in the PPP approximation the MCD spectra of the double cation and double anion derived from an alternant hydrocarbon should bear mirror image relationship to each other and it seems worthwhile to also investigate a few double ions derived from non-alternant hydrocarbons, where such a relation is not expected. Second, pentalene dianion 1A and heptalene dication 2C, both isoelectronic with the alternant hydrocarbon, naphthalene, turn out to have certain features in their excited states in which they resemble alternant π-electron systems, such as symmetry-allowed but "accidentally" forbidden transitions.[6a] These features are predicted to affect strongly parts of the MCD spectra. At the same time, they depend on the choice of parameters, permitting a sensitive testing of various approximations. A problem of considerable current interest has to do with inclusion of multiply excited configurations in PPP and similar semi-empirical models.[7-9] In some cases, their effect on the nature and ordering of low-lying excited states is profound (polyenes, benzene), in others, it is almost negligible (anthracene, fluoranthene). In most instances where their effect is marked it is not obvious that their inclusion improves agreement with experiment since the experimental data are too incomplete (cf. the notorious difficulties with assignment of excited states of benzene[10] and unsolved problems with polyenes[11]). Perhaps the only case of a hydrocarbon in which inclusion of doubly excited configurations has led to a clear-cut improvement in the predicted number and order of excited states is pleiadene,[8] so that much further work is required to settle the question. In the case of 1A and 2C the effect of doubly excited configurations on the results is quite striking and future comparison with experiment will also be of interest from this point of view.

$\overline{-}\ \overline{-}$: **1A**
$+\ +$: **1C**



$\overline{-}\ \overline{-}$: **2A**
$+\ +$: **2C**

Method of Calculation

All calculations used the simple PPP model. A discussion of the method and its applicability has appeared elsewhere.[1] A brief summary follows.

The usual perturbation formula for B is[2]

$$B(G \rightarrow F) = \mathrm{Im}\left\{\sum_{I,\, I \neq G} (\langle I|\hat{\vec{\mathcal{M}}}|G\rangle \langle G||\hat{\vec{M}}|F\rangle \mathrm{x} \langle F|\hat{\vec{M}}|I\rangle)/(W_I - W_G) + \sum_{I,\, I \neq F} (\langle F|\hat{\vec{\mathcal{M}}}|I\rangle \langle G|\hat{\vec{M}}|F\rangle \mathrm{x} \langle I|\hat{\vec{M}}|G\rangle)/(W_I - W_F)\right\},$$

where W_I is the energy of state $|I\rangle$, $\hat{\vec{M}}$ is the electric and $\hat{\vec{\mathcal{M}}}$ the magnetic dipole moment operator, and the summation index I runs over all molecular electronic states. The states $|I\rangle$ were represented by superpositions of spin-projected configurations built from SCF MO's using either all single excitations (SCI) or single and double

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excitations selected by the SECI-1 procedure[9] with cutoff parameters $\delta = 8$ eV, $\epsilon = 0{\cdot}1$, (for **1A**, $\epsilon = 0{\cdot}04$): a total of 48 configurations for **1A**, 26 for **1C**, 71 for **2A**, and 39 for **2C**. The MO's occupied in the ground configuration will be labelled $1, 2, 3, \ldots$, in the order of decreasing energy; those empty in the ground configuration $-1, -2, -3 \ldots$, in the order of increasing energy.

The parameters of the PPP model were $I_C = 11{\cdot}42$ eV, $\beta_{CC} = -2{\cdot}318$ eV, $\gamma_C = 10{\cdot}84$ eV, two-center electron repulsion integrals were obtained according to Ohno-Klopman (O–K)[12] or Nishimoto-Mataga (N–M)[13] formulas. Expressions for the matrix elements of one-electron electric and magnetic dipole moment operators $\hat{m}$ and $\hat{\mu}$ in AO representation were $\langle\kappa|\hat{m}|\lambda\rangle = -e\,.\,\vec{R}_\kappa\,.\,\delta_{\kappa\lambda}$ and $\langle\kappa|\hat{\mu}|\lambda\rangle = i(m/\hbar^2)\ \beta_{\kappa\lambda}(\vec{R}_\lambda \times \vec{R}_\kappa)$ in units of Bohr magneton, where $\vec{R}_\sigma$ is the position vector of AO σ and e, m stand for magnitude of electron charge and mass, respectively. The expression for $\langle\kappa|\hat{\mu}|\lambda\rangle$ follows from the requirement that the proper commutation relation between the position operator $\hat{r}$ and the Hamiltonian operator $\hat{H}$ be fulfilled in the PPP model,[14,15] and guarantees origin-independence of the B terms obtained from exact (full CI) PPP wavefunctions for π-electron systems of arbitrary symmetry.[1] Calculations for **1** and **2** assumed D_{2h} symmetry (regular polygons with 1·40 Å sides), and as a result, even approximate CI solutions (truncated CI expansions such as SCI and SECI-1) give origin-independent results for B.[15a]

For molecules without degenerate states, the peak of transition G → F in the MCD spectrum is related to its B term by[2]

$$[\Theta]_M = -21{\cdot}3458\, f_2 B,$$

where f_2 is a shape function. Note that a positive B term for a transition implies a negative peak in the MCD spectrum.

RESULTS AND DISCUSSION

The calculated transition energies, intensities, polarizations, and B terms are summarized in Tables 1–4. It is well known[16] that the ordinary PPP parameterization tends to overestimate the excitation energies of doubly negative hydrocarbon ions, at least at the SCI level. Too little is known experimentally about doubly positive ions to make a similar general statement. It appears likely that the overall nature of the absorption spectra predicted in Table 1 will agree with the experiment, but the exact positions of bands will deviate more than is usual in uncharged hydrocarbons. Fortunately, it turns out that most B terms originate by mutual mixing of only two excited states, so that the results should be largely independent of small errors in calculated excitation energies as long as the relative energies and ordering of states are correct. In order to check the sensitivity of the results to minor variations of the method, we have used both N-M and O-K parameter sets, and both SCI and SECI-1 procedures. This turned out to be quite important since in several instances doubt was cast on results which appear quite reasonable in any one calculation. Still, for B terms of most transitions, the differences between the three sets of results are only minor, and fairly reliable predictions are possible.

Pentalene Dianion (**1A**, Table 1). The main features of the calculated spectrum depend little on the choice of electron-repulsion integrals or extent of configuration interaction (SCI versus SECI-1). The spectrum starts with a medium intensity short-axis polarized transition described well as a one-electron jump 1 → −1, analogous to the ^1L_a transition of naphthalene. The analogy to naphthalene extends even farther in that the only other two allowed transitions in the conveniently accessible spectral region are both long-axis polarized, the lower energy one is quite weak and the higher energy one very strong, and both are well represented as mixtures of 2 → −1 and 1 → −3 excitations, and thus are strongly reminiscent of naphthalene transitions ^1L_b and ^1B_b except that in **1A** the orbital -3 plays the role of the orbital -2 in naphthalene. The degree of mixing of the two configurations is not exactly one to one and is somewhat dependent on the details of the calculation. As a result, the intensity of the lower of the two transitions, in which the transition moments contributed by the two configurations approximately cancel, also depends noticeably on the details of the method.

Table 1. Pentalene Dianion **1A**

		Transition													
		1		2		3		4		5		6		7	
N–M	E^a, sym	36·4	B_{2u}	42·1	B_{1u}	45·9	B_{3g}	50·7	B_{1u}	53·06	A_g	53·09	B_{3g}	59·6	B_{2u}
SCI	f_r^b, f_p^c	0·4	0·1	0·1	0·05	0·0	0·0	1·3	0·8	0·0	0·0	0·0	0·0	0·2	0·06
	B^d	−2·2		3·0		0·0		−1·9		0·0		0·0		0·7	
O–K	E^a, sym	36·1	B_{2u}	39·3	B_{1u}	46·4	B_{3g}	51·8	A_g	56·3	B_{1u}	56·4	B_{3g}	58·9	B_{2u}
SCI	f_r^b, f_p^c	0·3	0·1	0·2	0·1	0·0	0·0	0·0	0·0	1·3	0·6	0·0	0·0	0·2	0·06
	B^d	−6·7		7·8		0·0		0·0		−4·7		0·0		3·0	
O–K	E^a, sym	33·9	B_{2u}	38·6	B_{1u}	43·5	B_{3g}	49·6	A_g	50·8	B_{3g}	54·4	B_{1u}	58·6	B_{2u}
SECI-1	f_r^b, f_p^c	0·2	0·1	0·1	0·1	0·0	0·0	0·0	0·0	0·0	0·0	1·0	0·8	0·4	0·3
	B^d	−2·8		3·4		0·0		0·0		0·0		−3·1		2·5	

[a] Transition energy (10^3 cm^{-1}). [b] Oscillator strength from the dipole length formula. [c] Oscillator strength from the dipoile velocity formula. [d] B term in units of $10^{-3} \times$ debye^2 β_e/cm^{-1}.

Table 2. Heptalene Dication **2C**

		1		2		3		4		5		6		7		8		9		10		11		12	
N–M	E^a, sym	26·6	B_{2u}	29·0	B_{1u}	37·8	B_{3g}	39·1	B_{1u}	39·1	B_{3g}	40·4	A_g	42·2	B_{2u}	46·6	B_{3g}	50·1	A_g	50·8	B_{3g}	54·4	B_{2u}	55·0	B_{1u}
SCI	f_r^b, f_p^c	0·2	0·03	0·0002	0·0004	0·0	0·0	2·4	1·0	0·0	0·0	0·0	0·0	0·6	0·2	0·0	0·0	0·0	0·0	0·0	0·0	1·3	0·6	0·006	0·00007
	B^d	0·2		0·5		0·0		3·0		0·0		0·0		−3·3		0·0		0·0		0·0		−0·4		0·3	
O–K	E^a, sym	25·8	B_{2u}	27·3	B_{1u}	36·1	B_{3g}	38·9	A_g	43·7	B_{1u}	44·2	B_{3g}	44·7	B_{2u}	51·1	B_{3g}	52·9	B_{3g}	53·1	A_g	57·3	B_{1u}	58·0	B_{2u}
SCI	f_r^b, f_p^c	0·08	0·01	0·01	0·004	0·0	0·0	0·0	0·0	2·7	1·0	0·0	0·0	0·6	0·1	0·0	0·0	0·0	0·0	0·0	0·0	0·1	0·006	1·3	0·5
	B^d	4·3		−4·5		0·0		0·0		17·3		0·0		−16·5		0·0		0·0		0·0		2·6		−3·4	
O–K	E_a, sym	28·9	B_{2u}	30·1	B_{1u}	38·4	B_{3g}	39·7	A_g	41·4	B_{3g}	43·9	A_g	44·8	B_{1u}	45·2	B_{2u}	48·9	A_g	49·1	B_{3g}	50·6	B_{1u}	55·5	B_{3g}
SECI-1	f_r^b, f_p^c	0·06	0·04	0·0	0·0006	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	1·8	1·1	0·3	0·1	0·0	0·0	0·0	0·0	0·1	0·05	0·0	0·0
	B^d	0·3		0·02		0·0		0·0		0·0		0·0		43·0		−43·5		0·0		0·0		0·6		0·0	

[a] Transition energy (10^3 cm^{-1}). [b] Oscillator strength from the dipole length formula. [c] Oscillator strength from the dipole velocity formula. [d] B term in units of $10^{-3} \times \text{debye}^2\ \beta_e/\text{cm}^{-1}$.

Table 3. Pentalene Dication **1C**

		Transition 1	2	3	4	5	6	7	8	9	10
N–M	E[a], sym	10·9 B_{2u}	20·6 B_{1u}	34·3 B_{2u}	41·8 B_{1u}	45·2 A_g	53·6 B_{3g}	57·5 B_{3g}			
SCI	f_r[b], f_p[c]	0·0008 0·009	0·05 0·01	0·4 0·2	2·4 0·5	0·0 0·0	0·0 0·0	0·0 0·0			
	B[d]	−0·06	1·1	−0·8	0·3	0·0	0·0	0·0			
O–K	E[a], sym	8·2 B_{2u}	17·6 B_{1u}	33·9 B_{2u}	47·0 B_{1u}	47·1 A_g	56·5 B_{3g}	59·4 A_g			
SCI	f_r[b], f_p[c]	0·0002 0·1	0·05 0·01	0·4 0·2	2·6 0·5	0·0 0·0	0·0 0·0	0·0 0·0			
	B[d]	0·05	0·8	−0·6	0·4	0·0	0·0	0·0			
O–K	E[a], sym	14·7 B_{2u}	22·2 B_{1u}	24·2 A_g	29·6 B_{3g}	32·6 A_g	39·9 A_g	41·5 B_{2u}	41·9 B_{3g}	46·0 B_{3g}	49·6 B_{1u}
SECI-1	f_r[b], f_p[c]	0·002 0·006	0·05 0·03	0·0 0·0	0·0 0·0	0·0 0·0	0·0 0·0	0·4 0·3	0·0 0·0	0·0 0·0	1·2 0·7
	B[d]	0·2	0·4	0·0	0·0	0·0	0·0	−0·4	0·0	0·0	−0·2

[a]Transition energy (10^3 cm^{-1}). [b]Oscillator strength from the dipole length formula. [c]Oscillator strength from the dipole velocity formula. [d]B term in units of $10^{-3} \times$ debye^2 β_e/cm^{-1}.

Table 4. Heptalene Dianion **2A**

		1	2	3	4	5	6	7	8	9	10	11	12	13
N–M	E[a], sym	8·1 B_{2u}	13·6 B_{1u}	24·7 B_{2u}	33·8 B_{1u}	36·2 B_{3g}	40·7 B_{2u}	41·3 B_{3g}	42·2 A_g	45·3 A_g	46·1 B_{1u}	48·9 A_g	50·9 B_{3g}	53·4 B_{2u}
SCI	f_r[b], f_p[c]	0·01 0·02	0·008 0·0004	0·2 0·02	3·3 0·6	0·0 0·0	0·4 0·1	0·0 0·0	0·0 0·0	0·0 0·0	0·08 0·03	0·0 0·0	0·0 0·0	1·3 0·6
	B[d]	0·4	−1·4	0·5	2·6	0·0	−5·7	0·0	0·0	0·0	0·9	0·0	0·0	8·2
O–K	E[a], sym	6·1 B_{2u}	10·9 B_{1u}	24·5 B_{2u}	38·6 B_{3g}	39·2 B_{1u}	43·0 A_g	44·8 B_{3g}	44·8 B_{2u}	46·1 A_g	48·7 B_{1u}	50·8 A_g	53·8 B_{3g}	54·8 B_{1u}
SCI	f_r[b], f_p[c]	0·0009 0·2	0·006 0·0003	0·2 0·003	0·0 0·0	3·4 0·5	0·0 0·0	0·0 0·0	0·6 0·2	0·0 0·0	0·3 0·08	0·0 0·0	0·0 0·0	0·3 0·1
	B[d]	0·2	−0·8	0·2	0·0	4·5	0·0	0·0	−12·3	0·0	4·0	0·0	0·0	17·3
O–K	E[a], sym	11·0 B_{2u}	14·7 B_{1u}	20·4 A_g	23·9 B_{3g}	27·6 B_{3g}	29·0 A_g	30·8 A_g	30·8 B_{2u}	34·4 A_g	35·3 B_{3g}	36·8 B_{2u}	37·3 A_g	39·1 B_{1u}
SECI-1	f_r[b], f_p[c]	0·002 0·0001	0·004 0·001	0·0 0·0	0·0 0·0	0·0 0·0	0·0 0·0	0·0 0·0	0·03 0·009	0·0 0·0	0·0 0·0	0·3 0·1	0·0 0·0	1·3 0·7
	B[d]	0·2	−0·5	0·0	0·0	0·0	0·0	0·0	0·3	0·0	0·0	−5·3	0·0	4·4

[a]Transition energy (10^3 cm^{-1}). [b]Oscillator strength from the dipole length formula. [c]Oscillator strength from the dipole velocity formula. [d]B term in units of $10^{-3} \times$ debye^2 β_e/cm^{-1}.

Two symmetry-forbidden transitions are also calculated to be present, corresponding to almost pure $1 \rightarrow -2$ and $2 \rightarrow -2$ excitations. Similarly as in naphthalene, a short-axis polarized transition is calculated at about 60,000 cm^{-1}. It corresponds to a $2 \rightarrow -3$ electron jump and is analogous to the ^{1}B$_a$ transition in naphthalene.

All three calculations agree that the B terms of the transitions into the first two excited states are due virtually exclusively to their mutual mixing by the magnetic field, the first B term being negative, the second positive. The predicted negative B term for the very strong third allowed transition, which will be hard to observe in the usual ether solvents, results from a sum of several relatively small contributions, all of which are negative, in the N-M calculations, while in the O-K calculations, the dominant term originates from mixing with the fourth allowed transition.

The difference in size of the lowest two B terms obtained from the three calculations is related to the difference of the calculated dipole strength of the second transition in the two cases. As pointed out above, this transition is analogous to the ^{1}L$_b$ transition of naphthalene in that its transition dipole is a net result of cancellation of two large terms. In naphthalene, this cancellation is exact within the PPP model irrespective of the values of parameters, and it is necessary to go beyond the PPP model in order to account for its non-vanishing though very small magnitude. In **1A**, the cancellation is not exact and is somewhat sensitive to parameter choice. In all three instances tested by us the calculated value is sufficiently large to insure domination of the first two B terms by the effect of the mutual magnetic mixing of the two corresponding excited states.

Thus, experimental results for B terms of the first two bands in IA may be of particular interest for testing parameter selections in the PPP model. If the degree of cancellation of transition moments outlined above is described incorrectly by the common parameter choices used here, and the cancellation is nearly perfect, the magnetic mixing of the first two states will be unimportant and the B terms will be very small and dominated by small effects whose sign the PPP model cannot predict reliably, similarly as for the naphthalene ^{1}L$_b$ transition, where it predicts vanishing B terms (for both ^{1}L$_b$ and ^{1}L$_a$ bands). If the cancellation is incomplete, but in the opposite sense than calculated here, the two B terms will again be large, but their signs will be opposite than predicted here.

The mixing coefficients for configurations $2 \rightarrow -1$ and $1 \rightarrow -3$ are sensitive function of the diagonal matrix elements of the Hamiltonian. For both parameter sets, configuration $2 \rightarrow -1$ is of lower energy than $1 \rightarrow -3$, but the difference is only 0·4 eV for N-M parameters while it is 1·2 eV for O-K integrals. The magnitudes of transition moments of the two configurations are quite similar: the $2 \rightarrow -1$ transition density has only two important contributions, namely about $\frac{1}{4}$ e on atom 2 and about $-\frac{1}{4}$ e on atom 5, the $1 \rightarrow -3$ transition density has four, about $\frac{1}{4}$ e on atoms 4 and 6, and about $-\frac{1}{4}$ e on atoms 1 and 3.

The published experimental absorption spectrum[4] shows a peak near 33,000 cm^{-1} and an indistinct shoulder near 42,000 cm^{-1} and it is tempting to assign these to be the first two calculated transitions.

Heptalene dication (**2C**, Table 2). This other 10-π-electron system is predicted to have a somewhat more complicated spectrum starting at longer wavelengths than that of **1A**. Except for this shift, the low-energy part of the spectrum resembles strongly that of **1A** and is thus again analogous to that of naphthalene. The lowest-energy transition should be weaker than in pentalene, but again short-axis polarized, reasonably well described as a $1 \rightarrow -1$ excitation, but now with a sizeable contribution from $2 \rightarrow -2$, and analogous to the ^{1}L$_a$ transition in naphthalene. The following two long-axis polarized transitions are again analogous to the ^{1}L$_b$ and ^{1}B$_b$ transitions in naphthalene in that they are represented by mixtures of approximately equal contributions from two configurations, $2 \rightarrow -1$ and $1 \rightarrow -2$, and in that the one at lower energy is very weak and the one at higher energy very strong. For **2C**, the energies of these two configurations are virtually equal for N-M parameterization, and $1 \rightarrow -2$ is only 0·4 eV lower than $2 \rightarrow -1$ when O-K parameters are used. As a result, the uncertainties concerning the exact degree of cancellation are larger than was the case for **1A**.

This is clearly reflected in the predicted B terms. With O-K parameters at the SCI level, the transition moment of the second transition is still far from zero, and the B terms of transitions into the first two states are dominated completely by a single term due to the magnetic mixing of the two states. In contrast to **1A**, the lower of the two transitions is now predicted to have positive B, the higher one negative B. On the other hand, at the SECI-1 level or with N-M parameters, the cancellation is virtually complete and the very small resulting transition moment now has opposite direction. Contribution from mixing the first and second excited states thus is not only very small, but also of the opposite sign and tends to make B positive for the second transition and negative for the first one. No other terms of comparable magnitude contribute to the second B term, so that the predicted value remains small and positive, while several such small contributions to the first B term exist, mostly with positive sign, and as a result for N-M parameterization and for O-K parameters at SECI-1 level, the first two B terms are both predicted to be very small and positive.

Only one additional allowed transition is predicted below 50,000 cm^{-1}. It is short-axis polarized, rather intense, and the excited state is well represented as configuration $2 \rightarrow -2$ with considerable admixture of $1 \rightarrow -1$. It thus corresponds to the naphthalene ^{1}B$_a$ state. In addition to the allowed transitions, several symmetry-forbidden ones are expected.

The B terms predicted for the first two states have already been discussed. The first one should be positive, but no reliable prediction is possible for the second one, since the results at different levels of approximation differ so much. To the contrary, experimental results for this so far unknown species would be of great interest as a potential aid to evaluation of different parameter schemes. The B term of the intense long-axis polarized third allowed transition is determined by mixing with the nearby lying intense short-axis polarized fourth allowed transition and all other contributions are negligible. The first of these B terms should be positive, the second one negative. The prediction of signs appears to be quite safe, while magnitudes ought to be sensitive to the separation of the transitions. Since the two transitions are so close to each other, it is possible that their order is predicted incorrectly. If this were the case, sign of the denominator in the leading term for B would change, so that the then higher-energy long-axis polarized energy transition would have a negative B term and the then lower short-axis transition would have a positive one. This reversal of energies thus would not be apparent in the MCD spectrum since the lower transition would still have a positive and the higher one a negative B term.

Pentalene dication (**1C**, Table 3). The absorption spectrum of this so far unknown species should be beautifully simple. In the SCI approximation, only four electronic transitions are to be expected up to almost 50,000 cm^{-1}; all of them allowed, followed by four forbidden transitions at higher energies. At the SECI-1 level, the same transitions are predicted (at higher energies since the ground state is now 0·8 eV lower than in the SCI calculations due to strong mixing with several doubly excited configurations). However, at this level, many forbidden transitions into doubly excited states are predicted to lie at quite low energies. In the following, we shall only discuss the four symmetry-allowed transitions, for which B terms can be calculated easily. The first, very weak and short-axis polarized transition should lie in the IR region; the second, stronger and long-axis polarized, in the visible region; the third, stronger still and short axis polarized, in the near UV region; and the strongest fourth one, long-axis polarized, near the edge of the vacuum UV region. The description of these allowed transitions in terms of singly excited configurations is complicated by the fact that the order of SCF orbital enerries depends on the parameters used. Using the numbering obtained with N-M integrals ($1\!:\!b_{1g}$, $2\!:\!b_{2g}$, $3\!:\!b_{3u}$, $-1\!:\!b_{3u}$, $-2\!:\!a_u$, $-3\!:\!b_{2g}$, $-4\!:\!b_{3u}$, $-5\!:\!b_{1g}$), the first one is described as $1 \rightarrow -1$, the third one as $2 \rightarrow -2$, and the second and fourth as out-of-phase and in-phase superpositions of $1 \rightarrow -2$ and $2 \rightarrow -1$. At least formal similarity with pairing in excited states of neutral alternant hydrocarbons is again obvious. Of course, predicted transition energies are more reminiscent of spectra of double ions derived from alternant hydrocarbons.

However, mechanism by which calculated B terms arise is distinctly different. In double ions of linear polyacenes, magnetic mixing of the very low-lying first excited state into the ground state is calculated to play a substantial role.[17] In **1C**, and also **2A**, the symmetry of this low-lying excited state is unsuitable for such a mixing and all significant contributions to the B terms arise in the usual way, namely by magnetic mixing of the various excited states among themselves.

The calculated B term of the first transition in **1C** originates from mixing with the second transition and is too small to be considered significant; moreover, its sign depends on the parameters used. The dominant contribution to the B term of the second transition is provided by mixing with the third allowed transition, while mixing with the first excited state plays a negligible role because of the small magnitude of the first transition moment. The sign can be reasonably safely expected to be positive. The calculated magnitude is smaller in the SECI-1 calculations because of a large energy denominator. The same mixing of the excited states corresponding to the second and third allowed transitions also is the sole significant contributor to the B term of the third allowed transition, expected to be negative and of about the same magnitude as the second B term.

The B term of the fourth transition is the sum of several small contributions, mainly from mixing with high-lying transitions which are probably described rather poorly by the PPP model, and no sign can be predicted at this time.

The small values of all B terms in **1C** are easily understood to be a result of the large energy gaps from one state to the next and of the relatively small transition moments of most of the transitions.

Heptalene dianion (**2A**, Table 4): The absorption spectrum of **2A** is closely analogous to that of **1C**, except that all transitions are shifted to lower energies. Again, some of the doubly excited configurations mix strongly with the ground configuration, so that the SECI-1 excitation energies are higher. The four allowed transitions analogous to those of **1C** now all occur below 40,000 cm^{-1}, again in the order short, long, short, long-axis polarized, and with increasing intensity as one proceeds to higher energies, and again are well represented by configurations $1 \rightarrow -1$, then $2 \rightarrow -1$ mixed with $1 \rightarrow -2$, then $2 \rightarrow -2$, and finally $2 \rightarrow -1$ mixed with $1 \rightarrow -2$. Now, however, two additional allowed transitions occur below 50,000 cm^{-1}. The lower of these is short-axis polarized and is best represented as $1 \rightarrow -4$ (in the SECI-1 calculation it actually occurs below the highest of the above-mentioned four transitions), the other is long-axis polarized and best represented as $2 \rightarrow -4$. Numerous symmetry-forbidden transitions are also predicted, again at lower energies in the SECI-1 calculation than at the SCI level. Several of the corresponding excited states are of doubly excited nature.

The calculated B terms of the first three allowed transitions are quite small and comparison with experiment will again represent a fairly demanding test. The small positive B term of the first transition originates in magnetic mixing of the first and second excited states, other contributions being negligible. The second B term is a sum of two negative contributions, due to the mixing of the second excited state with excited states of both first and third allowed transitions. B term of the third allowed transitions is a sum of numerous small contributions and can hardly be considered reliable although it always came out positive. The physical significance of the higher B terms is in question since the SCI and SECI-1 results differ. Again, comparison with experiment might provide clues as to the appropriateness of the inclusion of multiply excited configurations in the PPP model.

SUMMARY

Excited states of the 10-π-electron ions **1A** and **2C** have much in common with those of naphthalene, including near cancellation of transition moments contributed by two configurations which are mixed in the same CI state, and resulting uncertainties in some of the B terms. Because of the sensitivity of the results for the lowest two B terms to the choice of electron repulsion integrals, these might serve as a useful check of the various possibilities. This test appears to be more sensitive than simple comparison of excitation energies which is usually used for parameter fitting.

On the other hand, absorption spectra of the 6- and 14-π-electron species **1C** and **2A** should resemble those of doubly charged ions of the polyacene series. Because of the symmetry of the first excited state, magnetic field cannot mix it with the ground state although they lie very close together. This should make the MCD spectroscopy of **1C** and **2A** distinctly different from that of polyacene double ions, in that B terms should be determined by mutual mixing among excited states only, as is common in molecules without low-lying excited states.

The ions **1** and **2** would represent good test cases not only for comparison of various parameter schemes, but also for an assessment of the importance of doubly excited configurations for the PPP model. It should be noted that we have used the same parameter values for both SCI and SECI-1, while they ideally should be optimized separately to ensure an objective evaluation of the two schemes. The values used are appropriate for the SCI approximation, so that it would not be surprising if the SECI-1 energies were in poorer numerical agreement with experiment. The evaluation should thus rely more on the predicted number of excited states, their polarizations, intensities, as signs of their B terms.

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