Magnetic Circular Dichroism and Molecular Orbital Studies on Condensed Thiadiazoles

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Magnetic circular dichroism (MCD) spectra of some thiadiazoles have revealed the characteristic $\pi \rightarrow \pi^*$ transitions in cata-condensed thiadiazoles. Within the framework of the PPP method quantum mechanical calculations have been carried out in order to give a reasonable explanation for the MCD spectra, resulting in a fairly good agreement between the experimental and theoretical Faraday parameters.

1. Introduction

Experimental and theoretical investigations of organosulfur compounds have attracted appreciable attention of many authors because of their characteristic electronic spectra. Johnstone and Ward [1, 2] have tried to elucidate the ultra-violet absorption spectra of the sulfur heterocycles within the framework of the PPP SCF MO CI method, while leaving the one-center and two-center core integrals as variable parameters. They have found a set of reasonable parameters which reproduces the observed electronic spectra. In their calculations, no 3d atomic orbitals on the S atom were taken into account.

Including variable π-electronegativity and σ-polarization, Hammond [3] has carried out LACO SCF CI calculations for heteroaromatics including N, S, O and B atoms in order to clarify their ionization potentials and electronic spectra. The agreement between theoretical and experimental data seems to be good, although 3d AO's were neglected in his calculation.

The electronic structure of thieno[3,4-d]thiepine has been investigated on the basis of the CNDO/2 and extended Hückel methods by Gleiter *et al.* [4], which revealed a small energy difference between planar and non-planar structures. The first four absorption bands have been elucidated in relation to those of azulene and assigned to the $\pi \rightarrow \pi^*$ electronic transitions on the basis of the virtual orbital approximation using the results of the CNDO/2 calculations.

While Grunwell and Balzer [5] have suggested that it is impossible to draw meaningful conclusions from such calculations about the necessity of 3d orbital participation, Johnson and Mellon [6] and Clark *et al.* [7] have pointed out its importance, even though it is small, in the explanation of the photoelectron spectra of thiophenes and thiadiazoles.

On the other hand, the magnetic circular dichroism (MCD) technique has been recognized to be a very powerful tool in analysing complicated electronic spectra of molecules and ions in their ground and excited electronic states [8]. Although simple organic molecules and their ions have been extensively studied, there have been very few MCD studies on heterocycles.

Several authors [9–13] have reported the MCD spectra of saturated thioketones and thiophenes along with their quantum mechanical calculations. In their MCD measurements on several saturated thioketones, Engelbrecht *et al.* have observed both singlet-singlet and singlet-triplet MCD bands associated with the $n \rightarrow \pi^*$ transition in the thioketone moiety. The MCD measurement on thiophene and the related compounds has revealed two electronic origins in the longest wavelength absorption band [10–13]. In the course of our MCD studies on benzenoid [14], non-benzenoid [15] and heterocyclic aromatics [16] quantum mechanical calculations of the Faraday parameters and excitation energies have played an important role in the interpretation of the observed MCD spectra and the spectroscopic assignment to the resolved MCD bands which are not found in the usual absorption measurement due to occasional overlapping. It seems interesting to extend this study to other

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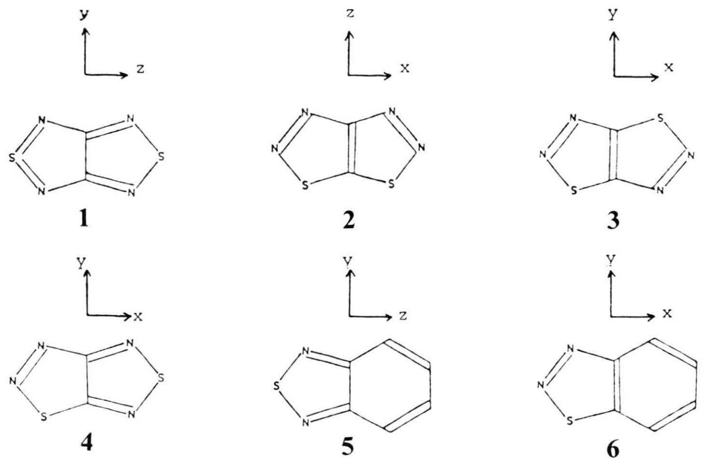

Fig. 1. Molecular skeletons of the condensed thiadiazoles and the choice of axes.

complicated systems, in view of the application and verification of the theoretical calculation within a semiempirical LCAO MO SCF framework. Herein we report on MCD of thiadiazoles (Fig. 1) in solution and its quantum mechanical interpretation.

2. Theoretical

In the absence of degeneracies, the quantum mechanical expressions for the Faraday B term and the dipole strength, D, associated with an electronic transition $a \leftarrow 0$ are,

$$B_{0a} = \frac{1}{3}\,\mathrm{Im}\left\{\sum_{b \neq 0} \frac{\hat{m}_{b0}}{\nu_{b0}} \cdot \hat{\mu}_{0a} \times \hat{\mu}_{ab} + \sum_{b \neq a} \frac{\hat{m}_{ab}}{\nu_{ab}} \cdot \hat{\mu}_{0a} \times \hat{\mu}_{b0}\right\} = B_{\mathrm{I}} + B_{\mathrm{II}}\,, \qquad (1)$$

$$D_{0a} = \hat{\mu}_{0a}^2\,, \qquad (2)$$

where $\hat{\mu}_{ab}$ and $\hat{m}_{ab}$ represent the off-diagonal matrix elements of electric and magnetic moment operators, respectively, whereas Im stands for taking the imaginary part of the bracketted expression of (1). The denominator is the energy difference between the states $|b\rangle$ and $|a\rangle$.

As was pointed out by several authors, however, the difficulties arise from an infinite sum in (1) over all molecular electronic states $|b\rangle$'s. In a practical treatment, the sum is so severely truncated that B_{0a} is origin dependent. To decrease this origin dependency, we set the origin at the center of the charge distribution of the molecule in its ground state in accord with the proposal by Caldwell and Eyring [17].

A LCAO MO SCF CI method was adopted within the framework of the PPP approximation in order to obtain transition energies and wavefunctions which are necessary in evaluating the Faraday B terms according to (1). The CI procedure was carried out among all singly excited configurations. The resonance integral $\beta_{\mathrm{rs}}^{\mathrm{c}}$ and two-center electron repulsion integrals γ_{rs} were estimated from the Wolfsberg-Helmholtz [18] and Nishimoto-Mataga equations [19], respectively. The transition and magnetic moments were calculated using the dipole length operator er and the magnetic moment operator $\mu_z = -(\beta/\hbar)\,L_z$, respectively. The atomic orbitals used in these calculations are the Slater AO's, with which the basis set χ^{λ} in the PPP procedure is expanded in terms of the overlap integral S according to the equation

$$\chi^{\lambda} = \chi\, S^{-1/2}\,.$$

Throughout the calculation, the molecules are assumed to be planar. The atomic distances are summarized and listed in Table 1, along with the values of the overlap and two-center core integrals

Table 1. Atomic distances R, overlap integrals S and two-center core integrals β^{c}.

Bond	R/Å	S	β^{c}/eV
C–C	1.35	0.266	−2.60
C–N	1.34	0.185	−2.05
C–S	1.73	0.177	−2.15
N–N	1.33	0.174	−2.15
N–S	1.60	0.166	−2.22

Table 2. Ionization potentials I_p, electron affinities A_p, one-center electron repulsion integrals γ_{pp} and the Slater exponents Z_p.

Atom	I_p/eV	A_p/eV	γ_{pp}/eV	Z_p
C	11.16	0.03	11.13	3.25
N	14.12	1.78	12.34	3.90
S	16.27	5.49	10.78	5.451

for the corresponding bonds. The bond angles were estimated assuming that the molecules have regular polygonal structures. The atomic quantities used in this work are taken from the table of Hinze-Jaffe [20] and summarized in Table 2.

3. Results

[1,2,5]-Thiadiazolo-[3,4-c][1,2,5]-thiadiazole **1**

The UV and MCD spectra of **1** are represented in Figure 2. The compound **1** exhibits an absorption at 32200 cm^{-1}, which seems to be single and isolated. In contrast, positive and negative extrema are observed in the MCD spectrum at 29900 cm^{-1} and 33700 cm^{-1}, respectively. An inflexion point coincides with the absorption maximum within the limits of experimental error. As the molecule belongs to the point group C_{2v}, the observed MCD is due to the sole contribution from the Faraday *B* term. Accordingly, the MCD technique reveals two components of absorption in the lowest wave number absorption band of **1**. From the observed intensity of absorption and MCD, the electronic transition associated with the lowest wave number absorption and MCD bands are considered to be $\pi \rightarrow \pi^*$ in nature. The experimental Faraday *B* values are roughly estimated to be $-171 \times 10^{-5} \beta$ Debye^2/cm^{-1} and $307 \times 10^{-5} \beta$ Debye^2/cm^{-1} for the first and second MCD bands, respectively. Unfortunately no distinct MCD has been observed in the region above 40000 cm^{-1}.

A theoretical result for **1** is listed in Table 3 and compared with experimental data. The lowest singlet-singlet transition is calculated to take place at 3.24 eV (26100 cm^{-1}) with its transition moment directed along the *y*-axis. The theoretical *B* term associated with this first transition is calculated to be negative, in agreement with experiment. Accordingly the lowest energy transition is assigned to the first positive MCD band.

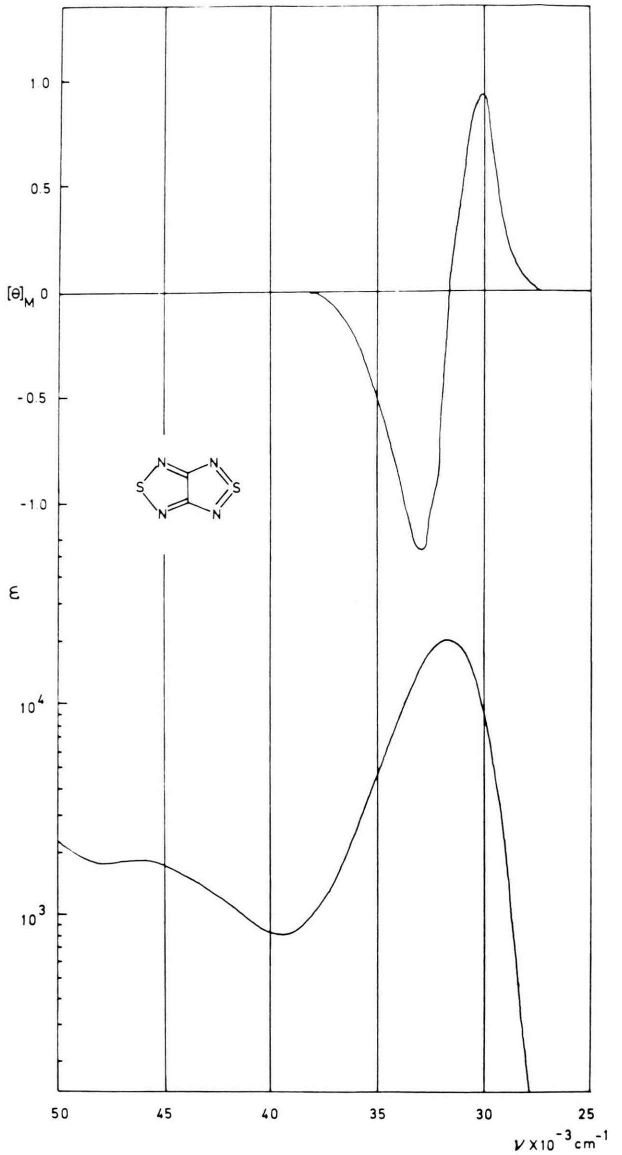

Fig. 2. The MCD (top) and absorption (bottom) spectra of [1,2,5]-thiadiazolo[3,4-c][1,2,5]-thiadiazole in ethanol at room temperature.

A *z*-axis polarized transition is calculated to occur at 4.47 eV (36100 cm^{-1}), which gives rise to appreciable intensity of absorption and negative MCD. The $A_1 \leftarrow A_1$ transition is assigned to the observed negative MCD band.

Agreement between theory and experiment is good as to the sign of MCD and the transition energies. The calculated *B* terms for the lowest

Table 3. Transition energies ΔE (eV) and Faraday B (β Debye^2/cm^{-1}) values in **1**.

	Theoretical			Experimental			
Sym.	$\Delta E(f)$	$B_{\mathrm{I}} \times 10^5$	$B_{\mathrm{II}} \times 10^5$	$B \times 10^5$	ΔE	$[\Theta]_{\mathrm{M}}$	$B \times 10^5$
$B_2 \leftarrow A_1$	3.24 (0.007)	−3.84	−14.47	−18.31	3.70	0.94	−171
$B_2 \leftarrow A_1$	3.86 (0.000)	0.00	0.00	0.00			
$A_1 \leftarrow A_1$	4.47 (0.143)	−6.66	11.11	17.77	4.07	−12.2	307
$B_2 \leftarrow A_1$	5.33 (0.000)	0.00	0.00	0.00			
$B_2 \leftarrow A_1$	6.63 (0.233)	9.21	79.12	88.33			

Table 4. Transition energies ΔE (eV) and the Faraday B ($\beta \cdot$ Debye^2/cm^{-1}) values in **2**.

	Theoretical			
Sym.	$\Delta E(f)$	$B_{\mathrm{I}} \times 10^5$	$B_{\mathrm{II}} \times 10^5$	$B \times 10^5$
$B_2 \leftarrow A_1$	4.42 (0.193)	0.42	22.98	23.40
$A_1 \leftarrow A_1$	5.11 (0.062)	−1.43	−25.62	−27.05
$B_2 \leftarrow A_1$	6.36 (0.133)	−5.93	−74.64	−80.57
$A_1 \leftarrow A_1$	6.39 (0.005)	7.81	79.36	87.17
$A_1 \leftarrow A_1$	7.09 (0.003)	2.45	−1.79	0.66

$B_2 \leftarrow A_1$ and $A_1 \leftarrow A_1$ transitions are equal in magnitude but opposite in sign, suggesting that the magnetic coupling takes place mainly between these two states. Unfortunately, however, the agreement between the theoretical and experimental B values is not good in a quantitative sense.

[1,2,3]-Thiadiazolo-[4,5-d][1,2,3]-thiadiazole **2**

A calculated result is summarized and listed in Table 4. The lowest energy transition, $B_2 \leftarrow A_1$, is predicted to take place at 4.42 eV (35600 cm^{-1}), with its transition moment directed along the x-axis. The theoretical values for B_{I} and B_{II} are $0.42 \times 10^{-5} \beta$ Debye^2/cm^{-1} and $23.0 \times 10^{-5} \beta$ Debye^2/cm^{-1}, respectively, so as to give negative MCD associated with this transition.

The next transition is predicted to occur at 5.11 eV (41200 cm^{-1}) with its transition moment directed along the z-axis. The B value is calculated to be $-27 \times 10^{-5} \beta$ Debye^2/cm^{-1}, indicative of positive MCD. Thus the present calculation predicts two opposite directed MCD bands in the lowest wave number region, where the first and second bands are expected to exhibit negative and positive MCD, respectively, in contrast to the first positive and second negative MCD bands of **1**.

[1,2,3]-Thiadiazolo-[5,4-d][1,2,3]-thiadiazole **3** *and [1,2,5]-Thiadiazolo-[3,4-d][1,2,3]-thiadiazole* **4**

Theoretical results are summarized and listed in Table 5 for **3** and in Table 6 for **4**. The lowest two transitions of **3** are predicted to take place at 4.16 eV (33500 cm^{-1}) and 4.95 eV (39900 cm^{-1}). The Faraday B values are calculated to be small for these two transitions as well as for the higher energy transitions.

The first transition of **4** which is calculated to occur at 4.27 eV (34400 cm^{-1}) is expected to exhibit positive MCD, while the second transition at 4.80 eV (38700 cm^{-1}) is expected to exhibit negative MCD, which is nearly equal in intensity with that of the first transition.

Table 5. Transition energies ΔE (eV) and the Faraday B ($\beta \cdot$ Debye^2/cm^{-1}) in **3**.

	Theoretical			
Sym.	$\Delta E(f)$	$B_{\mathrm{I}} \times 10^5$	$B_{\mathrm{II}} \times 10^5$	$B \times 10^5$
$B_u \leftarrow A_g$	4.16 (0.178)	−1.24	2.04	0.80
$A_g \leftarrow A_g$	4.95 (forb)	−0.19	−0.24	−0.43
$B_u \leftarrow A_g$	5.47 (0.026)	1.24	1.84	3.08
$A_g \leftarrow A_g$	6.57 (forb.)	1.48	0.06	1.54
$B_u \leftarrow A_g$	7.24 (0.004)	2.14	−0.21	1.93

Table 6. Transition energies ΔE (eV) and the Faraday B ($\beta \cdot$ Debye^2/cm^{-1}) values in **4**.

	Theoretical			
Sym.	$\Delta E(f)$	$B_{\mathrm{I}} \times 10^5$	$B_{\mathrm{II}} \times 10^5$	$B \times 10^5$
$A' \leftarrow A'$	4.27 (0.016)	−1.83	−41.13	−42.96
$A' \leftarrow A'$	4.80 (0.199)	1.38	19.11	44.34
$A' \leftarrow A'$	5.45 (0.126)	−13.89	42.80	28.91
$A' \leftarrow A'$	6.05 (0.032)	−0.73	3.09	2.36
$A' \leftarrow A'$	6.43 (0.031)	−1.93	−18.82	−20.75

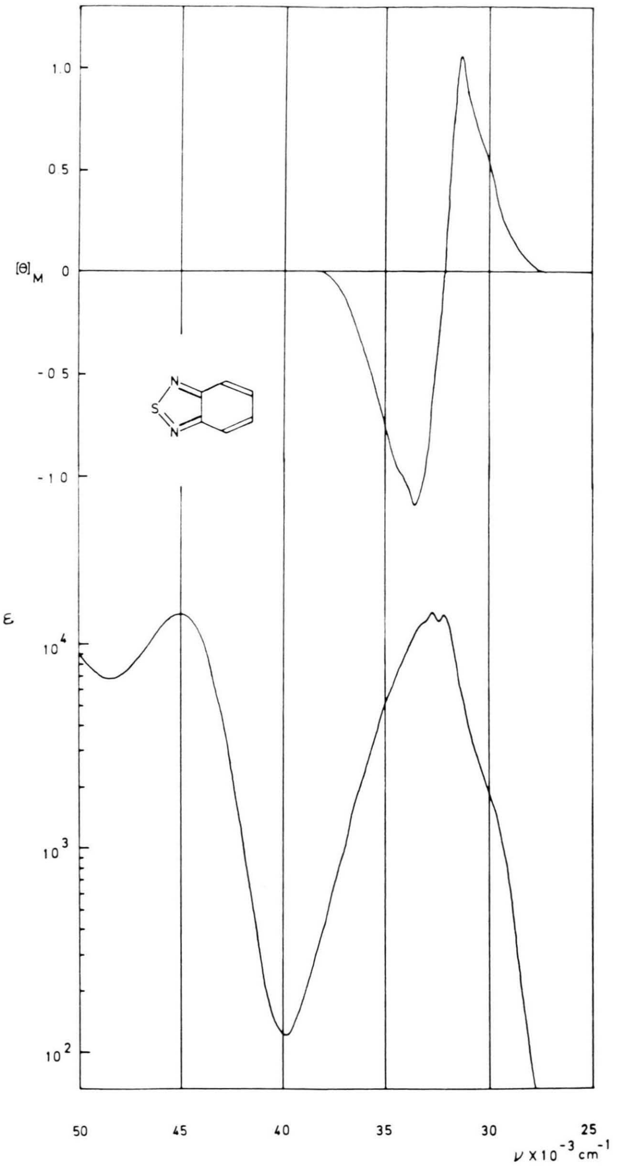

Fig. 3. The MCD (top) and absorption (bottom) spectra of benzo-[1,2,5]-thiadiazole in ethanol at room temperature.

Benzo-[1,2,5]-thiadiazole **5**

The UV and MCD spectra of **5** are represented in Figure 3. The first absorption band showing fine structure exhibits a maximum at 31400 cm^{-1} and a minimum at 33500 cm^{-1} in the MCD spectrum. The splitting is roughly estimated to be 2100 cm^{-1}. The observed two extrema are considered to be due to different electronic transitions in the benzothiadiazole skeleton. Absorption in the higher wave length region exhibits no distinct MCD.

In Table 7 theoretical results for **5** are summarized and listed along with experimental data. Two electronic transitions are predicted to take place in the lower energy region. One is a $B_2 \leftarrow A_1$ transition with an excitation energy of 3.50 eV (28200 cm^{-1}) and the other is an $A_1 \leftarrow A_1$ transition with an energy of 4.27 eV (34400 cm^{-1}). The former is calculated to exhibit positive MCD, and the latter negative MCD. The $B_2 \leftarrow A_1$ transition has to be assigned to the first MCD band and the $A_1 \leftarrow A_1$ transition to the second MCD band. Unfortunately, however, the calculated splitting is much larger than the experimental value.

Benzo-[1,2,3]-thiadiazole **6**

The calculated transition energies, oscillator strengths and the Faraday parameters are listed in Table 8. The lowest transition is predicted to exhibit positive MCD, while the second transition is expected to exhibit negative MCD. The *B* values associated with these MCD bands are equal in magnitude. Accordingly the MCD spectral feature will be the same as for **5**. It is noticed that the lowest transition energy of **6** is calculated to be higher than that of **5**. From an inspection of the present calculation, the N−S−N moiety seems to lower the energy of the first excitation of a molecule.

Table 7. Transition energies ΔE (eV) and the Faraday *B* ($\beta \cdot$ Debye^2/cm^{-1}) values in **5**.

	Theoretical				Experimental		
Sym.	$\Delta E (f)$	$B_{\mathrm{I}} \times 10^5$	$B_{\mathrm{II}} \times 10^5$	$B \times 10^5$	ΔE	$[\Theta]_M$	$B \times 10^5$
$B_2 \leftarrow A_1$	3.50 (0.021)	7.86	−34.04	−26.18	3.89	1.05	−194
$A_1 \leftarrow A_1$	4.27 (0.045)	−21.74	37.01	15.27	4.17	−1.13	279
$B_2 \leftarrow A_1$	5.11 (0.052)	21.94	71.10	93.04			
$B_2 \leftarrow A_1$	5.79 (0.000)	0.04	21.03	21.07			
$A_1 \leftarrow A_1$	5.83 (0.564)	131.09	−74.88	56.21			

Table 8. Transition energies ΔE (eV) and the Faraday B ($\beta \cdot$ Debye^2/cm^{-1}) values in **6**.

	Theoretical			
Sym.	$\Delta E(f)$	$B_{\mathrm{I}} \times 10^5$	$B_{\mathrm{II}} \times 10^5$	$B \times 10^5$
$A' \leftarrow A'$	4.18 (0.018)	−2.29	−70.35	−72.64
$A' \leftarrow A'$	4.51 (0.186)	−10.18	96.23	86.05
$A' \leftarrow A'$	5.46 (0.059)	−2.09	−2.63	−4.72
$A' \leftarrow A'$	6.25 (0.003)	−0.34	−2.32	−2.66
$A' \leftarrow A'$	6.56 (0.270)	−11.65	104.01	92.36

Discussion

The present PPP calculation gives a resonable explanation of the observed transition energies and sign of the MCD spectra in the longer wave length region. However, the theoretical B values are small compared with experimental values in most cases. This may be attributed to the underestimation of the magnetic moment in (1). As the electric moment, in general, becomes too high in such MO methods as the PPP method, the small B values obtained in this work are considered to arise from the small magnetic moment calculated. Inclusion of the 3d AO's in the calculation seems to improve the result, because the matrix elements $\langle 3d^{\mathrm{S}} | 1 | 2p^{\mathrm{N}} \rangle$ etc. will contribute appreciably.

As we have seen before, quantum mechanical calculations of the chemical and physical properties of sulfur heterocycles have been carried out on the basis of the different types of LCAO MO approximations. In these theoretical treatments, the 3d orbital participation on the S atom seems to have been of interest in order to explain not only the ground state stabilities but also some excited state properties of the sulfur heterocycles. The importance of the 3d orbital participation was first pointed out by Longuett-Higgins [21] in his HMO calculation of thiophene, leading to appreciable stability in its ground state. However, the unimportance of the contribution from the 3d orbital on the S atom to such properties as dipole moment [22], polarographic reduction potential [23], spin density [24], electronic absorption spectra [1−4] and photoelectron spectra [3, 4] has also often been stressed, and now it seems to be established that the 3d orbital participation is more or less unimportant.

In fact theoretical transition energies seem to reproduce fairly well the experimental values even in this calculation. As to the evaluation of the magnetic moments, however, 3d orbitals seem to need further confirmation.

As has been often pointed out, the calculated Faraday B terms associated with the first and second transitions are equal in magnitude but opposite in sign. Generally, the second term is larger than the first term in (1) because the energy difference ν_{ab} in the second term is smaller than ν_{b0} in the first term. Accordingly the second term often determines the MCD spectral features. The present calculation is in good agreement with this qualitative prediction in most cases. If we neglect the first term and further neglect non-adjacent excited states, the Faraday B term for the first $a \leftarrow 0$ and the second $b \leftarrow 0$ transitions are written as

$$B_{0a} \sim \operatorname{Im} \frac{\hat{m}_{ab} \cdot \hat{\mu}_{0a} \times \hat{\mu}_{b0}}{\nu_{ab}},$$

$$B_{0b} \sim \operatorname{Im} \frac{\hat{m}_{ba} \cdot \hat{\mu}_{0b} \times \hat{\mu}_{a0}}{\nu_{ba}}.$$

It is easily seen that $B_{0a} = -B_{0b}$ because $m_{ab} = -m_{ba}$, $\mu_{0a} \times \mu_{b0} = -\mu_{0b} \times \mu_{a0}$ and $\nu_{ab} = -\nu_{ba}$ although it is difficult to determine *a priori* which is positive and which is negative.

Equal Faraday B values for the first and second transitions in most molecules studied indicate that magnetic mixing takes place between these two excited states.

The present calculation gives no decisive conclusion for the difference between the Faraday B values of the lower and higher energy transitions, where those of the latter are very small as compared with those of the former. This may be attributed to the number of CI's included in the present calculation, in addition to the participation of the 3d orbital in the evaluation of the matrix elements.

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