Commentationes

Interpretation of Electronic Spectra of Aromatic Hydrocarbons by the "Molecules in Molecules" Method

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The "molecules in molecules" method has been applied to five groups of hydrocarbon molecules or ions. Energy, polarisation and intensity of electronic transitions have been compared with experimental data and previous theoretical results. The results show that the method is applicable even when there is relevant conjugation between the fragments.

Die "molecules in molecules"-Methode wurde auf fünf Gruppen von Kohlenwasserstoff-Molekülen angewandt. Energie, Polarisation und Intensität von elektronischen Übergängen wurden mit experimentellen und theoretischen Resultaten verglichen. Die Resultate beweisen, daß die Methode anwendbar ist, auch wenn eine wesentliche Konjugation zwischen den Fragmenten besteht.

La méthode "molecules in molecules" a été appliquée à cinq groupes de molécules ou ions d'hydrocarbures. On a comparé les energies, la polarisation et l'intensité des transitions électroniques avec les données experimentales et les données théoriques qu'on avait précedemment calculées. Les résultats indiquent que la méthode est appliquable, même lorsqu'on a une conjugaison assez importante entre les fragments.

1. Introduction

The method "molecules in molecules" (M.I.M.) first introduced by Longuet-Higgins and Murrell [1] has been used to discuss the electronic spectra of compounds in which two conjugated systems are connected by one bond characterized by a low value of the mobile bond order [2–5] or applied to aromatic systems carrying electron-donor and electron-acceptor substituents [6–10].

The agreement between experimental and calculated spectra is usually good. However in the case of acenaphthylene and fluoranthene Heilbronner *et al.* [11] pointed out that these systems could not be conveniently studied by this method, owing to the fact that, even in the lowest excited states of these molecules, locally excited configurations of the naphthalene fragment are involved which are not usually included in this kind of calculation. In the present paper we consider a number of molecules, including acenaphthylene and fluoranthene, in which naphthalene is one of the fragments, also molecules having strong electron delocalisation between different fragments, to test the validity of the M.I.M. method in such situations.

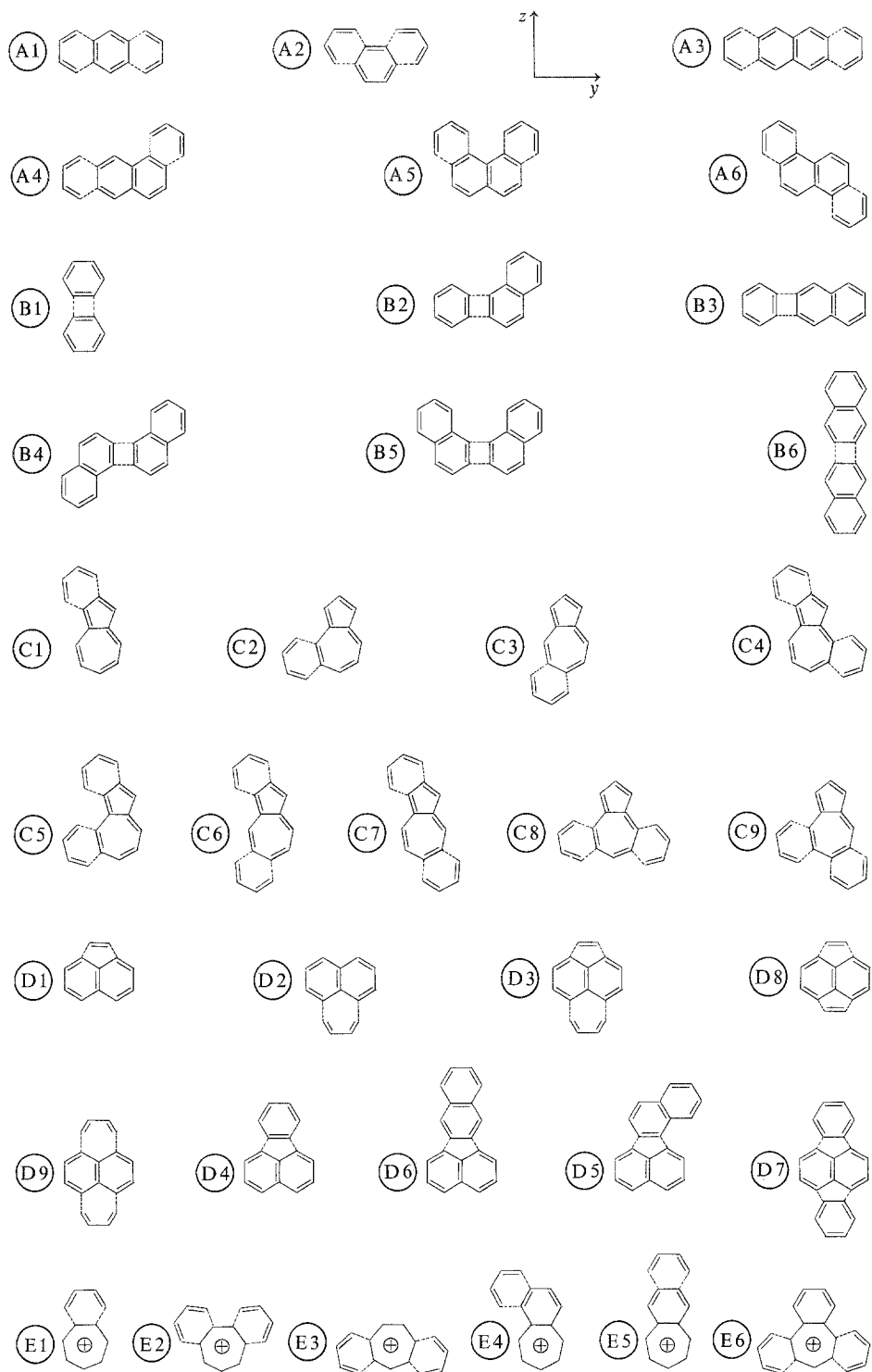* Present address: Institute of Physical Chemistry, Catania.

Fig. 1. Numbering of molecules within each group

2. Calculations

Calculations were performed for the molecules shown in Fig. 1, where dotted lines indicate interfragment bonds. The reference axes are shown following the prescriptions of the Joint Commission for Spectroscopy [12].

It is apparent from Fig. 1 that ethylene, cis-butadiene, benzene, naphthalene, azulene, and the tropylium and benzotropylium cations are the fragments. Five groups of molecules can be recognized (A to E): A and B include alternant hydrocarbons (in the molecules of the group B a four-membered ring is present); C and D include non-alternant hydrocarbons (molecules in group C contain the azulene fragment); derivatives of the tropylium ion are included in group E.

For each fragment Hückel molecular orbitals were used, except for butadiene, where SCF molecular orbitals were calculated. Following Heilbronner *et al.* [11] we used the highest occupied and the lowest unoccupied molecular orbital of ethylene and butadiene, the three highest occupied and three lowest unoccupied molecular orbitals for naphthalene, the two highest occupied and two lowest unoccupied molecular orbitals for other fragments.

We included the interaction between ground configuration and singly-excited configurations built by the above mentioned molecular orbitals.

The energies of the excited states of the fragments were taken from their spectra. For naphthalene we needed several energy values which cannot be obtained from the spectrum; these have been obtained from the calculated values through an interpolation procedure as shown in Fig. 2, together with renormalized wave functions. The experimental energies and wave functions for ethylene and for the tropylium and benzotropylium cations were taken from the literature [2] together with energy values for butadiene. For azulene the wave functions given by Pariser [13] were renormalized and the excitation energies were those of Mann and Platt [14].

The first ionisation potentials of ethylene, butadiene, benzene, naphthalene and azulene were taken from the literature [15].

Electron affinities of benzene and naphthalene as obtained from experiment [15] were used. For ethylene, butadiene and azulene electron affinities were calculated from experimental values of the ionisation potentials and of the first excitation energy through an empirical relationship [16]. Higher ionisation potentials and electron affinities were calculated from the experimental values of the first ionisation potentials and electron affinities and as well as the differences in the energies of the relevant orbitals as calculated by the Pariser and Parr technique. They are reported in Table 1. Energy values for charge-transfer configurations involving the tropylium and benzotropylium cations were empirically evaluated as follows: for the tropylium-butadiene pair we used the value given by Heilbronner *et al.* [2] and for the benzotropylium-butadiene pair we used the values for the benzotropylium-ethylene pair [2] corrected for the difference in electron affinities between butadiene and ethylene. The resonance integrals were assumed as empirical parameters; the standard value of $\beta = -2.50$ eV, corresponding to a distance of 1.40 Å, has been chosen, except for the molecules of group B where the value $\beta = -1.80$ eV has been used. This is justified by unusually low bond orders corresponding to bond-lengths of about 1.48 Å.
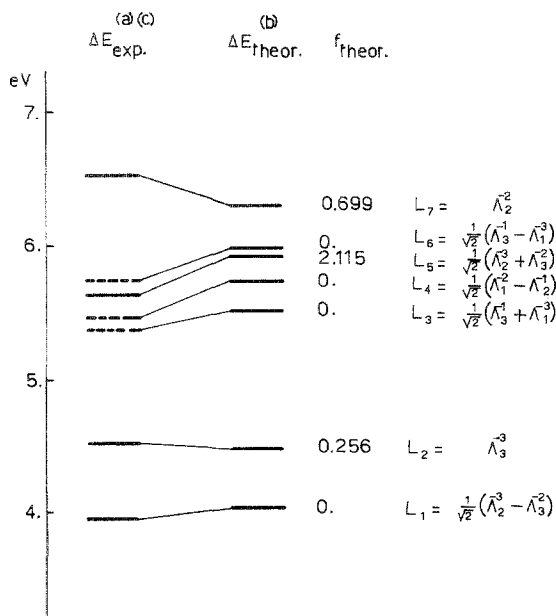
Fig. 2. Theoretical and experimental energies for naphthalene excited states. Calculated intensities are also shown, together with the main configurational functions for each state. $L_i^{\,j}$ is the wave-function for the configuration in which one electron has been excited from the i to the j molecular orbital. Only orbitals included in calculations have been numbered: bonding orbitals of increasing energy are numbered from 1 to k; antibonding orbitals from $-k$ to -1. Excited states Λ_m are numbered in order of increasing energy. a) Klevens, H. B., and J. R. Platt: J. chem. Physics; b) Pariser, R.: J. chem. Physics **24**, 250 (1956); c) dotted lines indicate interpolated values

The geometries of the molecules were obtained as follows: the experimental bond-length 1.34 Å [17] was used for ethylene; for *cis*-butadiene the experimental bond-lengths and angles of the *trans*-isomer [18] were used; all cyclic fragments were assumed to be regular polygons with each side 1.40 Å long.

The use of previously given β values and the assumption of planarity for all molecules completely define the geometry.

Coulomb integrals $\gamma_{\mu\nu}$ were calculated according to the previously given formula [19].

For 18 molecules our results are compared with experimental and previous theoretical results in the following section. Our results for the remaining molecules are collected in the Appendix A.

Table 1. *Ionisation potentials I and electron affinities A (in eV)* [a]

Naphthalene		Azulene	
I_1	10.34		
I_2	9.17	I_1	8.78
A_{-2}	-0.40	A_{-1}	-0.44
A_{-1}	-1.57		

[a] The subscript labels the donor or acceptor orbital.

Results

Group A (Alternant Hydrocarbons)

A-1: Experimental spectra for this molecule have been taken from different authors [20–24]. From the body of these results the following assignments may be made: the first band corresponds to a transition to a B_{2u} state at 3.40 eV ($f = 0.10$) with z polarization; a second very weak y-polarized band is concealed under the first band and has its 0—0 maximum at 3.46 eV.

The third band is y polarized and lies at 4.80 eV ($f = 1.60$). The fourth band, z polarized, lies at 5.60 eV ($f = 0.20$). The fifth band, z polarized, is found at 6.69 eV ($f = 0.40$). A number of theoretical treatments has been published for this molecule [13, 25–33]. All these authors use different modifications of the PPP-method [34] except Hummel and Ruedenberg [28] who use the so called "tight-binding" and "intra-ring" approximations, and Ham and Ruedenberg [26, 35] who use a method based on the inclusion of the electronic interaction in the "free electron model".

Our results allow a good interpretation of the spectrum. The weakest point is a low energy value for the fourth transition as compared with experiment and other theoretical treatments; our method however gives better agreement for the third band.

A-2: The experimental spectrum [20–22, 36] shows the following bands: 3.50 eV ($f = 0.003$), z polarized; 4.09 eV (0.18), y polarized; 4.87 eV (1.09) y polarized; 5.84 eV (0.60), z polarized; 6.62 eV (0.59) z polarized and 6.99 eV (0.29).

The third band might overlap a weak $A_1 \rightarrow A_1$ transition (we find a transition of this kind at 4.82 eV ($f = 0.15$).

There is some ambiguity in the interpretation of this spectrum with our results for the last two bands. The band at 5.84 eV corresponds to our calculated transition at 5.68 eV; we find a z polarized transition at 6.06 eV which might be assigned to the same band.

We find a y polarized transition at 6.63 eV corresponding to the z polarized band at 6.62 eV and a transition at 6.95 eV (y-polarized) corresponding to the highest experimental band, or, if we give more significance to the polarisation than to energy, our transition at 6.06 eV corresponds to the fifth experimental band and the transition at 6.63 eV to the highest experimental one.

Theoretical results from other authors do not provide better insight.

A-3: The experimental data for this molecule are due to Zimmermann [24] and Klevens and Platt [20, 21]. The intensity, polarization and energy data are shown in Table 2 together with results obtained by different authors using the PPP-method and with our results. The agreement between our results and experiment is excellent.

A-4: The correspondence between theoretical and experimental data is shown in Table 3.

Polarizations of transitions found in this molecule are shown in Fig. 3.

The first transition energy calculated by us is about 0.4 eV too low. The direction of the polarisation of this band is in agreement with the one calculated by Ham and Ruedenberg [26] while the direction of polarisation of the second band is in poor agreement with experimental and previous theoretical results.

G. Favini, A. Gamba, and M. Simonetta:

Table 2. *Energies, intensities and polarisations for the first bands in A-3*

	ΔE_1	f	pol.	ΔE_2	f	pol.	ΔE_3	f	pol.	ΔE_4	f	pol.	ΔE_5	f	pol.	ΔE_6	f	pol.
Exp.	2.62	0.08	z	3.22	—	y	4.55	1.85	y	5.39	0.28	—	5.88	0.45	—	6.62	0.27	—
Ref. [13]	3.11	0.44	z	3.56	0.00	y	5.09	3.78	y	4.68	0.16	z	6.54	0.00	z			
Ref. [26]	3.05	0.34	z	3.04	0.03	y	4.86	3.97	y	5.39	0.75	z						
Ref. [28]	2.53	0.33	z	3.22	0.31	y	4.94	4.59	y	5.08	0.03	z	6.08	0.04	z			
	2.66	0.37		3.33	0.15		4.95	3.29		5.26	0.08		6.13	0.07				
Ref. [29]	2.66	0.35	z	3.42	0.00	y	3.87	2.90	y	4.98	0.07	z	5.75	1.26	z			
Ref. [32]	3.02			3.44			4.44											
This work	2.46	0.06	z	3.48	0.00	y	4.60	2.68	y	4.98	0.20	z	5.77	0.22	z	6.64	0.02	y
																6.79	0.45	z

Table 3. *Energies, intensities and polarisations for the first bands in A-4*

	ΔE_1	f	ΔE_2	f	ΔE_3	f	ΔE_4	f	ΔE_5	f	ΔE_6	f
Exp.	3.22	0.004	3.62	0.15	4.31	1.30	4.82	0.58	5.60	0.67	6.15	0.54
Ref. [26]	3.57	0.03	3.78	0.21	4.84	2.67	5.09	0.85				
Ref. [28]	3.42	0.35	3.64	0.14	4.27	0.48	4.60	1.42				
	3.45	0.42	3.75	0.20	4.45	1.20	4.75	1.47				
Ref. [32]	3.60		3.73		4.50							
This work			3.58	0.68	4.19	0.53	4.86	0.19	5.49	0.14	6.05	0.41
	2.78	0.04	3.71	0.09	4.46	0.05	4.97	0.34	5.51	0.06	6.21	0.04
					4.58	0.04	5.08	0.50	5.88	0.01	6.31	0.07

A-5 and A-6: Theoretical and experimental data [20–22, 36] for these two molecules are collected in Tables 4 and 5.

The polarisation directions for chrysene are shown in Fig. 4.

The correspondence between our calculations and experiment for the molecules of this group oscillates between a very nice agreement (for example tetracene) and a large discrepancy for the third and fourth band in 3,4 benzophenanthrene. For the last molecule however it may be pointed out that X-ray structural analysis
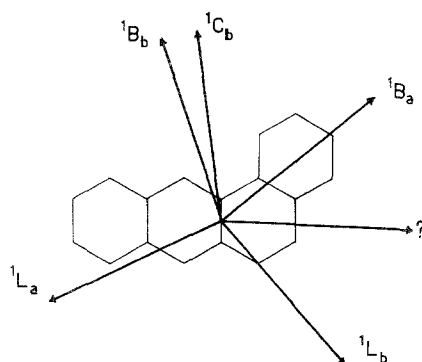
1,2-Benzanthracene

Fig. 3. Theoretical polarisation directions for the main bands of *A-4*

Table 4. *Energies, intensities and polarisations for the first bands in A-5*

	ΔE_1	f	pol.	ΔE_2	f	pol.	ΔE_3	f	pol.	ΔE_4	f	pol.
Exp.	3.31	0.006	y	3.76	0.12	z	4.41	1.57	y	5.65	1.38	z
Ref. [26]	3.47	0.00	y	3.91	0.38	z	4.92	2.81	y	5.36	1.14	z
Ref. [28]	3.65	0.02	y	3.85	0.02	z	4.42	1.39	y	4.86	0.79	z
				3.86	0.04		4.50	1.44		4.92	1.27	
Ref. [32]	3.87			4.17			4.74					
This work	3.19	0.01	y	3.57	0.07	z	3.80	0.44	y	4.17	0.72	z

Table 5. *Energies and intensities for the first bands in A-6*

	ΔE_1	f	ΔE_2	f	ΔE_3	f	ΔE_4	f	ΔE_5	f
Exp.	3.40	0.005	3.75	0.36	4.60	1.29	5.65	0.69	6.35	0.22
Ref. [26]	3.47	0.00	3.91	0.28	4.94	2.81	5.36	1.44		
							5.18	1.17		
Ref. [28]	3.75	0.15	3.80	0.44	5.05	0.65	5.32	1.51	6.40	0.30
	3.85	0.41	3.90	0.55	5.20	2.05	5.33	0.53	6.60	0.42
							5.55	1.46		
Ref. [30]	4.12	0.00	4.25	0.38	5.48	1.32	5.75	1.41	6.35	1.01
Ref. [32]	4.00		4.38		5.47					
			3.62	0.53						
This work	3.22	0.15	4.24	0.45	4.60	0.46	5.78	0.07	6.34	0.95

[37] reveals a geometry far from the planar one assumed in these calculations. This argument probably holds not only for the molecule in the crystal, but also for an isolated molecule, as most of the strain comes from the interaction between hydrogens in positions 4′–5 of the same molecule (the numbering is taken from Ref. [38]). The experimental distance between atoms 4′–5 is 3.00 Å while in our model it is assumed to be 2.42 Å. The difference is particularly relevant in the calculations of matrix elements containing electronic repulsion integrals, with significant consequences on the calculated interactions between locally excited configurations.
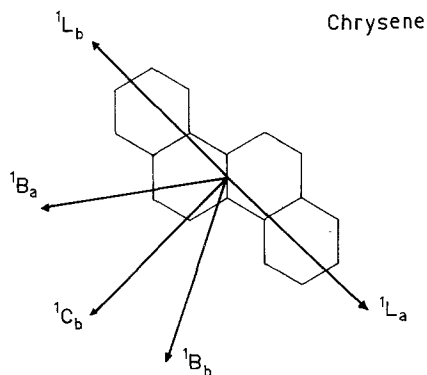

Fig. 4. Theoretical polarisation directions for the main bands of *A-6*

Group B (Biphenylene Derivatives)

B-1: The experimental data [39–41] show the existence of three regions of absorption: a weak band at about 3.18 eV, a medium intensity band at about 3.54 eV and a strong band at 5.16 eV.

The strong band is due to an allowed transition, which we find polarized along the z axis. Also the medium intensity band is due to an allowed transition for which we calculated a very low oscillator strength. According to our predictions the forbidden transition to the lowest B_{3g} state lies at a higher energy value than found experimentally (about 0.8 eV). The discrepancy is significant, but less than that observed in Skancke's [30] PPP calculations. Better agreement has been obtained by Hilpern [40] by "*ad hoc*" calibration of the β value for the "long" bonds and by Bloor *et al.* [35], who use a "variable resonance integral modification" of the PPP-method.

B-2: The experimental data [42, 43] show three regions of absorption: the first one at 3.16–3.45 eV ($f = 0.07$); the second one at 4.26–4.44 eV ($f = 0.31$) and the third one at 4.73–4.88 eV ($f = 0.63$). There is good correspondence with our calculated energy values for the first three allowed transitions.

B-3: Experimental [44] and calculated data agree in the positions of the first three allowed bands: experimental values are found at 3.38–3.56 eV; 4.19–4.35 eV; 4.69–4.86 eV.

B-4: Three bands were found experimentally [45] at 3.15–3.30 eV ($f = 0.07$); 4.17 eV ($f = 0.85$); 4.75 eV ($f = 0.38$).

The agreement with the results of our calculations is good both for the position and the intensity of the bands.

B-5: The spectrum of this molecule [42] shows four bands: at 2.95–3.10 eV ($f = 0.10$); 4.16 eV ($f = 1.02$); 4.75–4.82 eV ($f = 0.28$); 5.74 eV ($f = 0.68$).

Our calculations find four bands at about the right position and an extra band at 4.53 eV ($f = 0.13$), which might be masked under the second (strong) band, which shows a shoulder on the high energy side.

B-6: In the interpretation of this spectrum we meet the same difficulties as for the *B-1* molecule. There are three well defined bands [45] at 3.85 eV ($f = 0.13$), 4.30 eV ($f = 1.05$) and 5.71 eV ($f = 0.70$) showing good correspondence with our calculated energies and oscillator strengths. However the experimental spectrum shows a band at 3.05–3.42 eV ($f = 0.22$) with a strong vibrational structure; the first forbidden transition ($A_g \rightarrow B_{3g}$) from our calculations lies at 4.03 eV.

For this group of molecules the agreement between experiment and our calculations is fairly good with the exception of the first band of the *B-1* and *B-6* molecules (both with D_{2h} symmetry), which we found shifted to the higher energy side of the first allowed band. Further experimental studies of this group of molecules and the determination of the band polarisations would be desirable.

Group C (Azulene Derivatives)

The experimental spectra for *C-1*, *C-2*, *C-3*, and *C-4* are taken from Refs. [46–48].

Experimental data and the results of Heilbronner and Murrell [48] (Platt's perimeter model [49]), of Koutecky *et al.* [47] (PPP-method) and of the present paper are shown in Tables 6–9.

Table 6. *Energies and intensities for the first bands in C-1*

	E_1	f [a]	E_2	f	E_3	f	E_4	f
Exp. [b]	2.02	0.01	3.24	0.09	4.16	1.05	5.00	—
Ref. [48]	2.39		3.18		3.99			
Ref. [47]	1.50	0.03	2.91	0.12	3.98	1.34	4.26	0.23
							4.30	0.57
This work	1.92	0.04	3.07	0.05	3.91	0.93	5.03	0.12
					4.06	0.22	5.15	0.29
					4.33	0.44		

[a] Oscillator strengths values calculated by us from spectra of Ref. [46].
[b] Experimental data refer to spectra recorded in cyclohexane [46].

Table 7. *Energies and intensities for the first bands in C-2*

	E_1	f [a]	E_2	f	E_3	f	E_4	f
Exp. [b]	2.15	0.01	3.11	0.06	4.02	0.62	4.89	0.58
Ref. [48]	2.49		3.24		4.10		4.41	
Ref. [47]	1.44	0.03	2.82	0.06	3.82	1.17	4.20	0.20
							4.20	0.09
This work	1.92	0.06	3.09	0.03	3.92	0.82	4.80	0.21

[a, b] See Table 6.

Table 8. *Energies and intensities for the first bands in C-3*

	ΔE_1	f [a]	ΔE_2	f	ΔE_3	f	ΔE_4	f
Exp. [b]	2.22	0.01	3.48	0.01	4.30	1.02	4.90	0.55
Ref. [48]	2.45		3.21		3.95		4.46	
Ref. [47]	1.71	0.04	2.93	0.05	3.95	0.74	4.51	0.37
					4.18	0.85		
This work	1.96	0.04	3.06	0.03	3.91	0.43	4.96	0.05
					3.99	0.93	5.28	0.24
					4.36	0.64		

[a, b] See Table 6.

Table 9. *Energies and intensities for the first bands in C-4*

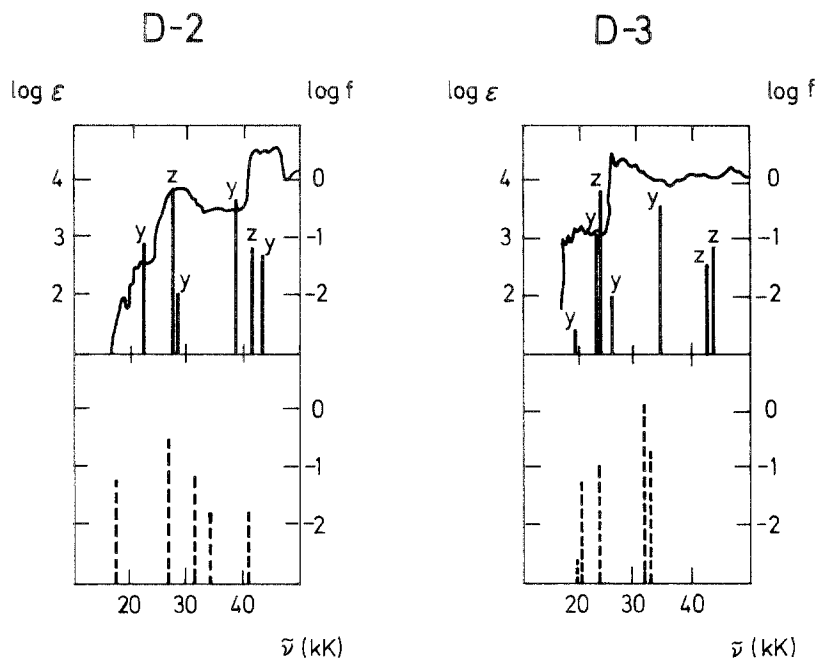|	ΔE_1	f [a]	ΔE_2	f	ΔE_3	f	ΔE_4	f
Exp. [b]	1.86		3.09		4.04		4.75	
			3.24					
Ref. [47]	1.71	0.04	2.93	0.05	3.95	0.74	4.51	0.37
					4.18	0.85		
This work	1.72	0.07	2.82	0.01	3.75	0.79	4.53	0.23
			3.48	0.02	3.87	0.31		
					4.07	0.16		

[a, b] See Table 6.

Fig. 5. Comparison of the calculated excitation energies of the D-2 and D-3 molecules with the experimental absorption curves. - - - - Ref. [47], —————— this work. The left-hand scale $\log \varepsilon$; the right-hand scale $\log f$

For the C-5 and C-6 molecules no experimental data are available; for comparison we report in Table 10 the results by Koutecky *et al.* [47]:

For the molecules of this group the agreement with experimental data, where available, is good both for transition energies and oscillator strengths.

Group D (Non Alternant Hydrocarbons)

D-1: Our results for this molecule are compared with experiment [11] and PPP calculations [47, 11] in Table 11.

D-2 and D-3: The experimental spectra for this molecule [50] are reproduced in Fig. 5.

Owing to the difficulties in the localisation of band maxima, our results together with those obtained by Koutecky *et al.* [47] are reported in the same figure.

The polarisation of the longest wave length band for *D-3* is in agreement with experiment [51].

D-4: Detailed experimental data for this molecule are available [11, 52]. They are compared with our and previous results in Table 12.

Our interpretation of this spectrum is good and it is perhaps the most satisfactory compared with other theoretical treatments.

D-5 and D-6: The spectra of these two molecules are known in dioxane [53] and ethanol [38b]. Experimental data in ethanol are shown in Figs. 6 and 7 together with Koutecky's and our results.

Table 10. *Energies, intensities and polarisations for the first bands of C-5 and C-6 taken from Ref. [47]*

	ΔE_1	f	$\cos\phi$	ΔE_2	f	$\cos\phi$	ΔE_3	f	$\cos\phi$	ΔE_4	f	$\cos\phi$	ΔE_5	f	$\cos\phi$
C-5	1.95	0.03	0.47	2.59	0.04	0.31	3.45	1.31	−0.99	3.61	0.17	−1.0	3.78	0.32	−0.94
C-6	1.98			2.91			3.71			4.10			4.30		

Table 11. *Energies, intensities and polarisations for the first bands in D-1*

	ΔE_1	f^{a}	pol.	ΔE_2	f	pol.	ΔE_3	f	pol.	ΔE_4	f	pol.	ΔE_5	f	pol.
Exp.	2.65	0.007	y	3.65	0.03	z	3.84	0.15	y	4.70	0.07	z	5.41	0.57	y
Ref. [48]	2.75	0.04	y	3.75	0.31	z	3.83	0.22	y	4.75	0.00	z	5.56	1.21	y
Ref. [47]	2.61	0.04	y	3.70	0.24	z	3.93	0.16	y	4.55	0.04	z	5.63	1.08	y
This work	2.65	0.04	y	3.65	0.63	z	3.56	0.12	y	4.76	0.01	z	5.09	0.55	y
													5.47	0.00	y

ᵃ See Table 6.

Table 12. *Energies, intensities and polarisations for the first bands in D-4*

	ΔE_1	f^{a}	pol.	ΔE_2	f	pol.	ΔE_3	f	pol.	ΔE_4	f	pol.	ΔE_5	f	pol.	ΔE_6	f	pol.	ΔE_7	f	pol.
Exp.	3.20	—	y	3.47	0.09	y	3.83	0.09	z	4.32	0.09	z	4.74	—	z	(4.96)ᵇ		y	5.25	0.67	y
Ref. [48]	3.32	0.01	y	3.51	0.52	y	3.93	0.08	z	4.48	0.22	z				5.26	0.60	z	5.39	1.28	y
Ref. [47]	3.33	0.02	y	3.58	0.64	y	4.09	0.07	y	4.58	—	y	4.70	0.20	z	5.20	0.03	y	5.25	0.00	z
This work	3.31	0.20	y	3.47	1.04	y	3.69	0.01	y	4.58	0.07	y	4.78	0.04	z	5.04	0.42	y	5.28	1.13	y

ᵃ See Table 6.
ᵇ Values in parenthesis refer to shoulders.

G. Favini, A. Gamba, and M. Simonetta:

Fig. 6. Comparison of the calculated excitation energies of the *D-5* molecule with the experimental absorption curve.- - – – – Ref. [47], ———— this work. The left-hand scale $\log \varepsilon$; the right-hand scale f
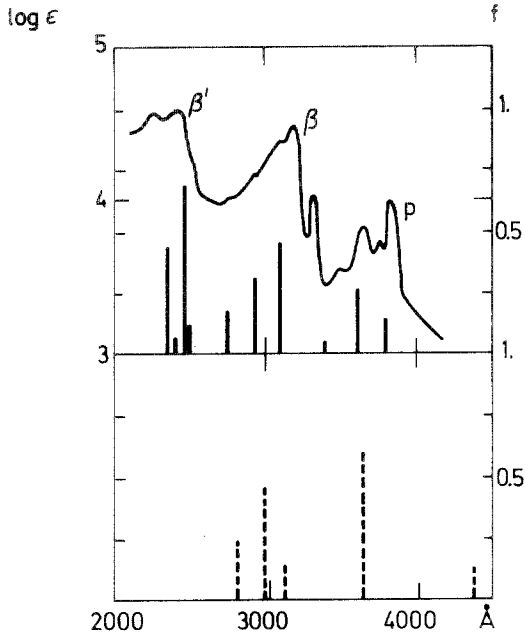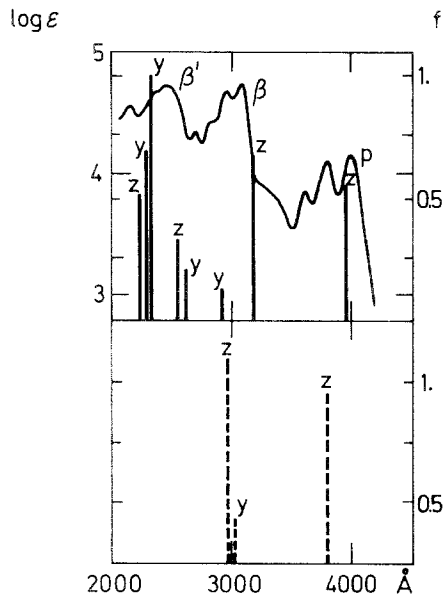

Fig. 7. Comparison of the calculated excitation energies of the *D-6* molecule with the experimental absorption curve.- - – – – Ref. [47], ———— this work. The left-hand scale $\log \varepsilon$; the right-hand scale f
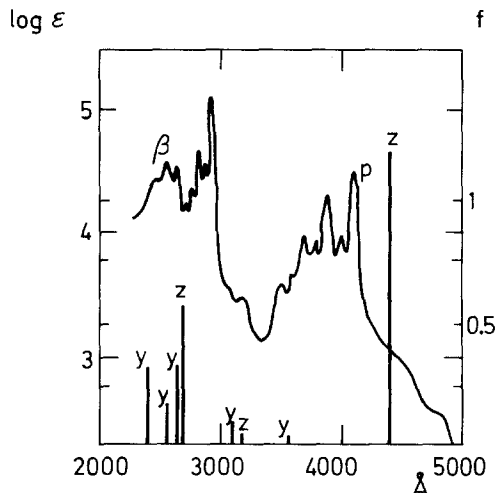
Fig. 8. Comparison of the calculated excitation energies of the *D-7* molecule with the experimental absorption curve. The left-hand scale $\log \varepsilon$; the right-hand scale f

D-7 and D-8: The spectrum in ethanol for *D-7* [38 b] is shown in Fig. 8 together with our results. The meagre reported experimental data for *D-8* [38 a] do not allow a discussion of the spectrum for this molecule[1].

Group E (Tropylium Cation Derivatives)

The experimental spectra for this group of molecules are taken from [54]. Calculations for this group of molecules were carried out by Heilbronner and Murrell [48] and by Koutecky *et al.* [47]. Experimental data and theoretical results are collected in Tables 13–18.

The interpretation of the spectra of this group is particularly difficult, since the solvent is concentrated sulphuric acid, so that strong interactions between the

Table 13. *Energies, intensities and polarisations for the first bands in E-1*

	ΔE_1	f^a	pol.	ΔE_2	f	pol.	ΔE_3	f	pol.	ΔE_4	f	pol.
Exp.	2.92	0.03		3.68	0.03		4.40	0.47		5.29	0.60	
Ref. [48]	3.16	0.20	y	3.71	0.01	z	4.66	2.56	z	4.91	0.60	y
Ref. [47]	2.88	0.09	y	3.64	0.00	z	4.67	1.53	z	5.51	0.44	z
							4.86	0.07	y			
This work	2.71	0.01	y	3.61	0.48	z	4.71	0.18	z	5.82	0.70	z
							4.80	0.22	y			

[a] Oscillator strength values were calculated by us from spectra reported in Ref. [54].

[1] One referee has pointed it out that for the molecules in Figs. 5–8 some peaks may be due to residual vibrational fine structure. Since the polarisations of the bands under consideration are not available a definite choice between the two interpretations is not yet possible.

Table 14. *Energies, intensities and polarisations for the first bands in E-2*

	ΔE_1	f^a	pol.	ΔE_2	f	pol.	ΔE_3	f	pol.	ΔE_4	f	pol.
Exp.	2.71	0.14		3.92 4.13	0.80		4.42	0.27		5.00	0.31	
Ref. [48]	2.94 3.10		z y	4.05		y	4.24		z			
Ref. [47]	2.61 2.81	0.06 0.25	y z	3.96 4.14	0.09 0.03	y z	4.54	0.21	z			
This work	2.31 2.43 3.01	0.01 0.01 0.19	y z y	3.90	0.27	z	4.52 4.66	0.02 0.08	y z	5.29	0.05	z

ª See Table 13.

Table 15. *Energies, intensities and polarisations for the first bands in E-3*

	ΔE_1	f^a	pol.	ΔE_2	f	pol.	ΔE_3	f	pol.	ΔE_4	f	pol.	ΔE_5	f	pol.
Exp.	2.30 2.44	0.05		3.12 3.27	0.11		4.05	0.59		4.61			5.23	0.20	
Ref. [48]	2.59		z	3.14		y	3.95		y	4.21		z			
Ref. [47]	2.55	0.17	z	3.24	0.04	y	3.68 4.44	0.06 2.69	y y	4.49	0.08	z			
This work	2.58 2.65	0.05 0.02	z y	2.85	0.27	y	4.12 4.53 4.62	0.02 0.03 0.00	z z y	4.84	0.02	z	5.50	0.04	y

ª See Table 13.

Table 16. *Energies, intensities and polarisations for the first bands in E-4*

	ΔE_1	f^a	$\cos\phi$	ΔE_2	f	$\cos\phi$	ΔE_3	f	$\cos\phi$	ΔE_4	f	$\cos\phi$	ΔE_5	f	$\cos\phi$
Exp.	2.71	0.06		3.18	0.34		4.20	0.19		4.85	0.50		5.40	0.45	
Ref. [48]	3.08			3.30			3.89			4.17					
Ref. [47]	2.66	0.19	0.82	3.02 3.55	0.01 0.35	−0.3 −0.9	3.99	0.74	0.8	4.48	0.22	0.97			
This work	2.66 2.79	0.15 0.25	0.42 −0.36	3.41	0.29	−1.0	4.08	1.02	1.0	4.61	0.73	−0.98	5.37 5.47	0.35 0.35	0.18 −0.04

ª See Table 13.

Table 17. *Energies, intensities and polarisations for the first bands in E-5*

	ΔE_1	f^a	pol.	ΔE_2	f	pol.	ΔE_3	f	pol.	ΔE_4	f	pol.	ΔE_5	f	pol.
Exp.	2.04	0.03		3.12	0.30		3.75 4.12	0.72		4.88	0.52		5.41	0.58	
Ref. [48]	2.24		y	3.22		z	4.06		z	4.62		y			
Ref. [47]	1.88	0.07	y	3.09	0.01	z	3.85 3.63	1.71 0.00	z y	4.40	0.05	y			
This work	2.37	0.14	y	2.87	0.74	z	3.90 3.97	0.62 0.03	z y	4.64 5.03	0.65 0.72	z y	5.68	0.13	y

ª See Table 13.

Table 18. *Energies intensities and polarisations for the first bands in E-6*

	ΔE_1	f [a]	pol.	ΔE_2	f	pol.	ΔE_3	f	pol.	ΔE_4	f	pol.
Exp.	2.22 (2.48)	0.04		3.03	0.06		(4.29)[b]	0.43		4.96	1.15	
Ref. [47]	2.44 2.61	0.28 0.09	z y	3.28	0.33	y	3.95 4.03	0.00 0.01	y z			
This work	2.34 2.43 2.59	0.01 0.02 0.01	y z y	3.40 3.54	0.19 0.01	z y	3.94 4.12	1.05 1.00	y z	5.07 5.07	0.11 0.19	y z

[a] See Table 13.
[b] Values in parenthesis refer to shoulders.

ions and the solvent itself may occur; also the assessment of empirical values for charge transfer configurations is difficult.

However the agreement between the results for energy, intensity and polarisation of the transitions obtained by different theoretical methods is rather satisfactory and the agreement with experiment is fair. No theoretical method can claim a significant superiority from this viewpoint.

Concluding Remarks

The "molecules in molecules" method has been applied to thirty six molecules belonging to different classes such as alternant and non alternant hydrocarbons (including azulenes), hydrocarbon cations and hydrocarbons containing a four membered ring.

No adjustable parameters have been included: only two values for the β resonance integral have been used, the difference being justified by the difference in bond lengths. A peculiarity of our application of this method, as compared with previous work, is the fact that the bonds between different fragments are by no means quasi-single bonds, but usually are bonds between different parts of the molecules connected by significant conjugation.

For the applicability of the M.I.M.-method to these molecules a stringent condition is that the geometry of each component fragment should not change significantly during the "building up" process.

The results for energy, intensity and polarisation of the transitions are on the whole better than those obtained by the PPP-method. This is especially evident if we consider the fact that most users of this method have adjusted their parameters to fit the experimental data for limited classes of compounds. On the other hand when the necessary data for the fragments are available, the amount of computational work is much less for the M.I.M.-method. This fact becomes of major importance when treating big molecules; it appears that the M.I.M.-method can be used as a procedure of "building up" spectra: from the known spectra of small molecules the spectra of bigger molecules can be interpretated or predicted.

An interesting feature of the method is that in the same energy range a higher number of electron transitions are obtained than with previous methods, suggesting that in some cases what we usually call a band may result from the overlapping of different transitions; so that the attribution of series of peaks to vibrational structure may be over-used. A more detailed study of the polarisation spectra seems necessary; the interpretation of experimental results by the M.I.M.-method might then gain popularity.

Calculations to explore the possibility of extending the M.I.M.-method to systems containing hetero-atoms are in progress.

Appendix

The results of our calculations are shown in part in the following tables. For molecules with symmetry the symmetry group is given after the molecule label; the headings of columns are self explanatory.

Table 1 A

A-1 (D_{2h})			A-2 (C_{2v})		
E_i (eV)	pol.	f	E_i (eV)	pol.	f
-2.166	—	—	-2.166	—	—
3.312	z	0.05	3.458	z	0.16
3.602	y	0.00	3.474	y	0.01
4.348	y	1.02	4.047	z	0.00
4.809	z	0.01	4.445	y	0.75
5.147	z	0.01	4.551	y	0.01
5.921	y	0.04	4.815	z	0.15
6.149	z	0.10	5.080	y	0.15
6.755	z	0.02	5.250	z	0.03
			5.681	z	0.19
			5.773	y	0.03
			6.055	z	0.02
			6.628	y	0.20
			6.950	y	0.00

Only results for allowed singlet states are given except for molecules B-1 and B-6.

Theoretical intensity of transitions has been calculated by the known relation:

$$f \text{ (oscillator strength)} = 1.085 \times 10^{-11} \, v M^2$$

where v and M represent the frequency (cm^{-1}) and the moment of the transition respectively.

The experimental f values were approximately calculated from the absorption curves ($f = 4.32 \times 10^{-9} \, \varepsilon_{max} \Delta v$, where Δv is the band width (in cm^{-1}) at half-maximum extinction).

The weights of the contributing configurations to each state are available upon request.

Table 2A

B-1 (D_{2h})			B-2			B-3 (C_{2v})			B-4 (C_{2h})			B-5 (C_{2v})			B-6 (D_{2h})		
E_i(eV)	pol.	f	E_i(eV)	$\cos\phi^a$	f	E_i(eV)	pol.	f	E_i(eV)	$\cos\phi$	f	E_i(eV)	pol.	f	E_i(eV)	pol.	f
-0.342	—	—	-0.293	—	—	-0.325	—	—	-0.236	—	—	-0.252	—	—	-0.274	—	—
4.021	z	0.00	3.596	-0.406	0.24	3.599	z	0.07	3.641	-0.866	0.01	3.039	y	0.26	3.906	z	0.02
4.088 [b]	—	—	4.457	0.454	1.69	4.354	y	0.33	4.114	0.130	1.57	4.387	y	1.61	4.031 [b]	—	—
4.813	z	0.16	4.760	-0.914	0.34	4.621	z	2.30	4.881	-0.951	0.63	4.528	z	0.13	4.481	y	0.88
5.750 [b]	—	—	5.460	0.682	0.01	4.799	y	0.01	5.045	0.982	0.11	4.820	y	0.25	4.719	y	0.02
5.795	y	0.04	5.646	-0.981	0.63	5.169	y	0.07	5.462	0.848	1.96	5.364	z	0.07	4.854	z	0.00
			5.979	0.113	0.28	5.541	y	0.07	5.711	-0.866	0.07	5.485	y	0.03	5.277	y	0.03
						6.070	z	0.26	5.934	0.866	0.02	5.549	y	0.01	5.375	z	0.00
									6.060	0.999	0.92	5.606	z	0.43	5.711	y	0.00
												6.074	z	2.91	5.807	z	0.69
															5.908	z	0.00

[a] ϕ is the angle formed by the z axis and the direction of the transition moment vector.
[b] Transitions to these states (symmetry B_{3g}) from the ground state are symmetry-forbidden.

Table 3A

C-5		C-6		C-7		C-8			C-9	
E_i(eV)	$\cos\phi^a$ f	E_i(eV)	$\cos\phi^a$ f	E_i(eV)	$\cos\phi^a$ f	E_i(eV)	pol.	f	E_i(eV)	$\cos\phi^a$ f
-1.582	— —	-1.502	— —	-1.469	— —	-1.507	—	—	-1.463	— —
1.628	-0.087 0.05	1.811	0.602 0.05	1.688	-0.087 0.03	1.651	y	0.03	1.795	-0.656 0.04
2.796	0.233 0.03	2.750	-0.946 0.03	2.708	-0.276 0.04	2.754	z	0.06	2.726	0.899 0.03
3.472	-0.191 0.25	3.462	-0.616 0.25	3.540	0.940 0.52	3.379	y	0.62	3.598	-0.970 0.18
3.696	-0.883 1.16	3.678	-0.993 1.16	3.672	0.951 0.24	3.739	y	0.16	3.744	0.552 0.11
3.917	-0.880 0.00	3.948	0.799 0.00	3.958	0.855 0.53	3.930	z	0.50	3.934	0.961 1.65
4.114	0.616 0.52	4.112	-0.883 0.52	4.070	-0.999 0.59	4.166	z	0.00	4.053	-0.940 0.00
4.520	0.174 0.04	4.297	0.477 0.04	4.326	0.927 0.17	4.533	y	0.00	4.257	0.454 0.12
4.664	0.000 0.04	4.885	0.000 0.04	4.764	0.000 0.05	4.841	z	0.12	4.540	0.552 0.04
4.866	-0.656 0.00	4.969	0.530 0.00	4.987	0.208 0.02	4.878	y	0.00	4.837	0.552 0.06
5.096	0.545 0.03	5.039	0.788 0.03	5.663	-0.537 0.02	5.032	y	0.04	4.978	0.000 0.04
									5.228	0.766 0.00

[a] ϕ is the angle formed by z axis and the direction of the transition moment vector.

G. Favini, A. Gamba, and M. Simonetta:

Table 4A

D-2 (C₂ᵥ)			D-3 (C₂ᵥ)			D-5			D-6 (C₂ᵥ)			D-7 (D₂ₕ)			D-8 (D₂ₕ)			D-9 (D₂ₕ)		
E_i(eV)	pol.	f	E_i(eV)	pol.	f	E_i(eV)	$\cos\phi^a$	f	E_i(eV)	pol.	f	E_i	pol.	f	E_i(eV)	pol.	f	E_i(eV)	pol.	f
−0.893	—	—	−1.984	—	—	−0.797	—	—	−0.458	—	—	−1.545	—	—	−2.110	—	—	−1.545	—	—
2.774	y	0.08	2.490	y	0.00	3.194	0.629	0.13	3.141	z	0.57	2.779	z	1.20	2.769	z	0.49	2.628	z	0.59
3.454	z	0.67	2.953	y	0.12	3.426	−0.783	0.26	3.717	y	0.03	3.434	y	0.02	3.149	y	0.15	3.096	y	0.01
3.539	y	0.01	2.969	z	0.66	3.662	0.000	0.03	3.820	y	0.01	3.863	z	0.04	3.643	y	0.24	3.449	y	0.15
4.900	y	0.44	3.323	y	0.01	3.959	−0.978	0.45	3.901	z	0.66	4.003	y	0.07	5.044	y	0.37	4.519	y	0.03
5.168	z	0.07	4.374	y	0.39	4.243	−0.358	0.31	4.259	y	0.11	4.601	z	0.57	5.668	y	0.37	5.111	y	1.08
5.368	y	0.05	4.495	z	0.00	4.511	0.946	0.13	4.745	y	0.21	4.645	y	0.32	6.153	z	0.02	5.975	z	0.00
			4.519	z	0.01	4.860	0.000	0.05	4.883	z	0.32	4.825	y	0.16						
			5.443	y	0.04	4.891	0.000	0.01	5.034	z	0.02	5.177	y	0.31						
						4.995	−0.552	0.12	5.165	z	0.07	5.539	z	0.12						
						5.048	−0.156	0.68	5.225	y	0.10									
						5.171	0.000	0.05	5.376	y	1.01									
						5.294	0.643	0.42	5.396	y	0.71									
						5.565	0.559	0.33	5.548	z	0.52									

[a] ϕ is the angle formed by z axis and the direction of the transition moment vector.

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