2548 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (10), 2548—2553 (1977) [Vol. 50, No. 10

Comparison of Experimental and Calculated Oscillator Strengths for Condensed Ring Compounds

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(Received March 18, 1977)

The electronic absorption spectra of eighteen aromatic condensed ring compounds (C_{2v} or D_{2h}) were studied by means of comparison between the calculated and experimental results in terms of three fundamental factors: the electronic transition energy, the direction of the electronic transition moment, and the oscillator strength. The three experimental factors were obtained from the component spectra polarized to the long and short axes of the molecule, which were determined by means of the dichroism analysis technique. The calculated oscillator strengths were obtained by the dipole-length, dipole-velocity, and mixed-dipole methods. From the comparison between experimental and calculated results, it was found that the mixed-dipole method gives the best fit of the values to the experimental ones.

As is well known, the electronic absorption spectrum is assigned on the basis of comparison between calculated and experimental results for three fundamental factors: the electronic transition energy, the direction of the electronic transition moment, and the oscillator strength. In most cases, however, the experimental results to be compared with the theory are not always valid for these items, since the results are obtained through band spectra in which most bands are composed of two or more overlapping transition bands. In order to make more precise assignments, therefore, it is necessary to separate the overlapping bands. One of the most useful methods for separating such bands for some symmetrical molecules is dichroism analysis using a stretched PVA [poly(vinyl alcohol)] film.

For a planar molecule of C_{2v} symmetry, for instance, the polarization direction of the π-π^* electronic transitions are restricted to directions parallel or perpendicular to the C_2 axis in the molecular plane. In such cases, the directions of polarization can easily be distinguished from one another by the use of the dichroism analysis. By means of this method, an absorption spectrum observed in non-stretched PVA film can be divided into two kinds of spectra in which the polarization directions are orthogonal to each other. When the divided spectra thus obtained are employed as experimental data, the comparison with the calculated results will become more precise in terms of the three factors mentioned above.

As for the theoretical calculation of the oscillator strength, the dipole-length method[1] has been extensively used. In recent years, however, the mixed-dipole method[2] and the dipole-velocity method[3-5] have also been employed, and comparisons of calculated with experimental values have been reported.

The first purpose in the present study is to determine the oscillator strength experimentally using the component spectra for many symmetrical molecules, such as condensed-ring compounds. The second purpose is to compare the oscillator strengths obtained by the dipole-length, mixed-dipole, and dipole-velocity methods with the experimental values.

Experimental

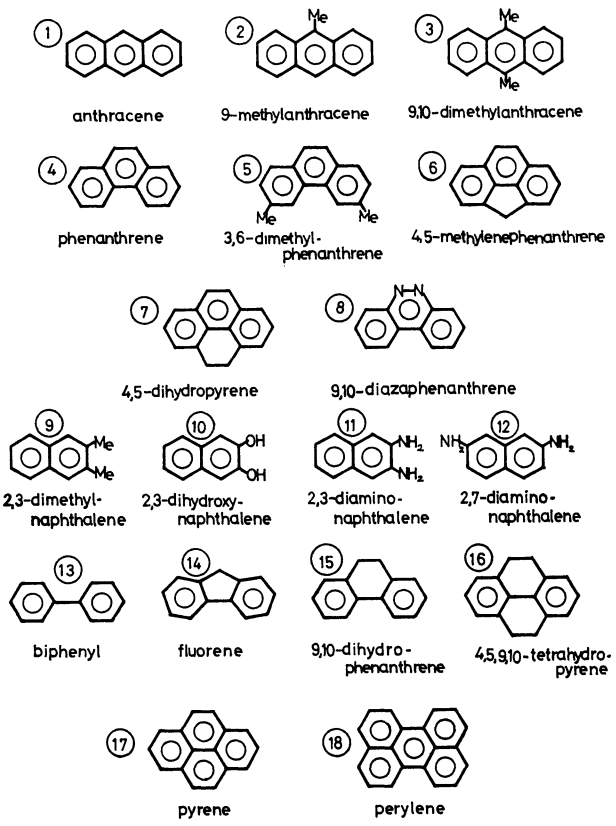

Fig. 1. Name, structures, and numbers for the compounds. (In Table 1, these numbers are employed instead of respective name of compound.)

Materials. The chemical structures and the names of the compounds used are shown in Fig. 1, along with the sample number to be referred to throughout this work.

The anthracene (U.P.; ultra-pure reagent), 9-methylanthracene (G.R.; guaranteed reagent), 9,10-dimethylanthracene (G.R.), 3,6-dimethylphenanthrene (G.R.), 4,5-methanophenanthrene (G.R.), 2,3-dimethylnaphthalene (G.R.), 2,3-naphthalenediol (G.R.), 2,3-naphthalenediamine (E.P.; extra pure reagent), 2,7-naphthalenediamine (E.P.), pyrene (U.P.), biphenyl (E.P.: >99%, G.C.), fluorene (U.P.), 9,10-dihydrophenanthrene (G.R.), and 4,5,9,10-tetrahydropyrene (G.R.) were commercially obtained from the Tokyo Kasei Kogyo Co., Ltd. The phenanthrene(fluorescence grade) and 5,6-phenanthroline were obtained from the Aldrich Chemical Company. Highly purified perylene was kindly offered by the Inokuchi Laboratory at the Institute for Solid State Physics, the University of Tokyo. The biphenyl, 2,3-dimethylnaphthalene, and other naphthalene derivatives were repeatedly recrystallized from the respective appropriate solvents. For 9,10-dihydrophenanthrene and 4,5,9,10-tetrahydropyrene, further purification was made by the Tokyo Kasei Kogyo Co., Ltd., at our request. For other compounds, no purification was made.

Measurement. The measurement of the polarized absorption spectra and the determination of the component spectra were carried out using the methods previously reported.[6)]

After the assignment of the electronic transition bands for the component spectra had been established, the experimental oscillator strength (f^{exp}) for the respective bands were determined by means of the well-known formula:*

$$f^{\text{exp}} = 4.32 \times 10^{-9}\int \varepsilon_\sigma d\sigma$$

where σ is the wave number in cm^{-1} and where ε_σ is the molar extinction coefficient in the PVA substrate. In the present work, however, we used ε_σ in ethanol instead of that in PVA, since the absorption curves in the PVA film generally resemble those in ethanol. In fact, for some compounds, such as anthracene, and phenanthrene, it was found that the ε_σ values in PVA were nearly equal to those in ethanol.

Calculation

The MO calculations were carried out using the Pariser-Parr-Pople SCF CI method.[7,8)] The one- and two-center electron repulsion integrals were evaluated by the Pariser-Parr equation[7)] and the Nishimoto-Mataga equation[9)] respectively. The valence-state ionization potentials ($I_p(r)$) and the electron affinities ($E_a(r)$) were as follows: $I_p(\text{C})=11.16$ eV, $E_a(\text{C})=0.03$ eV, $I_p(\text{-N=})=14.12$ eV, $E_a(\text{-N=})=1.78$ eV, $I_p(\text{-NH}_2)=24.80$ eV, $E_a(\text{-NH}_2)=8.04$ eV, $I_p(\text{-OH})=33.00$ eV, and $E_a(\text{-OH})=11.47$ eV.

For the "methyl" group, the hyperconjugation effect was taken into account after Morita,[10)] and the following values were used: $I_p(\text{H}_3)=10.08$ eV and $E_a(\text{H}_3)=0.19$ eV, the resonance integrals were $\beta(\text{C-C}')=-2.24$ eV and $\beta(\text{C}'\text{-H}_3)=-5.27$ eV where the primed carbon is for methyl carbon. For the methylene group, the same parameters were used as for the methyl group. All the molecules, including biphenyl, were regarded as planar. The geometrical structure of fluorene was determined by reference to the crystal structure.[11)]

The theoretical oscillator strengths, f^{cal}, were calculated by means of the following equations:[2,3)]

$$f_1 = 1.085\times 10^{11}\,\sigma M_1^2 \tag{1}$$

$$f_v = 1.463\times 10^5\, D_v^2/\sigma, \tag{2}$$

$$f_m = (f_1 \cdot f_v)^{1/2}, \tag{3}$$

$$M_1 = \langle \Psi_p | \sum_i r_i | \Psi_q \rangle,$$

$$D_v = \langle \Psi_p | \sum_i \text{grad}\, i | \Psi_q \rangle,$$

where σ is the transition energy in cm^{-1}, for which the calculated values were used. The calculation methods using Eqs. 1, 2, and 3 are referred to as the dipole-length, dipole-velocity, and mixed-dipole methods respectively. In these calculations, Slater's atomic orbitals were employed, and the overlap integrals were not neglected. Moreover, all the elements of the transition density matrix were included.

Results

Table 1 shows the experimental and calculated results for the allowed transitions of eighteen compounds. Roman numerals represent the calculated transition numbers. For example, in the case of anthracene (Sample Number 1), the I st, II nd, and VI th transitions are allowed, while the others are forbidden, in the region above 200 nm. Even if a transition is allowed, when the corresponding absorption is too low to be determined, the relevant columns for the experimental transition energy and also the oscillator strength (f^{exp}) are left blank, as may be seen for the 1st transition of Sample No. 5, for example. Moreover, even if a transition energy is determined, when not all of the band is observed, f^{exp} can not be determined and the relevant column is blank (see the *X*th transition of Sample No. 5).

In Table 1, the transition directions are designated by x and y for the long and short axes of the molecule respectively, and Platt's notations are shown in parentheses. The oscillator strengths calculated by the dipole-length, dipole-velocity, and mixed-dipole methods are denoted by f_1, f_v, and f_m respectively.

According to Table 1, the calculated transition energies as well as the transition directions agree very well with the experimental values. As for the oscillator strength, however, the calculated values are considerably different from the experimental ones in some cases. Moreover, some considerable differences between f_1 and f_v are observed.

Figure 2 shows the distributions of the experimental (f^{exp}) and calculated (f^{cal}) oscillator strengths for the about seventy transitions listed in Table 1. In the figure, the abscissa is divided into sections at 0.1 intervals: for example, the f^{exp} value, 1.54, of the VI th transition of Sample No. 1 is placed in the column between 1.5 and 1.6. Thus, the distributions for f^{exp}, f_1, f_v, and f_m are obtained as shown in Figs. 2(a), (b), (c), and (d) respectively. The f^{exp} and f^{cal} values did not exceed 1.6 and 2.6 respectively. Nearly 90% of all the f values fall in the range of $0<f<1$. The frequencies within $0<f<0.1$ are 30—40% and are the greatest in all classes.

Now, let us investigate the relation between the f^{exp} and f^{cal} values. First, let us select sample molecules in Table 1 for which the π-electron approximation will be completely valid in the present calculation; that is, the five molecules of Samples No. 1, 4, 8, 17, and 18 have a planar structure and no substituent groups. The ratios of the oscillator strength, $R(=f^{\text{cal}}/f^{\text{exp}})$, for the corresponding transitions are plotted in Fig. 3, in which the abscissa is the same as in Fig. 2 and in which the ordinate represents the frequency of R values. In Fig. 3, the R values for $f^{\text{exp}}<0.1$ are marked by oblique lines to distinguish them from the others.

According to Fig. 3(c) all the values of $R_v(=f_v/f^{\text{exp}})$

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* In general, f^{exp} is little affected by the medium. However, we neglected this correction in the present work, since there is some disagreement about this matter. See also Ref. 5 and especially the Ref. 17 in the Ref. 5.

TABLE 1. COMPARISON OF EXPERIMENTAL AND CALCULATED OSCILLATOR STRENGTHS

Sample No.[c]	Transition No.	Transition energy		Oscillator strength				Polarization[b]	
		Calcd kcm^{-1}	Exptl kcm^{-1}	Calcd[a] f_l	f_v	f_m	Exptl f^{exp}		
①	I	26.91	26.2	0.2437	0.0152	0.0609	0.0763	y	(L_a)
	II	28.10	27.6	0.0120	0.0063	0.0087	0.0194	x	(L_b)
	VI	39.17	38.9	2.4135	1.2801	1.7577	1.545	x	(B_b)
2	I	26.11	25.5	0.2614	0.0169	0.0664	0.0867	y	(L_a)
	II	27.82	27.0	0.0202	0.0063	0.0113	0.0201	x	(L_b)
	VI	38.83	38.4	2.4780	1.2159	1.7358	1.455	x	(B_b)
3	I	25.62	24.9	0.2775	0.0255	0.0841	0.127	y	(L_a)
	II	27.70	24.9	0.0188	0.0052	0.0099	0.0232	x	(L_b)
	VI	38.63	37.9	2.4427	1.1884	1.7038	1.080	x	(B_b)
④	I	29.00	28.9	5.9×10^{-4}	4.6×10^{-4}	5.2×10^{-4}	0.0027	y	(L_b)
	II	32.96	33.7	0.3298	0.1225	0.2010	0.171	x	(L_a)
	IV	39.85	(39)	0.4563	0.1213	0.2353	0.272	y	(B_b)
	V	39.87	39.2	1.3009	0.6735	0.8762	0.737	x	(B_a)
	VII	45.25	45.0	0.3078	0.1429	0.2097	0.101	y	
	X	48.85	(46)	0.0790	0.0263	0.0456		(x)	
5	I	28.67		7.3×10^{-4}	4.2×10^{-4}	5.5×10^{-4}		(y)	(L_b)
	II	32.15	33.1	0.4255	0.1847	0.2803	0.198	x	(L_a)
	IV	39.60	(38)	0.4591	0.1227	0.2373	0.352	y	(B_b)
	V	39.64	38.8	1.2838	0.7003	0.9482	0.613	x	(B_a)
	VII	43.79	43.9	0.4943	0.2475	0.3498	0.247	y	
	X	48.46	(46)	0.3208	0.1854	0.2439		(x)	
6	I	28.54		2.5×10^{-5}	1.0×10^{-5}	1.6×10^{-5}		y	(L_b)
	II	32.52	32.9	0.3107	0.1103	0.1851	0.187	x	(L_a)
	IV	38.28	39.1	0.7817	0.4645	0.6026	0.665	x	(B_a)
	V	38.67	37.6	0.4378	0.1192	0.2284	0.317	y	(B_b)
	VII	44.74	44.6	0.2920	0.1205	0.1876	0.223	y	
	X	47.39	43.9	0.4402	0.1885	0.2881	0.217	x	
7	I	28.63		0.0011	4.9×10^{-4}	7.3×10^{-4}		y	(L_b)
	II	32.69	33.1	0.3023	0.0959	0.1702	0.149	x	(L_a)
	IV	38.51	38.2	1.0222	0.5483	0.7486	0.396	x	(B_a)
	V	38.83	37.4	0.4475	0.1424	0.2524	0.279	y	(B_b)
	VII	44.82	43.9	0.3150	0.1232	0.1970	0.169	y	
	X	47.54	45.7	0.5597	0.2505	0.3391	0.317	x	
⑧	I	27.02	27.7	0.0457	0.0062	0.0168	0.0249	y	(L_b)
	II	29.36	31.8	0.5021	0.1364	0.2617	0.154	x	(L_a)
	V	40.11	39.2	1.0652	0.5262	0.7487	0.734	x	(B_a)
	VI	40.57	39.8	0.4609	0.1328	0.2474	0.191	y	(B_b)
	VIII	46.37	45.6	0.0704	0.0268	0.0434	0.071	y	
	IX	48.88	>46.5	0.2405	0.1102	0.1628		x	
9	I	30.66	31.3	0.0046	0.0022	0.0032	0.0011	x	(L_b)
	II	34.02	34.3	0.1596	0.0254	0.0637	0.0879	y	(L_a)
	III	42.90	43.5	1.9731	1.0321	1.4270	1.040	x	(B_b)
	IV	43.57		0.0036	0.0018	0.0026			
10	I	29.72	30.5	0.0439	0.0192	0.0290	0.0267	x	(L_b)
	II	33.41	33.9	0.1324	0.0189	0.0500	0.0581	y	(L_a)
	III	41.55	42.5	0.8730	0.4517	0.6280	0.836	x	(B_b)
	IV	43.04		0.6136	0.3260	0.4473		x	
	VI	44.61	44.1	0.3027	0.1237	0.1935	0.258	y	
11	I	26.55	28.9	0.1206	0.0474	0.0756	0.0572	x	(L_b)
	II	31.13	32.6	0.0382	0.0004	0.0039	0.0346	y	(L_a)
	IV	37.18	39.6	0.7162	0.3668	0.5125	0.642	x	(B_b)
	V	39.88		0.2168	0.1216	0.1624			
	VI	42.72	40.6	0.1215	0.0584	0.0842	0.274	y	
	VIII	45.37	46.0	0.5515	0.2917	0.4011		x	
12	I	26.88	29.4	0.0855	0.0334	0.0534	0.0409	x	(L_b)
	II	30.02	32.1	0.0658	0.0037	0.0156	0.0168	y	(L_a)
	III	36.09	39.6	1.0014	0.5530	0.7442	1.033	x	(B_b)
	V	41.97	45.8	0.3496	0.1490	0.2282	0.147	y	
	IX	48.05	48.0	0.3319	0.1438	0.2185		x	
13	I	34.63	34.5	6.0×10^{-4}	1.5×10^{-4}	3.0×10^{-4}	0.6×10^{-4}	y	
	III	36.40	39.0	0.7684	0.4420	0.5828	0.293	x	
	VI	48.85		0.8038	0.2970	0.4886		y	
14	I	33.95	32.6	0.0008	0.0026	0.0015	1.0×10^{-4}	y	
	II	34.62	33.1	0.0558	0.0230	0.0358	0.0623	x	
	III	35.76	37.6	0.4751	0.2811	0.3654	0.404	x	
	IV	45.09	44.9	0.2724	0.0986	0.1638		x	

Table 1. (continued)

Sample No.[c]	Transition No.	Transition Energy Calcd kcm^{-1}	Transition Energy Exptl kcm^{-1}	Oscillator strength Calcd[a] f_l	Oscillator strength Calcd[a] f_v	Oscillator strength Calcd[a] f_m	Oscillator strength Exptl f^{exp}	Polarization[b]	
15	I	34.15	31.7	8.2×10^{-5}	2.7×10^{-5}	4.7×10^{-5}	2.0×10^{-4}	y	
	II	34.59	33.2	0.0020	0.0029	0.0024	0.0369	x	
	III	35.86	37.3	0.6394	0.3472	0.4712	0.296	x	
	IV	45.33	45.3	0.1438	0.0444	0.0789	0.103	x	
	V	46.54	46	0.1709	0.0988	0.1299		y	
16	I	33.56	32.6	7.0×10^{-6}	1.1×10^{-5}	8.8×10^{-6}	4.4×10^{-4}	y	
	III	35.03	33.9	0.5460	0.3130	0.4143	0.298	x	
	VI	46.71	45.3	0.8172	0.4047	0.5751	0.578	y	
	VII	47.28	(46)	1.2852	0.4185	0.7334		x	
⑰	I	27.05	26.8	0.0034	0.0014	0.0022	0.0014	y	(L_b)
	II	28.00	29.4	0.6723	0.1841	0.3518	0.326	x	(L_a)
	V	38.17	36.4	0.8322	0.2401	0.4470	0.418	y	(B_b)
	IX	43.57	41.2	1.3143	0.6054	0.8920	0.750	x	(B_a)
⑱	I	23.40	22.6	0.8037	0.2126	0.4611	0.332	x	
	II	28.60	(27.3)	0.0121	0.0046	0.0074	(0.019)	y	
	IX	40.04	37.8	1.4677	0.5515	0.8025	0.592	y	

a) The calculated oscillator strengths, f_1, f_v, and f_m, represent the values from the dipole-length method, the dipole-velocity method, and the mixed-dipole method respectively. b) Where x and y show the polarization directions paralle to and perpendicular to the molecular long axis respectively; the signs in parentheses are Platt's notations. c) Circles indicated in the first column show the selected samples.

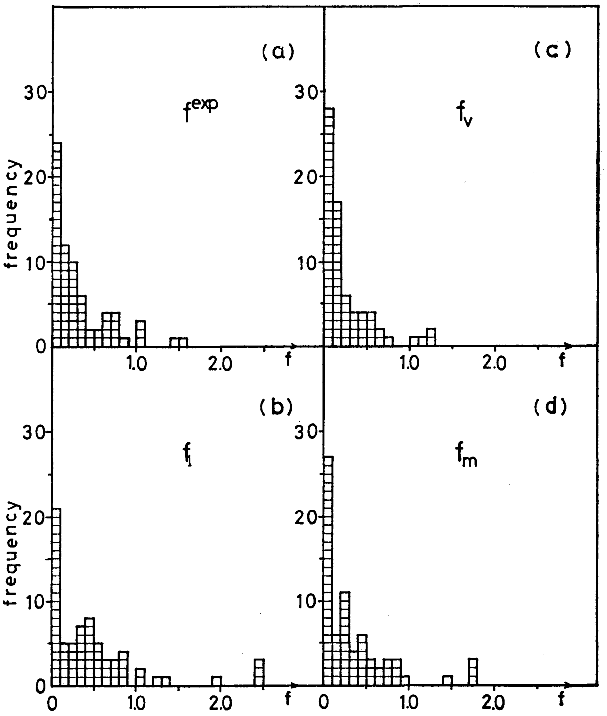

Fig. 2. Distributions of absolute oscillator strength for f^{exp} (a), f_l (b), f_v (c), and f_m (d); The ordinate, the number of frequencies and the abscissa, the absolute oscillator strength classed at 0.1 intervals.

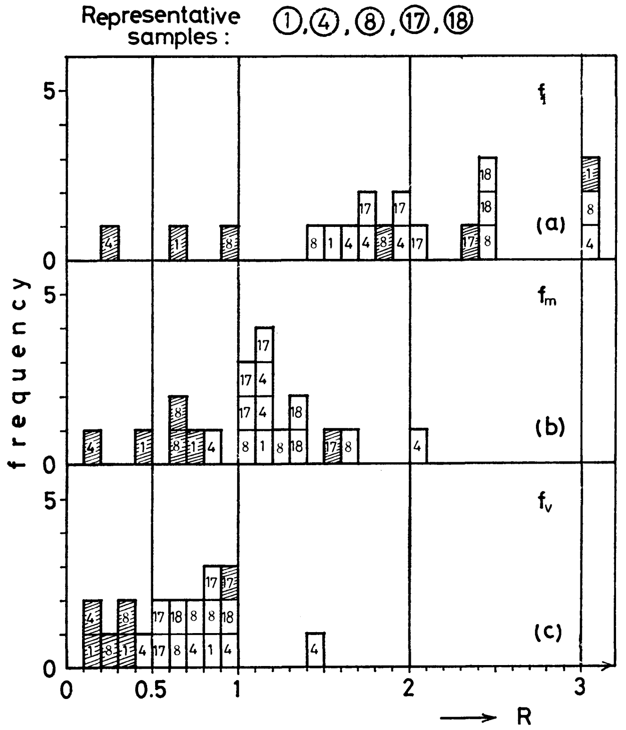

Fig. 3. Distributions of relative oscillator strength; (f_l/f^{exp}) (a), (f_m/f^{exp}) (b), and (f_v/f^{exp}) (c) for the representative compounds. The ordinate, the frequencies and the abscissa, the relative values, $R=(f^{cal}/f^{exp})$ at 0.1 intervals. The shaded parts represent the R values for $f^{exp}<0.1$.

except one ($R_v=1.5$, the VIth transition of Sample No. 2) are less than unity, and most of those for $f^{exp}<0.1$ are less than those for $0.1<f^{exp}$. On the other hand, Fig. 3(a) shows that the values of $R_l(=f_l/f^{exp})$ are scattered widely around 3. The values of $R_m(=f_m/f^{exp})$ shown in Fig. 3(b) fall between the former two values, and it is noticed that the values for $0.1<f^{exp}$ are concentrated in the range of 1.0—1.5.

Figure 4 shows the distributions of the R values for all the transitions in Table 1. The interrelation among R_v, R_m, and R_l is similar to that for the selected samples in Fig. 3.

From these results, the following relations are generally obtained:

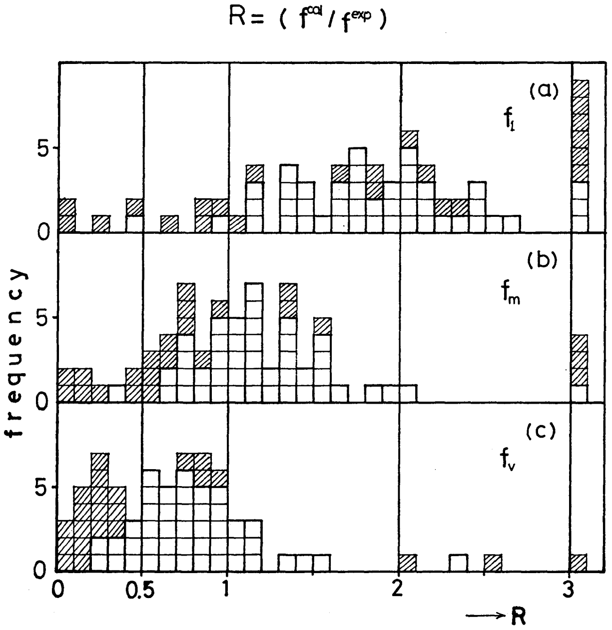

Fig. 4. Distributions of relative oscillator strength, $R = f^{\text{cal}}/f^{\text{exp}}$, for all compounds used in the present work. The shaded parts represent the R values for $f^{\text{exp}} < 0.1$.

$$f_v \lesssim f^{\text{exp}} \lesssim f_l, \text{ and } f_v \lesssim f_m \lesssim f_l.$$

Moreover, in the comparison of the experimental and calculated values, since, in practical absorption spectra, intensity-borrowing phenomena usually occur, even if the calculated values are exact ones, for weak intensity bands the $f^{\text{cal}} < f^{\text{exp}}$ relation is to be expected. In fact, in the figures of distributions of the R values for f_m and f_v, the shaded parts ($f^{\text{exp}} < 0.1$) mainly lie in the classes with relatively low values.

Discussion

In the present investigation, we determined the experimental oscillator strength (f^{exp}) from the component spectra obtained by the application of the dichroism analysis, thinking that the f^{exp} value to be compared with the calculated value should be determined for the corresponding single electronic band. That the f^{exp} values thus obtained are quite reasonable can be shown by the following example. For the first band of anthracene, the experimental oscillator strength has been given as 0.10—0.11.[13–15] It is well known that this band is composed of ^1L_a and ^1L_b bands. According to Table 1 (Sample No. 1), they are $f^{\text{exp}}(L_a) = 0.0763$ and $f^{\text{exp}}(L_b) = 0.0194$, the sum of these values gives 0.096, which is very close to the above conventional value. For the strong second band (^1B_b) of anthracene, the conventional values reported are 1.4—2.8;[13,15,16] among them, the value of $f = 1.56$ is considered as the best one.[5] Table 1 shows that $f^{\text{exp}}(^1B_b) = 1.545$. Since it is known that this band is a little overlapped, the value of $f = 1.56$ may be regarded as reasonable.

In view of the above, the f^{exp} values which used to be compared with f^{cal} in the studies of the oscillator strength were not always reliable. However, if the band in question is not overlapped, such as the first band of linear polyenes, its f^{exp} value is reliable.

From the study of the oscillator strength for the linear polyenes, biphenyl linear polyenes, *etc.*, Chong *et al.*[3,4] found that the f_l/f^{exp} ratio ranges from 2 to 5, whereas f_v/f^{exp} varies from 1 to 0.5; they concluded that f_v is much better than f_l. The same conclusion was derived from the study of naphthalene, anthracene, *etc.* by McHugh and Gouterman.[5] They obtained a quantity relatively independent of the overlapped bands and intensity borrowing by integration over the complete experimental absorption curve. Using these quantities, they compared M_l and D_v (see Eqs. 1—3) and found that D_v is superior to M_l and that consequently, f_v is superior to f_l, in comparison with the experimental (f^{exp}) value. Furthermore, they concluded that f_v is superior to the f_m employed by Hansen.[2]

On the other hand, as is shown in our results, both f_v and f_m are much better than f_l in comparison with the experimental (f^{exp}) values; moreover, f_m is superior to f_v, as is shown in Figs. 3 and 4. It is natural from the forms of Eqs. 1—3 that f_m falls between f_l and f_v. According to Hansen,[2] when the doubly excited configuration is taken into account, f_l and f_v are considerably changed, while f_m shows less sensitivity. This means that even if the electron correlation is taken into account, f_m is still superior to f_l and f_v.

Incidentally, one advantage of employing f_m is that the transition energy is unnecessary in the calculation. Therefore, in contrast to f_l and f_v, one can avoid the problem of whether to use the experimental or theoretical transition energy in the calculation of the oscillator strength. (In this connection, Chong *et al.* used the experimental values.)

De Bruijn[17] calculated f_l and f_v by considering the overlap integral and CI for alternant hydrocarbons. He concluded that a complete CI does not give much improvement in f^{cal} and that the failure in f^{cal} is partly attributable to the deficiency of the simpler MO-levels and partly to the neglect of the polarization of the σ-electrons. He pointed out that the overlap integral is effective in the f_v calculation. Especially, from a comparison of f_l and f_v for the S_j-S_0 transitions of naphthalene and anthracene, he concluded that the inference of Chong *et al.* is not generally valid. However, as has been already pointed out, these considerations do not seem appropriate, since the f^{exp} values employed in his study have some problems.

Finally, it should be emphasized here that the inclusion of the off-diagonal terms of the transition density matrix in the calculation of the oscillator strength, especially by the dipole-length method, sometimes becomes very important, though the off-diagonal elements have been disregarded in almost all cases.[18,19] An example is indicated for the very weak transitions on the longest-wavelength sides of the first bands for pyrene, phenanthrene, biphenyl, *etc.*, which are well known to be ^1L_b bands. (Ex.: for pyrene, $f^{\text{exp}} = 1.4 \times 10^{-3}$). For these transitions, the conventional calculated values are always zero; *i.e.*, $f_l(\text{diagonal}) = 0.000$. On the other hand, relatively good values for the corresponding f^{exp} values are obtained by the inclusion of off-diagonal terms. (Ex.: for pyrene,

f_1(diag.+off-diag.)$=3.4\times10^{-3}$.) (See Table 1.) The same relation holds for naphthalene, which was not taken up in the present study. This may also be extended to a general case; that is, the inclusion of the off-diagonal terms gives a non-zero finite value for a transition which is group-theoretically allowed, but f_1(diagonal) is zero.

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