Combining State Gap from Optical Dichroism of Diffuse Vibronic Spectra

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Abstract

Quantum-mechanical microscopic reversibility of vibronic transitions and Boltzmann thermal distribution of the initial (starting) states substantiate method to obtain pure-electronic transition frequency from diffuse absorption or emission spectra. It is shown, that the information is obtainable immediately from linear and circular dichroism spectra or ratio of polarization spectra when the spectra present non-identical ensembles of chromophores. The examples to obtain pure-electronic gap from experimental spectra of linear or circular dichroism are given. The approach allows selecting molecular chromophor ensembles by polarization and evaluating their combining states zero-gap.

Keywords: Linear Dichroism, Dissymmetry Factor, Combining States Zero-gap, Chirooptics, Magnetic Optical Activity, Chromophore Polymorphism.

Introduction

The ways to obtain zero-gap of states combining at optical vibronic transition by simple recalculation from separate diffuse absorption or emission spectra are proposed and testified for different media [1-7]. The approach was applied to molecular chromophores in vapor state [1-3], solutions [1, 2], as molecular markers [4], to F-centers and doped glasses [5], molecular crystals and quantum dots [6] and at optical activity [7]. General conclusion from the experimental tests is that the approach is actual for homogeneous chromophore ensembles. It shows that using maxima of spectra as levels zero-gap is rather approximate. At low temperature the method is complicated by narrow population zone, degeneration and inhomogeneity [6, 8]. Side result of the approach is the possibility to detect inhomogeneity of chromophores or chromophore incorporating cells qualitatively [4, 6]. In previous papers of the author the application to dichroism was given in passing. Here the approach to linear and circular dichroism is considered in some detail.

General conception

The polarized absorption or luminescence of homogeneous chromophore ensembles obeys crossection relations on the above model principles [1-7]. As chromophore optical crossection $s(n)$ is proportional to $e(n)/n$ or to $I(n)/n^4$ so the absorption coefficient $e(n)$ and emission intensity $I(v)$ include the frequencies of purely electronic transitions v_0 from the ground (n_0^a) in form

$$(e(n) / n) / \exp(hn / 2kT) = j^a(|n - n_0^a|), \quad (1)$$

and from the excited states (n_0^e) in form

$$(I(n) / n^4) \times \exp(hn / 2kT) = j^e(|n - n_0^e|) . \quad (2)$$

The functions j have extremum at n_0 and are symmetrical in the area of an order kT about that point [6, 8]. It was shown [3] that n_0 corresponds to frequency at minimum of average energies sum of combining states. As the relations (1) and (2) are actual for any not only orthogonal different polarizations of photons $i \neq j$ it results:

$$e_i(n) \, / \, e_j(n) = \; j_i^a(|\, n - n_{0i} \,|) \, / \, j_j^a(|\, n - n_{0j} \,|) \;\; (3)$$

and

$$I_i(n) \, / \, I_j(n) = \; j_i^e(|\, n - n_{0i} \,|) \, / \, j_j^e(|\, n - n_{0j} \,|) \, . \; (4)$$

So the normalized coefficients of dichroism and circular dissymmetry factors according (3) and (4) are of form

$$(\sigma_i(v)/\sigma_j(v)-1)/(\sigma_i(v)/\sigma_j(v)+1) =$$
$$= (\varphi_i(v)/\varphi_j(v)-1)/(\varphi_i(v)/\varphi_j(v)+1). \quad (5)$$

For $\sigma_i(v) \neq \sigma_j(v)$ in the relations (3), (4) and (5) the ratio of $j_i \, / \, j_j$ as of partial functions of parent constituents of chromophore ensemble has general extreme area. The extremums have an general point v_{0ij} which join the extreme points n_{0i} and n_{0j}. In the following the test will be done of the relations on experimental data.

Approaches

The linear and circular dichroism applies similar technology of measurements, but are different in physical nature. The linear one is based on electrical anisotropy, as circular one has additional magnetic components. It may differ in relation to basic here principle microreversibility. So we will divide in following the consideration on linear and circular dichroism.

1. Linear Dichroism

It was found [6] that regions of extreme point at n_0 found by (2) and (5) almost coincide. Fig. 1A shows that locations of n_0 obtained from excitation and coefficient anisotropy spectra of 1,3,5-triethynylbenzene–dithienyldiketopyrrolopyrrole–2,2':5',2''-terthiophene in a thin polymer film (Zeonex) [9] coincide. Fig. 1B presents 9-methyladenine in stretched PVA film spectra of isotropic absorption and reduced linear dichroism (LD$_r$), magnetic circular dichroism (MCD) measured in neutral aqueous solution, and fluorescence excitation anisotropy (FA) in EPA glass at 80 K (4) [10]. Calculated from absorption and MCD spectra

of $\ln\varphi^a$ and $\ln\varphi^{MCD}$ have the extremum which coincide with ones of LD_r and FA^- from [10]. All the extremum ranges locate the same ν_0.
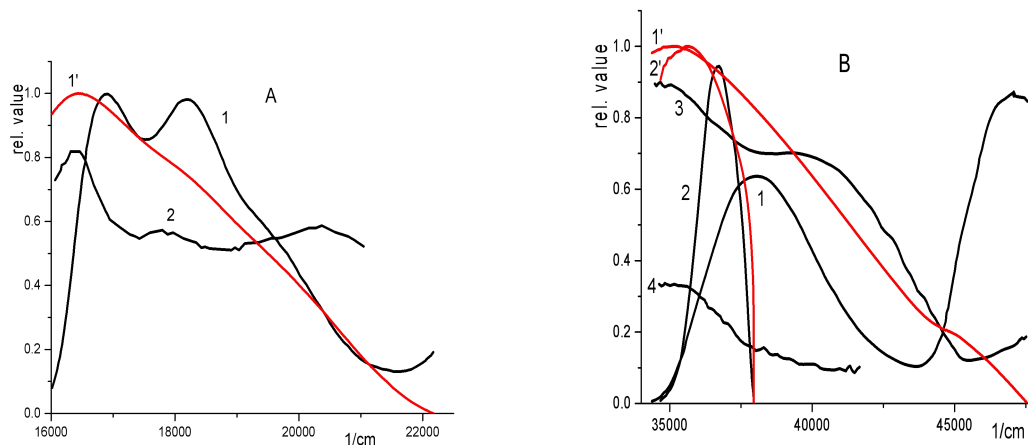

Figure 1. **Locations of n_0 for excitation and coefficient anisotropy spectra: A - excitation (1) and fluorescence anisotropy (FA) (2) spectra of 1,3,5-triethynylbenzene-dithienyldiketopyrrolopyrrole-2,2':5',2''-terthiophene in polymer film Zeonex [9]; and $\ln j^a(n)$ (1') spectrum; B - 9-methyladenine absorption (1), MCD (2), LD (3); FA in EPA glass at 80 K (4) [10]; $\ln\varphi^a$ (1') and $\ln\varphi^{MCD}$ (2') spectra.**

The molecular single crystals have rather homogeneous chromophore, as observed for single crystals of uracil and 1.3-dimethyluracil [11]. The coincidence of n_0 found by extreme point of j-function, or of e_i/e_j and of normalized LD coefficient $LD_r = (e_i/e_j - 1)/(e_i/e_j + 1))$ is shown in Fig. 2. The thymine single crystal absorption spectra for orthogonal polarization along axes a and c are given in Fig. 2A [11] as the spectra of e_c/e_a and of j^a. It is shown [11] that unit-cell of thymine crystal consist from four thymine molecules, which are differently oriented inside of unit-cell. So absorption spectrum $\|a$ is based on more homogeneous chromophore orientation in crystal unit-cell then of $\|c$ one as shown by extremum area of j-functions. Nevertheless n_0 from j^a-functions and from relation e_c/e_a coincide well. In Fig.

¯Here and in the preceding papers [1-7] the $\ln j(n)$ spectrum is usually applied to better oversee the extreme point region, but *it is crude to locate* n_0 as will be shown in figure 5B.

2B the spectra of single crystal of sodium uridine-5'-phosphate are presented. Here the absorptions for polarization in plane $\|Z$ and $\|X$ are considered, where Z and X are main optical axes of the crystal [11]. According to j^a spectra for both polarizations the chromophores are rather homogeneous though broadened differently. The reason of that may be difference in labilities of unit-cell molecules. Spectrum of e_X / e_Z shows narrow extreme point region (minimum) and fits the region of the absorption spectra.
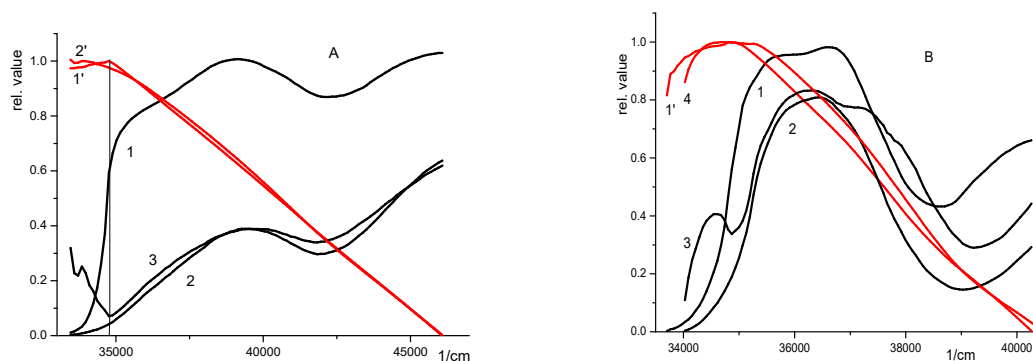

Figure 2. Spectra of single crystal absorption of orthogonal polarizations. Thymine (A): 1- absorption $\|$a axis plane, 2- absorption $\|$c axis plane [11]; 3- e_c / e_a , 1'- ln j_a^a , 2'-ln j_c^a spectra. Sodium uridine-5'-phosphate (B): 1- absorption $\|$Z plane, 2- absorption $\|$X plane [11]; 3- e_X / e_Z , 1'- ln j_Z^a , 2'- ln j_X^a spectra.

2. Chirooptical Dichroism

The basic assumption of the tested method is implied that probability of transitions between two elementary states under external optic perturbation is reversible if operator of perturbation is hermitian. The magnetic components in chirooptics bring additional physics into the mechanism of perturbation. The application of considered method in chirooptics will give additional information on the problem and actuality of tested approach. It will be shown by experimental data in what follows.

In Figure 3A n_0 obtained from extreme points of $j^a(e)$, j^{CD} and e^a / e^{CD} from absorption and circular dichroism (CD) spectra of thymidine at pH 7 in water [12] are determined. All locating v_0 extreme points coincide. The same result is obtained from fluorescence, CPL and absorption dissymmetry (g_{abs}) spectra of planar chiral 4,7,12,15-tetrasubstituted

[2.2]paracyclophane (S_p)CP3) film [13] that is shown in Figure 3B. (The mirror structure of the substance is on scheme (R_p)CP3 [13]). The shortwave shift of zero-point extremum of integral luminescence may be explained by input of non-chiral chromophores.
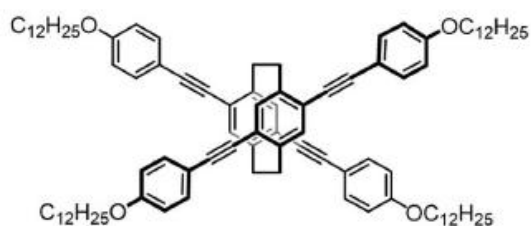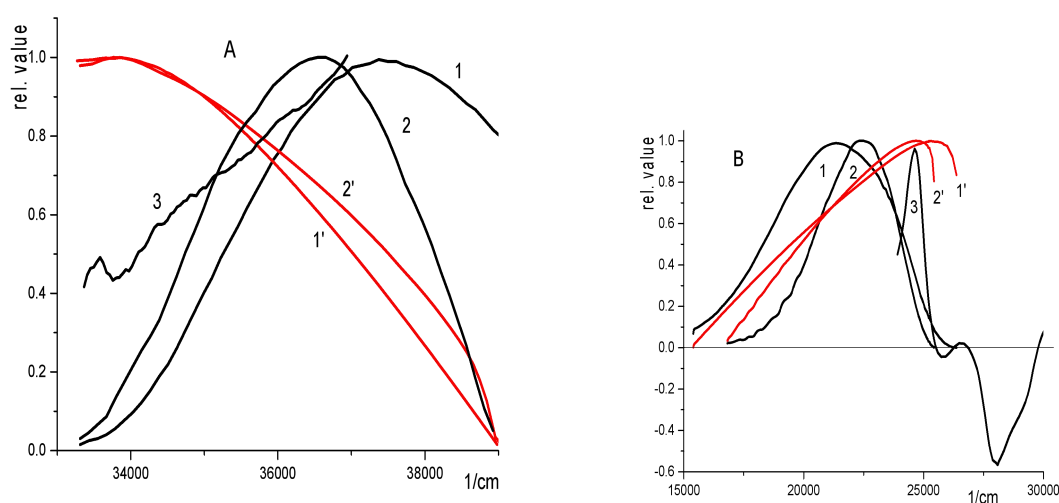

(R$_p$)CP3 [13]

Figure 3. A - Thymidine in water at pH 7: absorption (1), CD (2) and $\varepsilon_a^a / \varepsilon_{CD}^a$ (3) spectra [12]; and calculated ln $j^a(n)$ (1') and ln $j^{CD}(n)$ (2'). B – 4,7,12,15-tetrasubstituted [2.2]paracyclophane ((S_p)CP3) film: absorption (1), CPL (2) and absorption dissymmetry factor g_{abs} (3) spectra [13]; ln $j^e(n)$ and ln $j^{CPL}(n)$ spectra.

Figure 4 is based on thorough paper on circular dichroism (CD) and optical activity of luminescence (CPL) made by Morisaki et al. [14] of shown in insert [2.2]paracyclophane derivative structure. Chirooptical data show full coincidence locals of n_0 found by all three approaches. (The extreme point on the plot2' in region near 25000 cm^{-1} is the side-effect

because of overlapping of different electronic bands where the method is inoperative [3]). Quite different picture is seen in Figure 4 for the luminescence. Though the regions of integral luminescence and CPL extreme areas are close they are very broad. The narrow regions of extreme point in absorption indicate homogeneous distribution of ground state chromophores, contrary by luminescence manifested inhomogeneity of excited state chromophores. For integral luminescence $n_0 = 24900$ cm^{-1}, for CPL $n_0 = 25600$ cm^{-1} and for g_{lum} $n_0 = 24700$ cm^{-1}, as for absorption all values $n_0 = 24780 \pm 50$ cm^{-1}. The reason of excited state inhomogeneity may be emission on different time stage of prolonged the excited molecule relaxation. The broadened form of extremum of luminescence g_{lum} spectra is typical for all observed [2.2]paracyclophane extended π-system derivatives [14,15].
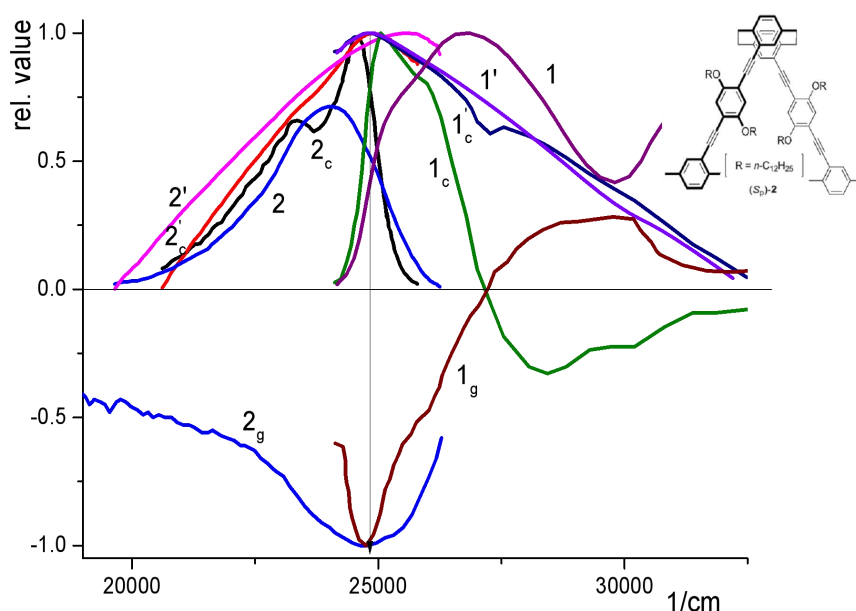

Figure 4. Spectra of [2.2]paracyclophane derivative (shown S$_p$ form) in CHCl$_3$ solution : absorption (1), CD (1$_c$) and g$_{CD}$ factor (1$_g$); integral fluorescence (2), CPL (2$_c$) and g$_{CPL}$-factor (2g) [14]. Calculated: 1' - $\ln j^a$ **,1'$_c$ -** $\ln j^{CD}$ **, 2' -** $\ln j^{FI}$ **, 2'$_c$ -** $\ln j^{CPL}$ **. The arrow indicates common** n_0 **.**

In Figure 3 and 4 it is shown that the substantiating assumptions in above hold for natural chirooptical vibronic spectra. A problem stayed with magnetic induced optical activity.

By above approaches the published magnetic chirooptical spectra are elaborated. In Figure 5 the values of n_0 of absorption and magnetic circular dichroism (MCD) spectra [16, 17] are compared. In Figure 5A the extreme points for n_0 of 2'.3'-isopropylidene-3.5'-cycloguanosine (IPG) at pH 2 and pH 7 are given [16]. At pH 2 the form and place of the extremum of absorption and magnetic circular dichroism (MCD) spectra coincide. At pH 7 they are shifted to longwave side and differ in extremum range and in frequency. The broad extremum range for integral absorption one may explain by presence of non-chirooptical absorbing chromophores. In Figure 5B the spectra of φ^a, φ^{MCD}, $\ln j^a$, $\ln j^{MCD}$ and e^a / e^{MCD} are compared. The minimum of e^a / e^{MCD} is near the range of j-extreme points. Note coinciding extreme points of MCD and of integral absorption.
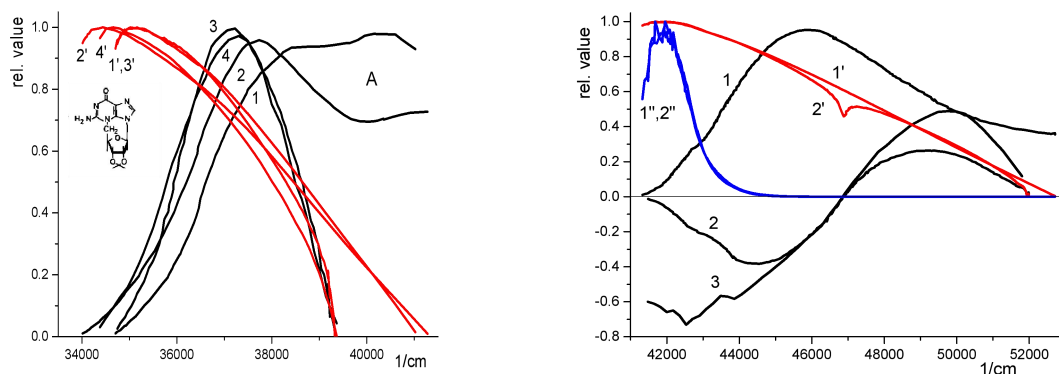

Figure 5. Absorption and MCD spectra. IPG absorption of solution at pH 2 (1) and pH 7 (2); MCD at pH 2 (3) and pH 7 (4), spectra [16] (A), and corresponding $\ln j$-value spectra (1'-4'). Absorption (1) and MCD (2) spectra of 2.5-Dimethylfuran in n-hexan [17] (B) and calculated spectra of $\ln j^a$ (1'), $\ln j^{MCD}$ (2') and e^a / e^{MCD} (3), φ^a (1"), φ^{MCD} (2").

Conclusion

All positive application of linear and circular polarization dichroism spectra for determining the zero-gap of vibronically combining states are supported by comparison with that obtained

from vibronic spectra. The approach is in some aspects preferable as to escape of recalculation φ-function and to use ratio of any pair of experimentally favorable polarizations spectra to determine ν_0, not only standard orthogonal ones. But is a complicated detail: there are many spectra of g_{abs} and g_{lum} in literature which are constant over the region of spectrum. That is not controversial to relations (3)-(5), as it shows direct identity of chromophor ensembles being relative to polarization.

The presented data shows that natural and magnetic induced circular dichroism follow the proposed microreversibility. It seems that there is no significant difference in presentation n_0 by CD or MCD of the same chromophor ensemble. The considered methods allow to manoeuvring at determination of the excited state gap, chromophor inhomogeneity and some other spectroscopy approaches. As the position of n_0 region for diffuse vibronic spectra usually is situated on low intensity antistokes wings of spectra, so the methods are very sensitive to chromophor non-homogeneity by another chromophore additives, impurities. Optical anisotropy methods allow to by-pass some obstacles to select the interesting chromophore ensembles.

Acknowledgement

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