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Chromophor Inhomogeneity Indication by Diffuse Vibronic Spectra

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Abstract: Determination of gap between optically combining states (0-0- transition) from diffuse vibronic absorption or emission spectra is possible now for homogeneous ensembles of chromophores. If the observed spectra present composite polymorphic chromophores or different species they are formed by partial spectra and differing electronic transitions. For these conditions the indicating pure-electronic transition frequency attribute is distorted, smeared or even absent. That behavior is qualitative indication of the chromophore inhomogeneity. The same would be because of impurities. It is shown that the approach of inhomogeneity qualitative indication by spectra is adaptable to different structural forms of chromophor and at polymorphic sites of containing the chromophore media. The experimental data show that the approach is applicable to see the chromophore inhomogeneity by linear and circular vibronic spectra even of molecular dye-labels. The examples of observed distortions for the spectra of different composite species in different media as manifestation of their inhomogeneity are given. As the region of indication 0-0-transition is situated at low intensity antistokes wings of spectra the sensitivity to inhomogeneity is high as to hindrance by impurities and measurement precision.

Keywords: Optical Spectra, 0-0-Electronic Transition, Inhomogeneity of Chromophores, Spectral Inhomogeneity, Impurities Indication, Molecular Labels Homogeneity

1. Introduction

The application of basic quantum-theoretical microscopic reversibility principle to forming spectra mechanism of vibronic transitions with the thermal equilibrium in optical transition starting state have lead to new method of determining gap between combining in vibronic transition electronic states. The method was applied to molecular chromophores in vapor state and solutions [1-3], molecular crystals and quantum dots [4], F-centers and doped glasses [5] and molecular markers [4, 6]. Everywhere the homogeneous forms of chromophor gave single definite gap of states combining in electronic transition. For all the media the inhomogeneity was observed in different forms of development. It was observed evolution of doped glass inhomogeneity with time of annealing up to homogeneous [7] or transformation of diamond nanoparticles with annealing temperature from inhomogeneous form to homogeneous one [8]. Recently it was found that the method is applicable in natural and magnetically induced chirooptics

[9]. It was shown by this highly selective spectroscopy of complex molecules that integral linear spectra of the chiral substances often show lower homogeneity than chiral spectra. It is understandable.

2. Theory

It is found [1, 3] that for homomorphic chromophores in the vicinity of pure-electronic transition the crossection spectra $\sigma(\nu)$ on the frequencies ν obey relation:

$$\sigma(\nu) \cdot \exp(\mp h\nu / kT) = \varphi(|\nu - \nu_0|) \qquad (1)$$

with "-" for absorption, "+" for emission; $h\nu_0$ is purely electronic gap between optically combining electronic states. The relation states symmetry around ν_0, extremum in the adjacent area. Function φ prevails in the regions $\nu > \nu_0$ for absorption and $\nu < \nu_0$ for emission, i.e., is valid in the Stokes regions where the involvement of initial, starting in the

transition sublevels is not limited by energy, but it extends to opposite side of ν_0 on range of the thermal kT order [4]. As the crossection $\sigma(\nu)$ in Eq. (1) is proportional to $\varepsilon(\nu)/\nu$ or $I(\nu)/\nu^4$ it is more convenient to use instead of (1) the usual absorption $\varepsilon(\nu)$ and emission spectra $I(\nu)$ in form:

$$\ln(\varepsilon(\nu)/\nu) - h\nu/2kT = \ln(\varphi^a(\nu)) \qquad (2)$$

or

$$\ln(I(\nu)/\nu^4) + h\nu/2kT = \ln(\varphi^e(\nu)) \qquad (3)$$

to analyze the location and form of $\varphi(\nu)$ extremum.

When the absorption coefficient $\varepsilon(\nu)$ at a given frequency ν is the sum of partial absorption coefficients $\varepsilon_i(\nu)$ of forms i chromophores in the medium, (1) becomes as:

$$\left[\sum_i \varepsilon_i(\nu)/\nu\right] \cdot \exp(-h\nu/2kT) = \sum_i \varphi_i(|\nu - \nu_{0i}|). \qquad (4)$$

It is vivid that it is not symmetric like Eq. (1) and even may have no extremum if ν_{0i} are not close [4, 6]. Similarly, for emission intensity $I(\nu)$ it is

$$\left[\sum_i I_i(\nu)/\nu^4\right] \cdot \exp(h\nu/2kT) = \sum_i \varphi_i^e(|\nu - \nu_{0i}|). \qquad (5)$$

The distorting of stating by (1), (2) or (3) extremum indicates that the chromophor is polymorphic according to (4) or (5) [4, 6]. The situation by (4) and (5) is observed too when the spectra of different electron transitions of the same chromophores overlap. The problem is complicated and the way to the approach was considered particularly [3].
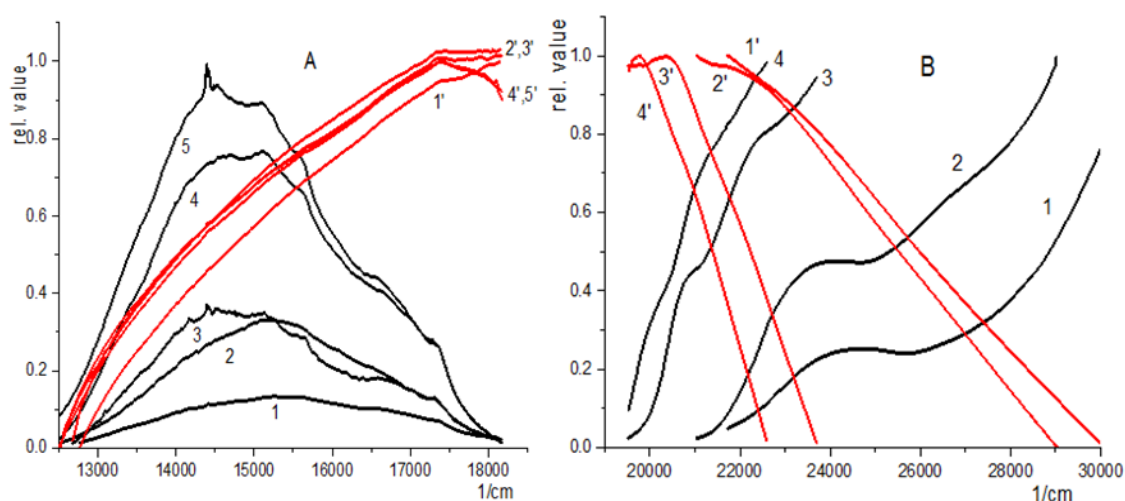

Figure 1. Transformation of micro object spectra along modification process. A are fluorescence spectra of diamond nanoparticles, obtained by oxidation in air with no annealing (1) and after annealing at temperatures 2- 650°C, 3- 700°C, 4- 800°C, 5- 900°C [8]; 1'-5'are the corresponding $\ln \varphi^e$ (as usual throughout normalized in interval [0,1]) [4]. B are the change of absorption spectrum of glass doped with $CdS_{0.9}Se_{0.1}$ crystallites after annealing at 650°C for 1 (1), 4 (2), 8 (3), and 16 h (4) [7] and the corresponding evolution of $\ln \varphi^a$ (1' - 4') [5].

3. Application

For example, absorption spectra of vapor state uracil and 1.3-dimethyluracil were compared in that way [2]. Their ν_0 was determined by jet-cool spectroscopy and theoretical calculations. Uracil does not show extremum. The explanation is the well-known extensive tautomerism (up to seven tautomers) that persists to the temperature of the given spectrum (211°C). Methyl substituents of 1,3-dimethyluracil prevent the tautomerism so ν_0 determined by this and jet-cool methods were practically the same. Compounds allowing tautomerism did not exhibit 0-0-transition extremum in the gas phase according to our observations. In a similar manner, the methyl substituents prevented tautomerism. For example, 1,3-dimethylhypoxanthine in the gas phase (200°C) by it's UV absorption spectrum exhibits a well-resolved 0-0-transition extremum about 32900 cm^{-1}. However, the 0-0-transition extremum is missing for the absorption spectrum of

9-methylhypoxanthine vapor (273°C) because the molecule tautomerism is activated at high temperatures. For example, that was observed for tautomerism behavior of uracil, adenine and hypoxanthine. The "anomalies" show the possibility to analyze chromophores inhomogeneity by this approach [4, 6], so have practical interest.

In Figure 1 are given examples of micro objects absorption and fluorescence spectra transformation along the processes of technical modification. In Figure 1A the processes of annealing of diamond nanoparticles are given [8]. It is seen that in the first stages at lower temperatures the extremum is absent. But for temperatures 800-900°C when the process of modification is finished the extremum and ν_0 are fixed well. Figure 1B shows process transformation of glass doped by annealing. $CdS_{0.9}Se_{0.1}$ crystallites in time [7]. At first stages of annealing the chromophores of glass are polymorphous. The results are in full absence of extremums. After longer time of annealing the chromophores ordered homogeneously and ν_0. is manifested.

In Figure 2 the emission spectra of graphene quantum dots (GQD) obtained by two different technologies are given and homogeneity of structure is determined. Figure 2A shows excited by different light waves emission spectra of obtained by chemical synthesis GQDs C132 [10, 11]. The spectra differ. It is because, probably, participating of differently populated emitting levels. But upper emitting level is conserved showing the homogeneity. On Figure 2B are given GQDs spectra produced by mechanical-chemical method [12]. They are inhomogeneous by technology. There are emission spectra of three forms of chemically modified GQDs but no one have signs of homogeneity.
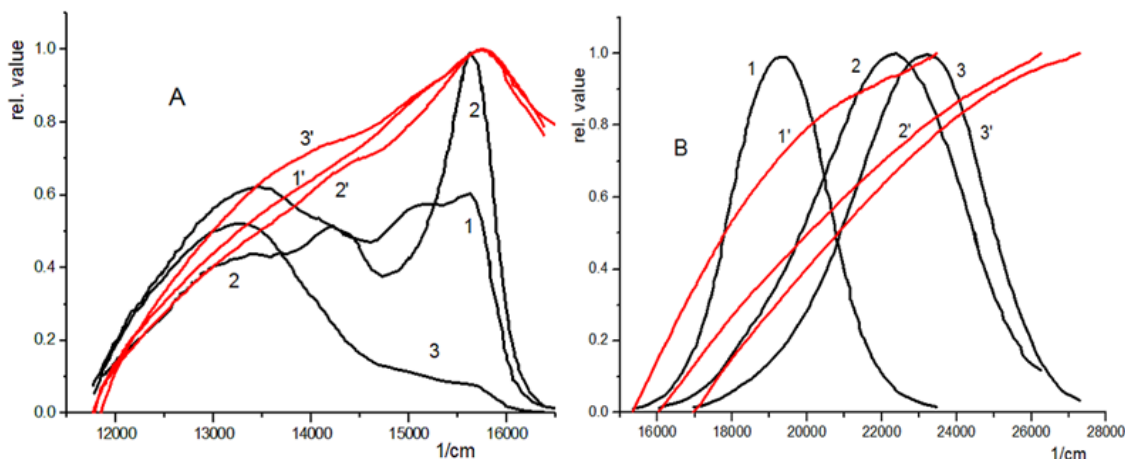

Figure 2. Emission spectra of GQD's: C132 obtained by chemical method: 1- λ_{ex} =337 nm, 2- λ_{ex} =479 nm, 3- λ_{ex} =532 nm [10, 11,] (A), and of GQD's obtained by mechanical-chemical method: 1- non modified (oxido-GQDs), 2- previous ones doped by aminogrups (m-GQDs), 3- obtained from (m-GQDs) by reduction (r-GQDs) [12], (B); 1'-3' are the corresponding $\ln \varphi$ [4].
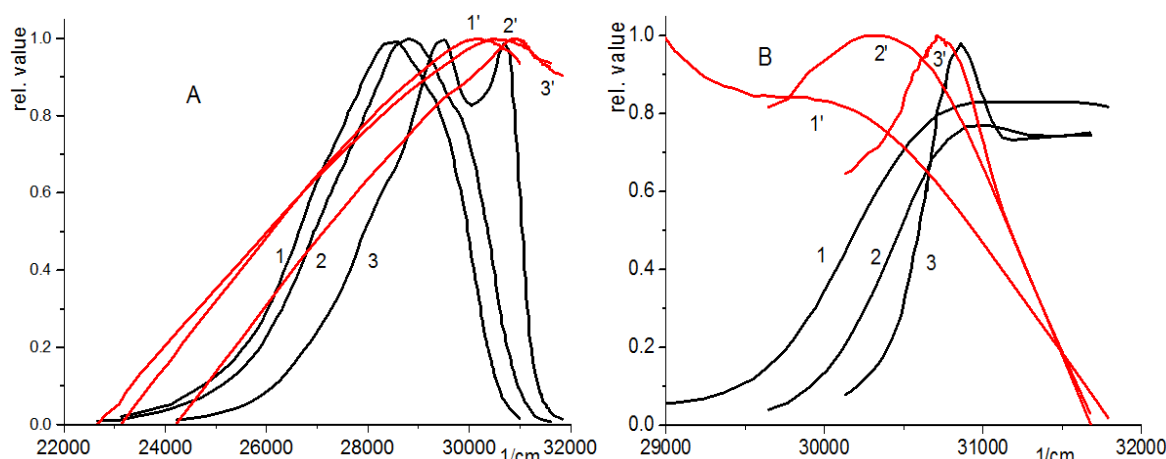

Figure 3. The fluorescence (A) and absorption (B) spectra of 2-dibenzofuranol in ethanol (1), acetonitrile (2) and cyclohexane (3) [13]; 1' -3' are corresponding $\ln \varphi$ spectra.

Let's view indication of molecular chromophores inhomogeneity. The examples of the composite extremes according (5) are given on Figure 3 for 2-dibenzofuranol [13]. The emission of ethanol, methanol and cyclohexane solutions in Figure 3A is presented by homogeneous excited state chromophores, perhaps of similar form. The opposite situation is for the ground state in Figure 3B. In cyclohexane solution for absorption v_0 is about 30700 cm^{-1}, for emission about 30900 cm^{-1}. For acetonitrile the values are 30350 and 30500 cm^{-1}. (The difference for absorption and emission v_0 is the typical as related to prerelaxational finish-state, vertical zero-gap between combining states). The ground, absorbing state in ethanol solution is inhomogeneous, as has no extremum, but broad expanded to longwave side band. The effect one can explain by capability to form hydrogen bonding by ethanol which can produce polymorphic system of hydrogen-bonded chromophores.

Solvent on general have different interaction forms with solute up to produce the chemical complexes. In Figure 4A the indication of homogeneity transformation of chromophores solution in cyclohexane with addition of methanol [14] is presented by proposed method. The specific action of methanol on solute by hydrogen bonding is well known. The addition of methanol multiplies forms of solute-solvent cages and increase inhomogeneity. The behavior of common in biology aqueous solvents mostly depends on pH. In Figure 4B the absorption spectra of deoxyadenosine at pH 1.5 and 7.9 are shown [15]. In alkali solution deoxyadenosine is homogeneous but in acidic solution the inhomogeneity, polymorphism is observed, as followed from deformation of characteristic function φ spectrum. It is known that the

alkali form of solution is preferable for homogeneity of many nucleotides, as has been confirmed by described method too [16].

Ultraviolet absorption (A) and magnetic circular dichroism (MCD) (B) spectra of oligopeptide antibiotics netropsin, distamycins A and D in aqueous 0.1 M NaCl solutions [17] are given in Figure 5. The application of 0-0-extremum method to the spectra show that MCD spectra gives clearly

defined extremum (ν_0) and homogeneity. The corresponding points on plate A are shown by arrows. As the MCD spectra give clear ν_0, so for integral absorption spectra, as noted by arrows, there are no extremums. The reason is that MCD spectra are spectra of chiral chromophores. The integral absorption spectra are spectra of general, may be even non-chiral structures and so are inhomogeneous.
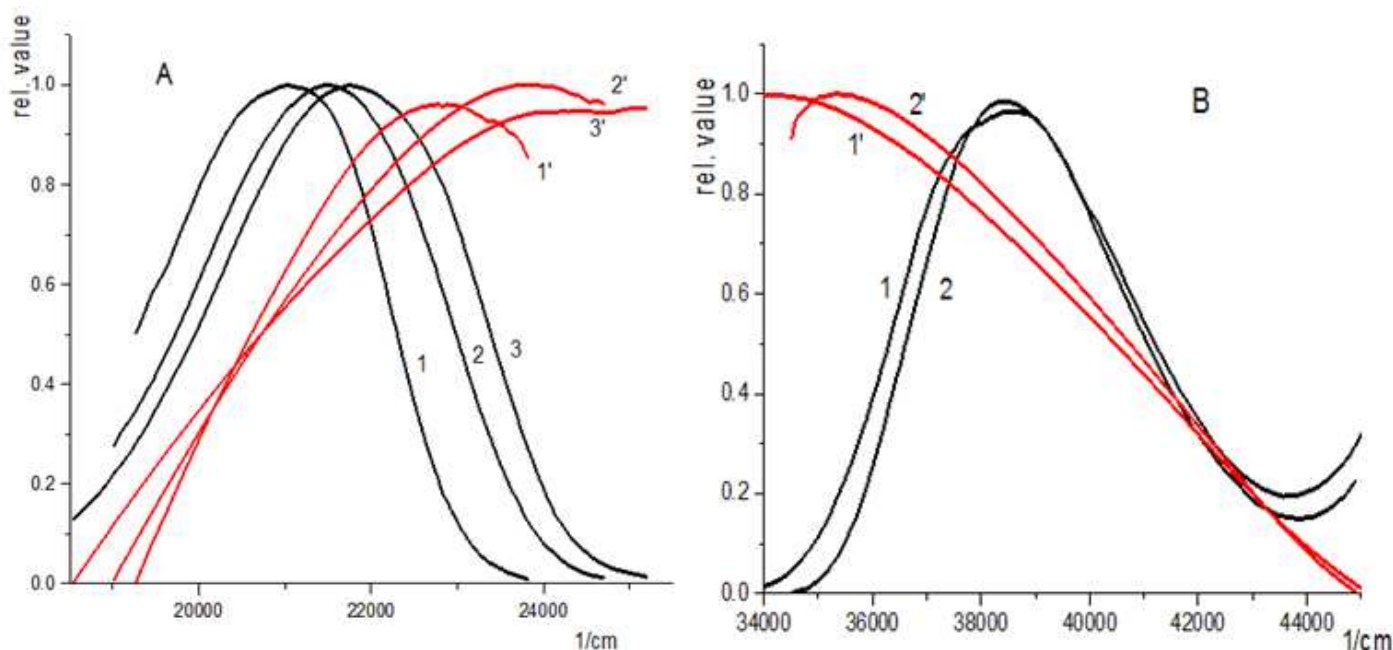

Figure 4. *Influence of solvent on solute homogeneity shown by absorption and emission spectra. On plane A the fluorescence spectra of (2-hydroxyphenyl) benzimidazole in cyclohexane-methanol mixture: 1 no methanol (Me), 2 0.2 M Me, 3 0.4 M Me [14]. On plane B absorption spectra of aqueous deoxyadenosine solution at pH 1.5 (1) and 7.9 (2) [15]. Corresponding* $\ln \varphi$ *are shown by primed numbers.*
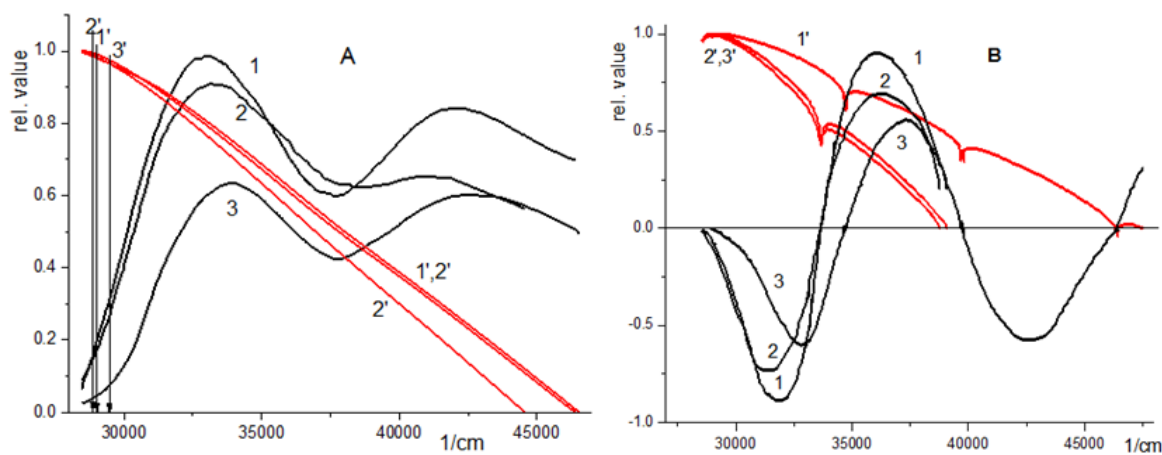

Figure 5. *Ultraviolet absorption (A) and MCD (B) spectra. Aqueous solutions of distamycin-A in H₂O (1); distamycin-D (2) and netropsin (3) in 0.1 M NaCl spectra [17] and corresponding* $\ln(\varphi^a)$ *spectra (1', 2', 3'). The arrows on plate A note the positions of* ν_0 *obtained in plate B.*

4. Conclusions

It is shown that analysis of 0-0-transition localization can be effective to determine the spectral homogeneity of relative chromophor ensembles or even purity of species. It fits to gaseous, crystalline and polymeric media. The best application of the method beside gap $h\nu_0$ determination is to

test homogeneity of molecular spectral labeling [3] and even of chromophor ensembles with chiroptical selection [17]. The main lack of the approach is location on low intensity antistokes wings of spectra, longwave in the absorption and short wave in the emission. So it is sensitive to overlapping spectra of different electronic transition and to measurement errors. The approach should be applied carefully at low temperatures [18].

Acknowledgements

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