New Opportunities for Analytical Use of Optical Diffuse Electronic Absorption and Emission Spectra

Vitaly Antonovich Tolkachev

Institute of Physics, National Academy of Sciences of Belarus, Minsk, Belarus

Abstract: *The short review is given on determination of gap between electronic states combining in vibronic transition from separate diffuse absorption or emission spectra. The basic concept of method is given. It is shown on experimental data that the approach fits to molecules in gaseous, condensed and crystal state, color centers and F-centers quantum dots and to optical activity. The main results are: method to find pure-electronic gap between combining states from diffuse separate absorption or emission spectra, the manifestation of difference in the gap and spectral maximum, visualization of inhomogeneity, polymorphism from spectra related system.*

Keywords: *Optically combining states, Pure-electronic transition, Diffuse spectrum, Optical activity, Chromophore polymorphism, Spectrum inhomogeneity,*

1. INTRODUCTION

In recent years, some progress has been achieved in the use of optical diffuse absorption and emission spectra [1-6]. It turned out that without any new specific technological conditions it is possible to obtain important additional information from the spectra. Applying the concept, known from the fundamentals of quantum mechanics, to the theory of the formation mechanism of optical spectra, that the *probability of a transition between two simple, elementary states under the influence of external influence does not depend on the direction of the transition if the perturbation causing the transition is real (the perturbation operator is Hermitian)* for trivial conditions when the initial state of the optical transition is in thermal equilibrium, we can obtain an additional condition to get the information on the molecule (chromophore). From that consideration for the spectra of sufficiently homogeneous molecular systems or quasimolecular chromophore centers, the possibility of a more accurate method for determining the distance between optically combining states of the spectrum follows. This concept was not usually applied to the complex systems that are characterized by diffuse spectra for obtaining information from spectra. It turned out that its application leads to a more accurate method, in comparison with existing methods, to determine the distance between combining states in a transition.

Previously, the position of the maximum of the spectrum was used as such distance for diffuse absorption or emission spectra, which yielded an overestimated value from the absorption spectrum and an underestimated value from the emission spectrum. The error usually amounted to tenths of electron-volts, which is significant for low-energy reactions and structural transformations.

THEORY.

For the above new conditions, it follows that in the vicinity of the transition between the lower (zero) initial and final states, in the 0-0-transition, for the spectrum of the transition cross section $\sigma(\nu)$ a simple relation holds:

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

where "-" is for absorption, and "+" is for emission of light, $h\nu_0$ is the difference in energy between the zero levels of the states combining in the optical transition (ν_0 is the frequency of the 0-0-transition). The relation gives from the absorption or emission spectrum a dependence f having an extremum symmetric with respect to ν_0 and so localizes the frequency of the determined 0-0-transition. The width of the extremum region is of order of the width of the thermal population of initial state. A decrease in temperature leads to a narrowing of the extremum region; therefore, room and higher temperatures are most favorable for applying this ratio.

DISCUSSION

The ratio was tested on the optical absorption and emission spectra of structures such as molecules [1,2] their composites [2,3] and other charge micro- and nanoformations - quantum dots, color centers of crystals, molecular crystals [4,5]. The comparison was made with the data on the 0–0-transition obtained by the methods of low temperature cooling and calculations. Experimental confirmation of the correctness of the approach used has expanded it to analytical application to optical centers - chromophores, and even to measurement methods.

The electronic 0–0-transition frequency (ν_0) could be determined from not only the frequency dependence of spectral transition cross sections σ(ν) but also from their relative changes with temperature if the elementary transition probabilities are temperature independent [2]. In this instance, ν_0 corresponds to a minimum in the dependence of the average energies of the combining states sum on frequency or an extremum of the function

$$2 \cdot \partial \ln \sigma(\nu) / \partial (1/kT) \mp h\nu \qquad (2)$$

where $-h\nu$ refers to absorption; the $h\nu$ to emission. The method was tested using gas-phase spectra of several compounds and showed better precision for determining ν_0 than the frequency dependence of the spectra (1), especially for overlapping of different transitions spectra [2].

So, the main achievement of this approach was the ability to determine the distance between the ground and excited states *separately* from the absorption or emission spectra. For the vast majority of molecules of biological structures, only diffuse absorption spectra are available, and usually in this case, the absorption spectra maximum is taken as the 0-0 distance, which is up to half electron-volt shifted to the short-wavelength side. Such an error in the calculation of reactions can significantly shift the results. Absorption spectra are also not always available, such as for phosphorescence transition, dispersed aggregate states, etc.

The above ratio, as noted, is suitable for fairly homogeneous systems, ensembles of chromophores. Testing on different types of chromophore ensembles showed that the heterogeneity of the ensemble forming the spectrum prevents the determination of the frequency of the 0–0-transition. This also follows from the above relation (1), where it is seen [3] that the total cross section of the inhomogeneous ensemble will give the total extremum region, distorted according to the structure of the inhomogeneity inputs. Such distortion is also a good indicator of the polymorphism of the studied object. That is general rule confirmed by experiment [4-6]. For example, in solutions where the solvent specifically interacts with the dissolved pure substance, a significantly wider region of the 0–0 extremum is observed or even its absence than in a neutral solvent. For F-centers formed in crystals by irradiation, a wide spectrum of defects is formed. The heterogeneity leads, as a rule, to the complete absence of a 0-0 extremum. The same is observed for graphene-based quantum dots formed by mechanochemical methods.

From relation (1), the possibility of using anisotropy methods to determine the distance between optically combining states also follows. In this case, the spectra of cross sections of different polarizations will be proportional only in the ideal case. Usually they are different due to different conditions for the corresponding ensembles of chromophores, and the ratio of the spectra of different polarizations, as well as the anisotropy coefficients, will give an averaged extremum and a generalized value of ν_0.

The proposed approach is applicable to optical activity spectra (OA) [6]. OA spectroscopy is of great importance in biology, making it possible to view the spectra of interest in a complex chemical-biological mixture. In the mechanism of optical transitions of this type, along with the electrical ones, the magnetic properties of chromophores also appear. Therefore, testing the given regularity for this case was of fundamental interest, as a confirmation in this case of the concept of equality of probabilities of direct and reverse transitions at the state elementary level. It has been established that all types of optical activity spectra of ensembles of homogeneous chromophores give under the specified conditions the positions of the corresponding 0–0-transitions. As expected, the spectra of circular dichroism, circularly polarized fluorescence, and integral fluorescence, as a rule, give the position of the 0–0-transition of their chromophore ensemble. Inhomogeneous ensembles are also indicated in this case by the absence of homogeneous characteristics, which is also a qualitative signs of practical importance [6].

To illustrate the significance of this approach, we consider it appropriate to give a table of differences in the frequencies of the maxima of long-wavelength absorption spectra of a series of nucleotide solutions under various conditions [7] and ν_0 frequencies derived from these spectra. The table 1 contains the pH constant of the solutions, the frequency ν_{max} and wavelength λ_{max} of the maxima of the spectra and, the wavelength λ_0 and frequency ν_0 of the obtained 0-0 transitions, as well as their difference $-\Delta \nu_0$. On average, by 33 spectra the difference is about 3600 cm^{-1} or 0.45 eV.

Table 1: Nucleotides ν_0 in water solutions

Substance	pH	λ_{max} , cm^{-1}	ν_{max} ,cm^{-1}	ν_0 ,cm^{-1}	λ_0 ,nm	$-\Delta\nu_0$, cm^{-1}
Adenine	7.0	260.5	38380	35200	284.1	3180
	2.5	262.5	38150	34700	288.2	3450
Adenosine	7.9	259.5	38560	35220	283.9	3340
	1.5	257	38910	34200	292.4	4710
Adenylic Acid	4.5	260	38360	34400	290.7	3960
Cytidine	8.2	271	37000	34040	293.8	2960
	2.2	280	35900	33150	301.7	4750
Cytidynic Acid	7.9	270	37130	33850	295.4	3280
	4.6	274	36560	33440	298.6	3120
	2.5	277	35990	33240	300.8	2750
Cytosine	8.8	267	36360	33240	300.8	3120
	2.5	276	37300	34420	290.5	2880
Deoxyadenosine	7.9	259.5	38550	35307	283.2	3243
	1.5	257	38450	34000	294.1	4450
Deoxyadenylic Acid	7.9	260	38600	34320	291.4	4280
	6.8	260	38390	35160	284.4	3230
	2.2	257.5	38600	34320	291.4	4280
Deoxycytidine	7.8	272	36870	34200	292.4	2670
	2.2	280	35810	33150	301.6	2660
Deoxycytidylic Acid	7.8	272	36900	34180	292.6	2720
	4.6	275	36250	32950	303.5	3300
	2.4	280	35800	33130	301.8	2670
Deoxyguanosine	5.4	252.5	39600	33260	300.7	5630
Guanine	6.2	275	36350	32960	303.4	3390
Guanosine	5.5	252.5	39700	33970	294.4	5730
Thymidilic Acid	7.1	268	37400	33340	299.9	4060
	4.6	267.5	37400	33340	299.9	4060
Thymidine	7.2	267	37520	33920	294.8	3600
Thymine	7.0	264.5	37700	34310	291.5	3390
Uracil	7.0	259	38450	35260	283.6	3190
Uridine	7.3	261	38340	34740	287.8	3600
Uridylic Acid	7.6	262	38320	34620	288.8	3700
	3.2	261.5	38400	34380	290.9	4020

The comments on publications

1. Establishment and testing of the considered regularity on diffuse electron-vibrational (vibronic) molecular spectra of vapors and solutions, separately, on absorption or emission. It was shown that the frequency of the 0–0-transition always differ with the frequencies of the spectral maxima [1].

2. It was shown that the frequency of the 0–0-transition corresponds to the minimum of the sum of the average energies of states that optically combine in the optical transition, and a method has been proposed for determination the frequency of the 0–0-transition from the temperature dependence of the spectrum [2].

3. It was shown that anomalies in the manifestation of an extremum in the region of the 0–0-transition, its smearing or even absence characterize heterogeneity, polymorphism of the chromophore medium and make it possible to use this in the analysis of matter [3, 4].

4. The possibility and efficiency of determination the frequencies of the zero-phonon transition from diffuse electronic spectra of color centers, crystals, glasses and F centers, as the assessment of the polymorphism and inhomogeneity of these centers are shown. [5]

5. It was shown that the optical activity spectra and dissymmetry coefficients make it possible to determine the frequencies of 0–0-transitions of their corresponding chromophore ensembles, as well as to determine the homogeneity of the corresponding chromophore ensembles. [6]

REFERENCES

[1] V. A. Tolkachev, "Determination of 0-0-Transition Frequencies from Diffuse Vibronic Spectra." *J. Appl. Spectrosc.*, vol. 84, pp. 668–673, 2017.

[2] V. A. Tolkachev, "Average Energies of Combining States and Purely Electronic Transition Frequencies in Vibronic Spectra." *J. Appl. Spectrosc.*, vol. 85**,** pp. 845-849, 2018.

[3] V. A. Tolkachev, "Manifestation of Molecular Chromophore Polymorphism in Diffuse Vibronic Spectra." *J. Appl. Spectrosc.*, vol. 85, pp. 220–224, 2018.

[4] V. A. Tolkachev, A. P. Blokhin. "Extraction of Pure-electronic Transition Frequency and Chromophor Polymorphism from Diffuse Vibronic Spectra," *Sci. J. Anal. Chem.,* vol.7, pp. 76-82, 2019.

[5] V. A. Tolkachev, "Zero-phonon Transition Frequency in Diffuse Electronic Spectra of Color Centers in Crystals and Glasses." *J. Appl. Spectrosc.,* vol. 86, pp. 504-507, 2019. DOI 10.1007/s10812-019-00848-8.

[6] V. A. Tolkachev, "Determination of 0-0-Transition Frequency from Optical Activity Spectra." *Zh. Prikl. Spektrosk.*, vol. 87, No. 3, pp. 492–497, 2020.

[7] D. Voet, W. B. Gratzer, R. A. Cox, P. Doty, "Absorption Spectra of Nucleotides, Polynucleotides, and Nucleic Acids in the Far Ultraviolet." *Biopolymers,* vol. 1, pp. 193-208, 1963.