

Extraction of Pure-electronic Transition Frequency and Chromophor Polymorphism from Diffuse Vibronic Spectra

Vitaly Antonovich Tolkachev*, Alexander Pavlovich Blokhin

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

Email address:

tolkachev@imaph.bas-net.by (V. A. Tolkachev), lsfm@imaph.bas-net.by (A. P. Blokhin)

*Corresponding author

To cite this article:

Vitaly Antonovich Tolkachev, Alexander Pavlovich Blokhin. Extraction of Pure-electronic Transition Frequency and Chromophor Polymorphism from Diffuse Vibronic Spectra. *Science Journal of Analytical Chemistry*. Vol. 7, No. 4, 2019, pp. 76-82.

doi: 10.11648/j.sjac.20190704.11

Received: July 19, 2019; Accepted: September 6, 2019; Published: September 21, 2019

Abstract: Background: The adiabatic approach and thermal population of starting state sublevels in vibronic transition at non degenerate combining states of molecular chromophores open ways to calculate pure-electronic transition frequency (combining states gap) individually from diffuse absorption or emission spectra. Results: Experimental data and the theory show, that the model fits to homogeneous chromophores at room and not low temperatures to escape degeneration and inhomogeneity. Side result of the approach is possibility to view inhomogeneity of chromophores or solvent site inhomogeneity. Conclusions: The approach is applied to vibronic spectra of molecular systems: molecules in different aggregate states, molecular crystals, color and F-centers, films and quantum dots. The trouble with the procedure is using wings of spectra, where the errors can be introduced by overlapping of impurities spectra and even by measurement inaccuracy.

Keywords: Diffuse Vibronic Spectrum, Pure-electronic Transition, Zero-Phonon Frequency, Chromophore Homogeneity, Quantum Dots Homogeneity, Molecular Crystals, F-centers and Color Centers

1. Introduction

It was shown recently [1-4], that frequency of purely electronic, 0-0-transitions could be determined from continuous diffuse cross-section spectra of only absorption or only emission (fluorescence, phosphorescence) for homomorphic chromophores (molecules, molecular complex, etc.) at equilibrium distribution of population upon initial-state sublevels. But the base of the procedure were rather complicated and discussed fluently. Though the idea has been confirmed by numerous experimental data [1-4] it needs to be revised, summed and commented.

2. Theory

2.1. General Conception

Optical electron-dipole transition proceeds as transformation of electronic component in ensemble "electrons+nuclei" because mobility of electronic component is substantially higher. The model with functions of starting $\Psi_i(x_i, q_k)$ and finishing $\Psi_j(x_j, q_k)$ states, where $x_{i,j}$ and q_k are generalized coordinate of electrons and nuclei, when in elementary state of the system dipole transition cross-sections are reversible, gives

$$|D_{i,j,k}|^2 = |\langle \Psi_i(x_i, q_k) | \vec{M}(q_k) | \Psi_j^*(x_j, q_k) \rangle|^2 = |\langle \Psi_j(x_j, q_k) | \vec{M}(q_k) | \Psi_i^*(x_i, q_k) \rangle|^2 \quad (1)$$

where $\vec{M}(q_k)$ are dipole moment of rigid nuclei structure. The value of dipole moment

$$|D_{i,i,k}|^2 = |\langle \Psi_i(x_i, q_k) | \vec{M}(q_k) | \Psi_i^*(x_i, q_k) \rangle|^2 \quad (2)$$

Corresponds to pure-electronic transition ($h\nu_0$), which at low temperature limit is 0-0-transition. In the scope of combining start (E_1) and finish (E_2) state the energies for depletion of transition quantum on $h\Delta\nu = h|\nu - \nu_0|$ about $h\nu_0$ the crossections are equal and proportional to

$$|D(E_1, E_2)|^2 = |D(E_2, E_1)|^2 = |D(E_1, E_1 \pm h\Delta\nu)|^2 = |D(E_1 \pm h\Delta\nu, E_1)|^2, \quad (3)$$

($E_1, E_2 > 0$). So the crossection for transition $E_1 \rightarrow E_1 + h\Delta\nu$ in Stokes region ($\nu > \nu_0$) at thermal equilibrium onsublevels of ground state is proportional to

$$\frac{\varepsilon(\nu_0 + \Delta\nu)}{\nu_0 + \Delta\nu} = \text{const} \cdot \int_0^\infty e^{-E_1/kT} \cdot g(E_1) \cdot g(E_1 + h\Delta\nu) \cdot |D(E_1, E_1 + h\Delta\nu)|^2 dE_1, \quad (4)$$

where $g(E)$ and $g(E+h\Delta\nu)$ are the statistical weights of combining states, ε - absorption coefficient. For mirror to (4) transitions ($E_1 + h\Delta\nu \rightarrow E_1$) with energy conservation one obtains

$$\frac{\varepsilon(\nu_0 - \Delta\nu)}{\nu_0 - \Delta\nu} = e^{-h\Delta\nu/kT} \cdot \frac{\varepsilon(\nu_0 + \Delta\nu)}{\nu_0 + \Delta\nu} - \text{const} \cdot e^{-h\Delta\nu/kT} \int_0^{h\Delta\nu} e^{-E_1/kT} \cdot g(E_1 + h\Delta\nu) \cdot g(E_1) \cdot |D(E_1 + h\Delta\nu, E_1)|^2 dE_1 \quad (5)$$

Multiplying (5) by $\exp(h\Delta\nu/2kT)$ and taking into account that at $\Delta\nu \leq 0$ the integral in (5) disappears we obtain

$$f^a(\nu_0, |\nu - \nu_0|) = \frac{\varepsilon(\nu_0 - \Delta\nu)}{\nu_0 - \Delta\nu} \cdot e^{h\Delta\nu/2kT} = e^{-h\Delta\nu/2kT} \cdot \frac{\varepsilon(\nu_0 + \Delta\nu)}{\nu_0 + \Delta\nu}, \quad (6)$$

the relation, which is symmetric about ν_0 . By similar way for emission $E_2 \rightarrow E_2 + h\Delta\nu$ with $\nu \leq \nu_0$ for emission intensity I one obtains

$$f^e(\nu_0, |\nu - \nu_0|) = \frac{I(\nu_0 + \Delta\nu)}{(\nu_0 + \Delta\nu)^4} \cdot e^{-h\Delta\nu/2kT} = \frac{I(\nu_0 - \Delta\nu)}{(\nu_0 - \Delta\nu)^4} \cdot e^{h\Delta\nu/2kT}. \quad (7)$$

As relations (6) and (7) are symmetric about ν_0 , so at that frequency functions $f^a(\nu_0, \Delta\nu^2)$ and $f^e(\nu_0, \Delta\nu^2)$ have extremum. The relative value of the integral in (5) depends on temperature by population of energy interval $[0, h\Delta\nu]$. Whentemperature rise the relative input of the interval population and the value of the integral in (5) drops, reducing asymmetry which is introduced by the integral in (5). So in region of $h\Delta\nu < kT$ one can observe approximated symmetry of f-functions about ν_0 . The same is for emission. That behavior was observed on experimental data [1-4]. As the relationships (6) and (7) operate in Stokes regions, it means, that

$$\frac{\varepsilon(\nu_0 + \Delta\nu)}{\nu_0 + \Delta\nu} \cdot e^{-h\Delta\nu/2kT} = f^a(\nu_0, \Delta\nu^2); \nu \geq \nu_0 \quad (8)$$

$$\frac{I(\nu_0 - \Delta\nu)}{(\nu_0 - \Delta\nu)^4} \cdot e^{h\Delta\nu/2kT} = f^e(\nu_0, \Delta\nu^2); \nu \leq \nu_0 \quad (9)$$

The practically more useful is logarithmic form, as applied in [1]-[4]:

$$\ln \frac{\varepsilon_a(\nu)}{\nu} - \frac{h\nu}{2kT} = \varphi^a(|\nu - \nu_0|), \nu \geq \nu_0 \quad (10)$$

$$\ln \frac{I(\nu)}{\nu^4} + \frac{h\nu}{2kT} = \varphi^e(|\nu - \nu_0|), \nu \leq \nu_0, \quad (11)$$

where φ are normalized to interval $[0, 1]$, though more sensitive and match to spectra order forms are non-logarithmic.

One can see, that the method allows to calculate Frank-Condon, vertical frequency ν_0 , where the finish state is a state of new configuration of electrons, but former, starting state of slow, nuclei system. The ν_0 achieved from absorption spectra and the one for excited state differ as the finish structures of slow, nuclei and the new electronic systems after transitions relax to match in between and medium.

2.2. Degeneration

Many examples of molecular systems from molecular vapor to F-centers were considered in the approach [1-4, 9]. The laser dye solutions as a rule have homogeneous chromophors and F-centers just opposite, what is vivid. The deviation from homogeneity at room and higher temperatures is structure or site inhomogeneity. At low temperatures the other mechanisms are added. Accepted as basic the condition (1) of

optical dipole transition reversibility on the elementary level is correct for non degenerate systems. The systems are, for examples, polyatomic molecules, where at usual and high temperatures there are many intramolecular mechanisms which destroy degeneration. The role and influence of the mechanisms rise up with temperature and drop when the temperature drops. Interaction of degenerate states in optical transition shows complicated effects, which are controversial to the reversibility on molecular elementary level ([5, 6] e. a.). At temperatures in dozen degrees Kelvin the extremum at ν_0 is as a rule not observed at all. The reasons of deviation from obtained above relations at low temperatures are not only degeneration, but cell site and chromophore polymorphism

From (10) and (12) it follows

$$-\partial \ln f^a / \partial(1/kT) = h\nu / 2 - \partial \ln(\varepsilon(\nu)) / \partial(1/kT) = (\bar{E}_a^* + (\bar{E}_a^* - h\nu) - 2\bar{E}) / 2. \quad (13)$$

The relation (13) is symmetrical about ν_0 too. Besides, one can see, that extremum of (13) is extremum of the average energies sum of states combining in optical transitions [3]. Like above, for emission by relation

$$-\partial \ln(I(\nu)) / \partial(1/kT) = \bar{E}_e^*(\nu) - \bar{E}^*, \quad (14)$$

with $\bar{E}_e^*(\nu)$ as the average energy of excited molecules emitting photons $h\nu$ and the average energy of all excited molecules \bar{E}^* [8] and (11) one obtains

$$-\partial \ln f^e / \partial(1/kT) = -h\nu / 2 - \partial \ln I(\nu) / \partial(1/kT) = (\bar{E}_e^* + (\bar{E}_e^* - h\nu) - 2\bar{E}^*) / 2 \quad (15)$$

As for absorption and emission the expressions (13) and (15) are symmetrical about ν_0 so ν_0 corresponds to minimal sum of combining states average energies.

2.4. Mixture of Chromophors

One of main shortage of the methods is basing on longwave in absorption and shortwave in emission low intensity wings of spectra. Overlapping the wings by other spectra adds problems. Overlapping spectra of n kinds of chromophore modifies the relations (8) and (9) to

$$\left(\sum_n \sigma_n(\nu) \right) \cdot \exp(-h\nu / (2kT)) / \nu = \sum_n f_n (|\nu - \nu_{n0}|) = f_{gen}^a \quad (16)$$

for absorption and

$$\left(\sum_n I_n(\nu) \right) \cdot \exp(h\nu / (2kT)) / \nu^4 = \sum_n f_n^e (|\nu - \nu_{i0}|) = f_{gen}^e \quad (17)$$

for emission.

The extremum will smear because displacement and overlapping of particular extremums at different ν_{n0} and determination of separate pure electronic transition is impossible. But the disappearance of extremum is a qualitative note of chromophore inhomogeneity [4, 9] and some will be added below.

When the spectra of different vibronic transitions overlap as for example in molecular UV-Vis absorption, their temperature dependence can help [3]. As the antistokes regions of spectra are more sensitive to temperature so their location indicate region of extremum.

because of slow relaxation of states and the other mechanisms.

2.3. Average Energies of Combining States

The spectral selectivity of vibronic transitions is reflected in statistical characteristics. It was shown [7], that the dependence from temperature of vibronic absorption spectra, when the transition probability depends on temperature by population Boltzmann factor, is connected to the average energies of excited $\bar{E}_a^*(\nu)$ and of all ground state molecules \bar{E} in vapor state by relation

$$-\partial \ln(\varepsilon(\nu)) / \partial(1/kT) = \bar{E}_a^*(\nu) - \bar{E} - h\nu. \quad (12)$$

3. Approaches

The results of above considered model are tested for the rather extensive types of electronic transitions [1-4] in molecular vapors, solutions, color centers, including F-centers. In following the new examples of the approach are demonstrated.

3.1. Molecular Crystals

It was not considered application the method to molecular crystals. The orientation of molecules in molecular crystals is very high [1-4]. But elementary cell in molecular crystal may consist from identical but differently oriented molecules, so

the spectrum would appear as completed from different, inhomogeneous chromophore nature. The particular inputs to spectrum depend on the cell structure and on the direction of light wave polarization. Figure 1 shows the absorption

spectra and ϕ -functions of crystal and vapor of 1.3-dimethyluracil. In both of aggregate states the absorbing structures are homomorphic, monochromoforic.

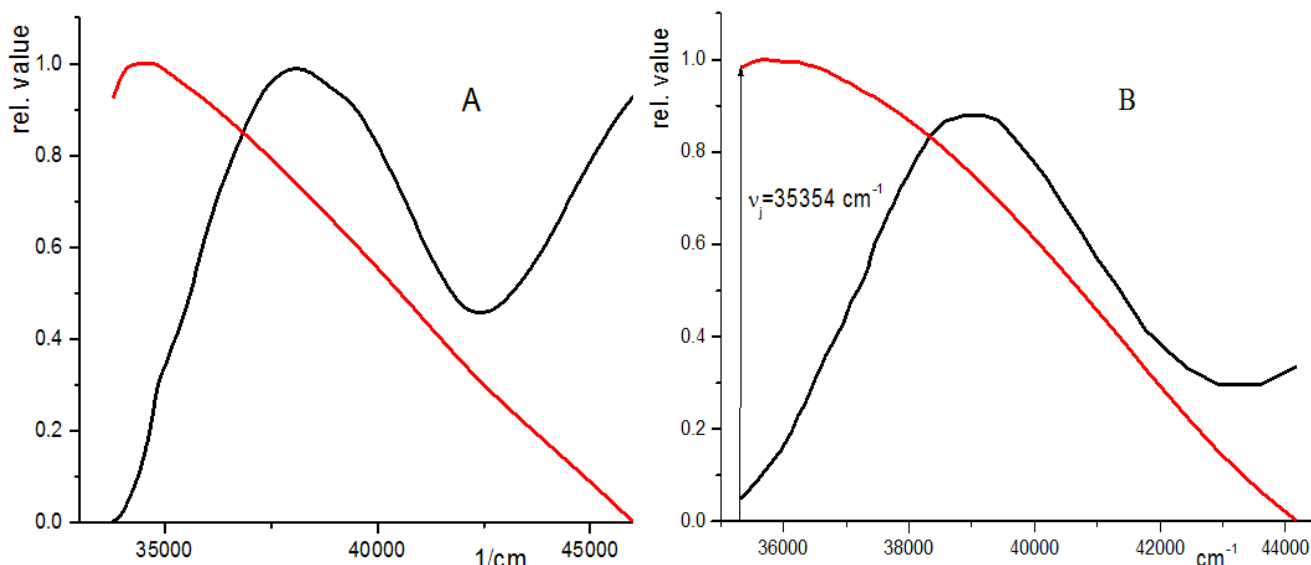


Figure 1. Absorption spectra of 1.3-dimethyluracil: A – crystal, polarization $\parallel Z'$ [10]; B – vapor [11] and corresponding functions $\phi = \ln(f)$. The arrow shows 0-0-transition (35354 cm^{-1}) found at jet-cooling [12].

Figure 2 gives the absorption spectra of uracil crystal at main and orthogonal optical axes of polarization. Here extremum is absent, indicating polymorphism of absorbing chromophors. Like shown in figure 2 the absorption spectra for polarizations $\parallel a$ and $\parallel c$ from [10] give polymorphism too. As it is known, uracil polymorphism is based on high lability of protons in the molecule. For the vapor state that polymorphism also found too [2]. The spike on ϕ^a in figure 1A at 34150 cm^{-1} possibly notes single prevailing orientation of uracil chromophore. The spikes like that, for example, are observed by authors in solutions of some dyes (Rh 4C in

ethanol, BBO in ethanol and dioxane a. o.). By this method were analyzed the absorption spectra of thymines and uracils crystals from [8] and was found, that predominantly the homogeneous chromophors are of crystals 1.3-dimethyluracil, 1.3-dimethylthimine, monohydrate thimine, calciumtimidilate; inhomogeneous are chromophors of 2-ethyl-5-methyluracil, uridine-5'-calciumphosphate, 1-methylthimine. As noted above, reason may be proton migration or different orientation of molecules in elementary cell of the crystals.

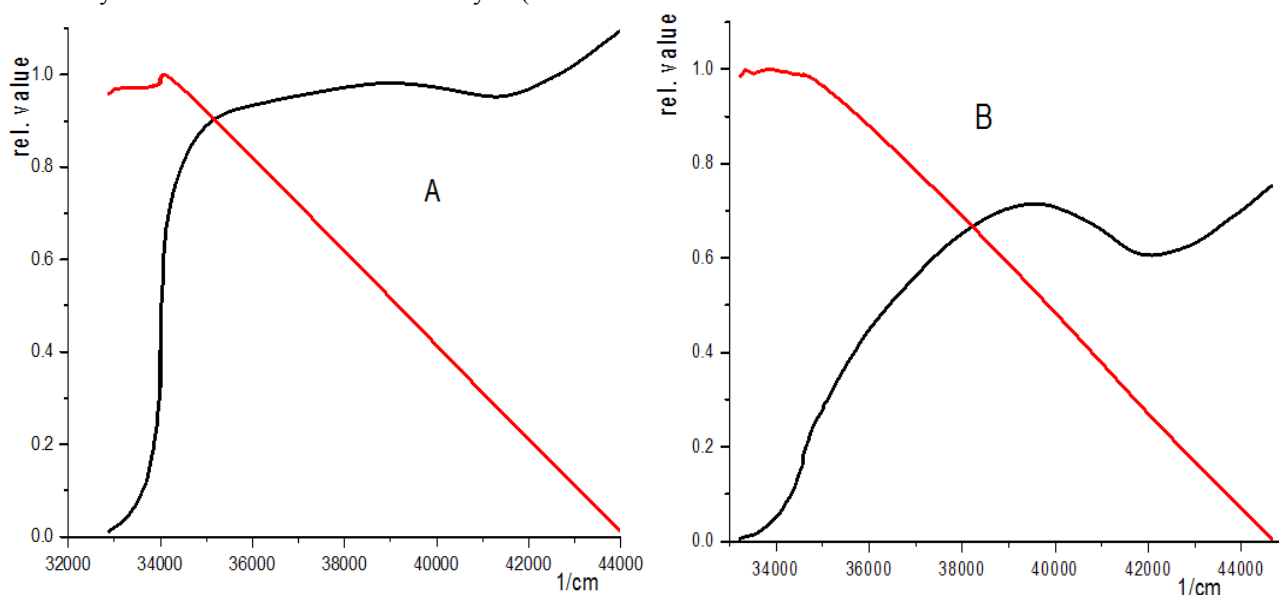


Figure 2. Absorption spectra of uracil crystals at room temperature for polarization along main optical axis Z' (A) and orthogonal X' (B) [10] and the corresponding ϕ -functions.

3.2. Quantum Dots

There are some interesting examples of definition of quantum dots electronic transition by this method. Best fit as it will be seen below is for graphene-based quantum dots (GQD). There are two fundamental approaches to produce GQD: “top-down” and “bottom-up” approaches. The “top-down” approach is most popular and based on fragmentation of huge graphene block into small particle with following

chemical modification. The rout “bottom-up” is synthesis of GQDs from molecular fragments of lower dimension. By chemical doping the GQDs of required properties, even luminescent, can be obtained. From much forms GQDs two luminescent forms of the GQD obtained by methods “bottom-up” and “top-down” were selected to the study. The emission spectra and ϕ -functions of the GQDs are shown in figure 3.

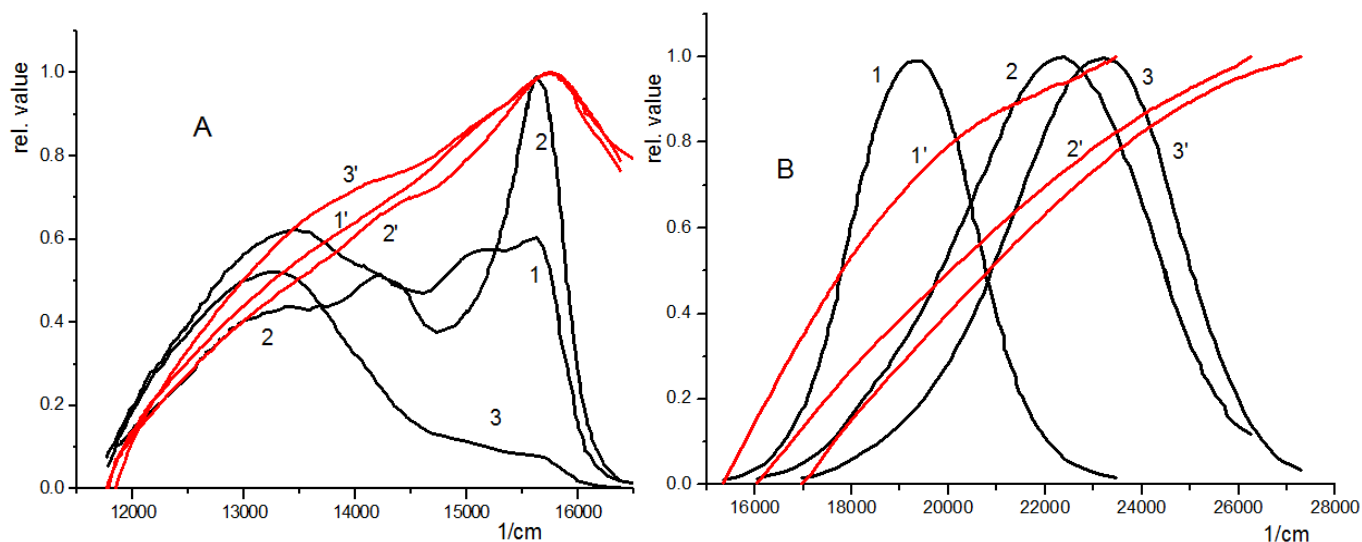


Figure 3. Emission spectra of GQD's: A- C132, obtained by method “bottom-up”: 1- $\lambda_{ex}=337$ nm, 2- $\lambda_{ex}=479$ nm, 3- $\lambda_{ex}=532$ nm [13, 14]; and (B) by “top-down” method: 1- non modified oxido-GQDs, 2- previous ones doped by aminogroups m -GQDs, 3- obtained from m-GQDs by reduction, r-GQDs [15]; 1'-3' – the corresponding ϕ -functions.

The homogeneity of shortwave emitting chromophore of C132 is very high for all emission spectra excited by light of different wavelengths. The lower excited emitting level is about 15760 cm^{-1} over the ground state. At about 14000 cm^{-1} there are next overlapped transition, which probably may be determined by variation of temperature method. The found homogeneity of longwave C132 chromophore by ϕ -functions is supported by reliably established in [13] homogeneity of its structure. Just opposite are results on figure 3B. All here shown GQD ensembles are mostly inhomogeneous. It is consistent with the production technology.

On figure 4 by the developed method evolution of diamond nanoparticle fluorescence spectra after oxidation and annealing [16] are analyzed. To obtain homogeneous concentration of NV-centers the nanoparticles were oxidized to depart unnecessary substituents and then annealed. It is seen, that the oxidized particles without annealing are mostly inhomogeneous. The annealing increases the homogeneity with temperature and at temperatures 800°C - 900°C attains the homogeneity. The pure electronic frequency is indicated at about 17390 cm^{-1} and is seen for all samples, but mostly sharp extremum is for homogeneous samples. The obtained transition frequency coincides with the transition of known NV° emission centers from state of symmetry 2A_1 to ground

state 2E [17, 18].

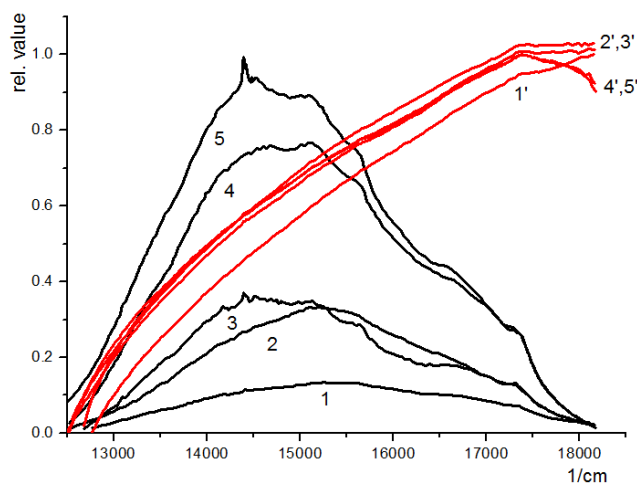


Figure 4. Fluorescence spectra of diamond nanoparticles, obtained by oxidation in air with no annealing (1) and after annealing at temperatures 2- 650°C , 3- 700°C , 4- 800°C , 5- 900°C [16]; 1'-5' – relative ϕ^{fl} - functions.

3.3. Dichroism

Figure 5 shows examples of correlation the dichroism spectra and of ϕ -functions. The dichroism of 9-methyladenine in stretched films PVA on figure 5A shows best correlation of dichroism and ϕ -function in longwave

wing of absorption spectra, though the spectrum is in some measure inhomogeneous. In figure 5B, as shown by the ϕ -function spectra, both forms of the proteins in anisotropic

polyacrylamide gel have rather low inhomogeneity, supported by dichroism spectra, though chromophors of the proteins have complicated orientation [19].

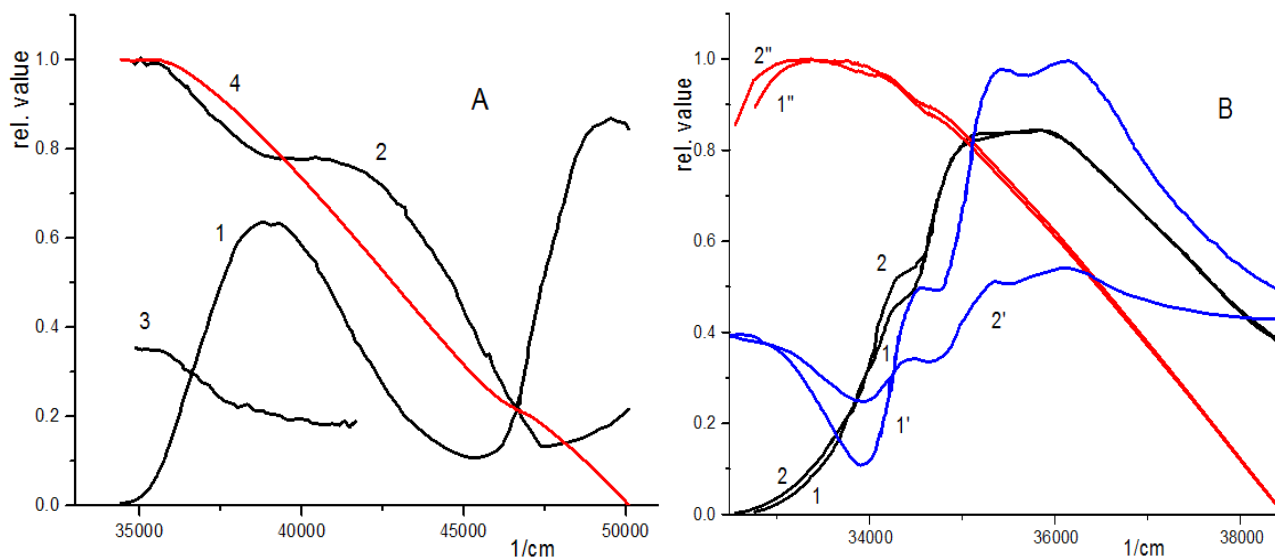


Figure 5. Absorption and dichroism spectra. A - 9-methyladenine in PVA film: 1 - absorption, 2 - linear dichroism; 3 - fluorescence anisotropy in EPA at 80 K [20], 4 - ϕ^e -function; B- proteins bovine γ II- and γ IVa-crystallins in anisotropic gel: 1, 2 - absorption spectra, 1', 2' - linear dichroism [19], 1'', 2'' - ϕ^e - functions.

3.4. Light Quenching

Figure 6 shows the correlation of fluorescence, relative yield of light quenching [21] and ϕ^e -function 1.1'.4.4'-tetraphenylbutadiene (TPB) spectra. The quenching goes by $S_1 \xrightarrow{h\nu_q} S_0$ mechanism. That kind of quenching must drop when $h\nu_q > h\nu_0$ as one can see here. Such dependence was observed in [21] for solutions of POPOP in hexane and benzene too, but TPB is demonstrated here, because the fluorescence spectra of POPOP are not diffuse.

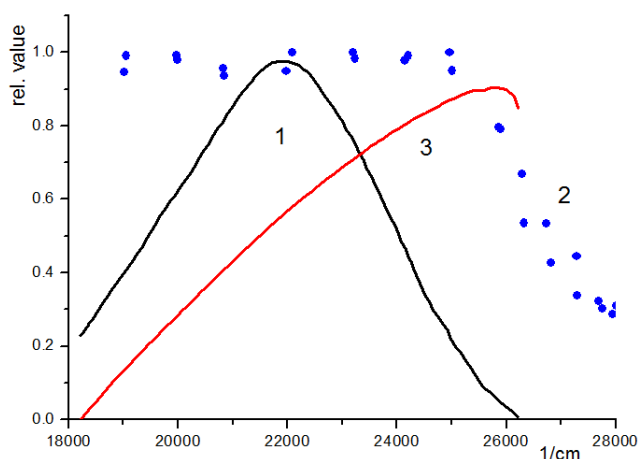


Figure 6. Solution of TPB in hexane. Fluorescence (1) and relative yield of fluorescence quenching by light (2) spectra [21], ϕ^e -function (3).

4. Conclusions

Obtained by this method ν_0 of molecular vapors and 0-0-transition found by jet-cool method differ less then 200-300

cm^{-1} (0.02-0.04 eV) though the temperatures differ on hundreds of degrees, but the differences between diffuse spectra maxima and ν_0 are about 0.1-0.4 eV [1, 2]. The analyzed above and tested in different situations method is useful not only by better location of electronic transition, but by possibility to determine the transitions from absorption or emission spectra separately, as the sample structure permits. A side capability is appeared to see the inhomogeneity of forming spectrum chromophors and some time to do the conclusion on chromophors media inhomogeneity. The approach is not free from limitation and shortcoming. The main vivid lacks are not determined levels of negative degeneration influence, of low temperature effect. The wings of spectra to use are uncomfortable for measurements: besides of different chromophors the errors can be introduced by impurities and even by measurements.

Acknowledgements

The authors thank the Belarusian Republican Foundation for Fundamental Research for supporting the work (Project F18UKA-030).

References

- [1] V. A. Tolkachev "Determination of 0-0-Transition Frequencies from Diffuse Vibronic Spectra". Journal of Applied Spectroscopy, 84, 2017, 668-673.
- [2] V. A. Tolkachev "Position of 0-0-Transition Frequency in Diffuse Vibronic Spectrum". Doklady Natsyonal'noi Akademii Nauk Belarusi, 61, 2017, 50-55 (rus.).

- [3] V. A. Tolkachev "Average Energies of Combining States and Purely Electronic Transition Frequencies in Vibronic Spectra". *Journal of Applied Spectroscopy*, 85, 2018, 845-849.
- [4] V. . Tolkachev "Manifestation of Molecular Chromophore Polymorphism in Diffuse Vibronic Spectra". *Journal of Applied Spectroscopy*, 86, 2019, 504-507.
- [5] C. J. Chen and R. Wiesendanger "Perturbation Theory of Exchange Interaction". *Physical Review B*, 74, 2006, 113102.
- [6] V. A. Tolkachev "Signs of Tunneling of (n, π) Excitation in Fluorescence of cis-Azoalkanes". *Journal of Applied Spectroscopy*, 81, 2014, 688-690.
- [7] V. Tolkachev "Dependence of Excitation Effective Energy of Vapor State Molecules on Exciting Light Frequency". *Izvestiya. Akademii Nauk SSSR, ser. fiz.*, 27, 1963, 584-587 (rus.).
- [8] V. A. Tolkachev and N. A. Borisevich "Average Energy of Fluorescing Molecules in Rarefied Vapors". *Optika i Spektroskopiya*, 15, 1963, 306-309. (rus.).
- [9] V. A. Tolkachev "Manifestation of Molecular Chromophore Polymorphism in Diffuse Vibronic Spectra". *Journal of Applied Spectroscopy*, 85, 2018, 220-224.
- [10] M. Tanaka and J. Tanaka "Electronic Absorption Spectra of Crystals of Thymine, Uracyl, and Their Derivatives". *Bulletin of the Chemical Society of Japan*, 44, 1979, 938-944.
- [11] M. J. Novak, K. Szczepaniak, A. Barski and D. Shugar "Spectroscopic Studies on Vapour Phase Tautomerism of Natural Bases Found in Nucleic Acids". *Z. Naturforsch.*, 33c, 1978, 876-883.
- [12] Y. Tsuchia, T. Tamura, M. Fujii and M. Ito "Keto-Enol Tautomer of Uracil and Thymine". *J. Phys. Chem.*, 92, 1988, 1760-1765.
- [13] X. Yan, X. Cui and L. Li "Synthesis of Large, Stable Colloidal Graphene Quantum Dots with Tunable Size". *J. Am. Chem. Soc.*, 132, 2010, 5944-5945.
- [14] H. Riesen, Ch. Wieber and S. Schumacher "Optical Spectroscopy of Graphene Quantum Dots: The Case of C132". *J. Phys. Chem. A*, 118, 2014, 5189-5195.
- [15] S. Zhu, J. Zhang, S. Tang, C. Qiao, L. Wang, H. Wang, X. Liu, B. Li, N. Yu, X. Wang, H. Sun and B. Yang "Photoluminescence Mechanism in Graphene Quantum Dots: Quantum Confinement Effect and Surface/Edge State". *Adv. Funct. Mater.*, 22, 2012, 4732-4740.
- [16] X. Song, G. Wang, X. Liu, F. Feng, J. Wang, L. Lou and W. Zhu "Generation of Nitrogen-Vacancy Color Center in Nanodiamonds by High Temperature Annealing". *Appl. Phys. Lett.*, 102, 2013, 133109.
- [17] G. Davies "The Jahn-Teller Effect and Vibronic Coupling at Deep Levels in Diamond". *J. Phys. C Solid State Phys.*, 12, 1979, 2551-2556.
- [18] S. Felton, A. M. Edmonds, M. E. Newton, P. M. Martineau, D. Fisher and D. J. Twitchen "Electron Paramagnetic Resonance Studies of the Neutral Nitrogen Vacancy in Diamond". *Phys. Rev. B*, 77, 2008, 081201.
- [19] M. Bloemendal, J. A. M. Leunissen, H. Amerogen and R. Grondelle "Average Orientation of Aromatic Residues in Proteins Determined from Linear Dichroism Spectroscopy". A Comparison of Results on Bovine γ -Crystallins with X-ray Data". *J. Mol. Biol.*, 216, 1990, 181-186.
- [20] A. Holmen, A. Broo, B. Albinsson and B. Norden "Assignment of Electronic Transition Moment Directions of Adenine from Linear Dichroism Measurements". *J. Am. Phys. Soc.*, 119, 1997, 12240-12250.
- [21] V. L. Bogdanov and V. P. Klochkov "Determination of excited state lifetime of molecules by method of light quenching". *Optika i Spektroskopiya*, 50, 1981, 1100-1106 (rus.).