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Pure electronic transition of n-methyl-4[1-(ethoxycarbonyl)-3 (methoxy carbonyl-indolizin-7-il]-pyridinium iodide

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The wavenumber of the pure electronic transition of N-methyl-4-(1-ethoxycarbonyl-3-methoxycarbonyl-indolizine-7-yl)-pyridinium iodide (MEMIPI) in different solvents was determined by three known methods. The obtained values for the wavenumbers corresponding to the pure eleectronic transition of MEMIPI depend on the solvent nature. The dependence of the wavenumber corresponding to the pure electronic transition on the solvent electric permittivity is a proof that the orientation-induction interactions are predominant in MEMIPI solutions.

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1. Introduction

The electronic absorption or fluorescence spectra of the non-planar molecules have continuous bands, large enough, so a single band can cover few thousands cm^{-1}.

The continuous aspect of the bands is due to the vibration levels of the electronic states that are very dense, forming a close continuous succession. Taking into consideration the rotation levels it results a continuum of levels; the levels lose their individuality [1-3].

Analyzing the mechanism of the electronic transitions, Leovshin empirically established the law of the mirror symmetry of electronic bands. This law was qualitatively confirmed for a great number of fluorescent molecules. In conformity with this law, if the first absorption band and the fluorescence band are normalized at the unity and they are rewritten in the scale of frequencies, then they have the same form and are situated symmetrically irrespective to the ν_{00} frequency corresponding to the intercept of the two bands; this frequency is placed at middle distance between the maxima of the two bands. It results that, in the case of the molecules having mirror symmetry of the electronic bands, a first method for determination of the pure electronic transition frequency ν_{00}, is based on the relation (1).

$$\nu_{oo} = \frac{\nu_{abs}^{max} + \nu_{fl}^{max}}{2} \qquad (1)$$

Stepanov [2] theoretically shown that the symmetry is better evidenced if the absorption band is represented in $\left(\frac{E_\nu}{\nu}, \nu\right)$ coordinates and the fluorescence band in $\left(\frac{I_\nu}{\nu^4}, \nu\right)$ coordinates; E_ν is extinction and I_ν is the intensity in the fluorescence spectrum, measured at the wavenumber ν. They can be represented in relative unities as in Fig.2.

For the case of free molecules (in the vapor state of the substance), Stepanov [2] demonstrated a low (named universal relation of Stepanov), which bonds the two types of spectra:

$$\frac{I_\nu}{E_\nu} = C\nu^3 e^{\frac{h(\nu_{00}-\nu)}{kT}} = C\nu^3 e^{\frac{h\delta\nu}{kT}} \qquad (2)$$

where C is a constant.

The purpose of this paper is to determine the values of the pure electronic wavenumbers of N-methyl-4-(1-ethoxycarbonyl-3-methoxycarbonyl-indolizine-7-yl)-pyridinium iodide (MEMIPI) in a few number of solvents.

Important information about the modification of the distribution of the spectrally active electronic levels in vacuum state or in their solutions achieved in various solvents can be obtained by the values of ν_{00}. The values are not affected by the vibration structure of the electronic levels.

2. Experimental

The analysed substances is N-methyl-4-(1-ethoxycarbonyl-3-methoxycarbonyl-indolizine-7-yl)-pyridinium iodide (MEMIPI) with general formula given in Fig. 1.

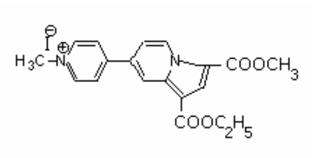

Fig.1. Chemical structure of MEMIPI

The structure and purity of this compound was verified by elemental and spectral analyses (NMR, IR, MS).

The bi-distilled water, chloroform, acetonitrile, DMF and ethanol were used as solvents. The used solvents, achieved from Merck Company, were spectrally grade.

The fluorescent spectra were recorded at a SLM 810 spectrophotometer with Data Acquisition System and the absorption spectra were recorded at a Specord UV-VIS Carl Zeiss Jena spectrophotometer with a Data Acquisition System.

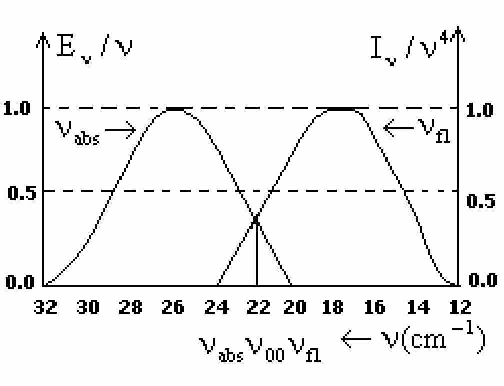

Fig. 2. Re-written spectra of the studied compound

In Fig. 2 are plotted the absorption and fluorescence spectra rewritten as Stepanov theory asks, in order to determine the frequency ν_{00} of the pure electronic transition.

From these spectra the value of ν_{00} was estimated using relation (1). In order to determine the ν_{00} value, by using either absorption, or fluorescence spectrum, relations (3) and (4), obtained from (2), were used.

$$\frac{\dfrac{E\left(\nu_{00}^{abs}+\delta\nu\right)}{\nu_{00}^{abs}+\delta\nu}}{\dfrac{E\left(\nu_{00}^{abs}-\delta\nu\right)}{\nu_{00}^{abs}-\delta\nu}}=e^{\frac{h\delta\nu}{kT}} \qquad (3)$$

In relations (3) and (4), ν_{00}^{abs} represents the frequency of the pure electronic transition determined from the absorption spectrum; ν_{00}^{fl} is the same frequency of the pure electronic transition, determined from the fluorescence spectrum; and $\delta\nu$ is a frequency interval considered at left and at right of ν_{00}. The values usually considered for $\delta\nu$ are given in Table 1, in which the values of the exponential function are also given for each $\delta\nu$.

$$\frac{\dfrac{I(\nu_{00}^{fl}-\delta\nu)}{(\nu_{00}^{fl}-\delta\nu)}}{\dfrac{I(\nu_{00}^{fl}+\delta\nu)}{(\nu_{00}^{fl}+\delta\nu)}}=e^{\frac{h\delta\nu}{kT}} \qquad (4)$$

For example, in order to determine the value of ν_{00}^{abs}, one choses an arbitrary value of ν_{00}^{abs}, at the left of the absorption curve, recorded in coordonates $(E_\nu/\nu,\nu)$ and one calculate the ratios from relation (3) for the values of $\delta\nu$ specified in Table 1.

Table 1. The chosen values for $\delta\nu$ and the values of the exponential.

$\delta\nu\left(cm^{-1}\right)$	100	200	300	400	500	600
$e^{\frac{h\delta\nu}{kT}}$	1.6	2.6	4.2	6.7	10.9	17.6

If the series of the obtained values for these ratios differ from the values calculated for the exponential function, one choses other ν_{00}^{abs} and so on, until the values of the ratios are the most closed to those of the exponential. In a similar way one determines the value of ν_{00}^{fl}, computing in a same way the ratios from relation (4).

A computational program has been realized for determination the values of ν_{00}^{abs} and ν_{00}^{fl}.

4. Results and discussion

In Table 2 the values of the maxima measured in the absorption and the fluorescence spectra of the MEMIPI in different solvents are given.

Frequency of the pure electronic transition of MEMIPI in different solvents, determined by three methods: ν_{00}^{abs}-from the absorption data; ν_{00}^{fl}-from fluorescence spectra; ν_{00} and by using Stepanov'formula are given in Table 3.

As the above data emphasized, the frequency of the pure electronic transition depends on the solvent nature.

In Fig. 3 is illustrated the dependence of the pure electronic transition wavenumber on the electric permittivity of the solvents. This depencence proves the prevalence of the orientation interactions in the solutions of the studied compound.

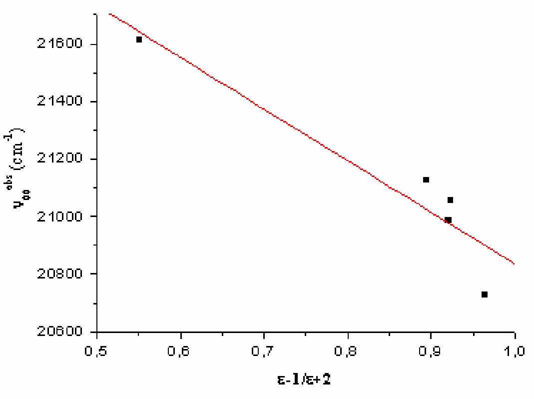

Fig.3. Pure electronic transition wavenumber of MEMIPI v.s. solvent electric permittivity

The wavenumber corresponding to the pure electronic transition of MEMIPI decreases when the electric permittivity of solvents increases (Fig.3). A study of this dependence in a bigger number of solvents with various polarities could offer more information regarding the influence of the intermolecular interactions on the electronic levels of MEMIPI.

Table 2. Wavenumbers of the absorption an fluorescence visible bands of MEMIPI

Solvent	ν^{abs} (cm^{-1})	ν^{fl} (cm^{-1})
Chloroform	23453	18581
Ethanol	23703	17940
Acetonitrile	24718	17845
DMF	23996	17905
Water	24259	18320

Table 3 Wavenumbers of the pure electronic transition of MEMIPI determined by three methods mentioned above.

Solvent	(cm^{-1})		
	ν_{00}^{abs}	ν_{00}^{fl}	ν_{00}
Chloroform	21613	21843	21017
Ethanol	21125	21245	20821
Acetonitrile	20988	21545	21281
DMF	21055	21978	20950
Water	20733	20824	21289

The method for determination of the pure electronic transition frequency, by using only the absorption spectrum, is important in the case of the molecules that does not have fluorescence properties, while the method that use the fluorescence spectrum can be applied in the case when the quantity of the substance does not permit the absorption spectrum recording, which asks a great quantity of substance than the fluorescence one. (We point out that the recordings of fluorescence spectra ask for a fewer quantity of substance, by tens or hundreds times smaller than for absorption spectra recordings).

The law of the mirror symmetry of the electronic spectra has important applications in the separation of the first absorption band when the first two absorption bands are partially superposed [3,4].

5. Conclusions

The wavenumber of the pure electronic transition of MEMIPI depend on the method used for its determination. It also depends on the electric permittivity of the solvents, showing that orientation-induction interactions are prevalent in solutions of MEMIPI.

The increase of the wavenumber in the visible electronic absorption spectrum is a proof of the charge transfer mechanismus responsible for the electronic visible band appearance.

References

[1] M. A. Eliaşevici, Spectroscopie Atomică şi Moleculară, Ed. Academiei RSR, Bucureşti, 1964.
[2] L. P. Kazacenko, B. I. Stepanov, Optika i Spektroscopia, **2** , 339 (1957).
[3] Otto S. Wolfbeis, Fuorescence Spectroscopy, New Meth ods and Aplications, Spinger-Verlag, 1993.
[4] K. Sarkunam, M. Nallu, J. Heterocyclic. Chem., **42**, 5 (2005).
[5] E. V Babaev, K. Y. Pasichnichenko, V. B. Rybacov, S. G. Zhukov, Chem. Het. Comp., **36**, 1192 (2000).
[6] P. L. Anderson, J. P. Hasak, A. D. Kahle, N. A. Paolella, M. J. Shapiro, *J. Heterocyclic Chem.,* **18** (6), 1149 (1981).
[7] B. Furdui, R. Dinica, I. Druta, M. Demeunynck, Synthesis, **16**, 2640 (2006).
[8] R. Dinică, C. Pettinari, Heterocyclic Comm., **07** (4), 381 (2001).
[9] F. Dellatre, P. Woisel, Ghe. Surpăţeanu, M. Bria, F. Cazier, P. Decock, Tetrahedron, **60**, 1557 (2004).
[10] A. Vlahovici, I. Druţă, M. Andrei, M. Cotleţ, R. Dinică, J. Luminescence, **82**, 155 (1999).
[11] A. Couture, A. Lablache-Combier, A. Pollet, H. Ofenberg, *Rev Roum.de Chimie,* **34** (11-12), 2087 (1989).
[12] L. Cireş, H. Ofenberg, T. Nicolaescu, C. Crăiţă, A. Pollet, J. Luminescence, **79** , 91 (1998).

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