Intermolecular Interactions in Non-Polar Liquids, Evidenced by Spectral Means

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The dispersive interactions acting in non-polar liquids are evidenced by spectral means. The vibronic absorption band of some non-polar aromatic compounds is used in order to obtain information about the strength of the dispersive forces in solutions achieved in non-polar solvents. A linear dependence between the spectral shifts (measured by passing the spectrally active molecule from its gaseous state into a non-polar solvent) and the dispersion function of the solvent have been evidenced. The proposed method can be used in determination of the molecular polarizabilities in the electronic excited states. So, the values of the electric polarizabilities in the excited state of the studied aromatic compounds are estimated with enough precision.

Keywords: chlorobenzene, nitrobenzene, 9,10 dicarbonitrileanthracene, dispersive interactions, electric polarizability

Intermolecular interactions act in the liquid state [1-5] between the atomic systems, determining a stabilization of the electronic levels. The strength of the intermolecular interactions depends on the following factors: nature of the atomic systems components of the liquid, temperature, presure and eventual external fields acting in liquid. These interactions can be of a specific (quasichemical, or short range) type, or of van der Waals (universal, or long range) type [4, 6-9]. The universal interactions are non-directed and non-oriented. Their direction is oriented along each radius of a sphere representing the atomic system. One from the atomic systems interacts with all systems placed on a given direction.

As London shown in 1930, dispersive forces [8,9] determined by the spontaneous electric dipole moments, act in the non-polar liquids. The dispersive forces have no equivalents in the classical electrodynamics, their action can be evaluated only in the limits of Quantum Mechanics. Two non-polar atomic systems, placed at relative small distances act by dispersive forces due to their spontaneous dipolar moments. The total energy of interaction by dispersive forces is usually obtained by summing the pair of interaction energies, taking into account the total number of pairs formed in the studied liquid. In nonpolar liquids only the dispersive interactions can be evidenced.

The electronic spectra, obtained by the valence electronic cloud reorganisation, are very sensitive to the universal interactions, reflecting the solvent global action on the spectrally active molecules used as sonds that measure the contribution of these interactions to the difference between their solvation energies in the electronic state participating to the electronic transition [10-12].

The strength of the local electric reactive field [4, 13-15], determined by the surounding molecules in the place where the spectrally active molecule is placed, is measured by the spectral shift in the corresponding (absorption or fluorescence) spectrum. The electronic band is shifted in the wavenumber scale with a quantity proportional to the difference between the solvation energies of the spectrally active molecule in their ground and excited (participating to the electronic transition) states. Spectral shifts are measured in a given solvent relative to the gaseous state of the spectrally active molecule (fig.1).

The spectral shifts of the electronic bands measured in the non-polar liquids in which non-polar spectrally active molecules are solved, compared with its gaseous state, are proportional to the energy of the dispersive interaction [4,16]. The concentration of the spectrally active molecules is very small, of about 10^{-3} - 10^{-5} mol/L, so the solution could be devided in independent subsystems consisting from a spectrally active molecule and an infinite number of solvent molecules surounding it. The number of the subsystems, giving the spectral intensity, is determined by the concentration of the spectrally active molecules in the analysed solution.

Theoretical notions

The dispersive interactions between two non-polar molecules labelled with u (for spectrally active molecule) and with v (for solvent molecule) is given by the following relation [4,10,13,16]:

$$w(r) = -\frac{3}{2}\frac{I_u I_v}{I_u + I_v}\alpha_u \alpha_v \frac{1}{r^6} \qquad (1)$$

In relation (1) the following notations are made: I-ionization potential; α-electric polarizability; r -distance between the centers of two spheres in wich are placed the interacting molecules. The indices u and v refer to the spectrally active and to the solvent molecules, respectively.

If one supposes that the dispersive interactions are additive and the solution is modelled as being devided in pairs of molecules, we can obtain the total energy of the interactions by integrating relation (1) from r_u to infinite.

The total energy of the dispersive interactions between the spectrally active molecule and the solvent [4] obtained by integrating relation (1) is given as:

$$\Delta W = -\frac{3}{2}\frac{I_u I_v}{I_u + I_v}\frac{\alpha_u}{r_u^3}\frac{\alpha_v}{r_v^3} \qquad (2)$$

The ratio $\frac{\alpha_v}{r_v^3}$ of a given solvent is equal to the function of its refractive index [4, 10]:

$$\frac{\alpha_v}{r_v^3} = \frac{n^2 - 1}{n^2 + 2} \qquad (3)$$

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This function is named function of dispersion, because the refractive index is a dispersive parameter. The energy ΔW can be considered as representing the interaction energy of the spectrally active molecule with the non-polar solvent:

$$\Delta W = -\frac{3}{2}\frac{I_u I_v}{I_u + I_v}\frac{\alpha_u}{r_u^3}\frac{n^2-1}{n^2+2} \quad (4)$$

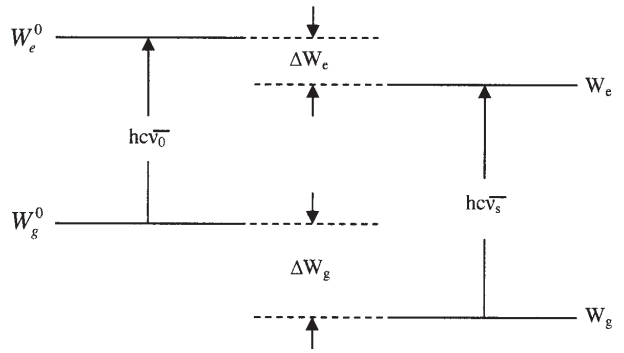

Fig.1 The solvation energies when the spectrally active molecule passes from its gaseous state into solution

By passing the spectrally active molecule from its gaseous state to the liquid state, its energy levels shift (fig.1) with solvation energy determined by the dispersive forces when the solution contains only non-polar molecules.

According to figure 1, the wavenumber in the maximum of the electronic absorption band of an isolated spectrally active molecule depends on the energies of the electronic levels participating to the considered transition.

$$h c\bar{\nu}_0 = W_e^0 - W_g^0 \quad (5)$$

In relation (5) W^0_e and W^0_g are the energies of the molecular levels participating to the electronic transition in the gaseous phase of the spectrally active molecule. Let be the solvation energies of the spectrally active molecule corresponding to the levels of the electronic transition ΔW_e and ΔW_g. The wavenumber in the maximum of the electronic band registered in a non-polar solution is expressed as a difference of the dispersion solvation energies of the spectrally active molecule in its electronic levels participating to the transition.

$$h c\bar{\nu}_s = W_e - W_g = \left(W_e^0 + \Delta W_e\right) - \left(W_g^0 + \Delta W_g\right) \quad (6)$$

Making the difference between relations (6) and (5), one obtains the spectral shift as a function of the solvation energies :

$$h c\left(\bar{\nu}_s - \bar{\nu}_0\right) = \Delta W_e - \Delta W_g \quad (7)$$

From relation (7) it results that, by measuring the spectral shift when the spectrally active molecule passses from its gaseous to liquid solution, we can obtain information on the difference of the electric polarizabilities in the ground and excited states of the spectrally active molecule. The radius of the molecular action sphere and the ionization potentials of the two types of molecules from the solution could be considered as being unchanged, in a first approximation.

$$h c\left(\bar{\nu}_s - \bar{\nu}_0\right) = -\frac{3}{2}\frac{I_u I_v}{I_u + I_v}\frac{\left(\alpha_{u,e} - \alpha_{u,g}\right)}{r_u^3}\frac{n^2-1}{n^2+2} \quad (8)$$

When there are information about the values of the parameters from relation (8), the difference of the molecular polarizabilities in the electronic states participating to the transition can be obtained. Additionally, if the electric polarizability in the ground electronic state is estimated by other methods, or computed by some methods of molecular computation [18-21], the value of the molecular electric polarizability in the excited state of the spectrally active molecule becomes available from (8).

Experimental part

The spectrally active molecules considered in this study were chlorobenzene, nitrobenzene and 9,10 dicarbonitrile anthracene. Only non-polar solvents were used for the electronic absorption spectra recordings. The solvents were carefully purified by known methods [22].

The solutions were prepared in the same conditions. The concentrations were of $0.5\ 10^{-3}$ mol/l in the case of benzene derivatives and of $0.5\ 10^{-4}$ mol/L for the dicarbonitrile anthracene. The ionization potential were obtained from literature [17] and the molecular radius was estimated by using the formula:

$$r_u = \sqrt[3]{\frac{3M}{4\pi N_A \rho}} \quad (9)$$

were:

M - molar mass,

N_A – Avogadro number,

ρ - density.

Table 1

THE REFRACTION INDEX, THE IONIZATION POTENTIAL AND THE X PARAMETERS OF THE USED SOLVENTS

Nr.	Solvent	n	I_v (eV)	$10^{24} * X\ (cm^{-4})$		
				Clorbenzen	Nitrobenzen	9,10 Dicarbonitril -antracen
1	Cyclopentane	1.407	10.56	638.560	505.880	128.619
2	Pentane	1.358	10.53	-	451.704	114.775
3	Cyclohexane	1.423	9.80	636.473	503.483	128.212
4	Hexane	1.37	10.13	575.334	455.364	116.119
5	Heptane	1.388	10.1	600.038	474.847	120.991
6	Decane	1.42	10.2	646.224	511.500	130.278
7	Dodecane	1.422	9.6	-	498.259	-
8	Octane	1.397	9.82	602.030	-	125.210

Table 2

THE IONIZATION POTENTIAL AND THE RADIUS FOR THE SPECTRALLY ACTIVE MOLECULES

Chloro-benzene		Nitro-benzene		9,10 Dicarbonitrile - anthracene	
I_u (eV)	r_u (Å)	I_u (eV)	r_u (Å)	I_u (eV)	r_u (Å)
9.06	2.82	9.86	2.97	8.25	4.78

Table 3

PARAMETERS FROM (11), LINEAR REGRESSION COEFFICIENT R, STANDARD DEVIATION SD AND THE POLARIZABILITIES IN THE ELECTRONIC STATES OF THE STUDIED COMPOUNDS

Benzene derivative	$\nu_0(cm^{-1})$	$A(cm^3)$	R	SD(cm^{-1})	α_g ($10^{24}cm^3$)	α_e ($10^{24}cm^3$)
Chloro-benzene	37207	-0.6683	0.963	5.88303	12.36	13.03
Nitro-benzene	42145	-5.2092	0.984	25.72723	11.07	16.28
9,10 Dicarbonitrile anthracene	26514	-9.4025	0.963	18.11935	28.68	38.08

An UV VIS spectrophotometer Carl Zeiss Jena with data aquisition system, having a precission of 25 cm^{-1} was used. The refractive indices were determined by an Abbe refractometer. The obtained data are given in table 1.

The studied solutions are made by the studied solute in non-polar solvents. The obtained wave number values were compared by the existent in literature data for the benzene derivatives [23-25] and for the anthracene derivatives [26, 27, 30], respectively. A good accordance was obtained.

Results and discussions

One can consider, in a first approximation, that only the dispersive forces act in the benzene derivatives solutions in non-polar solvents. Shall we introduce the X parameter by the equality:

$$X = \frac{3}{2}\frac{I_u I_v}{I_u + I_v}\frac{8066}{r_u^3}\frac{n^2-1}{n^2+2} \qquad (10)$$

The factor 8066 results by ionisation potential transformation from eV into cm^{-1}.

The relation (8) becomes:

$$\nu = \nu_0 + A \cdot X \qquad (11)$$

From the relations (8), (10) and (11) it results:

$$A = \alpha_{u,g} - \alpha_{u,e} \qquad (12)$$

that is :

$$\alpha_{u,e} = \alpha_{u,g} - A \qquad (13)$$

The parameters of the solvents that have been used and of the spectrally active molecules are given in the table 1 and 2.

For all the aromatic compounds that have been studied, the slope of the line (10) is negative, evidencing an arise of the electric polarizability through excitation.

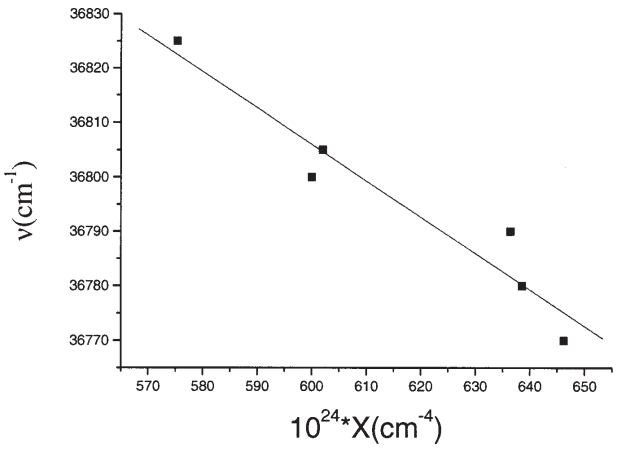

Fig.2 Spectral shifts vs. dispersion function for chlorobenzene

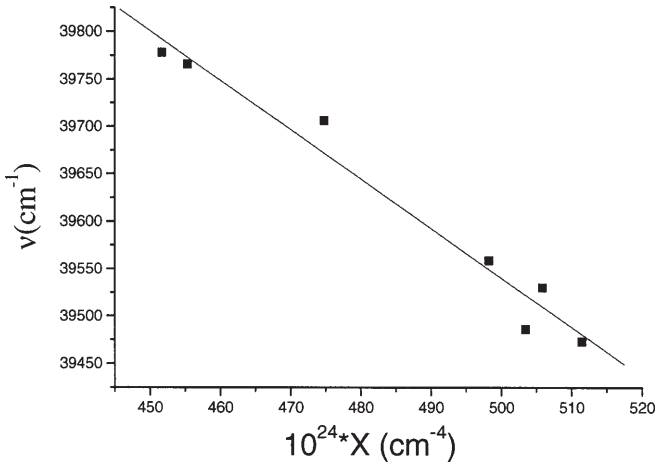

Fig.3. Spectral shifts vs. dispersion function for nitro-benzene

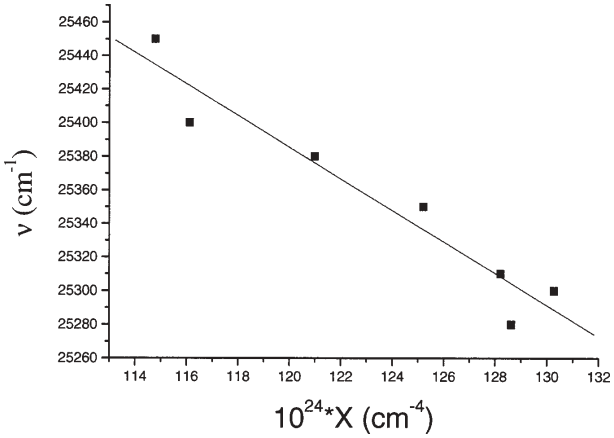

Fig.4 Spectral shifts vs. dispersion function for 9,10 dicarbonitrile-anthracene

The slope of the lines (10) equalise the difference of the polarizabilities in the two electronic state participating to the electronic absorption transition, as relations (8) and (11) show. The polarizabilities in the excited states of the studied benzene derivatives for which a linear dependence of the type (10) was evidenced, are listed in table 3. The polarizabilities in the ground states were estimated by using QSAR [28] application of the HyperChem software [29].

The cut at origin (intercept of the line (10) with Ov axis (figs. 2-4) signifies the wavenumber in the maximum of the electronic absorption band recorded in the gaseous phase of the spectrally active molecule.

An increase of the molecular polarizability by excitation in the visible range for all studied spectrally active molecule was evidenced in this study.

Conclusions

When the dispersive interactions are separated by using non-polar solutions some information about the electro-

optical parameters in the electronic state participating to the transition are obtained from the dependence of the spectral shifts on the X-parameter, directly dependent on the solvent dispersive function. Additionally, if the parameters ν_0 and A are statistically determined, the contribution of the other types of interactions at total spectral shift (recorded in polar solvents) could be estimated by substracting the contribution of the dispersive interactions.

Bibliography

1.BROWN, F., Handbook der Physics, Band **XVII**, 1958, p. 28
2.HIRSCHFELER, I., MEATH,W., Intermolecular forces, Sydhey Interscience, 1967
3. MATAGA, N., KUBOTA,T., Intermolecular Interactions and Electronic Spectra, Dekker, New York, 1970
4.BAKHSHIEV, H.G.,Spectroscopia Mejmoleculiarn'x Vzaimodeistvii, Izd. Nauka, Leningrad, 1972
5.LIPTAY, W., SCHLOSSER, H., DUMBACHER, B., HUNG,S., Zs. Naturforsch, **23a**, 1968, p.1613
6. SIMPSON, W., J. Am. Chem. Soc., **73**, 1950, p. 5359
7. PLATT, J., J. Chem. Phys., **25**,1956, p.80
8. BAYLISS, N., J. Chem. Phys., **18**, 1950, p. 292
9. BAYLISS, N., MC RAE,E. , J. Chem. Phys, **58**, 1954, p. 1002
10. MC RAE, E., J. Phys. Chem., **61**, 1957, p. 562
11. LONGUET-HIGGINS, H., POPLE, J., J. Chem. Phys., **27**, 1957, p. 192
12.BAKHSHIEV, H.G. , Opt.i. Spektrosc., **10**, 1961, p. 717
13.ABE,T., Bull. Chem. Soc. Japan, **38**,1965, p.1314; **39**, 1966, p. 936; **40**, 1967, p. 1571
14. BAKHSHIEV, H.G., Opt.i. Spektrosc., **16**, 1964, p. 821
15.BAKHSHIEV, H.G., GHIRIN, O.P., PITERSKAIA, I.B., Opt.i. Spektrosc., **64**, 1968, p. 901
16.DOROHOI, D., Fizica Stãrii Lichide, Ed. Gama, Ia°i, 1994
17. LIDE, D. R, (ed.), C R C Handbook of Chemistry and Physics, Boca Raton, Florida, CRC Press, 2005
18. DOROHOI, D.O., SURPATEANU,G., GHEORGHIES,L., Balkan Physics Letters, **6**, nr. 3, 1998, p. 198
19.DOROHOI, D.O, .J. Mol.Struct. **704**, 2004, p. 31
20.DOROHOI, D.O., J. Mol.Struct., **792**, 2006, p. 86
21.DIMITRIU, M., IVAN. M., DOROHOI,D.O.,in press
22.WEISSBERGER, A., PROSKAUER, E.S., BIDDIK, J.A., TOOPS, E. E., Technique et Organic Chemistry, Vol.VII, Organic Solvents, 2th Edition, Interscience, New York, 1955
23.MACOVEI, V., Rev. Roum. Chim., **20**, 1975, p.1413
24.MACOVEI, V., Rev. Roum. Chim, **21**, 1976, p.193
25.MACOVEI, V., Rev. Roum. Chim, **21**, 1976, p.1147
26.POP, V., DOROHOI,D.O., HOLBAN, V., An ªtiin. Univ. Al.I.Cuza, Ia°i, sIb, Fizicã, **TXLII-XLIV**, 1997/1998, p. 37
27.STRAT, G., STRAT,M., GRECU,I., Rev. Chim.(Bucure°ti) , **54** , nr. 2, 2003, p. 106
28. TARKO, L., Rev. Chim. (Bucure°ti), **55** nr. 3, 2004, p. 169
29.*** HyperChem5.02, Molecular visualization and Simulation Program Package, Hypercube, Inc., Gainesville, Fl, 32601
30.HUMELNICU, I., CONSTANTINESCU,M., VOICU,I., GHIRVU,C., Rev. Roum. Chim., **47**, nr. 8 – 9, 2002, p. 817

Manuscript received: 18.07.2007