EXCIPLEXES Of FULLERENE C$_{60}$ With AROMATIC SOLVENTS

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ABSTRACT

The solvent induced spectral shift method is applied to study stacking interactions between aromatic solvents molecules, such as benzene and toluene from one side, and solute fullerene C$_{60}$. Ratios of high-energy transitions shifts to calculated shifts under dispersion interactions are considered. It is concluded that in contrast to aromatic molecules containing two or three rings which do not form complexes with aromatic solvents, fullerene forms exciplexes with high-energy excited states involved in more strong interactions rather than low-energy one. The higher is excited state, the stronger is interaction.

Key words: fullerene C$_{60}$, exciplexes with aromatics, spectral shiftin a series AN > AMP > ATP, i.e., with the enhancement of the hydrophilicity and the solubility of these compounds in water.

INTRODUCTION

Recently we have shown [1, 2] that apolar aromatics with a few rings, such as naphthalene, phenanthrene and anthracene, do not demonstrate symptoms of stacking interactions with aromatic solvents. Fullerene C$_{60}$ has more complex system of conjugated bonds than any of mentioned molecules. So, it looks interesting to know, if molecule C$_{60}$ posses the same property. The study carries out with spectral shift method.

SOLVENT INDUCED SPECTRAL SHIFT

A shift of an electronic spectrum of molecules in a solvent from the spectrum in the gas phase is:

$$\Delta v = \Delta v_{disp} + \Delta v_{elst} + \Delta v_{oth,} \tag{1}$$

where $\Delta v_{disp} = - C(\alpha_i - \alpha_0)\varphi(\boldsymbol{R}, \boldsymbol{r})f(n)$, C is a positive factor dependent on solute properties, α is polarizability of the solute in the i-th or in the 0-th electronic states, $\varphi(\boldsymbol{R}, \boldsymbol{r})$ is a geometrical factor, it is $R^3/[r^3(2R - r)^3]$ in the quasi spherical approximation, R is an effective radius of the cavity occupied by a

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solute molecule whose effective radius is r, $f(n) = (n^2 - 1)/(n^2 + 2)$, n is refractive index of solvent, $\Delta v_{elst} = -0.5(\alpha_i - \alpha_0)\Sigma E_k$, E_k is electric field created by the k-th origin (ion, dipole,…) on the solute, and Δv_{oth} is a contribution of all other sources into the shift. Eq. (1) is valid when the electronic state in consideration does not depend on other ones. It is readily seen from Eq. (1) that for different electronic transitions of an apolar molecule

$$\eta = \Delta v_{j0}/\Delta v_{i0} = (\alpha_j - \alpha_0)/(\alpha_i - \alpha_0) \qquad (2)$$
$$\text{if } \Delta v_{oth} = 0.$$

One may rewrite equation for the shift

$$\Delta v = -C_k f(n) + \Delta v_{elst} + \Delta v_{oth}$$

in the cases when R keeps constant for all solvents in study. Here k indicates the transition in consideration. So it is expedient to compare relations

$$\eta_k = \Delta v_k/[-C_k f(n)]$$

EXPERIMENTAL

Spectrophotometers Specord UV Vis (Germany) and Perkin Elmer lambda 3S (UK) were used for recording spectra. Fullerene was produced in Institute of Surface Chemistry NASU. Solvents of chemical grade were made in Novocherkassk Chemical Plant (Russia).

RESULTS AND DISCUSSION

As it is shown in ref. [3], aromatic molecules dissolved in n-alkanes show linear dependence of v on solvent function $f(n)$ which extrapolates to wave number in the gas phase at temperature of solvents. Similar dependences for some bands of C_{60} electronic spectrum are as follows. Assignment is taken from ref. [4].

Band γ_0, transition $1^1T_{1g} \leftarrow 1^1A_g$: $v_{\gamma 0} = -1363.3f(n) + 16444$ cm^{-1}, correlation factor $\rho = 0.998$, root-mean-square uncertainty for the factor at $f(n)$, $\sigma_A = 88.8$ cm^{-1}, and the similar value for free term, $\sigma_B = 22$ cm^{-1}.

Band γ_2, $1^1T_{1g} \leftarrow 1^1A_g$ or $1^1T_{1u} \leftarrow 1^1A_g$: $v_{\gamma 2} = -1463.5f(n) + 17064$ cm^{-1}, $\rho = 0.998$, $\sigma_A = 99.3$ cm^{-1}, $\sigma_B = 24.4$ cm^{-1}

Band γ_3, $1^1T_{1g} \leftarrow 1^1A_g$ or $1^1T_{2g} \leftarrow 1^1A_g$: $v_{\gamma 3} = -1695.9f(n) + 17341$ cm^{-1}, $\rho = 0.999$, $\sigma_A = 86.6$ cm^{-1}, $\sigma_B = 21$ cm^{-1}

Two last bands are prominent enough for watching them. Nevertheless, they merge together due to broadening under aromatic solvent influence (*Fig. 1*). Therefore we use a half of the sum of these bands frequencies for comparison maxima positions of broadened bands:

$v_{\gamma 23} = (v_{\gamma 2} + v_{\gamma 3})/2 = - 1579.7f(n) + 17202.5$ cm^{-1}

Band A$_1$, $1\,^1T_{1u} \leftarrow \,^1A_g$: $v_{A1} = - 1616f(n) + 25182$ cm^{-1}, $\rho = 0.992$, $\sigma_A = 201.7$ cm^{-1}, $\sigma_B = 49$ cm^{-1}.

Band C, $3\,^1T_{1u} \leftarrow 1\,^1A_g$: $v_C = - 2490.9f(n) + 31122$ cm^{-1}, $\rho = 0.999$, $\sigma_A = 95$ cm^{-1}, and $\sigma_B = 23$ cm^{-1}.
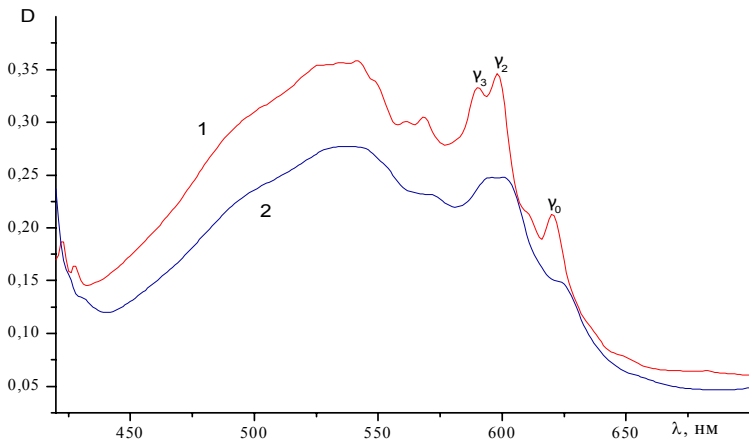

Fig. 1 – 1 - C$_{60}$ in N-heptane, 2 – C$_{60}$ in Benzene

One can see from the *Table* that all values of η_g equal to unity with uncertainty which does not exceed 0.001. This fact means that all interactions between solutes and solvents except for dispersion ones may be neglected for this transition.

Table – Spectral shifts and ratios $\eta_k = \Delta v_k/[C_k f(n)]$

Solvent	- Δv_{g23}, cm^{-1}	-$A_g \cdot f(n)$, cm^{-1}	η_g	-Δv_{A1}, cm^{-1}	-$A_{A1} \cdot f(n)$, cm^{-1}	η_{A1}	-Δv_C, cm^{-1}	$A_C \cdot f(n)$, cm^{-1}	η_C
n-C$_5$H$_{12}$	346	346.4	0.999	352	354.4	0.993	547.5	546.3	1.002
n-C$_6$H$_{14}$	362	361.7	1.001	372	370.1	1.005	568.5	570.4	0.997
n-C$_7$H$_{16}$	372	372.5	0.999	383	381.1	1.005	589	587.4	1.003
n-C$_8$H$_{18}$	381	381	1.000	393.5	389.6	1.010	599.5	600.6	0.998
n-C$_{10}$H$_{22}$	392	391.6	1.001	397	400.6	0.991	616.5	617.5	0.998
n-C$_{11}$H$_{24}$	397	397.4	0.999	403.5	406.6	0.992	627.5	626.7	1.001
n-C$_{13}$H$_{28}$	404	403.9	1.000	415	413.2	1.004	636	636.9	0.999
n-C$_{15}$H$_{32}$	410	409.8	1.001	420	419.2	1.002	647.5	646.1	1.002
c-C$_6$H$_{12}$	405	405.2	1.000	412	414.5	0.994	643	638.9	1.006
C$_6$H$_6$	466	465.8	1.000	558	476.6	1.171	1187	724.6	1.616
C$_6$H$_5$CH$_3$	465	461.4	0.999	565	472	1.197	1214	727.6	1.669

One can readily see from the table that high-energy transitions suffer additional shifts under aromatic solvents influence comparing to those under n-alkanes. The higher electronic level is situated, the higher the addition is. So, interaction affects rather upper states then lower ones. Hence the staking interaction consists in formation of exciplexes in high-energy states.

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