Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

On the solvatochromism of the $n \leftrightarrow \pi^*$ electronic transitions in ketones

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Using the Abe's approach (38) we have evaluated the changes undergone by the ketone compounds on electronic photoexcitation in its dipole moments and isotropic polarizability. This approach is given by the equation :

$$[(\mu_i)^2 - (\mu_0)^2] + (\alpha_i) \cdot A = B$$

Where μ_i and μ_0 are the dipole moments of the chromophore in the excited and ground states, respectively, which are involved in the electronic transition, and α_i is the isotropic polarizability of the excited electronic state. of its slope we can obtain the isotropic polarizability for the chromophore, and of its ordinate at the origin we can obtain the dipole moment for the excited electronic state.

Where

$$A = 3 \times [(2(\varepsilon^s - (n^s)^2)(\varepsilon^s + (n^s)^2)) / \varepsilon^s ((n^s)^2 + 2)^2 + ((n^s)^2 - 1) / ((n^s)^2 + 2)]^{-1} \times [kt \times ((\varepsilon^s - (n^s)^2) (2\varepsilon^s + (n^s)^2) / \varepsilon^s ((n^s)^2 + 2)^2 + 0.5 ((n^s)^2 - 1) / ((n^s)^2 + 2))) (I^s(I - h c \nu)) / (I^s + I - h c \nu)]$$

and

$$B = 3 \times [(2(\varepsilon^s - (n^s)^2)(\varepsilon^s + (n^s)^2)) / \varepsilon^s ((n^s)^2 + 2)^2 + ((n^s)^2 - 1) / ((n^s)^2 + 2)]^{-1} \times [kt \times ((\varepsilon^s - (n^s)^2) (2\varepsilon^s + (n^s)^2) / \varepsilon^s ((n^s)^2 + 2)^2 + 0.5 ((n^s)^2 - 1) / ((n^s)^2 + 2))) \times (I^s \times I / I^s +)) (\alpha_0) - 8.351 \times 10^{-42} \times (\rho^s/M^s)^{1/3} \times \Delta\nu \times (((M/\rho)^{1/3} + (M^s/\rho^s)^{1/3})^{-4} + ((M/\rho)^{1/3} + 3(M^s/\rho^s)^{1/3})^{-4} + ((M/\rho)^{1/3} + 5 (M^s/\rho^s)^{1/3})^{-4})^{-1}]$$

The notations s will refer to solvent.

The values of A and B can be calculated from observed values of : molecular weight (M), densities (ρ), refraction index (n), dielectric constant(ε), ionization potential(I) and electronic transition energies(ν), which are gathered in the following Table:

Solvent	n	ε	M	ρ	I	ν	Δν
2-methylbutane	1.354	1.84	72.15	0.62	10.30	35881	-199
n-pentane	1.357	1.84	72.15	0.626	10.59	35861	-219
n.heptane	1.388	1.92	100.20	0.684	10.35	35845	-235
Cyclohexane	1.426	2.02	84.16	0.779	9.86	35806	-274
Undecane	1.417	2.0	156.31	0.74	9.56	35850	-230
Tetradecane	1.429	2.04	198.39	0.762	9.91	35841	-239
Decalin	1.474	2.20	138.25	0.987	9.25	35806	-274
perFluorohexane	1.252	1.69	338.04	1.669	13.2	35986	-94
Carbontetrachloride	1.460	2.24	153.82	1.594	11.00	35768	-312
Chloroform	1.446	4.89	119.38	1.492	11.37	36300	220
Dichloromethane	1.424	8.93	84.93	1.325	11.32	36327	247
Chlorobutane	1.402	7.28	92.57	0.886	10.84	36155	75
Diethyl ether	1.356	4.34	74.12	0.706	9.72	36050	-30
Tetrahydrofuran	1.472	7.58	72.11	0.889	9.41	36232	152
Methanol	1.328	32.66	32.04	0.791	10.83	37045	950
Ethanol	1.361	24.55	46.07	0.806	10.59	36768	688
1-propanol	1.386	20.45	60.10	0.804	10.15	36756	676
2-propanol	1.377	19.92	60.10	0.785	10.10	36705	625
Tert-butanol	1.387	12.5	74.12	0.775	10.25	36579	499
n-pentanol	1.410	13.9	88.15	0.811	10.42	36685	605
n-decanol	1.437	10.20	158.28	0.829	9.65	36621	541
Water	1.333	78.36	18.02	1.000	12.63	37715	1635