Semiempirical Calculation of the Absolute Solvation Shift of Electronic and Vibrational Spectra of Molecules in the Gas–Solution Phase Transition

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Received February 12, 2001

Abstract—Calculations of the main components of the absolute solvation shift $Δν_Σ^{a,f,R}$ of optical absorption, emission, and Raman spectra of molecules in the gas–solution phase transition for solutions of several diatomic (HCl, DCl, H$_2$, D$_2$) and polyatomic (anthracene, 3- and 4-aminophthalimide) substances in some polar and nonpolar solvents are presented. The calculations are made by a new method of the semiempirical theory, which was proposed by the author earlier and makes such calculations possible for the first time. It is shown that the given theory adequately describes the photophysical effect under study and provides a correct prediction of the values of $Δν_Σ^{a,f,R}$, which differ for different systems by more than three orders of magnitude (from several inverse centimeters for vibrational spectra of H$_2$ and D$_2$ to many thousands of inverse centimeters for electronic fluorescence spectra of solutions of aminosubstituted derivatives of phthalimide). © 2001 MAIK “Nauka/Interperiodica”.

INTRODUCTION

In recent decades, interest in new methods of quantitative description of solvatochromic and solvatofluorochromatic processes has been growing [1–5]. In particular, concrete approaches to determining manifestations of intermolecular repulsion forces in optical spectra of solutions, which is an important and complicated problem, appeared. In the author’s papers [6–9], a new version of the semiempirical theory was proposed, which makes it possible for the first time to estimate the effect of dielectric and optical processes of individual solvents on the absolute shift $Δν_Σ^{a,f}$ of optical absorption and emission spectra of solutions of di- and polyatomic molecules in the gas–solution phase transition. As showed in preliminary tests of this theory, by using vibrational spectra of some simple molecules as an example, the values $Δν_Σ^{a}$ are in good quantitative agreement with the experimental values [6, 7]. In view of the aforesaid, it is of interest to make a wider comparison of experimental data with the theoretical relations derived in [8, 9] and describing not only the absorption spectra, but also the emission spectra of solutions, this being the aim of the present study.

RESULTS AND DISCUSSION

According to [8, 9], the complete expression for the absolute spectral shift $Δν_Σ^{a,f}$ of absorption ($a$) or emission ($f$) bands is written in the form

$$Δν_Σ^{a,f} = ν_Σ^{a,f} - ν_G^{a,f} = Δν_{re}^{a,f} + (Δν_{or}^{a,f} + Δν_{ind}^{a,f} + Δν_{disp}^{a,f} + Δν_{ind-res}^{a,f})_{att},$$

where the terms on the right-hand side are determined by intermolecular repulsion forces (rep); the attraction forces (att) of orientational (or), induction (ind), dispersion (disp), and induction-resonance (ind-res); and $ν_Σ^{a,f}$ and $ν_G^{a,f}$ are the frequencies of quantum transitions (the frequencies of band peaks) in the corresponding spectra of the solution ($S$) and the gas phase ($G$). In [8, 9], all the main components of the absolute shift of spectral bands were calculated within the framework of the continual approach (approximation), which is based on the joint use of representations and models of the statistical theory of liquids and physics of liquid dielectrics. The theoretical relations obtained there for the electronic and vibrational absorption spectra of solutions have the form

$$hΔν_{re}^{a} = \frac{2(α_e - α_s)}{3} \frac{α_e}{a_e^2},$$

$$hΔν_{or}^{a} = \frac{2μ_e^2}{α_e} + \frac{3kT}{α_e} f(ε, n) + \left[\frac{μ_e^2}{α_e} + \frac{3}{2} \frac{J_Γs}{J_Γs + 2J_Γs} f(n)\right],$$

$$hΔν_{ind-res}^{a} = \frac{2μ_e(μ_e - μ_s \cos φ)}{α_s^2} f(ε, n),$$

$$hΔν_{disp}^{a} = \frac{2μ_e^2}{α_e} + \frac{3}{2} \frac{J_Γs}{J_Γs + 2J_Γs} f(n).$$
One can write the expressions of the universal interaction that are determined by the dielectric properties of cases is insignificant and is noticeable only for some solutions of nonpolar substances in polar solvents.

Here \( \mu_i, \mu_e, \) and \( \alpha_g, \alpha_e \) are dipole moments and polarizabilities, respectively, of solute molecules in the ground (g) and excited (e) states, which correspond to the given solution; \( \varphi \) is the angle between the moments \( \mu_g \) and \( \mu_e \); \( J \) and \( J_S \) are the first ionization potentials of interacting molecules (the subscript \( S \) corresponds to a solvent molecule); \( e \) and \( m \) are the electron charge and mass; \( f^a \) is the oscillator strength for the absorption band under study; \( \alpha_g \) is the equilibrium value of the effective radius of a solute molecule (Onsager radius of a solute molecule) for the ground state; and \( f(\varepsilon, n) \) and \( f(n) \) are functions of the universal interaction that are determined by the generalized dielectric and optical properties of a medium. One can write the expressions

\[
\begin{align*}
\Delta\nu^a_{\text{ind}} &= \frac{1}{\mu_\alpha^2} f(n) + 3kT \frac{\alpha_e - \alpha_g}{\mu_\alpha^2} f(\varepsilon, n), \\
\Delta\nu^a_{\text{disp}} &= \frac{3}{2} \frac{(\alpha_e - \alpha_g)}{\mu_\alpha^2} \frac{J_J}{J + J_S} f(n), \\
\Delta\nu^a_{\text{ind-res}} &= \frac{1}{4\pi^2 me_g^2 a_g^2} \frac{n^2 - 1}{2n^2 + 1}. \tag{6}
\end{align*}
\]

where \( \varepsilon \) and \( n \) are the static dielectric constant and the refractive index of a solvent respectively, and \( \mu_{\alpha(G)} \) is the dipole moment of a solute molecule in the gas phase \((\alpha = g, e)\).

As noted in [8], the analysis of expressions (2)–(6) shows that all of them, except for relation (2), which was first obtained in [8], coincide with the corresponding formulas of the theory of solvatochromism based on the model concepts of the physics of dielectrics [1–4] or very close to them. This is especially true for relations (3), (5), and (6) determining the orientational, dispersion, and induction-resonant components of the absolute solvation shift of absorption bands, respectively. Some distinctions are present only in the expression for the induction shift component (4), in which a new term depending on the dielectric constant and the refractive index of a solution appeared. However, estimates show that the influence of this term in the majority of cases is insignificant and is noticeable only for some solutions of nonpolar substances in polar solvents.

In the calculations using formulas (2), (5), and (6), we used the following values for physical and chemical parameters for the anthracene molecule [11, 12]: \( \Delta\alpha_{ge} = (\alpha_e - \alpha_g) = (–40 \pm 5) \text{Å}^2; \ a_g^3 = (200 \pm 40) \text{Å}^3; J = 7.4 \text{eV}; \ f^a = 3.5–5 \) (Table 1), and \( \nu^a = 40000 \text{cm}^{-1}. \) The quantity \( J_S \) was taken to be equal to 10 eV for all the solu-

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( f^a )</th>
<th>( \Delta\nu^a_{\text{disp(calc)}} )</th>
<th>( \Delta\nu^a_{\text{rep(calc)}} )</th>
<th>( \Delta\nu^a_{\text{ind-res(calc)}} )</th>
<th>( \Delta\nu^a_{\text{calc}} )</th>
<th>( \Delta\nu^a_{\text{exp}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Heptane</td>
<td>4.9</td>
<td>–3.0</td>
<td>+2.0</td>
<td>–0.75</td>
<td>–1.75 ± 0.5</td>
<td>–1.59 ± 0.4</td>
</tr>
<tr>
<td>CCl₄</td>
<td>3.5</td>
<td>–4.2</td>
<td>+2.8</td>
<td>–0.60</td>
<td>–2.0 ± 0.6</td>
<td>–1.78 ± 0.4</td>
</tr>
<tr>
<td>Dioxane</td>
<td>3.8</td>
<td>–3.6</td>
<td>+2.4</td>
<td>–0.60</td>
<td>–1.80 ± 0.5</td>
<td>–1.83 ± 0.4</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.2</td>
<td>–3.9</td>
<td>+2.6</td>
<td>–0.70</td>
<td>–2.0 ± 0.6</td>
<td>–2.04 ± 0.4</td>
</tr>
<tr>
<td>Methanol</td>
<td>5.0</td>
<td>–2.1</td>
<td>+1.4</td>
<td>–0.65</td>
<td>–1.35 ± 0.4</td>
<td>–1.49 ± 0.4</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>4.8</td>
<td>–2.4</td>
<td>+1.6</td>
<td>–0.65</td>
<td>–1.45 ± 0.4</td>
<td>–1.49 ± 0.4</td>
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