Electronic and Electrical Effects of Solvents

11.1 THEORETICAL TREATMENT OF SOLVENT EFFECTS ON ELECTRONIC AND VIBRATIONAL SPECTRA OF COMPOUNDS IN CONDENSED MEDIA

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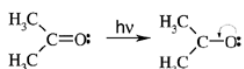
11.1.1 INTRODUCTION

The electronic-vibrational spectra of molecules can be substantially influenced by the surrounding condensed medium. The resultant effects arise from a variety of intermolecular interactions between the chromophoric solute and the solvent molecules in such media. Experimentally, these effects can be observed as
- the shifts of the spectral maxima (solvatochromic shifts)
- the change in the intensity of the spectral line or band
- the change of the shape and width of the spectral band

Each of those, so-called solvent effects can be described theoretically using different model approaches.

The solvatochromic spectral shifts are expected to arise from the difference in the solvation of the ground and the excited states of the molecule. As a result of the spectroscopic excitation, the charge distribution of the molecule changes and thus the interaction will be different in the ground state and in the excited state of the molecule. The direction and size of the respective spectral shift depends directly on the difference in the solvation energy of the molecule in those two states. The larger solvation energy of the ground state (S_0), as compared to that of the excited state (S_1), results in the negative solvatochromic shift (blue shift) of the spectral maximum (cf. Figure 11.1.1a). Alternatively, the stronger solvation of the excited state, as compared to the solvation of the ground state, leads to the decrease of the excitation energy and is reflected by the positive solvatochromic shift (red shift) in the spectrum of the compound (Figure 11.1.1b).

In each case, the direction and the size of the shift depends on the nature and electronic structure of the ground and excited state. For example, in the case of the $n \rightarrow \pi^*$ transition in acetone (Scheme 11.1.1) an electron from the n-orbital (lone pair) is transferred to the antibonding π^* orbital localized on the C=O double bond. In
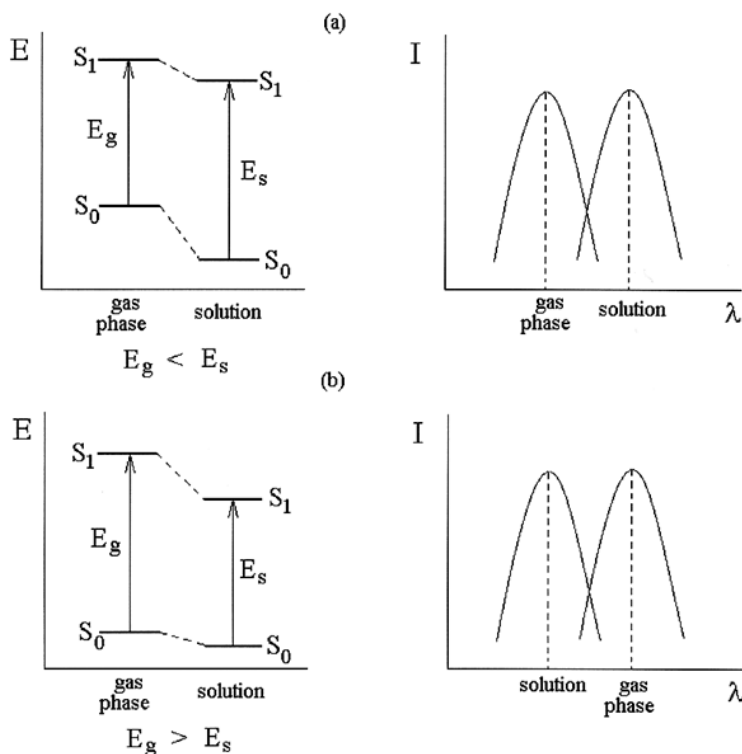
Scheme 11.1.1.

Figure 11.1.1. The origin of two types of solvatochromic shifts in the spectra of chromophoric compounds.
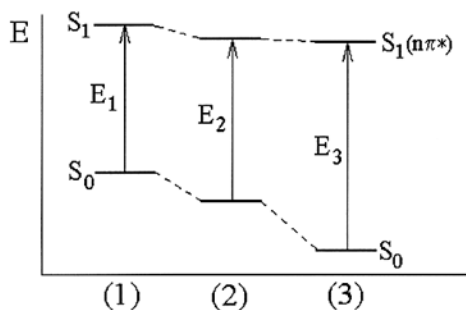

Figure 11.1.2. The schematic representation of the change of the solvation energy of the ground (S_0) and excited state (S_1) of acetone moving from a non-polar solvent (1) to a polar non-hydrogen bonded solvent (2) to a polar hydrogen-bonded solvent (3).

the ground state, the acetone molecule has a significant dipole moment (2.7 D) arising from the polarity of the C=O bond. Because of the difference in the electronegativity of bonded atoms, the electron distribution is shifted towards the oxygen that could be characterized by a negative partial charge on this atom. However, in the excited state the electron cloud is shifted from the oxygen atom to the bond and, correspondingly, the dipole moment of the molecule is substantially reduced. In result, the interaction of the dipole of the solute (acetone) with the surrounding medium in more polar solvents is larger in the ground state as compared to the excited state (Figure 11.1.2).

        Thus, the energy of the ground state is lowered more by the electrostatic solvation than the energy of the excited state. Consequently, the excitation energy increases and the respective spectral maximum is shifted towards the blue end of spectrum (negative solvatochromic shift). In the hydrogen-bonding solvents, the ground state of acetone is ad-

ditionally stabilized by the hydrogen bonding of the oxygen lone pair by the solvent that leads to further increase of the excitation energy (Figure 11.1.2) and the respective blue shift of the spectral maximum. Notably, the formation of this hydrogen bonding is impossible in the $S_1(n\pi^*)$ excited state of the acetone because of the electron transfer from the oxygen lone pair to the antibonding π^* orbital.
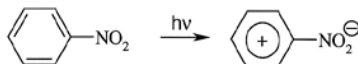
Scheme 11.1.2.

In many cases, the dipole moment increases in the excited state. For instance, in the nitrobenzene (Scheme 11.1.2) the $\pi \to \pi^*$ transition leads to the substantial redistribution of the electronic charge reflected by the shift of negative charge on the nitro-group. The real excited state is given by a combination of the L_a and L_b states. Nevertheless, the dipole moment of nitrobenzene is substantially increased in the first excited state (S_1). Because of the substantial charge redistribution in such excited states, they are often called the charge-transfer (CT) states. The much larger dipole of the nitrobenzene in the $S_1(\pi\pi*)$ state is additionally stabilized by a more polar solvents that leads to the decrease in the excitation energy (Figure 3) and to the corresponding solvatochromic red shift of the spectral maximum.
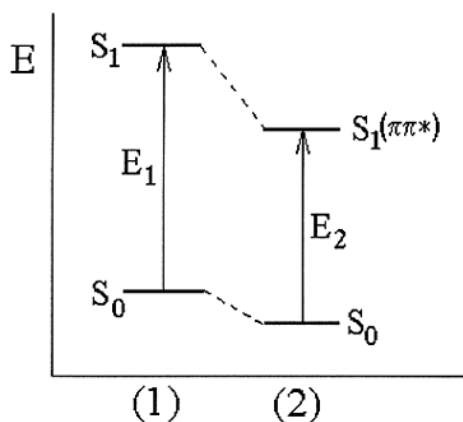

Figure 11.1.3. The relative energies of the ground (S_0) and the first excited state ($S_1(\pi\pi^*)$) of nitrobenzene in non-polar (1) and polar (2) solvents.

In Table 11.1.1, the solvatochromic shifts characterizing various positively and negatively solvatochromic compounds are listed. In most cases, the theoretical treatment of the solvatochromic shifts has been based on the calculation of the solvation energies of the chromophoric molecule in the ground and excited states, respectively.

Table 11.1.1. The solvatochromic shifts for various positively and negatively solvatochromic compounds

Compound	ν_{max} (non-polar solvent), cm^{-1}	ν_{max} (polar solvent), cm^{-1}	$\Delta\nu_{max}$, cm^{-1}	Ref.
(Scheme 3)	30000 (hexane)	25760 (CF$_3$CH$_2$OH)	+4240	(a)
(Scheme 4)	30170 (hexane)	26140 (water)	+4030	(b)
(Scheme 5)	20640 (hexane)	16860 (water)	+3780	(c)
(Scheme 6)	22620 (hexane)	19920 (DMSO)	+2700	(d)
(Scheme 7)	20730 (hexane)	18410 (methanol)	+2320	(e)
(Scheme 8)	27400 (cyclohexane)	23230 (water)	+4170	(f)
(Scheme 9)	43370 (isooctane)	41220 (water)	+2150	(g)
(Scheme 10)	14600 (toluene)	24100 (water)	-9500	(h)

Compound	ν_{max} (non-polar solvent), cm^{-1}	ν_{max} (polar solvent), cm^{-1}	$\Delta\nu_{max}$, cm^{-1}	Ref.
(Scheme 11)	15480 (tetrahydrofuran)	24450 (water)	-8970	(i)
(Scheme 12)	20410 (chloroform)	22080 (water)	-1670	(j)
(Scheme 13)	20160 (chloroform)	22370 (water)	-2210	(j)
(Scheme 14)	16080 (chloroform)	22170 (water)	-6090	(k)
(Scheme 15)	35870 (CCl$_4$)	37735 (CF$_3$CH$_2$OH)	-1865	(l)
(Scheme 16)	16390 (pyridine)	21280 (water)	-4890	(m)
(Scheme 17)	19560 (chloroform)	22060 (water)	-2500	(n)

(a)   S. Spange, D. Keutel, *Liebig's Ann. Chim.*, 423 (1992).
(b)   S. Dähne, F. Shob, K.-D. Nolte, R. Radeglia, *Ukr. Khim. Zh.*, **41**, 1170 (1975).
(c)   J.F. Deye, T.A. Berger, A.G. Anderson, *Anal. Chem.*, **62**, 615 (1990).
(d)   D.-M. Shin, K.S. Schanze, D.G. Whitten, *J. Am. Chem. Soc.*, **111**, 8494 (1989).
(e)   E. Buncel, S. Rajagopal, *J. Org. Chem.*, **54**, 798 (1989).
(f)   M.J. Kamlet, E.G. Kayser, J.W. Eastes, W.H. Gilligan, *J. Am. Chem. Soc.*, **95**, 5210 (1973).
(g)   E.M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958).
(h)   L.S.G. Brooker, A.C. Craig, D.W. Heseltine, P.W. Jenkins, L.L. Lincoln, *J. Am. Chem. Soc.*, **87**, 2443 (1965).
(i)   M.A. Kessler, O.S. Wolfbeis, *Chem. Phys. Liquids*, **50**, 51 (1989).
(j)   H. Ephardt, P. Fromherz, *J. Phys. Chem.*, **97**, 4540 (1993).
(k)   H.W. Gibson, F.C. Bailey, *Tetrahedron*, **30**, 2043 (1974).
(l)   G.E. Bennett, K.P. Johnston, *J. Phys. Chem.*, **98**, 441 (1994).
(m)   N.S. Bayliss, E.G. McRae, *J. Am. Chem. Soc.*, **74**, 5803 (1952).
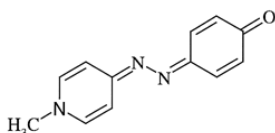(n)   E.M. Kosower, B.G. Ramsay, *J. Am. Chem. Soc.*, **81**, 856 (1959).
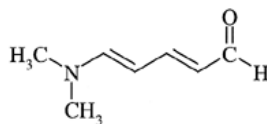
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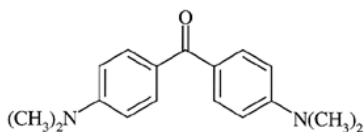
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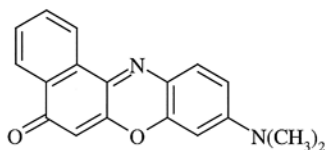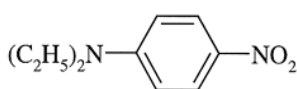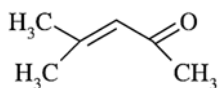
Scheme 5

Scheme 6

Scheme 7

Scheme 8

Scheme 9

Scheme 10
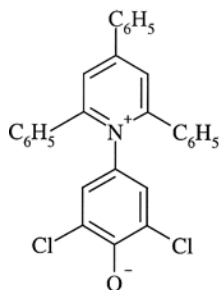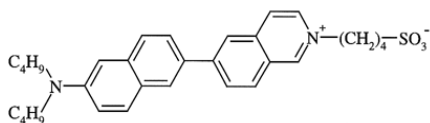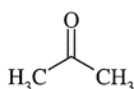
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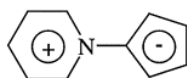
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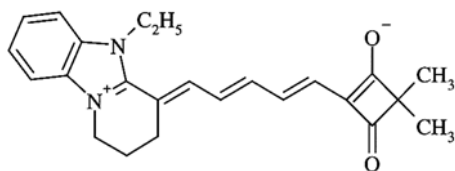
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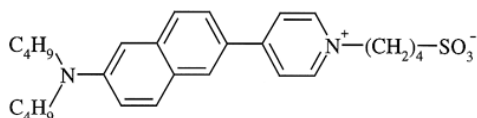
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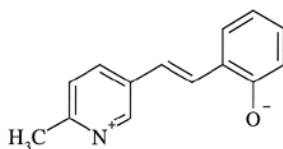
Scheme 15

Scheme 16

Scheme 17
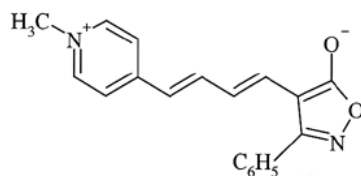
The solvent-induced broadening of the spectral lines and bands arises primarily from the variation of the local environment of the chromophoric solute molecule in the condensed medium caused by the thermal motion of the surrounding solvent molecules. At any given instant of time, there is a distribution of differently solvated solute molecules, each of which has characteristic transition energy to the excited state. The respective distribution of the transition energies leads to the broadening of the spectral band. It has to be kept in mind, however, that the broadening of spectral lines and bands can be also originated from adjoin-

ing the rotational and vibrational energy levels in the polyatomic molecule or from the Doppler and natural broadening of spectral lines. Those are more significant in the case of atoms and small molecules. The theoretical assessment of the solvent-induced spectral broadening has thus to rely on a proper statistical treatment of the solvent distribution around the chromophoric solute molecule, both in the ground and in the excited state of the latter.

The surrounding solvent can also influence the intensity of the spectral transition (absorption or emission). The intensity of the spectral transition is usually characterized by the oscillator strength f defined as follows

$$f = \left(\frac{8\pi m \overline{\nu}}{3he^2}\right)|M|^2 \qquad\qquad [11.1.1]$$

where m and e are the electron mass and the electron charge, respectively, h is the Planck's constant, M is the transition moment and $\overline{\nu}$ is the mean absorption wavenumber. Following the last equation, the intensity of the spectrum is proportionally related to transition energy, provided that the transition moment M is independent of the surrounding medium (solvent). This may, however, be not the case. The definition of the transition moment[1]

$$M = \sum_i \psi_0 |q_i r_i| \psi_1^* \qquad\qquad [11.1.2]$$

includes, apart from the charges (q_i) and their position-vectors (r_i) in the molecule, the wave function of the molecule in the ground state (ψ_0) and in the excited state (ψ_1^*), respectively. Therefore, whenever the solvent affects the wavefunction of the molecule either in the ground state or in the excited state, the intensity of spectral transition is further influenced by the change of the respective transition moment.

The analysis of the solvatochromic effects on molecular absorption and emission (fluorescence and phosphorescence) spectra is further complicated by the variation of time scales for the solvent relaxation after the spectral excitation of the solute molecule. The spectral transition is a very fast process that takes place within approximately 10^{-16} s. Thus, during this short period of time the atomic nuclei do not practically move. The excited state reached by the respective vertical transition is often called the Franck-Condon state (Figure 11.1.4).

The lifetime of the fluorescent excited state may be long enough (10^{-7} - 10^{-9} s) to allow in addition to the intramolecular nuclear relaxation (10^{-12} s), also the solvent orientational relaxation. The latter, which is characterized by the relaxation times ranging from 10^{-10} s up to infinity (in the case of solids) may bring up the additional, sol-
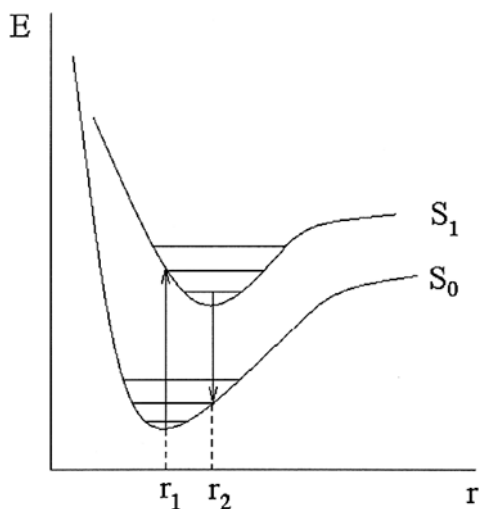
Figure 11.1.4. The Franck-Condon transitions during the excitation and the de-excitation of the molecule.

vent-induced stabilization of the relaxed excited state as compared to the Franck-Condon state. Thus, as a rule, the solvatochromic shifts in the absorption and fluorescence spectra are not equal.

The theoretical treatment of the time-dependent effects on molecular spectra in condensed phases is extremely complicated.[2] In most cases, it is assumed that only the electronic polarization of the solvent contributes to the solvation energy of the Franck-Condon state (S_1 in the case of absorption and S_0 in the case of emission). In the case of long-living states, i.e., the ground state and the relaxed excited state, a full relaxation of the solvent is assumed in the field of the solute molecule. The solvation energy of different states at different degrees of relaxation will thus be rather different that may result in rather different dependence of the absorption and emission transition energies on the polarity of the solvent. Some examples of solvatofluorochromical compounds are given in Table 11.1.2.

Table 11.1.2. The solvatofluorochromic shifts for various positively and negatively solvatochromic compounds

Compound	ν_{max} (non-polar solvent), cm^{-1}	ν_{max} (polar solvent), cm^{-1}	$\Delta\nu_{max}$, cm^{-1}	Ref.
(Scheme 18)	24400 (hexane)	16500 (water)	+7900	(a)
(Scheme 19)	21980 (cyclohexane)	18210 (water)	+3770	(b)
(Scheme 20)	~20000 (cyclohexane)	~17000 (CH$_3$CN)	+3000	(c)
(Scheme 21)	23530 (pentane)	22730 (water)	+800	(d)
(Scheme 22)	24150 (hexane)	21850 (methanol)	+2300	(e)

(a)   I.A. Zhmyreva, V.V. Zelinskii, V.P. Kolobkov, N.D. Krasnitskaya, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **129**, 1089 (1959).
(b)   M. Maroncelli, G.R. Fleming, *J. Chem. Phys.*, **86**, 6221 (1987).
(c)   A. Safarzadeh-Amini, M. Thompson, U.J. Krall, *J. Photochem. Photobiol., Part A.*, **49**, 151 (1989).
(d)   M.S.A. Abdel-Mottaleb, F.M. El-Zawawi, M.S. Antonious, M.M. Abo-Aly, M. El-Feky, *J. Photochem. Photobiol., Part A.*, **46**, 99 (1989).
(e)   J. Catalán, C. Díaz, V. López, P. Pérez, *J. Phys. Chem.*, **100**, 18392 (1996).

Scheme 18   Scheme 19
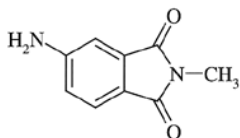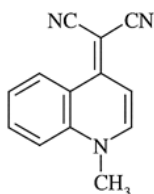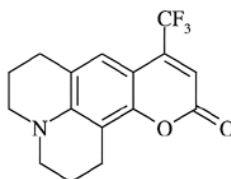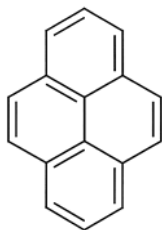
Scheme 20

Scheme 21   Scheme 22
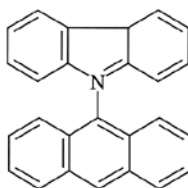
All theoretical treatments of solvatochromic shifts proceed from modelling the solvational interactions in the liquids and solutions. Theoretically, the interaction potential between a solute molecule and the surrounding solvent molecules Φ is given by the following integral

$$\Phi = C \int_0^\infty \varphi(R) g(R) R^2 dR \qquad\qquad [11.1.3]$$

where $\varphi(R)$ and $g(R)$ are the pair interaction potential between the solute and the solvent molecule and the solvent radial distribution function around the solute molecule, respectively, and C is a constant depending on the density of the system. The integration in the last formula is carried out over the distance between the solute and the solvent molecule, R. The equation [11.1.3] is derived proceeding from the assumption that the intermolecular forces in the condensed medium are additive. This assumption may be, however, violated because of possible three- and many-body interactions between the molecules in the solution. For most of the real systems, the application of Eq. [11.1.3] directly is rather impractical because of the low precision of $\varphi(R)$ and $g(R)$, particularly in the case of many-atomic molecules. Moreover, this equation will be strictly valid only for the solute-solvent systems in thermodynamic equilibrium and thus not applicable for the Franck-Condon states. Thus, almost all theoretical calculations of solvatochromic effects proceed from different physical models describing the intermolecular interactions in liquids and solutions.

Traditionally, the solvation energy of a molecule E_{solv} in a given solvent can be divided into the following terms[3]

$$E_{solv} = E_{cav} + E_{disp} + E_{elst} + E_{H-bond} \qquad\qquad [11.1.4]$$

each of which corresponds to a certain type of intermolecular interaction in the condensed media. Thus, E_{cav} denotes the energy of the cavity formation for the solute in the solvent, E_{disp} is the dispersion energy and E_{elst} the electrostatic energy of the interaction of the solute with the surrounding solvent molecules. The term E_{H-bond} accounts for the energy of the hydrogen bond formation between the solute and solvent molecules. The value of each of the above terms will change as a result of the Franck-Condon excitation of the solute molecule. First, the size of the molecule increases, as a rule, during the excitation. However, as the excitation process is practically instantaneous, the position and orientation of the solvent molecules in the solvation sheath of the chromophoric solute will not change. This means that

the average distance between the surface of the solute and the solvent molecules will decrease in the Franck-Condon excited state of the former that normally causes the enhanced solute-solvent repulsion in that state. At the same time, the dispersion energy that stabilizes the solute-solvent system will also increase in the absolute value, but to the opposite direction. In consequence, both effects may cancel each other and the net effect will be close to zero. For the polar solutes, both in the ground and in the excited state, the electrostatic solvation energy is therefore often considered as the most important term in Eq. [11.1.4].

During the excitation or de-excitation of the molecule, the molecular electronic wavefunction and the electron distribution may change significantly. In result, substantial differences are expected in the electrostatic and dispersion solvation energies of the ground and the excited state, respectively. In addition, the hydrogen bonding between the solute and solvent molecules may be affected by the excitation of the solute molecule that will be reflected as another contribution to the difference in the solvation energy of solute in the ground and in the excited state, respectively. In the following, we proceed with the systematic presentation of the theoretical methods developed for the description of the solvatochromic effects on molecular electronic and vibrational spectra in condensed disordered media (liquids, solutions, glasses etc.).

11.1.2 THEORETICAL TREATMENT OF SOLVENT CAVITY EFFECTS ON ELECTRONIC-VIBRATIONAL SPECTRA OF MOLECULES

As described above, the change (increase) in the size of the molecule during the excitation will result in increased van-der-Waals repulsion between the electron clouds of the chromophoric solute and the solvent molecules. Alternatively, the size of the molecule is expected to shrink as a result of the de-excitation of the molecule back to the ground state. In such case, the repulsion between the solute and solvent molecules will be reduced correspondingly. The respective energetic effect may be modeled as the difference in the cavity formation energies for the solute molecule in two states. The dependence of the cavity formation energy on the cavity size has been derived using several different model concepts.

The simplest approach is based on the concept of microscopic surface tension on the boundary between the solute cavity and the solvent. Within this approach, the free energy of cavity formation is assumed simply proportional to the surface of the solute cavity, S_M:

$$\Delta G_{cav} = \sigma S_M \qquad [11.1.5]$$

where σ is the surface tension of the solvent. This formula has been applied for the evaluation of the free energy of transfer of electroneutral solutes between different solvents.[4] It has been extended to account for the size of the solvent molecule as follows:

$$\Delta G_{cav} = \sigma S_M - RT \ln(1 - V_s n_s) \qquad [11.1.6]$$

where V_S is the intrinsic volume of a solvent molecule and n_S is the number density of the solvent. In order to account for the chemical individuality of constituent atoms, it has been suggested to use different surface tension values σ_i for different atomic types in the solute molecule.[5] Thus,

$$\Delta G_{cav} = C + \sum_i \sigma_i A_i \qquad [11.1.7]$$

where A_i are the solvent-accessible surface areas of different atoms in the solute molecule and C is an empirically adjustable parameter. The quality of the description of experimental data has been, however, not significantly improved by the introduction of individual atomic surface tension characteristics.

Another theoretical approach for the calculation of the free energy of cavity formation proceeds from the theory of microscopic curved surfaces. According to this theory,[6]

$$\Delta G_{cav} = k_s^g \left(\frac{V_S}{V_M} \right) \sigma S \qquad\qquad [11.1.8]$$

where S is the area of the cavity and $k_s^g (V_S / V_M)$ is a correction factor, characteristic of a given solvent and depending on the ratio of molecular volumes of the solvent and solute. This factor has been approximated by the following formula

$$k_s^g \left(\frac{V_S}{V_M} \right) = 1 + \left(\frac{V_S}{V_M} \right)^{2/3} \left[k_s^g (1) - 1 \right] \qquad\qquad [11.1.9]$$

where $k_s^g (1)$ is estimated from the solubility of a given solute in a given solvent. The main deficiency of this approach is connected with the introduction of additional empirical information, often not readily available.

The free energy of cavity formation has been also estimated from the data on isothermal compressibility, β_T, as follows[7]

$$\Delta G_{cav} = \frac{V_{cav}}{\beta_T} + C \qquad\qquad [11.1.10]$$

where V_{cav} is the volume of the cavity and C is a constant term. However, the microscopic isothermal compressibility of water, calculated from the slope of Eq. [11.1.10], was found to be about an order higher than the respective experimental value for water ($\beta_T(calc) = 23.5$ vs. $\beta_T(exp) = 3.14$). Therefore, the use of the macroscopic surface tension or compressibility of the solvent for the respective microscopic model quantities is questionable.

An entropic approach to the calculation of the free energy of cavity formation proceeds from the scaled particle theory (SPT).[8,9] The free energy of the formation of a spherical cavity in a solvent, ΔG_{cav}, can be calculated proceeding within the framework of SPT as follows

$$\Delta G_{cav} = RT \left\{ 1 - \ln(1-y) + \left(\frac{3y}{1-y} \right) \frac{a_M}{a_S} + \left[\frac{3y}{1-y} + \frac{9}{2} \left(\frac{y}{1-y} \right)^2 \right] \left(\frac{a_M}{a_S} \right)^2 \right\} \qquad [11.1.11]$$

where

$$y = \frac{4\pi\rho a_s^2}{3} \qquad\qquad [11.1.12]$$

is the reduced number density of the solvent. In the two last equations, a_M and a_S denote the intrinsic radii of the solute and solvent molecules, respectively, and ρ is the number density of the solvent. In the case of an ellipsoidal solute cavity, the SPT cavity formation energy has been given by the following equation[10]

$$\Delta G_{cav} = RT\left\{1 - \ln(1-y) + \left(\frac{\alpha y}{1-y}\right)\frac{a}{a_S} + \left[\frac{\beta y}{1-y} + \gamma\left(\frac{y}{1-y}\right)^2\right]\left(\frac{a}{a_S}\right)^2\right\} \qquad [11.1.13]$$

where α, β and γ denote the geometrical coefficients and a is the characteristic length of the ellipsoid (the major semi-axis). The scaled particle theory has been extended to dilute solutions of arbitrary shaped solutes and has been successfully applied for the calculation of the solvation free energy of hydrocarbons in aqueous solutions.[11]

For most practical applications that involve the lowest excited states of the molecules, the increase in the cavity size during the excitation of the solute molecule would not be accompanied with a significant energetic effect. However, it may be important to account for the so-called Pauli repulsion between the solute electronic system and the surrounding medium. This interaction will force the solute electrons to stay inside the cavity and not to penetrate into the dielectric continuum (consisted of electrons, too) that surrounds it. The Pauli repulsion has been modeled by the respective model potentials, e.g., by expanding the potential in spherical Gaussian shells as follows:[12]

$$V_{PR} = \sum_i b_i \exp\left[-\beta_i(r - r_{o,i})^2\right] \qquad [11.1.14]$$

where b_i are the weight factors, β_i the exponents and $r_{0,i}$ the radii of spherical shell functions. In general, the electrons in the solvent cavity could be treated as confined many-electron systems.[13]

11.1.3 THEORETICAL TREATMENT OF SOLVENT ELECTROSTATIC POLARIZATION ON ELECTRONIC-VIBRATIONAL SPECTRA OF MOLECULES

The origin of the solvatochromic shifts in the electronic spectra is related to the change in the electrostatic and dispersion forces between the solvent and the chromophoric solute molecule in the ground and in the excited state, respectively. The semiclassical approach to the treatment of the respective effects is based on the assumption that the solute and the solvent molecules are sufficiently separated to neglect the overlap between the electron distribution of these two molecular systems. The wave function for the whole system can then be approximated as the product of the wavefunctions of each individual system, i.e., the solute and individual solvent molecules:

$$\Psi = \psi^0_{s(1)}\psi^0_{s(2)}\cdots\psi^0_{s(n)}\psi^{(v)}_a \qquad [11.1.15]$$

where $\psi^0_{s(1)}, \psi^0_{s(2)}, \cdots \psi^0_{s(n)}$, etc. are the wavefunctions of the respective solvent molecules in the ground state and $\psi^{(v)}_a$ is the wavefunction of the solute molecule in the v-th state. The antisymmetry of the total electronic wavefunction is ignored as the individual molecules are assumed separated enough not to allow the electron exchange. This approximation may not be valid in the case of strong semichemical interactions between the solute and the solvent

molecules such as the hydrogen bonding or the formation of charge-transfer complexes. In such cases, the system consisting of the central solute molecule and the adjacent solvent molecules has to be treated as a supermolecule.

In the absence of strong semichemical interactions between the solute and solvent molecules, the interaction energy between them can be derived using the perturbation theory.[14] In the first approximation, the interaction between the nonionic molecules can be reduced to the dipole-dipole interaction between the molecules. The following perturbation operator can describe this interaction

$$\hat{\mathbf{H}}' = \sum_i \frac{\hat{\mu}_\alpha^{(v)} \hat{\Theta}_{ai} \hat{\mu}_{s(i)}}{R_{ai}^3} \qquad [11.1.16]$$

where $\hat{\mu}_\alpha^{(v)}$ and $\hat{\mu}_{s(i)}$ are the dipole moment operators for the solute a in the v-th state and for the i-th solvent molecule in the ground state, respectively, R_{ai} is the distance between the charge centroids of the interacting molecules and

$$\hat{\Theta}_{ai} = \hat{\mathbf{1}} - 3\vec{R}_{ai}\,\vec{R}_{ai} \qquad [11.1.17]$$

is the angular term describing the relative orientation of these two molecules in the space. The subsequent application of the perturbation theory to derive the energy of interaction between a pair of a solute and a set of N solvent molecules gives the following result[15]

$$\Delta E_a = \sum_{i=1}^{N} \frac{\mu_a^{(v)} \Theta_{ai} \mu_{s(i)}}{R_{ai}^3} - \frac{1}{2} \sum_{i=1}^{N} \frac{\mu_a^{(v)} \Theta_{ai} \alpha_s \Theta_{ai} \mu_a^{(v)}}{R_{ai}^6} -$$

$$- \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\mu_{s(i)} \Theta_{ai} \alpha_a^{(v)} \Theta_{aj} \mu_{s(j)}}{R_{ai}^3 R_{aj}^3} - \sum_{i=1}^{N} \sum_{p \neq 0} \sum_{\lambda \neq v} \frac{\mu_{s(i)}^{(0p)} \Theta_{ai} \mu_a^{(\lambda v)} \mu_a^{(\lambda v)} \Theta_{aj} \mu_{s(i)}^{(0p)}}{R_{ai}^6} \qquad [11.1.18]$$

with the following notations:

$$\mu_a^{(v)} = \left\langle \psi_a^{(v)} \middle| \hat{\mu}_a \middle| \psi_a^{(v)} \right\rangle \qquad [11.1.19]$$

is the dipole moment of the solute in the v-th state,

$$\mu_{s(i)} = \left\langle \psi_{s(i)}^0 \middle| \hat{\mu}_s \middle| \psi_{s(i)}^0 \right\rangle \qquad [11.1.20]$$

is the dipole moment of the i-th solvent molecule in the ground state,

$$\alpha_a^{(v)} = 2 \sum_{\lambda \neq v} \frac{\left\langle \psi_a^{(v)} \middle| \hat{\mu}_a \middle| \psi_a^{(\lambda)} \right\rangle \left\langle \psi_a^{(\lambda)} \middle| \hat{\mu}_a \middle| \psi_a^{(v)} \right\rangle}{E_v - E_\lambda} \qquad [11.1.21]$$

is the polarizability tensor of the solute molecule in the v-th state,

$$\alpha_s = 2 \sum_{p \neq 0} \frac{\left\langle \psi_s^0 \left| \hat{\mu}_s \right| \psi_s^{(p)} \right\rangle \left\langle \psi_s^{(p)} \left| \hat{\mu}_s \right| \psi_s^0 \right\rangle}{E_{0s} - E_{ps}}$$ [11.1.22]

is the polarizability tensor of the solvent molecule in the ground state, respectively, and

$$\mu_{s(i)}^{(0p)} = \left\langle \psi_{s(i)}^0 \left| \hat{\mu}_a \right| \psi_{s(i)}^{(p)} \right\rangle$$ [11.1.23]

and

$$\mu_a^{(\lambda v)} = \left\langle \psi_a^{(\lambda)} \left| \hat{\mu}_a \right| \psi_a^{(v)} \right\rangle$$ [11.1.24]

are the transition dipoles between the two states $(0 \rightarrow p)$ in the solvent and in the solute $(\lambda \rightarrow v)$ molecules, respectively. In the last formulae, E_v and E_λ denote the energy of the solute molecule in the respective (v-th and λ-th) states, and E_{ps} and E_{0s} - the energy of a solvent molecule in the p-th and in the ground state, respectively. The first term in equation [11.1.18] represents therefore the electrostatic interaction of the unperturbed charge distribution of the two molecules, given as the interaction between the respective permanent point dipoles. The second term in this equation corresponds to the interaction of the permanent dipole of the solute with the dipole induced in the solvent whereas the third term reflects the interaction of the permanent dipole of the solvent with the induced dipole of the solute. The last term represents the second-order interaction of both molecules in excited states and quantifies thus effectively the dispersion interaction in the solute-solvent system.

The equation [11.1.18] refers, of course, to a single fixed configuration of the solute and the solvent molecules. In order to find the effective interaction energy in the liquid medium, an appropriate statistical averaging over all configurations has to be carried out. In most practical applications, this procedure is very complicated and thus the semiclassical continuum approaches are employed to describe the solvent. The description of the electrostatic interactions between the solute and the solvent has been based on the Onsager's reaction field model. According to this model, the energy of electrostatic interaction between an arbitrary charge distribution inside the solute molecule and the surrounding polarizable dielectric medium is given by the following equation[16]

$$E_{el} = \frac{1}{8\pi} \int_V \mathbf{E}_s \mathbf{E}_o (\varepsilon - 1) dV$$ [11.1.25]

where $\mathbf{E}_o$ is the electrostatic field of the charges in the molecule in vacuo and $\mathbf{E}_s$ is the modified field in the presence of dielectric medium. Notably, within the formalism of the last [11.1.25], the dielectric constant ε of the medium is still a function of the space coordinates, i.e., both the interior of the molecule and the surrounding medium are treated by the same equation. However, the integral in the last equation cannot be found analytically and even the numerical integration over the space presents a difficult mathematical task. Therefore, the electrostatic equation is usually simplified by the application of the Gauss divergence theorem. According to this theorem, the volume integral in [11.1.25] is transformed into a surface integral over some boundary

$$E_{el} = \frac{\varepsilon - 1}{8\pi} \int_S \Phi_S E_o \vec{n} dS \qquad\qquad [11.1.26]$$

where S is the boundary surface, $\vec{n}$ the outward normal unit vector on S and the reaction potential Φ_s is defined as follows: $\mathbf{E_s} = $ -grad Φ_S. Depending on the shape of solute molecular cavity, different approaches have been applied for the calculation of the electrostatic solvation energies of compounds in liquids. Within the classical reaction field theory of Kirkwood and Onsager,[17,18] the solute molecule is represented by a set of point charges fixed inside of sphere of a radius a_0 and the electrostatic equation [11.1.26] is solved by applying the appropriate boundary conditions inside and outside the sphere. It is also assumed that the dielectric constant inside the cavity (sphere) is equal to unity (vacuum) and outside the cavity has a constant value, corresponding to the macroscopic dielectric constant of the medium studied. In that case, the energy of the electrostatic interaction between the solute charge distribution and the surrounding dielectric medium is given by the following infinite expansion

$$E_{el} = \frac{1}{2} \sum_{i,j} e_i e_j \sum_{l=0}^{\infty} \left[\frac{(l+1)(1-\varepsilon)}{\varepsilon(l+1)+1} \right] \frac{r_i^l r_j^l}{a_0^{2l+1}} P_l\left(\cos\theta_{ij}\right) \qquad\qquad [11.1.27]$$

where e_i and e_j are the charges inside the sphere at positions $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively, and θ_{ij} is the angle at the center of the sphere between the vectors $\mathbf{r}_i$ and $\mathbf{r}_j$. In the last equation, the summation proceeds over all charged particles (nuclei and electrons) of the solute and $P_l(\cos\theta_{ij})$ are the Legendre polynomials of l-th order. By expressing the Legendre polynomials as the products of the respective spherical harmonics of order m ($-l \le m \le l$), equation [11.1.27] can be rewritten as

$$E_{el} = -\frac{1}{2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} R_l^m M_l^m \qquad\qquad [11.1.28]$$

where

$$R_l^m = f_l M_l^m \qquad\qquad [11.1.29]$$

and

$$f_l = \frac{(l+1)(\varepsilon-1)}{(l+1)\varepsilon + 1} \frac{1}{a_0^{2l+1}} \qquad\qquad [11.1.30]$$

In these equations, M_l^m and R_l^m represent the electrical momentum and the respective reaction field component. The first term (l = 0) in the expansion [11.1.27] gives the interaction of the excess (ionic) charge of the solute with the respective reaction field created in the dielectric medium (Born term)

$$E_{Born} = \frac{1-\varepsilon}{2\varepsilon} \frac{Q^2}{a_0} \qquad\qquad [11.1.31]$$

where Q is the numerical value of the ionic charge. The next term ($1 = 0$) corresponds to the total dipole interaction with the corresponding reaction field (Onsager dipolar term)

$$E_{Onsager} = \frac{(1-\varepsilon)}{(2\varepsilon + 1)} \frac{\bar{\mu}^2}{a_0^3}$$ [11.1.32]

where $\bar{\mu}$ is the dipole moment of the solute. In most applications, only these two terms that are the largest by size are considered in the calculation of the electrostatic interaction energy. However, depending on system studied, the interaction of higher electrical moments with the corresponding reaction field may become also significant and the terms corresponding to higher moments of order 2^l (quadruple, octuple, hexadecuple, etc.) should be taken into account.

In many cases, the shape of the solute molecule may be very different from the sphere and therefore, it is necessary to develop the methods of calculation of the electrostatic solvation energy for more complex cavities. In the case of the ellipsoidal cavity with main semiaxes **a**, **b**, and **c**, the analytical formulas are still available for the calculation of the charge and dipolar terms of the electrostatic interaction with the reaction field. The charge term is simply

$$E_{Born}^{ell} = \frac{(1-\varepsilon)}{2\varepsilon} \frac{Q^2}{abc}$$ [11.1.33]

whereas in the respective dipolar term[19]

$$E_{Onsager}^{ell} = R\bar{\mu}$$ [11.1.34]

the reaction field **R** is presented using a special tensor as follows

$$R = \begin{pmatrix} \dfrac{3A_a(1-A_a)(1-\varepsilon)\mu_a}{abc[\varepsilon + (1-\varepsilon)A_a]} & 0 & 0 \\ 0 & \dfrac{3A_b(1-A_b)(1-\varepsilon)\mu_b}{abc[\varepsilon + (1-\varepsilon)A_b]} & 0 \\ 0 & 0 & \dfrac{3A_c(1-A_c)(1-\varepsilon)\mu_c}{abc[\varepsilon + (1-\varepsilon)A_c]} \end{pmatrix} \bar{\mu}$$ [11.1.35]

where A_a, A_b and A_c are the standard ellipsoidal shape factor integrals, and μ_a, μ_b and μ_c are the dipole moment components along the main semiaxes of the ellipsoid. Several methods have been developed to define the semiaxes of the ellipsoidal cavity. For instance, these have been taken collinear with the axes of the solute dipole polarizability tensor, and their lengths proportional to the respective eigenvalues.[20] Another definition proceeds from the inertia tensor of the van-der-Waals solid, i.e., a solid or uniform density composed of interlocking van-der-Waals spheres.[21] Also, the ellipsoidal surface has been defined in terms of the best fitting of a given molecular electrostatic isopotential surface.[22]

The above-discussed theoretical formulation of the electrostatic solute-solvent interaction is applicable for the fixed charge distribution inside the solute molecule. However, the solvent reaction field may cause a redistribution of the charge inside the solute. The

magnitude of this redistribution depends on both the dielectric constant of the solvent and the polarizability of the solute molecule. Within the approximations of the spherical solute cavity and the point dipole interactions between the solute and solvent, the dynamically changed Onsager reaction field can be expressed by the following formula[14]

$$R_l = \frac{\mu_a^{(v)} + \alpha_a^{(v)} R_l}{a_0^3} \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)}$$

[11.1.36]

Notably, the use of the macroscopic dielectric constant $\varepsilon = \varepsilon_0$ in the last formula is justified only when the lifetime of the solute molecule in a given (v-th) state is much longer than the rotational-vibrational relaxation time of the solvent at given temperature. This is not a valid assumption in the case of the Franck-Condon states, which have the lifetime much shorter than the rotational-vibrational relaxation time of the solvent. Therefore, the solvent is only partially relaxed for these states and the corresponding reaction field is characterized by the dielectric constant at infinite frequency of external electric field, ε_∞. By inserting the expression for the reaction field [11.1.36] into the equation [11.1.18] and assuming that the static polarizability of the solute molecule is approximately equal to the one third of the cube of Onsager's cavity radius

$$\alpha_a^{(v)} \approx \frac{a_0^3}{3}$$

[11.1.37]

the following semiclassical equation can be obtained for the solvation energy of the v-th (Franck-Condon) state of the solute molecule[14]

$$E_s = -\left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} - \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right)\left[\frac{2\mu_a^0\mu_a^{(v)}}{a_0^3} + \frac{2\mu_a^0\mu_a^{(v)}}{a_0^3}\left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\right)\right] - \frac{2\left(\mu_a^{(v)}\right)^2}{a_0^3}\left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right) +$$

$$+\left[\left(\frac{3}{2\varepsilon_0 + 1}\right)\frac{(2\varepsilon_0 + 1)^2(\varepsilon_0 - \varepsilon_\infty)^2}{(2\varepsilon_0 - \varepsilon_\infty)\varepsilon_0}\frac{kT}{3a_0^3} + \left(\frac{2\varepsilon_0 - 2}{2\varepsilon_0 + 1}\right)^2\right]\sum_{\lambda \neq v}\frac{\left(\mu_a^{(\lambda v)}\right)^2}{E_\lambda - E_v} +$$

$$+\left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right)\frac{2}{a_0^3}\sum_{\lambda \neq v}\left(\mu_a^{(\lambda v)}\right)^2\left(1 - \frac{E_v - E_\lambda}{E_{0s} - E_{ps}}\right)$$

[11.1.38]

The solvatochromic shift due to the difference in the electrostatic solvation energy of the ground state and the excited state of the solute, respectively, is thus given as follows:

$$\Delta E_s = \frac{2}{a_0^3}\left\{\left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} - \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right)\left(\frac{2\varepsilon_0 + 1}{\varepsilon_0 + 2}\right)\left[\left(\mu_a^0\right)^2 - \mu_a^0\mu_a^{(v)}\right] + \left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right)\left[\left(\mu_a^0\right)^2 - \left(\mu_a^{(v)}\right)^2\right]\right\}$$

$$+\left\{\left(\frac{3}{2\varepsilon_0 + 1}\right)\frac{(2\varepsilon_0 + 1)^2(\varepsilon_0 - \varepsilon_\infty)}{(2\varepsilon_0 - \varepsilon_\infty)\varepsilon_0}\frac{kT}{3a_0^3}\left[\sum_{\lambda \neq 0}\frac{\left(\mu_a^{(0\lambda)}\right)^2}{E_0 - E_\lambda} - \sum_{\lambda \neq v}\frac{\left(\mu_a^{(v\lambda)}\right)^2}{E_v - E_\lambda}\right]\right\} +$$

$$+\left(\frac{2\varepsilon_0-2}{\varepsilon_0+2}\right)^2\left[\frac{(\mu_a^{(v)})^2}{a_0^6}\sum_{\lambda\neq v}\frac{(\mu_a^{(v\lambda)})^2}{E_v-E_\lambda}-\frac{(\mu_a^{(0)})^2}{a_0^6}\sum_{\lambda\neq 0}\frac{(\mu_a^{(0\lambda)})^2}{E_0-E_\lambda}\right]+$$

$$+\left(\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\right)\frac{2}{a_0^3}\left[\sum_{\lambda\neq 0}(\mu_a^{(0\lambda)})^2\left(1-\frac{E_\lambda-E_0}{E_{0s}-E_{ps}}\right)-\sum_{\lambda\neq v}(\mu_a^{(v\lambda)})^2\left(1-\frac{E_\lambda-E_v}{E_{ps}-E_{0s}}\right)\right] \qquad [11.1.39]$$

The last expression represents the solvent effect on the transition energy of the 0-0 band of the solute molecule.

McRae[15,23] has given a different derivation of the electrostatic solvation energy based on semiclassical reaction field approach. The final result is however similar to the above equation for the solvatochromic shift in the electronic transition:[15]

$$\Delta E_s = \frac{2}{a_0^3}\left\{\left(\frac{\varepsilon_0-1}{\varepsilon_0+2}-\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\right)\left(\frac{2\varepsilon_0+1}{\varepsilon_0+2}\right)\left[(\mu_a^0)^2-\mu_a^0\mu_a^{(v)}\right]\right\}+$$

$$+\frac{1}{a_0^3}\left(\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\right)\left[(\mu_a^{(v)})^2-(\mu_a^0)^2\right]-\frac{1}{2}\alpha_a^{(v)}\left|\boldsymbol{E}_a^{(v)}\right|^2+\frac{1}{2}\alpha_a^0\left|\boldsymbol{E}_a^0\right|^2+D_a^{(v)}-D_a^0 \qquad [11.1.40]$$

where $\boldsymbol{E}_a^0$ and $\boldsymbol{E}_a^{(v)}$ are the solvent fields due to the permanent dipole moments of the solvent molecules applying to the ground state and to the excited state of the solute molecule, respectively. The terms D_a^0 and $D_a^{(v)}$ denote the solute-solvent intermolecular dispersion energies in the corresponding states.

Abe[24] has developed an alternative semiclassical theory of the solvent effects on electronic spectra. This theory is based on the averaging of the intermolecular interaction energy over all solute-solvent configurations within the approximation of pair interactions. The theory involves the dipole moments and polarizabilities of the solute molecule and takes into account the temperature dependence arising from the Boltzmann factor.

In all above-listed theoretical approaches, the response of the solute charge distribution to the solvent field is expressed by using the static polarizability of the solute molecule. However, it would be plausible to account for this response directly within the quantum mechanical theoretical framework. The quantum-chemical approaches to the calculation of the solvation effects on the ground and excited states of the molecules in the solution can be classified using two possible ways. First, it can be based on the traditional division of the quantum chemistry into the non-empirical (ab initio) and the semiempirical methods. Within both those classes of methods, the Hartree-Fock method based on the independent particle model and the methods accounting for the static and dynamic electron correlation are usually distinguished. The second way of classification of methods can be based on the differences of the models used for the description of solute-solvent interactions. In general, these interactions can be taken into account in the framework of continuum representation of the solvent or using the resolution of solute-solvent interactions at molecular level. In the following, we first proceed with the review of models used for the solute-solvent interactions, with the subsequent elaboration of the quantum-chemical methodology for the calculation of the solvent effects on spectra.

The simplest continuum model is based on the classical Onsager reaction field theory assuming the spherical or ellipsoidal form of cavities for the solute molecules in dielectric

media. The respective interaction energy is accounted for as a perturbation $\hat{\mathbf{V}}(a_0, \varepsilon)$ of the Hamiltonian of the isolated solute molecule, $\hat{\mathbf{H}}^0$.

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}^0 + \hat{\mathbf{V}}(a_0, \varepsilon) \qquad [11.1.41]$$

Within the approximation of electrostatic interaction between the solute dipole and the respective reaction field, the perturbation term is simply

$$\hat{\mathbf{V}}(a_0, \varepsilon) = \Gamma \hat{\mu}_a^2 \qquad [11.1.42]$$

where

$$\Gamma = \frac{2(1-\varepsilon)}{(2\varepsilon + 1)a_0^3} \qquad [11.1.43]$$

In the case of ellipsoidal cavities, the last coefficient has to be substituted by the tensor given in equation [11.1.35].

A self-consistent reaction field method (SCRF) has been developed at the level of Hartree-Fock theory to solve the respective Schrödinger equation[25]

$$\hat{\mathbf{H}}\Psi = E\Psi \qquad [11.1.44]$$

Proceeding from the classical expression for the electrostatic solvation energy of a solute molecule in a dielectric medium in the dipole-dipole interaction approximation, the total energy of the solute is presented as follows[26]

$$E = E^o - \frac{1}{2}\Gamma\left(\langle\psi|\hat{\mu}|\psi\rangle\langle\psi|\hat{\mu}|\psi\rangle + 2\vec{\mu}_{nuc}\langle\psi|\hat{\mu}|\psi\rangle + \vec{\mu}_{nuc}^2\right) \qquad [11.1.45]$$

where $E^o = \langle\psi|\hat{\mathbf{H}}^0|\psi\rangle$, $\hat{\mathbf{H}}^0$ is the Hamiltonian for the reaction field unperturbed solute molecule and ψ is the molecular electronic wave function. From the last equation, one can construct the variational functional

$$L = E^o - \frac{1}{2}\Gamma\left(\langle\psi|\hat{\mu}|\psi\rangle\langle\psi|\hat{\mu}|\psi\rangle + 2\vec{\mu}_{nuc}\langle\psi|\hat{\mu}|\psi\rangle + \vec{\mu}_{nuc}^2\right) - W(\langle\psi|\psi\rangle - 1) \quad [11.1.46]$$

where W is the Lagrange multiplier ensuring the normalization of the variational wave function. The variation of the last equation with respect to the parameters of the wave function yields

$$\delta L = \delta E^o - \Gamma\left(\langle\delta\psi|\hat{\mu}|\psi\rangle\langle\psi|\hat{\mu}|\psi\rangle + \vec{\mu}_{nuc}\langle\psi|\hat{\mu}|\psi\rangle\right) - W\delta(\langle\psi|\psi\rangle)$$

$$= \langle\delta\psi|\hat{\mathbf{H}}^0|\psi\rangle - \Gamma\langle\delta\psi|\hat{\mu}|\psi\rangle\vec{\mu}_{tot} - W\langle\delta\psi|\psi\rangle + c.c. = 0 \qquad [11.1.47]$$

where $\hat{\mu}_{tot} = \hat{\mu}_{nuc} + \langle\psi|\vec{\mu}_{el}|\psi\rangle$ is the total dipole moment of the solute molecule. The latter is calculated during the SCRF procedure simultaneously with the total energy of the system.

From equation [11.1.47], the following Schrödinger equation is obtained for the electronic state $|\psi>$ of the solute molecule

$$\hat{H}^0 - \Gamma\langle\psi|\hat{\mu}_{tot}|\psi\rangle\hat{\mu}_{el} = W|\psi\rangle \qquad [11.1.48]$$

W plays the role of the quantum mechanical motif that is directly obtained from the Schrödinger equation as follows

$$W = \left\langle\psi\left|\hat{H}^0 - \Gamma\langle\psi|\hat{\mu}_{tot}|\psi\rangle\hat{\mu}_{el}\right|\psi\right\rangle = \left\langle\psi\left|\hat{H}^0\right|\psi\right\rangle - \Gamma\langle\psi|\hat{\mu}_{tot}|\psi\rangle\langle\psi|\hat{\mu}_{el}|\psi\rangle \qquad [11.1.49]$$

By adding the part for the interaction of the nuclear component of the solute dipole with the total reaction field and assuming

$$\left\langle\psi\left|\hat{H}^0\right|\psi\right\rangle \approx \left\langle\psi^0\left|\hat{H}^0\right|\psi^0\right\rangle \qquad [11.1.50]$$

where ψ^0 is the wavefunction of the solute molecule, unperturbed by the reaction field, one obtains that

$$E_{el} = E_{rf} - E_0 = \left\langle\psi\left|\hat{H}^0\right|\psi\right\rangle - \Gamma\left(\langle\psi|\hat{\mu}_{el}|\psi\rangle + \vec{\mu}_{nuc}\right)^2 - \left\langle\psi^0\left|\hat{H}^0\right|\psi^0\right\rangle \approx -\Gamma\langle\vec{\mu}_{tot}\rangle^2 \qquad [11.1.51]$$

The comparison of the last equation with the starting equation [11.1.44] reveals a difference by the factor of two in the final result. Of course, the approximation [11.1.50] brings up a certain error and it has been therefore proposed[25,27] to correct the last formula by the addition of the "solvent cost", i.e., the additional work required to reorganize the solvent due to the electrostatic field of the solute

$$E_{el} = E_{rf} - E_0 + \frac{1}{2}\Gamma\langle\vec{\mu}_{tot}\rangle^2 \qquad [11.1.52]$$

Alternatively, the electrostatic solvation energy can be derived proceeding from the following variational functional[27]

$$L = E^0 - \frac{1}{4}\Gamma\left(\langle\psi|\hat{\mu}|\psi\rangle\langle\psi|\hat{\mu}|\psi\rangle + 2\vec{\mu}_{nuc}\langle\psi|\hat{\mu}|\psi\rangle + \vec{\mu}_{nuc}^2\right) - W(\langle\psi|\psi\rangle - 1) \qquad [11.1.53]$$

This leads to a Schrödinger equation which eigenvalue is directly related to the total electrostatic (dipolar) solvation energy, E_{el},

$$\left(\hat{H}^0 - \frac{1}{2}\Gamma\langle\psi|\hat{\mu}_{tot}|\psi\rangle\hat{\mu}_{el}\right)|\psi\rangle = E_{el}^{(e)}|\psi\rangle \qquad [11.1.54]$$

$$E_{el} = E_{rf}^{(e)} - \frac{1}{2}\Gamma\vec{\mu}_{nuc}\vec{\mu}_{tot} - E_0 \qquad [11.1.55]$$

For the solution of equation [11.1.54], the molecular wavefunction can be presented as a proper spin-projected antisymmetrized product of molecular (or atomic) orbitals[27]

$$|\psi\rangle = O_s A[\phi_1, \cdots, \phi_n]$$ [11.1.56]

Recalling that the dipole moment operator is a one-electron operator (as are all electric moment operators), the following orbital equations are obtained

$$\mathbf{f}(k)\phi_i(k) = \varepsilon_i \phi_i(k)$$ [11.1.57]

with

$$\mathbf{f}(k) = \mathbf{f}_0(k) - \Gamma\langle\psi|\hat{\mu}_{tot}|\psi\rangle\hat{\mu}_{el}(k)$$ [11.1.58]

or

$$\mathbf{f}(k) = \mathbf{f}_0(k) - \frac{1}{2}\Gamma\langle\psi|\hat{\mu}_{tot}|\psi\rangle\hat{\mu}_{el}(k)$$ [11.1.59]

where $\mathbf{f}_0(k)$ is the usual Fock operator for the isolated molecule, ε_i is the molecular orbital energy for $|\phi_i\rangle$ and $\hat{\mu}_{el}(k)$ is the electronic part of the dipole moment operator. Both equations are solved iteratively, using the usual SCF procedure and the expectation value of the total dipole moment from the previous SCF cycle.

A scheme for the treatment of the solvent effects on the electronic absorption spectra in solution had been proposed in the framework of the electrostatic SCRF model and quantum chemical configuration interaction (CI) method.[27] Within this approach, the absorption of the light by chromophoric molecules was considered as an instantaneous process. Therefore, during the photon absorption no change in the solvent orientational polarization was expected. Only the electronic polarization of solvent would respond to the changed electron density of the solute molecule in its excited (Franck-Condon) state. Consequently, the solvent orientation for the excited state remains the same as it was for the ground state, the solvent electronic polarization, however, must reflect the excited state dipole and other electric moments of the molecule. Considering the SCRF Hamiltonian

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}^0 + \Gamma\langle\phi|\hat{\mu}_{tot}|\phi\rangle\hat{\mu}$$ [11.1.60]

it is possible to write for the state $|\psi_I\rangle$ the following expression

$$H_{II} = \langle\psi_I|\hat{\mathbf{H}}^0 + \Gamma\langle\psi|\hat{\mu}|\psi\rangle\hat{\mu}|\psi_I\rangle = \langle\psi_I|\hat{\mathbf{H}}^0|\psi_I\rangle - \Gamma\langle\psi_0|\hat{\mu}|\psi_0\rangle\langle\psi_I|\hat{\mu}|\psi_I\rangle$$ [11.1.61]

that is the zeroth order estimate of the energy of the state $|\psi_I\rangle$. Then, for a single excitation, $I \rightarrow A$, the excitation energy is given as follows

$$\Delta E_{ia} = \varepsilon_a - \varepsilon_i - J_{ia} + \begin{Bmatrix} 2 \\ 0 \end{Bmatrix} K_{ia} = \varepsilon_a^0 - \varepsilon_i^0 - J_{ia} + \begin{Bmatrix} 2 \\ 0 \end{Bmatrix} K_{ia} -$$
$$-\Gamma \langle \psi_0 | \hat{\mu} | \psi_0 \rangle [\langle \psi_i^a | \hat{\mu} | \psi_i^a \rangle - \langle \psi_0 | \hat{\mu} | \psi_0 \rangle]$$

[11.1.62]

where J_{ia} and K_{ia} are the respective Coulomb' and exchange matrix elements and Γ is the reaction field tensor at the dipole level. The terms ε_i^0 are the eigenvalues of the Fock operator for the k-th electron in the isolated solute molecule. The off-diagonal CI matrix elements are given by

$$H_{IJ} = \langle \psi_I | \hat{H}^0 + \Gamma \langle \psi | \hat{\mu} | \psi \rangle \hat{\mu} | \psi_J \rangle = \langle \psi_I | \hat{H}^0 | \psi_J \rangle - \Gamma \langle \psi_0 | \hat{\mu} | \psi_0 \rangle \langle \psi_I | \hat{\mu} | \psi_J \rangle$$

[11.1.63]

Equations [11.1.60] - [11.1.63] demonstrate that some part of the solvent effect is already included in the ordinary CI treatment when proceeding from the SCRF Fock matrix. It has to be noticed that the terms $\langle \psi_0 | \hat{\mu} | \psi_0 \rangle$ should represent the ground-state dipole moment after CI, and therefore, an iterative procedure would be required to obtain a proper solution. However, at the CIS (CI single excitations) level, commonly used for the spectroscopic calculations, this is no concern because of Brillouin's theorem, which implies that the CI does not change the dipole moment of the molecule. Even at higher levels of excitation in CI, this effect should not be large and might be estimated from the respective perturbation operator.[27]

There are two approaches to address the instantaneous electronic polarization of the solvent during the excitation of the solute molecule. In the first case, the following correction term has to be added to the CI excitation energy

$$\Delta E_I = \frac{1}{2} \Gamma(\varepsilon_\infty) \left[\langle \psi_0 | \hat{\mu} | \psi_0 \rangle \langle \psi_I | \hat{\mu} | \psi_I \rangle - |\langle \psi_I | \hat{\mu} | \psi_I \rangle|^2 \right]$$

[11.1.64]

where $\Gamma(\varepsilon_\infty)$ is the reaction field tensor for the optical relative dielectric permittivity of the solvent, ε_∞. In the last equation, the first term removes the incorrect term arising from the SCRF orbitals and energies in forming the CI matrix whereas the second term adds the response of the electronic polarization of the solvent to the dipole of the excited state. Equation [11.1.64] is first order in electron relaxation. Higher orders can be examined by defining the perturbation

$$X^{(I)} = \lambda \Gamma(\varepsilon_\infty) \frac{\left[\langle \psi_0 | \hat{\mu} | \psi_0 \rangle - \langle \psi_I | \hat{\mu} | \psi_I \rangle \right]}{2}$$

[11.1.65]

which is clearly different for each excited state and would, if pursued, lead to a set of excited states that were nonorthogonal. In principle, these corrections need not to be small.

Depending on the Fock operator used (equation [11.1.58] or [11.1.59]), the excitation energy from the ground state $|\psi_0\rangle$ to the excited state $|\psi_I\rangle$ of a solute molecule in a dielectric medium is given as follows

$$W_I^A - W_0^A = \langle \psi_I | \hat{H} | \psi_I \rangle - \langle \psi_0 | \hat{H} | \psi_0 \rangle + \frac{1}{2} \Gamma \langle \psi_0 | \hat{\mu} | \psi_0 \rangle [\langle \psi_I | \hat{\mu} | \psi_I \rangle - \langle \psi_0 | \hat{\mu} | \psi_0 \rangle] -$$

$$-\frac{1}{2}\Gamma(\varepsilon_\infty)\langle\psi_I|\hat{\mu}|\psi_I\rangle\Big[\langle\psi_I|\hat{\mu}|\psi_I\rangle-\langle\psi_0|\hat{\mu}|\psi_0\rangle\Big]\qquad\qquad\text{[11.1.66]}$$

in the first case, and

$$W_I^B-W_0^B=\langle\psi_I|\hat{H}|\psi_I\rangle-\langle\psi_0|\hat{H}|\psi_0\rangle-\frac{1}{2}\Gamma(\varepsilon_\infty)\langle\psi_I|\hat{\mu}|\psi_I\rangle\Big[\langle\psi_I|\hat{\mu}|\psi_I\rangle-\langle\psi_0|\hat{\mu}|\psi_0\rangle\Big]\quad\text{[11.1.67]}$$

in the second case. The last two equations are first order in electron polarization of the solvent.

The second approach to the calculation of spectra in solutions is based on the assumption that the ground and excited states are intimately coupled in an instantaneous absorption process.[28,29] In this model, the solute ground state electron distribution responds to the electron distribution in the excited state through the instantaneous polarization of the solvent. In such a case, the energy of the absorbing (ground) state is shifted by the following amount

$$\frac{1}{2}\Gamma(\varepsilon_\infty)\langle\psi_0|\hat{\mu}|\psi_0\rangle-\langle\psi_0|\hat{\mu}|\psi_0\rangle-\frac{1}{2}\Gamma(\varepsilon_\infty)\langle\psi_0|\hat{\mu}|\psi_0\rangle\Big[\frac{1}{2}\langle\psi_I|\hat{\mu}|\psi_I\rangle-\langle\psi_0|\hat{\mu}|\psi_0\rangle\Big]\qquad\text{[11.1.68]}$$

In the last equation, the first term removes the first order in the electron polarization part of the dielectric relaxation included in the SCRF of the ground state, and the second term adds back the appropriate interaction of the ground state with the "mean" reaction field, created by the excited state, $|\psi_I\rangle$. This leads to the following equation for the excitation energy

$$W_I^A-W_0^A=\langle\psi_I|\hat{H}|\psi_I\rangle-\langle\psi_0|\hat{H}|\psi_0\rangle+\frac{1}{2}\Gamma\langle\psi_0|\hat{\mu}|\psi_0\rangle\Big[\langle\psi_I|\hat{\mu}|\psi_I\rangle-\langle\psi_0|\hat{\mu}|\psi_0\rangle\Big]+$$

$$-\frac{1}{4}\Gamma(\varepsilon_\infty)\langle\psi_I|\hat{\mu}|\psi_I\rangle\Big[\langle\psi_I|\hat{\mu}|\psi_I\rangle-\langle\psi_0|\hat{\mu}|\psi_0\rangle\Big]^2\qquad\qquad\text{[11.1.69]}$$

for the Fock operator [11.1.58] and

$$W_I^B-W_0^B=\langle\psi_I|\hat{H}|\psi_I\rangle-\langle\psi_0|\hat{H}|\psi_0\rangle+\frac{1}{4}\Gamma(\varepsilon_\infty)\Big[\langle\psi_I|\hat{\mu}|\psi_I\rangle-\langle\psi_0|\hat{\mu}|\psi_0\rangle\Big]^2\qquad\text{[11.1.70]}$$

for the Fock operator [11.1.59]. However, it should be noticed that all four equations for spectral transition energies [[11.1.66], [11.1.67], [11.1.69] and [11.1.70]] yield very similar results when $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transition solvatochromic shifts have been compared between the nonpolar and polar solvents.[27] In Table 11.1.3, the results of the INDO/S (ZINDO)[30,31] SCRF CIS calculated spectroscopic transition energies are given for some solvatochromic dyes. The relative shifts due to the solvent are reproduced theoretically in most cases. Even the absolute values of the spectroscopic transition energies are in satisfactory agreement with the respective experimental values, which demonstrates the applicability of the spectroscopic INDO/S parameterization for the spectra in solutions.

Table 11.1.3. INDO/S SCRF CI calculated and experimental spectroscopic transition energies of some dyes in different solvents[27]

Molecule	Solvent	ν_{calc}, cm^{-1}	ν_{exp}, cm^{-1}
(Scheme 23)	Gas phase Cyclohexane Water	29,700 26,300 22,500	- 27,400 23,300
(Scheme 24)	Gas phase n-Hexane Water	36,900 34,800 31,100	- 30,200 26,100
(Scheme 25)	Gas phase Chloroform Water	20,200 21,800 24,600	- 19,600 22,100

Scheme 23
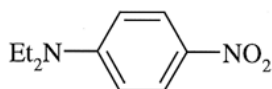
Scheme 24
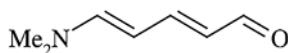
Scheme 25
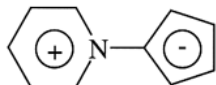
The INDO/S SCRF CI method has been also successfully applied for the prediction of the solvatochromic shifts in various nitro-substituted porphyrins.[32]

The SCRF methodology has been employed also for the prediction of the solvatochromic shifts on emission spectra.[33,34] A satisfactory agreement was obtained between the calculated and experimental fluorescence energies of p-N,N-dimethylaminobenzonitrile in different solvents. Finally, the solvent-induced shifts in the vibrational spectra of molecules have been also calculated using the SCRF theory.[35]

The SCRF approach has been also implemented for the treatment of solute-continuum solvent systems at the ab initio Hartree-Fock level of theory.[36,37] In addition, a general SCRF (GSCRF) approach has been proposed to account for the interaction of the solvent reaction field with the arbitrary charge distribution of the solute molecule. According to this theory,[38,39] the effective Hamiltonian of the solute in the solvent has the following form

$$\hat{H}_s = \hat{H}_s^0 + \int d\mathbf{r}\Omega_s(\mathbf{r})\left[V_m^0(\mathbf{r}) + \int d\mathbf{r}' G(\mathbf{r},\mathbf{r}')\Omega_s(\mathbf{r}') \right] \qquad [11.1.71]$$

where $\Omega_s(\mathbf{r})$ is the solute charge density operator given by

$$\Omega_s(\mathbf{r}) = -\sum_i \delta(\mathbf{r}-\mathbf{r}_i) + \sum_a Z_a\delta(\mathbf{r}-\mathbf{R}_a) \qquad [11.1.72]$$

where $\mathbf{r}_i$ stands for the i-th electron position vector operator, $\mathbf{R}_a$ is the position vector of the a-th nucleus with the charge Z_a in the solute and $\delta(\mathbf{r})$ is the Dirac's delta function. The first term in square brackets in Eq. [11.1.71], $V_m^0(\mathbf{r})$, represents the electrostatic potential created by the solvent in the absence of the solute and the second, integral term corresponds to the reaction potential response function of the polarizable solvent. Together these terms produce the reaction field potential applying to the solvent molecule in the polarizable dielectric medium. Notably, a principal part of the Hamiltonian [11.1.71] is the solute charge density that can be represented using different approximations of which the multipolar expansion has been mostly applied. By using the distributed multipole model, it is possible to obtain the GSCRF equations for the molecules of a complex shape. However, it has been mentioned that the use of multipole expansions of the solvent electrostatic and reaction potentials in Eq. [11.1.71] may cause this Hamiltonian to become unbound and special damping procedures have been invented to overcome this difficulty.

The GSCRF total energy of the solute is given by the following equation

$$E_{GSCRF} = \left\langle \psi \left| \hat{H}^0 \right| \psi \right\rangle + \left\langle \psi \left| \int d\mathbf{r}\Omega_s(\mathbf{r})V_m^0(\mathbf{r}) \right| \psi \right\rangle + \frac{1}{2}\left\langle \psi \left| \int d\mathbf{r}\Omega_s(\mathbf{r}) \right| \psi \right\rangle \int d\mathbf{r}'G(\mathbf{r},\mathbf{r}')\Omega_s(\mathbf{r}') \quad [11.1.73]$$

This energy expression can be used to build up the respective variational functional to get the molecular orbitals [above]. A crucial step in the general self-consistent reaction field procedure is the estimation of the solvent charge density needed to obtain the response function $G(\mathbf{r},\mathbf{r}')$ and the reaction potential. The use of Monte Carlo or molecular dynamics simulations of the system consisting the solute and surrounding solvent molecules has been proposed to find the respective solvent static and polarization densities.

Several methods have been developed to account for the solute cavities of arbitrary shape in the solution. The polarizable continuum model (PCM) is based on the numerical integration of the relevant electrostatic equations describing the electrostatic interaction between the molecular charge distribution and the charge created on the boundary surface between the solute molecule and surrounding dielectric continuum.[40-45] Within this method, the solute cavity is usually constructed from the overlapping van der Waals spheres of constituent atoms in the solute molecule and the solvent reaction field arising from the solute charge distribution is calculated numerically. Alternatively, the cavity can be defined as constructed from the electron isodensity surface around the solute molecule (IPCM).[46] According to the classical electrostatics, the electrostatic potential at any point in the space can be described in terms of the apparent charge distribution, σ, on the cavity surface. It consists of two terms

$$\Phi_s = \Phi_M + \Phi_\sigma \qquad [11.1.74]$$

the first of which (Φ_M) corresponds to the electrostatic potential created by the charge distribution of the solute and the second (Φ_σ) is due to the reaction potential by the solvent. The latter is directly connected with the apparent charge distribution on the surface of the cavity as follows:

$$\Phi_\sigma(\mathbf{r}) = \int_\Sigma \frac{\sigma(\mathbf{s})}{|\mathbf{r} - \mathbf{s}|}d^2\mathbf{s} \qquad [11.1.75]$$

where Σ is the cavity surface and $\mathbf{s}$ vector defines a point on Σ. The Σ surface is usually divided into appropriate number of triangular small areas (tesserea), each of which has an area ΔS_k and contains the charge q_k in some internal point $\mathbf{s}_k$. Thus, according to this, so-called boundary element method, the reaction potential is found as the following sum over all tesserea

$$\Phi_\sigma(\mathbf{r}) = \sum_k \frac{q_k}{|\mathbf{r} - \mathbf{s}_k|} \qquad [11.1.76]$$

with

$$q_k = \Delta S_k \sigma(\mathbf{s}_k) \qquad [11.1.77]$$

In the application of the boundary element method, it is crucial to select appropriate boundary surface for the solute cavity and to proceed as accurate as possible tessellation (triangulation) of this surface. For instance, it has been proposed that in the case of the cavity formation from overlapping van-der-Waals spheres, the atomic van-der-Waals radii should be multiplied by a coefficient equal to 1.2. Other possibilities of the surface definition include the closed envelope obtained by rolling a spherical probe of adequate diameter on the van-der-Waals surface of the solute molecule and the surface obtained from the positions of the center of such spherical probe around the solute.

Within the quantum-mechanical theory, the PCM model proceeds from the following Schrödinger equation for a solute molecule in the dielectric continuum

$$\left(\hat{\mathbf{H}}^0 + \hat{V}_{PCM}\right)\Psi = E\Psi \qquad [11.1.78]$$

where the reaction field potential is given by equation [11.1.76] as follows

$$\hat{V}_{PCM} = \sum_k \frac{q_k}{|\mathbf{r} - \mathbf{s}_k|} \qquad [11.1.79]$$

The charges on the boundary are found from the electrostatic polarization of the dielectric medium on the surface of the cavity due to the potential derived from the charge distribution of the solute and from other (induced) charges on the surface. The induced surface charge is evaluated iteratively at each step of the SCF procedure to solve the Schrödinger equation [11.1.78]. It has been reported that a simultaneous iteration of the surface charge with the Fock procedure reduces substantially the computation time without the loss in the precision of calculations.

Also, it has been shown that the expressions which determine the charges q_k may be given as a set of linear equations. In the matrix form[42]

$$\mathbf{D}\mathbf{q}^{0f} = \mathbf{E}_{in} \qquad [11.1.80]$$

where $\mathbf{D}$ is a square nonsymmetric and nondiagonal matrix with the dimension equal to the number of surface elements, derived from the curvature of the surface and $\mathbf{q}^{0f}$ is a column

vector, containing the unknown surface charges. $\mathbf{E}_{in}$ is also a column vector collecting the effective components of the solute electric field multiplied by the surface elements

$$E_{in,k}^{0} = -\Delta S_k \vec{\nabla}\Phi_{M,in}(\mathbf{s}_k)\mathbf{n}_k \qquad\qquad [11.1.81]$$

The $\mathbf{D}$ matrix depends only on the shape of the cavity and the dielectric constant of the medium. Therefore, when the system of linear equations [11.1.80] has to be solved several times with different $\mathbf{E}_{in}$, as in the case of the polarizable solute, it may be convenient to work with the single inversion matrix $\mathbf{D}^{-1}$.

The PCM model has been implemented for the calculation of the electronic excitation energies of solvated molecules within the quantum-mechanical configuration interaction method.[47,48] The respective final expression for the excitation energy from the ground state (0) to the I-th state has the following form

$$\Delta W^{(0I)} = \Delta E_{CI}^{(0I)} - \frac{1}{2}\left[\mathbf{J}_{20}(\mathbf{P}_I - \mathbf{P}_0) + \mathbf{P}_0\mathbf{T}_0(\mathbf{P}_I - \mathbf{P}_0)\right] +$$
$$+ \frac{1}{2}\left[\mathbf{J}_{2\infty}(\mathbf{P}_I - \mathbf{P}_0) + \mathbf{P}_I\mathbf{T}_\infty(\mathbf{P}_I - \mathbf{P}_0)\right] \qquad [11.1.82]$$

where $\mathbf{P}_I$ and $\mathbf{P}_0$ are the electronic density matrices of the solute in the excited state and in the ground state, respectively,

$$\Delta E_{CI}^{(0I)} = E_I - E_0 + \frac{1}{2}\left[2(\mathbf{P}_I - \mathbf{P}_0)\mathbf{T}_0\mathbf{P}_0 + (\mathbf{P}_I - \mathbf{P}_0)\mathbf{J}_{10} + \mathbf{J}_{20}(\mathbf{P}_I - \mathbf{P}_0)\right] \qquad [11.1.83]$$

are the diagonal elements of CI matrix, and

$$\mathbf{T} = C^t\mathbf{W}^{-1}\partial\hat{C} \qquad\qquad [11.1.84]$$

$$\mathbf{J}_1 = C\mathbf{W}^{-1}\partial\hat{\mathbf{M}}\mathbf{Z} \qquad\qquad [11.1.85]$$

$$\mathbf{J}_2 = \mathbf{Z}^t\mathbf{M}^t\mathbf{W}^{-1}\partial\hat{C} \qquad\qquad [11.1.86]$$

$$\mathbf{B} = \mathbf{Z}^t\mathbf{M}^t\mathbf{W}^{-1}\partial\hat{\mathbf{M}}\mathbf{Z} \qquad\qquad [11.1.87]$$

In the last equations, C and $\partial\hat{C}$ are the matrices representing the electrostatic potential and the electric field generated from the electron distribution in the solute molecule, respectively. The matrices $\mathbf{M}$ and $\partial\hat{\mathbf{M}}$ are the matrices representing the electrostatic potential and the electric field generated from the nuclear charges in the solute molecule, respectively. The diagonal elements of the matrix $\mathbf{W}$ are defined as the following function of the dielectric constant of the solvent

$$W_{ii} = \frac{\varepsilon + 1}{\varepsilon - 1} \qquad\qquad [11.1.88]$$

The subscripts 0 and ∞ in the $\mathbf{J}_1$, $\mathbf{J}_2$, and $\mathbf{T}$ matrices in equation [11.1.82] correspond to the static and optical dielectric constant of the solvent. Equation [11.1.82] can be considered

as an analog of equation [11.1.66] for the case of arbitrary cavity shape. The PCM-CI method has been applied for the calculation of solvatochromic shifts in the spectrum 4-[(4'-hydroxyphenyl)azo]-N-methylpyridine in a variety of solvents.[48]

An integral equation formalism (IEF) has been developed as particularly suitable for the description of solvent effects on spectral transition energies within the PCM model.[49] The respective theoretical equations have been applied for the calculation of solvatochromic shifts of several carbonyl-group containing molecules at the self-consistent field (SCF), configuration interaction (CI) and multiconfiguration self-consistent (MC SCF) field level of theory. The calculated spectral shifts accompanying the transfer of a solvatochromic compound from the gas phase to water were comparable with the experimental data. In Table 11.1.4, the results of calculations are presented for three carbonyl compounds, formaldehyde, acetaldehyde and acetone.

Table 11.1.4. The calculated and experimental solvatochromic shifts (from the gas phase to water) in the spectra of some carbonyl compounds (cm^{-1})[49]

Compound	ΔSCF	CI(SDT)	CAS SCF	Exp.
Formaldehyde	1889	839	944	1700-1900[a]
Acetaldehyde	1854	979	1049	1700-1900[a]
Acetone	2273	1574	1259	1539-1889

[a]an estimate from other compounds

The advantage of the PCM method is in that it is applicable to the solute cavity of practically any shape in the solution. However, it is not clear how precisely should the molecular cavity be defined bearing in mind the classical (quasi-macroscopic) representation of the solvent. It is difficult to perceive that the solvent, e.g., the water molecules, can produce the electrical polarization corresponding to the statistically average distribution in the macroscopic liquid at infinitely small regions on the cavity surface. However, it is conceivable that larger chemical groups in the molecules may possess their own reaction field created by their charge distribution and the reaction fields of other groups in the solute molecule. A multi-cavity self-consistent reaction field (MCa SCRF) has been proposed[50] for the description of rotationally flexible molecules in condensed dielectric media. It proceeds from the observation that the interaction of the charge and higher electrical moments of a charge distribution in a spherical cavity with the corresponding reaction fields localized in the center of the cavity does not depend on the position of charge or (point) multipole centers in this cavity. Therefore, it is possible to divide a rotationally flexible solute molecule or a hydrogen-bonded molecular complex between two or more spherical cavities that embed the rotationally separated fragments of the solute or solute and solvent molecules, respectively. Assuming the classical Born-Kirkwood-Onsager charge density expansion (Eq. 11.1.27) for each of these fragments, the total energy of the solute in a dielectric medium can be expressed as a sum of terms that correspond to the energies arising from the interaction of the partial charge and the electric moments of a given molecular fragment with the reaction field of its own and the reaction fields of other fragments, as well as from the interaction between the reaction fields of different fragments. The Hartree-Fock-type equations derived from the variational functional for the total energy E can then be solved iteratively using the

SCRF procedure. The PCM approach has been further refined to account for the curvature of surface elements.[4] Also, this approach has been applied within different quantum-chemical frameworks.[47]

An alternative method for the description of solute-continuum electrostatic interaction has been developed as based on the notion that the electrostatic equations referring to the boundary surface between the solute and dielectric medium can be substantially simplified if to assume that the solvent is a homogeneous ideally conducting medium. Within this method (called the COSMO method), the electrostatic screening energy of a solute is given by the following equation (in matrix form)[51]

$$\Delta E = -\frac{1}{2} \mathbf{QBA}^{-1} \mathbf{BQ}$$ [11.1.89]

with the following matrix elements

$$b_{ik} \approx \left\| \mathbf{t}_k - \mathbf{r}_i \right\|^{-1}$$ [11.1.90]

for the point charges and

$$b_{ik} \approx \int_{\mu,\nu \in i} \frac{\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r})}{\left\| \mathbf{t}_k - \mathbf{r} \right\|} d^3\mathbf{r}$$ [11.1.91]

for the continuous charge distribution, and

$$a_{kl} \approx \left\| \mathbf{t}_k - \mathbf{t}_l \right\|^{-1}, \quad k \neq l, \quad a_{kk} \approx 3.8 \left| S_k \right|^{-1/2}$$ [11.1.92]

In the last equations, $\mathbf{t}_k$ denotes the position vectors of the centers of small surface elements k on the arbitrary cavity surface; $\mathbf{r}_i$ are the position vectors of the point charges in the solute molecule; $\mathbf{r}$ is the vector for electronic charge position described on the atomic basis $\{\chi_\mu(\mathbf{r})\}$ and S_k are the areas of the surface elements. In equation [11.1.82], $\mathbf{Q}$ is the matrix of source charges in the solute.

The COSMO model has been extended to account for the solvents with any dielectric constant.[52-54] Within the respective GCOSMO method,[53] the surface charges $\sigma(\mathbf{r})$ on the boundary between the solute and continuum solvent are first determined for the medium with the infinite dielectric constant under the assumption that the electrostatic potential on the surface S is zero. For a dielectric medium specified by the dielectric constant ε, the actual surface charges are then calculated by scaling the screening conductor surface charge $\sigma(\mathbf{r})$ by a factor of $f(\varepsilon) = (\varepsilon - 1)/\varepsilon$. This scaling preserves the validity of the Gauss theorem for the total surface charge. The boundary element method is applied for the calculation of the surface charge density, with the boundary divided into small areas and the surface charge approximated as the point charge in the center of this area. The charges are calculated either using the charge distribution in the molecule or by minimizing variationally of the total electrostatic solvation energy. The total free energy of the system of solute and surface charges is then calculated within the Hartree-Fock theory as

$$E_{tot} = \left[P_{\mu\nu} \left(H_{\mu\nu}^0 + H_{\mu\nu}^s \right) + \frac{1}{2} \left(G_{\mu\nu}^0 + G_{\mu\nu}^s \right) \right] - \frac{1}{2} f(\varepsilon) \mathbf{Z}^\dagger \mathbf{B}^\dagger \mathbf{A}^{-1} \mathbf{BZ} + E_{nn} + E_{nes} \quad [11.1.93]$$

where E_{nn} is solute nuclear-nuclear repulsion and E_{nes} is the solvation energy related to the dispersion and repulsion between the solute and solvent, and cavity formation; $H_{\mu\nu}^0$ and $G_{\mu\nu}^0$ are the one-electron and two-electron parts of the Fock matrix for the isolated solute, respectively, and $P_{\mu\nu}$ are the density matrix elements. The solvent perturbations to the corresponding operators have been expressed as

$$H_{\mu\nu}^s = -f(\varepsilon) \mathbf{Z}^\dagger \mathbf{B}^\dagger \mathbf{A}^{-1} \mathbf{B} L_{\mu\nu} \quad [11.1.94]$$

and

$$G_{\mu\nu}^s = -f(\varepsilon) \left(\sum_{\lambda,\sigma} P_{\lambda\sigma} L_{\lambda\sigma}^+ \right) \mathbf{A}^{-1} \mathbf{L}_{\mu\nu} \quad [11.1.95]$$

where $\mathbf{A}$ and $\mathbf{B}$ are the N x N square matrices (N - number of atomic nuclei in the solute molecule) with the elements defined by equations [11.1.90] and [11.1.92]. The matrices $\mathbf{L}_{\mu\nu}$ consist of the one-electron integrals [11.1.91]. The first and second derivatives needed for the calculation of the molecular potential surfaces and the respective solvent effects on vibrational spectra have been also supplied within the framework of GCOSMO approach.[53] A semi-quantitative agreement between the computational and experimental results has been obtained for the vibrational frequencies of acetone in water.

Several approaches have been developed to account for the electron correlation effects on the solvation energy of both the ground and the excited states of the molecule in the solution. A multiconfigurational self-consistent reaction field (MC SCRF) theory has been proposed as based on the classical Onsager's reaction field model.[55] Notably, the higher order electrical moments of the solute molecule and the respective reaction field in the solvent were taken into account within this method. Thus, the dielectric solvation energy of a solute in a given state embedded into a linear isotropic medium has been calculated as the product of the expectation values for the reaction field $\langle \mathbf{R}_l^m \rangle$ and the respective multipole charge moments $\langle \mathbf{M}_l^m \rangle$ of the solute[55-58]

$$E_{el} = -\frac{1}{2} \sum_{l,m} \langle \mathbf{R}_l^{m^+} \rangle \langle \mathbf{M}_l^m \rangle \quad [11.1.96]$$

where

$$\langle \mathbf{M}_l^m \rangle = \sum_k Z_k S_l^m (R_k) - \langle S_l^m \rangle \quad [11.1.97]$$

$$\langle \mathbf{R}_l^m \rangle = f \langle \mathbf{M}_l^m \rangle \quad [11.1.98]$$

and

$$f_l = \frac{(l+1)(\varepsilon-1)}{1+\varepsilon(l+1)} \frac{1}{a^{-(2l+1)}} \qquad\qquad [11.1.99]$$

$$S_l^m(\mathbf{r}) = \left[\frac{4\pi}{2l+1}\right]^{1/2} \mathbf{r}^l Y_{lm}(\theta,\varphi) \qquad\qquad [11.1.100]$$

where $Y_{lm}(\theta,\varphi)$ are the Legendre' polynomials.

Interestingly, it had been suggested that the dispersion interaction energy between the solute and the solvent could be accounted for, in principle, in the framework of this approach as related to the full distribution of dielectric relaxation frequencies of the solvent. Thus, the formula for the MC SCRF solvation energy has been expressed as follows

$$E_{el} = -\frac{1}{2}\sum_{l,m} f_l (T_{lm})^2 \qquad\qquad [11.1.101]$$

with the terms T_{lm} obtained from the expectation values of the nuclear and electronic solvent operators

$$T_{lm} = T_{lm}^n - T_{lm}^e \qquad\qquad [11.1.102]$$

$$T_{lm}^n = \sum_a Z_a R^{lm}(\mathbf{R}_a) \qquad\qquad [11.1.103]$$

$$T_{lm}^e = R^{lm}(\mathbf{r}) \qquad\qquad [11.1.104]$$

where R^{lm} are the special solvent effect integrals.[55]

The solvent contributions have been developed also for the multiconfigurational energy gradient and Hessian, necessary for the solution of the MC SCRF equations. Notably, the results of the model calculations on water molecule implied that the higher multipole terms might play a significant role in the total electrostatic solvation energy of the molecule. Thus, the quadrupole term consisted approximately 20% of the dipolar term whereas the 4-th order term was even more significant (~ 30% of the dipolar term). The MC SCRF method has been applied for the calculation of the solvent effects on the spectral transitions of water and formaldehyde in different media.[59] The MC SCRF methodology has been further refined in the framework of the response theory approach.[60] This development describes the response of the solute or the solute-solvent complex to a time-independent or time-dependent high-frequency perturbation such as the spectral excitation.

In order to take into account the electron correlation effects, another combination of the self-consistent reaction field theory with the configuration interaction formalism has been introduced as follows.[61] Within this approach, the usual CI wavefunction has been constructed as follows

$$\Psi_{CI} = \sum_{a=1}^{N} C_a D_a \qquad\qquad [11.1.105]$$

where C_a are the CI expansion coefficients and D_a are the basis functions (Slater determinants or their linear combinations). In the case of orthogonal basis functions, the normalization condition of the function Ψ_{CI} is given as

$$\sum_{a=1}^{N} C_a^2 = 1 \qquad [11.1.106]$$

and the coefficients C_a are determined from the following equation

$$\left(\hat{H}^0 + \hat{V}_{rf}\right)\Psi = E\Psi \qquad [11.1.107]$$

where $\hat{H}^0$ is the Hamiltonian for the molecule, unperturbed by the reaction field and $\hat{V}_{rf}$ is the reaction field perturbation. The latter can be presented, for example, in the framework of the boundary element method as follows (cf. Eq. [11.1.75])

$$\hat{V}_{rf} = \int d^2\mathbf{r} \frac{\sigma(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad [11.1.108]$$

where $\sigma(\mathbf{r}')$ is the charge density on the surface of the cavity.

For the spectroscopic applications, it would be again instructive to separate the noninertial and inertial components of the electrostatic polarization of the dielectric medium. The first of them corresponds to the electrostatic polarization of the electron charge distribution in the solvent that is supposedly instantaneous as compared to any electronic or conformational transition of the solute. The second component arises from the orientational polarization of the solvent molecules in the electrostatic field of the solute. The noninertial polarization can be described by the optical dielectric permittivity of the solvent that corresponds to the infinite frequency of external electromagnetic field ($\varepsilon_\infty \approx n_D^2$) whereas the inertial polarization represents the slow, orientational part of the total dielectric constant of the solvent, ε. In order to separate the noninertial polarization, it is helpful to determine the solute charge density as the sum of the respective nuclear and electronic parts

$$\rho = \rho_n + \rho_e = \sum_A \delta(\mathbf{r} - \mathbf{r}_A)Z_A + \sum_{a,b} C_a C_b (ab|\mathbf{r},\mathbf{r}') = \sum_{a,b} C_a C_b \rho_{ab} \quad [11.1.109]$$

where $\delta(\mathbf{r} - \mathbf{r}_A)$ is the Dirac's delta function and $(ab|\mathbf{r},\mathbf{r}')$ are the elements of the single-determinant matrices of transitions between the configurations. Notably, the values of

$$\rho_{ab} = \delta_{ab}\rho_n - \rho(ab|\mathbf{r},\mathbf{r}') \qquad [11.1.110]$$

do not depend on the coefficients C_a and C_b. The noninertial component of the polarization field, $\Phi_\infty(\mathbf{r})$, is always in equilibrium and thus it can be represented as follows

$$\Phi_\infty(\mathbf{r}) = \sum_{a,b} C_a C_b \Phi_{ab}^{(\infty)}(\mathbf{r}) \qquad [11.1.111]$$

where $\Phi_{ab}^{(\infty)}(\mathbf{r})$ is the solution of equation [11.1.107] for the basic charge distribution ρ_{ab}. Since the latter does not depend on the coefficients C_a and C_b, the values of $\Phi_{ab}^{(\infty)}(\mathbf{r})$ can be

determined before the calculation of the wavefunction Ψ_{CI} [11.1.105]. The coefficients C_a can be calculated, as usual, from the matrix equation

$$\mathbf{H}|C\rangle = E|C\rangle \qquad\qquad [11.1.112]$$

where $|C\rangle$ denotes the column-vector of the coefficients and the elements of the matrix $\mathbf{H}$ are given as follows[61]

$$H_{ab} = \left\langle D_a \left| \hat{\mathbf{H}}^0 \right| D_b \right\rangle + \sum_{a,b} C_a C_b \int d^3\mathbf{r}\rho_{ab}\Phi_{ab}^{(\infty)} + \int d^3\mathbf{r}\rho_{ab}\Phi_0 \qquad [11.1.113]$$

where Φ_0 is inertial (nuclear) part of the polarization field. For a given Φ_0, the set of equations [11.1.98] can be solved iteratively. Implicitly, the last equations describe both the electron subsystems of the solute and solvent, the latter being taken into account as the field of noninertial (electron) polarization of the solvent, $\Phi^{(\infty)}$.

The electron correlation effects on the solvation energy of a solute have been also accounted for within the framework of the perturbation theory.[62,63] By starting from the Hamiltonian of the solute molecule as follows

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}^0 - M_l^m f_l^m \left\langle \psi \middle| M_{l'}^{m'} \middle| \psi \right\rangle \qquad\qquad [11.1.114]$$

where ψ denotes the exact (correlated) wavefunction, the Hartree-Fock operator may be written as

$$\mathbf{F} = \mathbf{F}^0 - M_l^m f_l^m \left\langle \psi_0 \middle| M_{l'}^{m'} \middle| \psi_0 \right\rangle \qquad\qquad [11.1.115]$$

where ψ_0 denotes the electronic wavefunction at the Hartree-Fock level. The Hamiltonian may be then written as a perturbed expression of the Hartree-Fock operator

$$\hat{\mathbf{H}} = \mathbf{F} + \left(\hat{\mathbf{H}}^0 - \mathbf{F}^0\right) + M_l^m f_l^m \left(\left\langle \psi_0 \middle| M_{l'}^{m'} \middle| \psi_0 \right\rangle - \left\langle \psi \middle| M_{l'}^{m'} \middle| \psi \right\rangle\right) \qquad [11.1.116]$$

The perturbation has two contributions, the standard Møller-Plesset perturbation and the non-linear perturbation due to the solute-solvent interaction. If $C_j^{(i)}$ denotes the coefficient of the eigenstate $|J\rangle$ in the corrections of ψ to the i-th order, then the perturbation operators $H^{(i)}$ of the i-th order are given by the following formulae

$$\hat{\mathbf{H}}^{(1)} = \hat{\mathbf{H}}^0 - \mathbf{F}^0 \qquad\qquad [11.1.117]$$

$$\hat{\mathbf{H}}^{(2)} = -2\sum_{I \neq 0} C_I^{(1)} M_l^m f_l^m \left\langle 0 \middle| M_{l'}^{m'} \middle| I \right\rangle \qquad\qquad [11.1.118]$$

$$\hat{\mathbf{H}}^{(3)} = -2\sum_{J \neq 0} C_J^{(2)} M_l^m f_l^m \left\langle 0 \middle| M_{l'}^{m'} \middle| J \right\rangle - \sum_{J \neq 0}\sum_{P \neq 0} C_J^{(1)} C_P^{(1)} M_l^m f_l^m \left\langle I \middle| M_{l'}^{m'} \middle| P \right\rangle \quad [11.1.119]$$

The calculation is performed, as usual, by comparing the coefficients of the Schrödinger equation to successive orders.

The first order energy is the same as given by the usual Møller-Plesset treatment, $<0|\hat{H}^0|0>$ and the first order electrostatic contribution to the free energy of solvation is identical to the result obtained at the Hartree-Fock level of theory. The second order correction to the free energy is given as

$$\Delta G_s^{(2)} = 2\sum_{S\neq 0} C_S^{(2)} \left\langle 0\left|M_{l'}^{m'}\right|S\right\rangle f_l^m \left\langle 0\left|M_{l'}^{m'}\right|0\right\rangle + \sum_{D\neq 0}\sum_{D'\neq 0} C_D^{(1)} C_{D'}^{(1)} \left\langle D\left|M_{l'}^{m'}\right|D'\right\rangle f_l^m \left\langle 0\left|M_{l'}^{m'}\right|0\right\rangle \qquad [11.1.120]$$

where $|S\rangle$ stands for the singly excited states, and $|D\rangle$ and $|D'\rangle$ for a pair of doubly excited states different by just one orbital. Without excessive difficulty, it is possible to derive the correction terms to the electrostatic free energy of solvation of higher orders.

A many-body perturbation theory (MBPT) approach has been combined with the polarizable continuum model (PCM) of the electrostatic solvation.[64-66] The first approximation called by authors the perturbation theory at energy level (PTE) consists of the solution of the PCM problem at the Hartree-Fock level to find the solvent reaction potential and the wavefunction for the calculation of the MBPT correction to the energy. In the second approximation, called the perturbation theory at the density matrix level only (PTD), the calculation of the reaction potential and electrostatic free energy is based on the MBPT corrected wavefunction for the isolated molecule. At the next approximation (perturbation theory at the energy and density matrix level, PTED), both the energy and the wave function are solvent reaction field and MBPT corrected. The self-consistent reaction field model has been also applied within the complete active space self-consistent field (CAS SCF) theory[12,67] and the complete active space second-order perturbation theory.[12,67,68]

Several groups[69-73] have also proposed the quantum mechanical density functional theory (DFT) based methods for the calculation of the electrostatic solvation energy in dielectric media. However, the application of this theory for excited states is not straightforward.[74,75]

11.1.4 THEORETICAL TREATMENT OF SOLVENT DISPERSION EFFECTS ON ELECTRONIC-VIBRATIONAL SPECTRA OF MOLECULES

The dispersion interaction between two atomic or molecular systems can be theoretically presented at different levels of theory.[76-78] The modelling of the dispersion interactions in condensed media is more complicated and proceeds either from the discrete molecular description of the liquid or from the continuum model. According to a contemporary classification,[4] the theoretical approaches to the dispersion effect in solutions can be divided into following classes:

- pair-potential approaches
- reaction field based approaches
- cavity surface-dispersion energy relationship approaches

The pair-potential approach is based on the discrete representation of the pairs of solvent and solute molecules or some fragments of them. The respective dispersion potentials are expressed as truncated asymptotic expansions in powers of 1/r, the reciprocal of the distance between the interacting entities[4]

$$U_{ms}(disp) = \sum_{k=6,8,10} d_{ms}^k r_{ms}^{-k} \qquad [11.1.121]$$

where the indexes m and s denote the structural entities (atoms, bonds, chemical groups) belonging to the solute and solvent molecules, respectively. The powers in expansion [11.1.121] are based on the formal theory of two-body interactions. In the practical calculations, only the first term of the expansion (k = 6) is frequently applied. The expansion coefficient $d_{ms}^{(6)}$ can be calculated using the London formula

$$d_{ms}^{(6)} = -\frac{3}{2}\alpha_m\alpha_s\frac{\bar{I}_m\bar{I}_s}{\bar{I}_m+\bar{I}_s} \qquad [11.1.122]$$

where α_m and α_s are the isotropic polarizabilities for interacting systems and $\bar{I}_m$ and $\bar{I}_s$ are the mean excitation energies of these systems. This approximate formula is, in principle, valid only for interacting atoms. In the case of molecular systems, the atomic or group polarizabilities and local excitation energies are, as a rule, not isotropic and require the use of the respective tensor quantities. The absence of information about of accurate solute-solvent atom-atom distribution functions in dense media complicates further the accurate treatment of the dispersion interaction. These distribution functions can be calculated either using the molecular dynamics or Monte Carlo computer simulations or from the experimental scattering data on the respective systems. However, almost all these methods give only the averaged distribution functions and lack, therefore, the information about the local anisotropy of the atom-atom distributions.

Similarly to the treatment of electrostatic effects, the dispersion potential can be limited to the dipole-dipole term and the mean excitation energies are approximated by the respective ionization potentials for the solute and solvent molecules. Thus, when a small cluster of solvent molecules surrounds the solute molecule, the first approximation of the dispersion energy can be presented by the following formula:[79]

$$U_{MS}(disp) = -\frac{x}{4}\frac{\bar{I}_M\bar{I}_S}{\bar{I}_M+\bar{I}_S}\sum_{u=1}^{B_M}\sum_{v=1}^{B_S}\left\{r_{uv}^{-6}Tr[\mathbf{T}_{uv}\mathbf{A}_u\mathbf{T}_{uv}\mathbf{A}_v]\right\} \qquad [11.1.123]$$

where B_M and B_S are the number of bonds in the solute and in the solvent molecules, respectively, $\bar{I}_m$ and $\bar{I}_s$ are the corresponding mean excitation energies, $\mathbf{T}_{uv}$ is the tensor

$$\mathbf{T}_{uv} = 3\frac{\mathbf{r}_{uv}}{r_{uv}}\otimes\frac{\mathbf{r}_{uv}}{r_{uv}} - 1 \qquad [11.1.124]$$

where r_{uv} and $\mathbf{r}_{uv}$ are the distance and the radius-vector between the bonds u and v, respectively, and $\mathbf{A}_u$ is the polarizability tensor for bond u. The factor x in equation [11.1.123] is introduced to achieve the agreement between the molecule-molecule pair dispersion potential and a simpler expression derived on the basis of assumption that the dispersion energy between two molecules may be reduced to the sum of independent atom-atom contributions[80]

$$U_{MS}(disp) = \sum_m\sum_s d_{ms}^{(6)}r_{ms}^{-6} \qquad [11.1.125]$$

A scheme has been developed that reduces the spatial representation of the dispersion interaction into a surface representation of this interaction.[4] According to this approach, the average dispersion-repulsion energy of a solute-solvent system has been written as follows:

$$\left\langle E_{disp-rep} \right\rangle = \int \cdots \int U(\Omega)\, g(\Omega)\, d\Omega \qquad [11.1.126]$$

where Ω stands for the set of all coordinates of the molecules involved, $g(\Omega)$ is the solute-solvent pair distribution function and $U(\Omega)$ is expressed as a sum of two-body dispersion-repulsion potentials. In the case of the fixed geometry of the solute molecule

$$\left\langle E_{disp-rep} \right\rangle = n_S \sum_{s \in S} N_S \sum_{m \in M} \sum_k d_{ms}^{(k)} \int r_{ms}^{(k)} g_{ms}(\mathbf{r}_{ms})\, dr_{ms}^3 \qquad [11.1.127]$$

The integrals in the last formula can be limited only to a certain minimum distance defined, for instance, by the van-der-Waals envelopes of interacting molecules. By introducing the auxiliary vector functions $A_{ms}^{(k)}(\mathbf{r}_{ms})$ such that

$$\vec{\nabla} A_{ms}^{(k)}(r_{ms}) = d_{ms}^{(k)} \mathbf{r}_{ms}^{-k} g_{ms}(\mathbf{r}_{ms}) \qquad [11.1.128]$$

the average dispersion-repulsion energy between the solute and solvent molecules in solution may be written as follows

$$\left\langle E_{disp-rep} \right\rangle = n_S \sum_{s \in S} N_S \sum_{m \in M} \sum_k \int_{\Sigma_s} \mathbf{A}_{ms}^{(k)} \mathbf{n}_\sigma d\sigma \qquad [11.1.129]$$

where $\mathbf{n}_\sigma$ is the outer normal to the surface Σ_s at the position σ. The integral in the last equation may be calculated numerically using an appropriate partitioning (tessellation) of the surface.

A quantum-mechanical method of calculation of the dispersion energy has been developed on the basis of the above-cited semiclassical Abe's theory.[81] According to this method, the dispersion energy, E_{disp}, for a solute molecule in a spherical cavity is given as follows

$$E_{disp} = -\frac{2}{3} \frac{1}{a_S^3 a_M^3} \sum_{J \neq I} \sum_{K \neq O} \frac{\left(\mu_{IJ}^M\right)^2 \left(\mu_{KO}^S\right)^2}{E_K^S - E_O^S + E_J^M - E_I^M} \qquad [11.1.130]$$

where the superscript S refers to the solvent molecule and the superscript M to the solute molecule. Thus, μ_{IJ}^M and μ_{KO}^S are the transition dipoles between the respective states of the solute (I and J) and the solvent (K and O) molecules. In equation [11.1.130], E_K^S, E_O^S and E_J^M, E_I^M denote the energies of the K-th and O-th state of the solvent and of the J-th and I-th state of the solute molecule, respectively. The cavity radii for the solvent and solute molecules are denoted as a_S and a_M, respectively.

Table 11.1.5. The INDO/CI calculated solvatochromic shifts Δν (from the gas phase to cyclohexane) of some aromatic compounds and the respective experimental data in low polarity solvents (cm⁻¹)[81]

Compound	Transition	Δν (calc)	Δν (exp)
Benzene	$^1B_{2u}$	-316	-209[a]
Naphthalene	$^1L_b(x)$ $^1L_b(y)$	-332 -879	-300[b]; -275[a] -950[b]; -902[a]
Chrysene	$^1L_b(^1B_u)$ $^1L_a(^1B_u)$ $^1B_b(^1B_u)$	-243 -733 -1666	-252[a] -1030[a] -1620[a]
Azulene	$^1L_b(y)$ $^1L_a(x)$ $^1K_b(y)$ $^1B_b(x)$	+162 -288 -446 -1475	+164[c] -333[c] -285[c] -1650[c]

[a]in n-pentane, [b]in cyclohexane, [c]in 2-chloropropane

The equation [11.1.130] has been used within the semiempirical quantum-chemical INDO/CI formalism to calculate the solvent shifts of some aromatic compounds in cyclohexane.[81] The results compare favorably with the experimental data for some nonpolar solvents (cf. Table 11.1.5).

11.1.5 SUPERMOLECULE APPROACH TO THE INTERMOLECULAR INTERACTIONS IN CONDENSED MEDIA

The supermolecule approach to the calculation of solute-solvent interaction energies is based on the discrete molecular representation of the solvent. The supermolecule can be treated quantum-mechanically as a complex consisting of the central solute molecule and the surrounding closest solvent molecules. This supermolecule complex can be treated individually or as submerged into the dielectric continuum.[82] In the last case, some continuum theory (SCRF, PCM) is applied to the supermolecule complex consisting of the solute molecule and the solvent molecules in its first coordination sphere.[83-86] Therefore, the short-range solute-solvent electron correlation, dispersion and exchange-repulsion interactions are taken into account explicitly at the quantum level of theory as the electrons and nuclei both from the solute and solvent are included explicitly in the respective Schrödinger equation. The long-range electrostatic polarization of the solvent outside the first coordination sphere is, however, treated according to the dielectric continuum theory. Thus, the energy of solvation of a solute molecule can be expressed as follows:

$$E_{sol} = \left\langle \Psi_{SM} \middle| \hat{H}_{SM}^{(S)} \middle| \Psi_{SM} \right\rangle - \left\langle \Psi_{SM} \middle| \hat{H}_{M}^{(0)} \middle| \Psi_{SM} \right\rangle - n\left\langle \Psi_{SM} \middle| \hat{H}_{S}^{(0)} \middle| \Psi_{SM} \right\rangle \qquad [11.1.131]$$

where $\hat{H}_{SM}^{(S)}$ is the Hamiltonian for the supermolecule in the solution, and $\hat{H}_{M}^{(0)}$ and $\hat{H}_{S}^{(0)}$ are the Hamiltonians for the isolated solute and the solvent molecules, respectively. In the last equation, n denotes the number of the solvent molecules applied in the supermolecule, Ψ_{SM} is the total wavefunction of the supermolecule immersed into dielectric medium, and Ψ_M and Ψ_S are the wavefunctions for isolated solute and solvent molecules, respectively.

For instance, the $n \rightarrow \pi^*$ electronic transition ($1^1A_1 \rightarrow 1^1A_2$) of formaldehyde solvated by varying number of water molecules has been investigated using multi-reference CI calculations.[87] This simple supermolecule approach has given already satisfactory results as compared to experimental shifts in liquid water. However, it has been shown that in general, both the short-range quantum mechanical effects and the long-range solvent polarization play important role in determining the spectral shifts in liquid media. Thus, the INDO/S SCRF CIS theory alone has explained the solvatochromic shifts of azoles in different solvents, except those observed in water (Table 11.1.6).[85] In both the water and acetonitrile, the compounds are predicted to have practically the same shift that is not the case in experiment. The explicit bonding of two water molecules to the nitrogen lone pairs leads in the cases of pyrimidine and pyridazine to the calculated large red shift instead of the experimentally observed solvatochromic blue shift. However, by treating the complex of an azole and two water molecules quantum-mechanically in the surrounding reaction field leads to quantitatively correct blue shifts.

Table 11.1.6. The INDO/S SCRF/CI calculated and experimental spectral transition energies in different solvents for azoles (cm^{-1})[85]

Molecule	Solvent	ν_{calc}, cm^{-1}	ν_{exp}, cm^{-1}
Pyrimidine	gas phase	32966	-
	isooctane	33559	34200
	diethyl ether	34127	34400
	acetonitrile	34697	34800
	water	34743	36900
	2H$_2$O	30982	36900
	water + 2H$_2$O	36572	36900
Pyridazine	gas phase	28329	-
	isooctane	29460	29740
	diethyl ether	30382	30150
	acetonitrile	31296	31080
	water	31368	33570
	2H$_2$O	26490	33570
	water + 2H$_2$O	33927	33570
Pyrazine	gas phase	30387	-
	isooctane	30387	31610
	diethyl ether	30387	31610
	acetonitrile	30387	31740
	water	30387	33160
	2H$_2$O	32900	33160
	water + 2H$_2$O	33301	33160

As a general remark, in the calculations of the intermolecular interactions using the supermolecule approach, the "size-extensivity"[88] of the methods applied is of crucial importance. Furthermore, the interaction energies calculated in the supermolecule approach usually suffer from what is called the basis set superposition error (BSSE),[89] a spurious energy improvement resulting from the use of truncated basis sets. This error seems to be unavoidable in most practical calculations except for very small systems.[90]

The intermolecular interactions that correspond to the fixed geometry of the solute-solvent complex can be also studied by a perturbation approach.[91,92] It has been suggested that the perturbation theory has some advantages over the supermolecule approach and may therefore be considered conceptually more appropriate for the calculation of intermolecular interaction energies. In this case, the interaction energy is calculated directly and it may be separated into components of well-defined physical meaning.

Within the direct reaction field (DRF) method,[93-96] the classical part of the solute-solvent system (solvent) is treated as a distribution of the polarizable point dipoles, interacting with each other. The DRF Hamiltonian of the solute-solvent system is thus given by the following formula:

$$\hat{\mathbf{H}}_{DRF} = \hat{\mathbf{H}}^0 - \frac{1}{2}\sum_{i,j}\sum_{p,q}\mathbf{F}_{ip}^+\alpha_{pq}\mathbf{F}_{jq} \qquad\qquad [11.1.132]$$

where indices i an j correspond to the solute particles (electrons and nuclei) and p and q run over the external polarizable points. $\mathbf{F}_{ip}$ is the field of the particle i at the position p, and α_{pq} gives the induced dipole at point q by a field applied at point p. The respective Schrödinger equation can be solved directly, without the iterative adjustment of the solvent charge distribution and the respective reaction field potential. The DRF method proceeds from the direct reaction field obtained as the linear solute-solvent interaction operator, proportional to the square of the electric field operator while the GSCRF approach uses the average reaction field model. It has been suggested that the additional energy contributions can be interpreted as due to the dispersion interaction between the solute and solvent molecules.[97] More recently, the DRF approach has been combined with the continuum approach by dividing the space around the solute into a closer surrounding treated by direct reaction field method and to more distant space represented by the macroscopic dielectric properties of the solvent.[98,99] A good quantitative agreement has been obtained between the experimental and DRF calculated solvatochromic shifts of the $n \rightarrow \pi^*$ transition of acetone in different solvents.[100,101]

Nevertheless, even at the highest theoretical level accessible for practical calculations, the static approach is strictly valid only for the description of the molecular clusters of fixed geometry. However, in the cases of strong and weak intermolecular interactions, the energy of interaction in the molecular cluster in the gas phase or on the inert-gas matrix is substantially different from the total solvation energy in the condensed phase.[102] A direct solution of a time-dependent Schrödinger equation for the condensed low-order bulk matter, needed to overcome this problem, is premature. Therefore, the molecular dynamics method (MD)[103-105] based on the computer modelling of a system of molecules which interact by the known model potential to each other and undergoes the rotational and translational movement in the field caused by this interaction according to the classical (Newtonian) mechanics is widely applied for this purpose. By applying various boundary conditions and performing the calculation of the potential energies and forces for hundreds of thousands configurations obtained by step-by-step time evolution the time - averages such as internal energy (or enthalpy) can be obtained. An alternative is the stochastic Monte Carlo method that is based on the ergodic theorem and provides the ensemble averages calculated from randomly generated and weighted configurations. These methods suffer from several shortcomings, of which the problem of the applicability of the ergodic theorem (i.e., the identity

of the time-averaged and ensemble-averaged thermodynamic and dynamic observables), the path sampling and difficulties to obtain precise intermolecular interaction potentials are most serious. Also, the real dense systems, i.e., liquids and solutions are intrinsically quantified systems and therefore a quantum molecular dynamics should be developed which accounts for the quantum effects in the microscopic system from the first principles. The combined quantum-mechanical/molecular dynamics (QM/MD) or quantum-mechanical/molecular mechanics (QM/MM) approaches have been used for the calculation of solvatochromic shifts in different media.[106-108]

Numerous computational schemes have been developed to calculate the total molecular solvation energy or free energy using the combination of different theoretical solute-solvent interaction models. From these, one of the most popular is the SMx methodology.[109,110] This methodology proceeds from the division of the total molecular solvation energy into the solute-solvent electrostatic and inductive polarization terms, standard-state free energy of cavity creation in the solvent plus the solute-solvent dispersion interaction, and an empirical part of the nuclear motion free energy. The solvent polarization term is presented using the generalized Born formula:

$$G_p = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\sum_{k=1}^{N}\sum_{k'=1}^{N} q_k q_{k'} \gamma_{kk'} \qquad [11.1.133]$$

where the double summation is performed over all atomic partial charges q_k in the solute molecule, ε is the relative dielectric permittivity of the solvent and $\gamma_{kk'}$ - the Coulomb' integral between two centers k and k', parameterized for the interactions with the solvent. The cavity creation plus dispersion term is calculated as

$$G_{CD}^0 = \sum_{k=1}^{N} \sigma_k A_k \qquad [11.1.134]$$

where N is the number of atoms in the solute, A_k is the solvent accessible surface area of a given atom and σ_k is the parameter for this atom that is called the accessible surface tension. The latter is obtained from the fit with the experimental data and is, thus, essentially an empirical parameter for a given type of atom. Thus, in essence the SMx methodology represents a semiempirical approach to the calculation of solvent effects.

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11.2 DIELECTRIC SOLVENT EFFECTS ON THE INTENSITY OF LIGHT ABSORPTION AND THE RADIATIVE RATE CONSTANT

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11.2.1 THE CHAKO FORMULA OR THE LORENTZ-LORENZ CORRECTION

The intensity of light absorption by a molecule is generally altered when the molecule is immersed in a solvent or transferred from one solvent to another. The change may be small if the solvents are inert and non-polar, but often a significant increase or decrease is observed. The first attempt to correlate such effects with the nature of the solvent was made by Chako[1] in 1934. Chako's formula reads as

$$\frac{f''}{f} = \frac{\left(n^2 + 2\right)^2}{9n}$$

[11.2.1]

where:

f	oscillator strength of an absorption band of a molecule
f′	apparent oscillator strength of the molecule in solution
n	refractive index of the solution at the absorbing frequency

The apparent oscillator strength is proportional to the integrated intensity under the molar absorption curve. To derive the formula, Chako followed the classical dispersion theory with the Lorentz-Lorenz relation (also known as the Clausius-Mosotti relation), assuming that the solute molecule is located at the center of the spherical cavity in the continuous dielectric medium of the solvent. Hence, the factor derived by Chako is also called the Lorentz-Lorenz correction. Similar derivation was also presented by Kortüm.[2] The same formula was also derived by Polo and Wilson[3] from a viewpoint different from Chako.

Chako's formula always predicts an increase of the absorption intensity with the refractive index. This does not hold, for instance, for the allowed $\pi \rightarrow \pi^*$ electronic transitions of cyclohexadiene and cyclopentadiene,[4] and monomethyl substituted butadienes.[5]

11.2.2 THE GENERALIZED LOCAL-FIELD FACTOR FOR THE ELLIPSOIDAL CAVITY

A natural generalization of the Chako formula was made by generalizing the spherical cavity to an ellipsoidal cavity. Such a generalization was shown by Shibuya[6] in 1983. The generalized formula derived by him reads as

$$\frac{f''}{f} = \frac{\left[s\left(n^2 - 1\right) + 1\right]^2}{n}$$

[11.2.2]

where:

s	shape parameter which takes a value between 0 and 1

This parameter s is more generally known as the depolarization factor, whose values are listed for special cases in general textbooks.[7] For the spherical cavity, s = 1/3 in any axis; for
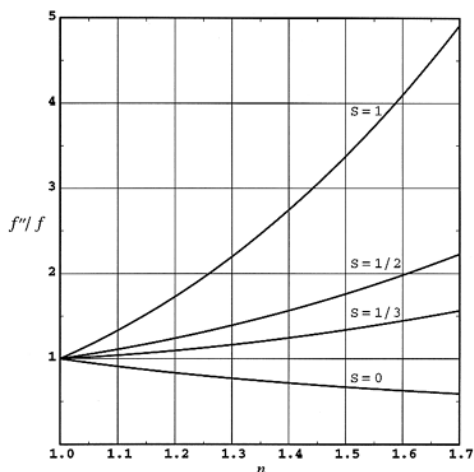
Figure 11.2.1. Dependence of f''/f on the refractive index n for different values of s. [After reference 6]

a thin slab cavity, s = 1 in the normal direction and s = 0 in plane; and for a long cylindrical cavity, s = 0 in the longitudinal axis and s = 1/2 in the transverse direction. The shape of the ellipsoidal cavity is supposed to be primarily determined by the shape of the solute molecule. Typical cases are long polyenes and large planar aromatic hydrocarbons. One can assume s = 0 for the strong $\pi \rightarrow \pi^*$ absorption bands of these molecules. For smaller molecules, however, one should assume $s \approx 1/3$ regardless of the shape of the solute molecule, as the cavity shape then may be primarily determined by the solvent molecules rather than the solute molecule. Note that Eq. [11.2.2] gives the Chako formula for s = 1/3, i.e., for the spherical cavity.

For transitions whose moments are in the longitudinal axis of a long cylindrical cavity or in the plain of a thin slab cavity, Eq. [11.2.2] with s = 0 leads to $f''/f = 1/n$, so that the absorption intensity always decreases with the refractive index. If the transition moment is normal to a thin slab cavity, Eq. [11.2.2] with s = 1 leads to $f''/f = n^3$. The dependence of the ratio f''/f on the refractive index n according to Eq. [11.2.2] is illustrated for different values of s in Figure 11.2.1. The slope of the ratio is always positive for s > 1/4. For 0 < s < 1/4, it is negative in the region $1 \leq n \leq \sqrt{(1-s)/3s}$ and positive in the other region.

Eq. [11.2.2] can be also written as the following form:

$$\sqrt{(nf'')} = \sqrt{f} s(n^2 - 1) + \sqrt{f} \qquad [11.2.3]$$

This equation shows a linear relationship between $\sqrt{(nf'')}$ and $(n^2 - 1)$. If a set of measured values of f'' vs. n are provided for a solute, the least-squares fitting to Eq. [11.2.3] of $\sqrt{(nf'')}$ against $(n^2 - 1)$ gives the values of f and s for the solute molecule. Note that f'' and f in Eq. [11.2.3] can be replaced by any quantities proportional to the oscillator strengths. Thus, they can be replaced by the integrated intensities or by their relative quantities.

Figure 11.2.2 shows such plots for the $\pi \rightarrow \pi^*$ absorption bands of β-carotene and the $n \rightarrow \pi^*$ absorption bands of pyrazine measured[8] in various organic solvents. Here, the relative intensities f''/f_c'', where f_c'' is the absorption intensity measured in cyclohexane as the reference solvent, are considered, and $y = \sqrt{nf''/f_c''}$ is plotted against $x = n^2 - 1$. The least-squares fittings give s = 0 for the allowed $\pi \rightarrow \pi^*$ transition of β-carotene and s = 0.29 for the vibronic $n \rightarrow \pi^*$ transition of pyrazine. Note that in this case the least-squares fitted line gives $\sqrt{f/f_c''}$ as its intercept and $s\sqrt{f/f_c''}$ as its slope so that s is given as the ratio of the slope divided by the intercept. A similar study was made[9] on the $n \rightarrow \pi^*$ absorption bands of acetone and cyclopentanone, giving the results s = 0.88 and $f = 1.8 \times 10^{-4}$ for acetone and s=0.72 and $f = 2.2 \times 10^{-4}$ for cyclopentanone.

A similar generalization was also made by Buckingham.[10] He followed Kirkwood's idea[11] in deriving the electric moment of a dielectric specimen produced by a fixed mole-
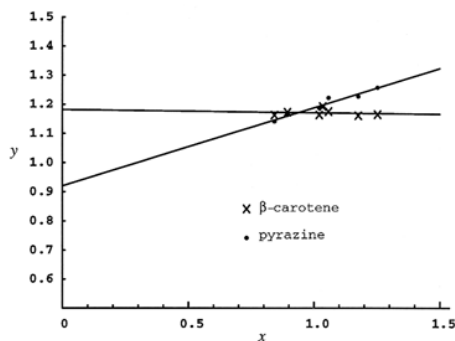
Figure 11.2.2. Plots of $y = \sqrt{nf''/f_c'}$ vs. $x = n^2 - 1$ for the $\pi \to \pi *$ absorption bands of β-carotene (crosses) and the $n \to \pi *$ absorption bands of pyrazine (solid circles). [After reference 6]

cule in its interior and Scholte's extension[12] of the cavity field and the reaction field in the Onsager-Böttcher theory[13,14] to an ellipsoidal cavity. Buckingham's formula involves the polarizability of the solute molecule and appears quite different from Eq. [11.2.2]. It was shown[6] that the Buckingham formula reduces to Eq. [11.2.2].

11.2.3 DIELECTRIC SOLVENT EFFECT ON THE RADIATIVE RATE CONSTANT

The radiative rate constant is related to the absorption intensity of the transition from the ground state to the excited state under consideration. The application of Eq. [11.2.2] leads[15] to

$$k_r''/k_r = n\left[s\left(n^2 - 1\right) + 1\right]^2 \qquad [11.2.4]$$

where:

k_r'' apparent radiative rate constant of the solute molecule measured in a solvent of the refractive index n

k_r radiative rate constant of the molecule in its isolated state

Note that the local-field correction factor $n[s(n^2 - 1) + 1]^2$ varies from n to n^5 as s varies from 0 to 1. For 9,10-diphenylanthracene (DPA), the correction factor was given[15] as $n[(0.128)(n^2 - 1) + 1]^2$, which lies between n and n^2. This agrees with the observed data[16] of fluorescence lifetimes of DPA in various solvents.

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