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Molecular Simulations of Outersphere Reorganization Energies in Polar and Quadrupolar Solvents. The Case of Intramolecular Electron and Hole Transfer

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Outersphere reorganization energies (λ) for intramolecular electron and hole transfer are studied in anion- and cation-radical forms of complex organic substrates (*p*-phenylphenyl-spacer-naphthyl) in polar (water, 1,2-dichloroethane, tetrahydrofuran) and quadrupolar (supercritical CO_2) solvents. Structure and charge distributions of solute molecules are obtained at the HF/6-31G(d,p) level. Standard Lennard-Jones parameters for solutes and the nonpolarizable simple site-based models of solvents are used in molecular dynamics (MD) simulations. Calculation of λ is done by means of the original procedure, which treats electrostatic polarization of a solvent in terms of a usual nonpolarizable MD scheme supplemented by scaling of reorganization energies at the final stage. This approach provides a physically relevant background for separating inertial and inertialless polarization responses by means of a single parameter ϵ_∞, optical dielectric permittivity of the solvent. Absolute λ values for hole transfer in 1,2-dichloroethane agree with results of previous computations in terms of the different technique (MD/FRCM, Leontyev, I. V.; et al. *Chem. Phys.* **2005,** *319,* 4). Computed λ values for electron transfer in tetrahydrofuran are larger than the experimental values by ca. 2.5 kcal/mol; for the case of hole transfer in 1,2-dichloroethane the discrepancy is of similar magnitude provided the experimental data are properly corrected. The MD approach gives nonzero λ values for charge-transfer reaction in supercritical CO_2, being able to provide a uniform treatment of nonequilibrium solvation phenomena in both quadrupolar and polar solvents.

1. Introduction

The present article extends our earlier work treating approximately the solvent electronic polarization in molecular dynamic (MD) simulations of equilibrium and nonequilibrium solvation energies in polar solvents.[1−4] In this study we will focus on the MD simulations of the outersphere reorganization energies of intramolecular electron and hole transfer in water, 1,2-dichlorethane, tetrahydrofuran, and supercritical CO_2, described by simple site-based intramolecular potential models. The *equilibrium* solvation energy of an arbitrary solute in polar or quadrupolar solvent may be calculated with a relatively high accuracy in terms of continuum models by using different approaches with existing codes.[5−7] Conventional MD simulations are sometimes applied for this purpose [8,9] but, as noted recently,[10] they require a refined parametrization. However, implementation of a nonpolarizable MD approach for treating *nonequilibrium* solvation energies is not straightforward due to the problem of separation of inertial and inertialless components of the total medium response to the electric field, created by a given solute charge distribution.[2−4,11]

It is well-known that charge reactions in polar solvents are accompanied by significant charge redistribution and thus include strong medium reorganization. The dispersion of relaxation times for different medium modes becomes decisive when such reorganization is a rate-limiting kinetic step. The simplest approach explicitly considers only two types of medium motion: inertial (slow or nuclear, including the slow part of electronic polarization adjusted to the solvent charge distribution) modes associated with orientational and translational degrees of freedom of solvent molecules and inertialless (fast or electronic) variables describing the electronic polarization of the solvent adjusted to the solute charge. In earlier continuum theories of charge transfer[12] the separation of inertial and inertialless components (polarizations) was performed by means of the Pekar factor:[13]

$$(1/\epsilon_\infty - 1/\epsilon_0) \qquad (1)$$

where ϵ_∞ and ϵ_0 are optical and static dielectric permittivities of the solvent. In recent dielectric continuum theories the response field is a solution of the Poisson equation with proper matching conditions on the boundary of the solute cavity, where solvent cannot penetrate. Most popular is the polarized continuum model (PCM).[14] Separation of inertial and inertialless polarizations in this technique reduces to performing two PCM computations with different values of dielectric permittivity ϵ ($\epsilon = \epsilon_0$ or ϵ_∞) outside the solute cavity.[14−16] However, in studies of solvent reorganization energies λ, accompanying intramolecular electron or hole transfer, this methodology strongly overrated λ values.[16]

A more elaborated technique[17] supplemented the solute region of excluded volume (where $\epsilon = 1$) by the dielectric continuum layer with $\epsilon = \epsilon_\infty$ surrounding this cavity. Such two-cavity

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construction was surrounded by the external region where $\epsilon = \epsilon_0$, as in PCM. The Poisson equation was then solved with the pertaining boundary conditions. The scheme was called FRCM (the frequency resolved cavity model).[17] It worked efficiently for computing solvent reorganization energies in a number of intramolecular electron and hole transfer reactions. The main drawbacks of FRCM are inherent to all local continuum theories:[18] among them difficulties with describing a temperature dependence of λ and problems with λ computations in quadrupolar solvents, for which $\epsilon_0 = \epsilon_\infty$, are well-known.

To overcome these difficulties, a combined molecular/continuum approach (MD/FRCM) was developed.[2] An essential feature of this approach is the implicit account of electronic polarization in a MD simulation in terms of nonpolarizable solvent models. The price for this simplification is the appearance of the parameter ϵ_∞, which is identified with the optical dielectric permittivity of the solvent. The latter value cannot be introduced self-consistently in terms of the conventional nonpolarizable solvent models.[19] The MD/FRCM approach enables one to describe the temperature dependence of λ[4] and, in principle, can operate with quadrupolar solvents. MD/FRCM computations of electrostatic energies combine a molecular level treatment of the inertial component of polarization with a continuum model for the inertialess component. The latter part requires a PCM-like procedure introducing the solute cavity in terms of overlapped atomic spheres with electrostatic radii R_i(el).[2] They are connected to the van der Waals radii R_i(vdW) by R_i(el) $= æR_i$(vdW). The experience of previous computations in water suggests the value of scaling factor $æ \approx 0.8/0.9$.[3] (It should be noted, that small variations of $æ$ lead to strong variations of the computed value of equilibrium solvation energies.) The size and shape of the cavity is fixed in MD/FRCM. Long-range electrostatics is treated in terms of the Reaction Field method.[20] As a result, the second ("external") cavity appears at the stage of the solvation energy computations, see Figure 1 in ref 2. Due to the "external" cavity, coupled within a continuum computation to the solute cavity, the computed value of the inertial component of the solvation energy depends, implicitly, on the van der Waals radii of solute atoms.

The present treatment elaborates further the idea of MD/FRCM. Long-range electrostatics is treated in terms of the Ewald technique.[21] This enables one to suppress the "external" cavity in the solvation energy computations. Moreover, when only inertial polarization is of interest, the suggested approach does not at all need continuum computations during the evaluation of λ. As a result, the cavity parameter $æ$ is eliminated. The aim of the present study is 3-fold: (1) to develop computationally this molecular simulation method that does not invoke the concept of cavity in the treatment of the inertial part of electrostatic energies; (2) to apply it for calculations of λ values accompanying intramolecular charge transfer in complex organic substrates in polar solvents, for such systems which were studied experimentally; and (3) to demonstrate that the developed approach gives realistic λ values in quadrupolar solvents.

2. The MD Computations of λ

Within the two-state ET model[22] we consider two electronic diabatic states of complex organic substrate, in which donor and acceptor are separated by inert rigid spacers (D-Sp-A). The initial state (the reactant species) is labeled as I and the final state (the product species) is labeled as II. The charge densities of these states are a composition of point charges q_i^I and q_i^{II}, respectively, located at atomic sites i of the solute molecule:

$$\rho^J = \sum_i q_i^{\,J} \delta(r - r_i), \qquad J = \text{I or II} \qquad (2)$$

here r_i denote positions of the solute atoms. These point charge distributions are calculated for the particular solute with quantum-chemical methods. They should be discriminated from empirical point charges used in the simple site-based potential models of solvent molecules. The latter charges are adjustable parameters evaluated for a description of some microscopic (dipole and quadrupole moments) and macroscopic properties of bulk pure solvents in standard nonpolarizable MD simulations.

The statistical ensembles of solvent molecular configurations are equilibrated respectively to ρ^I and ρ^{II} by means of the MD simulations by using Ewald summation method for treating long-range interactions. This enables one to evaluate the average response field $\Phi^J_{MD}(r_i)$, created by solvent molecules at the i atom of the solute molecule and adjusted to a particular solute charge density ρ^J ($J = $ I or II).

The key point of the suggested approach is based on the idea originally formulated by Dogonadze, Kornyshev, and Kuznetsov.[23] According to it, the inertialess polarization can be treated as a local continuum with $\epsilon = \epsilon_\infty$. This model was incorporated in nonlocal electrostatic theories, e.g., see ref 24. It was shown earlier[2] that the inertial polarization component can be obtained by scaling of the response field $\Phi^J_{MD}(r_i)$ by the factor $1/\epsilon_\infty$:

$$\Phi^J(r_i) = \frac{1}{\epsilon_\infty} \Phi^J_{MD}(r_i) \qquad (J = \text{I or II}) \qquad (3)$$

Such scaling is valid provided full long-range interaction is treated at a molecular level, as in the Ewald technique. The Reaction Field technique implemented earlier[2-4] postulates the existence of external continuum and this is why eq 3 could not be used.

Following the earlier prescriptions in refs 2, 4, and 25, solvent reorganization energy λ accompanying intramolecular electron or hole transfer is

$$-\lambda \approx \frac{1}{2}\{\langle \rho^I | \Phi^I \rangle + \langle \rho^{II} | \Phi^{II} \rangle - \langle \rho^I | \Phi^{II} \rangle - \langle \rho^{II} | \Phi^I \rangle\} \quad (4)$$

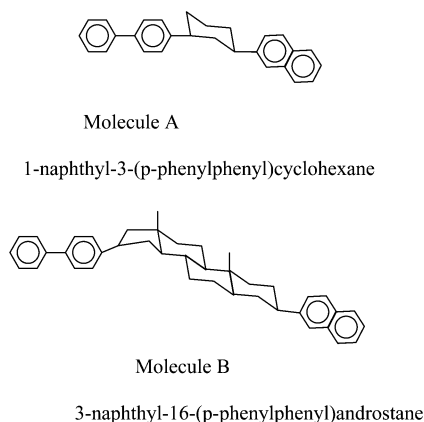where $\langle ... \rangle$ means integration over r. Using (3), eq 4 can be rewritten as

$$-\lambda \approx \frac{1}{2\epsilon_\infty}\{\langle \rho^I - \rho^{II} | \Phi^I_{MD} \rangle + \langle \rho^{II} - \rho^I | \Phi^{II}_{MD} \rangle\} \qquad (5)$$

When solute charge distributions are treated as collections of point charges (2), all functions and integrals reduce respectively to vector-arrays and sums representing their scalar products.

3. The D-Sp-A Molecules and Details of Calculation

We considered intramolecular electron (hole) transfer in organic radical anions (cations) of the two D-Sp-A molecules, in which the aromatic donor (*p*-phenylphenyl) and acceptor (naphthyl) groups are held at fixed distances by rigid saturated hydrocarbon spacer groups.

The rates of intramolecular electron and hole transfer ($^-$D-Sp-A $\rightarrow$ D-Sp-A$^-$ and $^+$D-Sp-A $\rightarrow$ D-Sp-A$^+$) were measured[26-28] and the outersphere (solvent) reorganization energies λ were extracted in terms of the complicated multiparameter procedure[26,27] fitting the Golden Rule rate expression to the observed electron- or hole-transfer rate constants. It should

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Molecule A

1-naphthyl-3-(p-phenylphenyl)cyclohexane

Molecule B

3-naphthyl-16-(p-phenylphenyl)androstane

TABLE 1: Solvent Reorganization Energies λ (kcal/mol) for the Hole-Transfer Reaction in DCE

solute	present study	MD/FRCM[a]	experiment[b]
molecule A	17.3 (16.6)[c]	16.5 (18.8)	12.2 (14.7)
molecule B	24.7	23.9 (25.5)	17.8 (23.1)

[a] Computed in ref 4 using GROMACS[43] and GROMOS-96[45] (in parentheses) Lennard-Jones parameters for the CH1, CH2, and CH3 aliphatic groups; [b] These values were estimated in refs 26 and 27 from experimental rate constants; the values in parentheses were obtained with eq 6, see Section 5; [c] The value in parentheses was calculated with the partial charges on DCE changed by ±0.027 ae in comparison with the charges used in the simple site-based model of DCE,[36] see Section 4.1.

be noted that the free energy changes of these reactions are small, <1 kcal/mol.[27]

3.1. Solute Structure and Charge Distributions. Ab initio methods were employed to obtain geometry and atomic charge distribution for the reactant (-1 or $+1$ on biphenyl) and the product (-1 or $+1$ on naphthalene) states of the radical anions or cations. Outersphere reorganization energies were considered in the present study. It implies that the same (fixed) geometry was used for the initial and final states. This geometry may not be favorable to either of the strongly localized diabatic radical anion or cation states. Several possible ways of preparing such geometry were considered in refs 16−18. Following ref 4, we used geometry obtained after optimization of the neutral delocalized system in vacuo, computed at the HF/6-31G(d,p) level. Atomic point charge distributions for reactant and product species were calculated by the SCRF-PCM method at the ROHF/6-31G(d,p) level[5] followed by the ESP[29] procedure of fitting atomic charges to reproduce electrostatic potential of the considered system. Next, these sets of atomic point charges were used as solute charge distributions ρ^I and ρ^{II}. In the SCRF-PCM calculations several solvents were considered: water, 1,2-dicloroethane, tetrahydrofuran.[30] CO_2 is absent in Gaussian 03 and argon was used instead of CO_2 as a solvent (they have the same value of dielectric permittivity $\epsilon_0 = \epsilon_\infty \approx 1.4^{31,32}$).

The method of obtaining the two SCF solutions with different charge localizations at the optimized geometry of the neutral system in vacuo is described earlier.[4] It should be noted that the computed values of point charges on solute atoms are quite sensitive to the particular solvent used in SCRF-PCM calculations.

3.2. The MD Simulations. The GROMACS package[33,34] has been used. All computations were performed with a rectangular cell. The solutes were rigid and fixed at the origin. All point charges, including those of H atoms, were explicitly counted. On the other hand, when LJ interactions were considered, we used the GROMACS atomic group parametrization in which hydrogen atoms were suppressed. So the different carbon groups are the following: C (C), no hydrogen atoms attached, aliphatic CH (CH1), CH_2 (CH2), CH_3 (CH3), and aromatic CH (CR), where symbols in brackets indicate the atomic code. Values of the van der Waals radii were borrowed from the recently elaborated refined force field.[10] Nonpolarizable models of water,[35] 1,2-dichlorethane (DCE),[36] tetrahydrofuran (THF),[37−39] and the rigid model of carbon dioxide[40] were used in simulations. The ultimate size of the equilibrium cells[41] was established by using the following densities of the solvents: 1.00 g/cm^3 for water, 1.23 g/cm^3 for DCE,[36] 0.882 g/cm^3 for THF,[37] and 1.07 g/cm^3 for supercritical carbon dioxide (scCO$_2$)[42] and the

excluded volume of the solute molecule, computed using the PCM cavity. The NVT ensemble was used in all simulations. MD simulations were performed at 300 K in the case of water, DCE, and THF and at 318 K in the case of scCO$_2$.[42] The coupling constant with the Berendsen thermostat was 0.3 fs. The trajectory step size was 2 fs and the pairlist was updated after every 3 steps. In the case of THF the step size was 0.5 fs and the pairlist was updated after every step. The Ewald PME technique[21] was used for treating the long-range Coulomb sums, and the cutoff radius was 9 Å. The preliminary equilibration step for every trajectory was performed during 100 ps. The following main step with a length of 200 ps produced the set of equilibrium solvent configurations.

3.3. Extraction of the Solute−Solvent Interaction. Evaluation of the solvent reorganization energy λ was based on two MD trajectories, in which solvent molecular configurations are equilibrated to ρ^I and ρ^{II} solute charge densities, see Section 2. The electrostatic energy computed with a given MD trajectory by means of the Ewald (PME) technique (GROMACS) contains three different contributions, originating from the solute−solute, solvent−solvent, and solute−solvent interactions. Only the last one is considered in eq 5. Extraction of the solute−solvent interaction was done using the *rerun* option.[43] Consider, e.g., the MD trajectory, equilibrated to ρ^I. One has to perform *rerun* computations with the three different sets of charges: (i) the ($\rho^I - \rho^{II}$) solute charge density and the "standard" partial charges on the solvent molecules; (ii) zero partial charges on the solute and the "standard" partial charges on the solvent molecules; and (iii) the ($\rho^I - \rho^{II}$) solute charge density and zero partial charges on the solvent molecules. Subtraction of electrostatic energies, computed at steps ii and iii from that one, calculated at step i, gives the requested solute−solvent electrostatic interaction energy. For all solvents it was assumed that $\epsilon_\infty = n^2$, with a refraction index n borrowed from Table 1 of ref 32 and Table 6 of ref 44.

4. Results

4.1. Outersphere Reorganization Energies: Simulations vs Experiment. The λ values for hole transfer in DCE, computed in the present study, are compared in Table 1 with the available experimental data[26,27] and our previous results,[4] obtained in terms of MD/FRCM. Agreement between the two sets of theoretical values is good. Both treatments have predicted reasonable but exaggerated values of λ. Our experience shows that this is not a consequence of improper Lennard-Jones parameters for solute molecules. In MD/FRCM the two different parameter sets for solute atomic groups involving combinations of C and H atoms were tested (column 3 of Table 1) with no significant effect on the resulting λ values. The refined force field[10] used in the present study (column 2 in Table 1) gives the λ values that locate just between GROMOS and GROMACS

TABLE 2: Solvent Reorganization Energies λ (kcal/mol) for the Electron-Transfer Reaction in THF

solute	present study	experiment[a]
molecule A	14.8	12.0
molecule B	19.4	17.3

[a] These values were estimated in refs 27 and 28 from experimental rate constants; see Section 3.

values. To check how important the details of the DCE charge distribution are, the computations for molecule A were repeated with partial charges on the solvent, changing by ±0.027 ae relative to the charges used in the simple site-based model of DCE[36] ($\pm$ means that the value of partial charge on chlorine was increased from -0.227 to -0.200 ae, while the value of partial charge on the CH2 group was decreased from 0.227 to 0.200 ae). Note that the calibration of parameters in ref 36 was not addressed for computations of solvation free energies. One can see that proper tuning of the corresponding parameters reduces the magnitude of the computed value by $1-2$ kcal/mol. However, the theoretical λ values are still systematically higher than the experimental ones. Possible sources for this discrepancy are discussed in Section 5.

The present study of outersphere reorganization energies for intramolecular electron transfer in anion-radical forms of the D-Sp-A molecules in THF comprises a first MD simulation of this problem. Similar to the hole-transfer reaction in DCE, the absolute values of λ are larger than those estimated from the experimental data, see Table 2. However, the difference between computed and experimental values for electron transfer in THF equals ca. 2.5 kcal/mol, i.e., much smaller than that (ca. 6 kcal/mol) found for hole-transfer in DCE. Two points should be stressed here: (i) Computed λ values for anions in THF are lower than the corresponding values for cations in DCE, cf. Tables 1 and 2. This has an important consequence, which is discussed in Section 5. (ii) The difference between the computed λ for B and A equals $\sim$4.5 kcal/mol, in agreement with the corresponding experimental difference of $\sim$5.5 kcal/mol.[27]

4.2. Outersphere Reorganization Energies: Quadrupolar vs Polar Solvents. Conventional continuum solvent models are not appropriate for investigations of charge-transfer reactions in quadrupolar solvents.[18,32,46] To overcome this problem, different advanced continuum models were developed, e.g., see refs 47 and 48. They are cumbersome and use additional parameters determined from the experiment as discussed in ref 46. The present approach can give naturally a uniform treatment of nonequilibrium solvation phenomenon in quadrupolar and polar solvents. To show this, the λ value for hole-transfer in scCO2 was computed and compared with λ values computed in water and DCE. The scCO2 seems to be a convenient *model* quadrupolar solvent because equilibrium and nonequilbrium solvation phenomena in it were studied by different experimental and simulation methods[49-53] and its force-field parameters are well elaborated giving a reasonable description of different experimental properties.[40,42,52,53]

The computed λ value for hole-transfer in the cation-radical of molecule A in scCO2 equals 4.8 kcal/mol (Table 3). Experimental λ values for charge-transfer reactions in scCO2 are not available in the literature. However, their magnitude can be estimated. The experimental value of the (total) reorganization energy for electron transfer in porphyrin$-$fullerene dyad in benzene equals 5.3 ± 0.3 kcal/mol.[54] The values of reorganization energies in benzene and scCO2 should be close, because the Stokes shifts accompanying electronic excitation in coumarin 153 are very close for these solvents.[32]

TABLE 3: Calculated Values of Outersphere Reorganization Energy λ for the Intramolecular Hole-Transfer Reaction in Molecule A in Different Solvents

solvent	ϵ_0; ϵ_∞[a]	λ, kcal/mol
water	78; 1.8	25.3 (24.8)[b]
DCE	10.4; 2.08	17.3
scCO2	$\sim$1.4; $\sim$1.4	4.8

[a] See Table 1 in ref 32 and Table 6 in ref 44. [b] The value in parentheses was calculated by using the MD/FRCM method, see Table 1 in ref 4.

According to this reasoning, computed λ in scCO2 can be treated as a measure of reorganization energy in quadrupolar solvents. A smaller magnitude of λ for a charge separation reaction in *n*-hexane was found in the polarizable MD simulations.[46]

Table 3 illustrates the dependence of λ on the solvent polarity, i.e., the ϵ_0 value. Decrease of ϵ_0 leads to strong reduction of λ. Obtained results correlate with the results of the experimental[32] and theoretical[48] studies of the Stokes shift dependence on ϵ_0: the value of the Stokes shift in acetonitrile ($\epsilon_0 = 35.9$) is $\sim$1.5 times larger than that in THF ($\epsilon_0 = 7.6$) and $\sim$3.5 times larger than those in scCO2 ($\epsilon_0 \sim 1.4$).

5. Discussion

The values of outersphere (solvent) reorganization energies λ computed in the present study seem to be systematically larger than the data reported in the experimental work.[26-28] However, the data, referred to as "experimental" values above, should be considered with a piece of criticism. They are not a result of explicit experiment, being derived from true experimental measurements after invoking several assumptions. Even the most reliable result, the value of λ for anion B, measured in 2-methylTHF and transferred to THF,[26] was extrapolated from another one, with much larger reaction free energy, ΔG, by means of an approximate Golden Rule relationship between the logarithm of the electron-transfer constant and the corresponding driving force ΔG. This relationship was applied[26,27] to a series of electron-transfer substrates with the same donor (*p*-phenylphenyl) fragment and the same spacer (specific for structure B), whereas the acceptor fragment was varied. An extra assumption was added in order to treat the series of cations in DCE. It suggested that λ must be the same for cations and anions of the same structure and even independent of a solvent. In this way the λ value for cationic structure B in DCE was equated to its counterpart for anionic structure B in THF.[28] Finally, λ values for structures A (as well as other ones in the reaction series with the same donor and acceptor fragments with changing spacers) were extrapolated, based on known λ values for structures B. Here two approximate theoretical relationships (one for the electron-transfer constant and another for λ) were used in the framework of a multiparameter fitting procedure.[26-28]

It should be mentioned here that the second assumption for cations in DCE has no solid background. According to our earlier simulations of λ values for similar cations and anions in water[4] it introduces a significant error. As an alternative, we suggest utilizing the difference:

$$\Delta\lambda = \lambda(\text{cation, DCE}) - \lambda(\text{anion, THF}) \qquad (6)$$

extracting it from the present MD simulations. From Tables 1 and 2 we find $\Delta\lambda = 5.3$ and 2.5 kcal/mol for structures B and A, respectively. By adding these corrections to the "experimental" λ values of Table 1 (based on the incorrect assumption that $\Delta\lambda = 0$) we obtain the "corrected experimental values", given

in parentheses. They show much better agreement with the computed data, comparable in quality with the similar correlation in Table 2.

On the other hand, mistakes due to several drawbacks of the computational methodology cannot be eliminated. Two possible sources of doubt are evident. The first one regards the computation of solute charge distributions, sensitive to the way in which two diabatic electron- or hole-transfer states are constructed. More refined procedures for fixing the geometry and localization of wave functions of diabatic states can be devised. The second one is the choice of solvent parameters implemented in MD simulations, keeping in mind that the existing parametrizations for both DCE[36] and THF[37,39] were never tested in reproducing solvation and reorganization energies. Here the solvent effective charges become of major importance (their impact is illustrated in Table 1). Thereby, if one accepts the "corrected" λ values for DCE in Table 1 as "experimental" ones, our simulation results look reasonable for both THF and DCE. The remaining misfits between the simulation and experiment could be further reduced by fine-tuning force field parameters of a simulation scheme (provided the experimental value is indeed reliable).

The present simulations also provide some evidence on the validity of the linear response approximation in its application to studies of solvent reorganization effects. This theme had been repeatedly discussed in the context of equilibrium solvation energies (see refs 1, 55−57 and references therein). For the case of hydration free energies of monatomic ions the contribution of nonlinearity constitutes less than 10% of their total values.[1] The case of solvent reorganization energies considered here can be analyzed in terms of eq 4 where the main nonlinearity contribution appears via ρ-dependence of the integral kernel $K_J(r,r')$ in the expression $\Phi^J(r) = \int d^3 r' K_J(r,r')\rho(r')$ for the response fields $\Phi^J(r)$ ($J = $ I or II). This dependence on ρ, i.e., on the particular MD trajectory, is known to be the basic source of discrepancy between values of λ for cations and anions originating from the same parent neutral system, such as the $\Delta\lambda$ value (6), provided the solvent is the same. It has been discussed in detail earlier[2,4] and does not exceed 5−6 kcal/mol according to the present computations. However, only the change of ρ in a given process related to a single substrate with states I and II, i.e., $\rho^{II} - \rho^{I}$, is important when we estimate λ in terms of eqs 4 or 5. Such change is significantly smaller than that arising due to the inversion of the charge sign in a charged substrate as considered above. As a quantitative measure of the nonlinearity in this case can serve the discrepancy of two off-diagonal terms in eq 4, namely $1/\epsilon_\infty\langle r^I|\Phi^{II}\rangle$ and $1/\epsilon_\infty\langle r^{II}|\Phi^I\rangle$. It is indeed very small: for instance, these terms are 9.9 and 10.1 kcal/mol (the absolute values) for cation A in DCE; the effect for other systems is of similar magnitude. This example demonstrates that the concept of reorganization energy, essentially based on the linear response approximation, can be consistently introduced within the molecular level computations.

6. Conclusions

In the present work we have modified the combined molecular/continuum simulation procedure elaborated earlier for calculations of outersphere (solvent) reorganization energies (λ) in charge transfer reactions. This new approach accounts explicitly for solvent electronic polarization effects and performs separation of inertial and inertialess polarization components. It requires a standard nonpolarizable MD simulation of a reaction system with Ewald treatment of long-range Coulomb interactions, the result of which is corrected by scaling at the final stage in order to extract the inertial part of the reorganization energy.

We implemented this approach for computing λ values in water and several nonaqueous solvents for real electron- and hole-transfer sybstrates. However, computed λ values are systematically larger than experimental ones. For the case of the model quadrupolar solvent (supercritical CO_2) the present computational scheme provided an absolute value of λ, which is qualitatively in accord with the experimental data found for different solutes in benzene and supercritical CO_2. Our studies of λ values in polar solvents were addressed to the solutes for which experimental rate constants have been measured. The computed λ values are qualitatively correct and the trends they show in a series of changing solutes seem to be quantitatively correct. The absolute values, for the cases studied so far, seem to be close to the experimental estimates provided the latter are properly corrected. Further work with different reaction systems, based on more solid experimental background, is required to verify ultimately predictive potentialities of our method at a quantitative level.

During the past decade important progress was gained in computations of electronic coupling matrix elements evaluation,[58−60] and innersphere reorganization energies[61,62] for charge-transfer processes. Outersphere (solvent) reorganization energies comprise the third and extremely important ingredient to be calculated for theoretical computations of the pertaining rate constants. The computational methodology, considered in the present study, seems to be useful for attaining this goal.

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