BNL-77280-2006-BC

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Marshall D. Newton

To be published in "Continuum Solvation Models in Chemical Physics: From Theory to Applications"

November 2006

Chemistry Department

Brookhaven National Laboratory
P.O. Box 5000
Upton, NY 11973-5000
www.bnl.gov

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BNL-77280-2006-BC

THE ROLE OF DIELECTRIC CONTINUUM MODELS IN ELECTRON TRANSFER: THEORETICAL AND COMPUTATIONAL ASPECTS

MARSHALL D. NEWTON

Department of Chemistry, Brookhaven National Laboratory, Upton NY 11973 USA
Email: Newton@bnl.gov

I. INTRODUCTION

Condensed phase physical and chemical processes generally involve interactions covering a wide range of distance scales, from short-range molecular interactions requiring orbital overlap to long-range coulombic interaction bewteeen local sites of excess charge (positive or negative monopoles). Intermediate-range distances pertain to higher-order multipolar as well as inductive and dispersion interactions. Efforts to model such condensed phase phenomena typically involve a multi-tiered strategy in which quantum mechanics is employed for full electronic structural characterization of a site of primary interest (eg, a molecular solute or cluster), while more remote sites are treated at various classical limits (eg, a molecular force field for discrete solvent molecules or a dielectric continuum (DC) model, if the solute is charged or has permanent multipole moments).

In particular, DC models have been immensely valuable in modeling chemical reactivity and spectroscopy in media of variable polarity. Simple DC models account qualitatively for many important trends in the solvent dependence of reaction free energies, activation free energies, and optical excitation energies, and many results of semiquantitative or fully quantitative significance in comparison with experiment have been obtained, especially when detailed quantum chemical treatment of the solute is combined self consistently with DC treatment of the solvent (eg, as in the currently popular PCM ('polarized continuum model') approaches).

Solvation effects are especially crucial in a class of transformations known as electron transfer (ET) processes, in which a charge ('electron' is typically used generically to denote electron or hole) is transferred between local donor (D) and acceptor (A) sites, over a distance (characterized by an effective D/A separation distance r_{DA}), which is at least as large as the distance scales of the local D and A sites (with effective radii r_D and r_A)); ie, $r_{DA} > r_D + r_A$. Eq. (1) nominally depicts 'intermolecular' ET between disjoint 'solutes' (ie, two separate molecular species, which may be in non-bonded contact or separated by solvent):

$$D^+A^- \rightarrow DA \tag{1}$$

Alternatively, in 'intramolecular' ET, D and A are linked covalently by a bridge (B), as shown schematically in Figure 1).

As a result of the appreciable change in local charge density, ET energetics are strongly coupled to the polarization modes of the solvent environment. Since ET does not involve the types of bonding rearrangements which characterize chemical reactions in general, they provide ideal tests of solvation models, free of many of the issues pertaining to electron correlation in chemical bonding. In this chapter we review the role of DC models (including PCM and its variants) in characterizing the solvent dependence of the energetics needed to model thermal and optical ET (the different types of ET are categorized in Section II). While ET is fundamentally a dynamical process, we will show, nevertheless, how the relevant energetics (both equilibrium and nonequilibrium) can be expressed in terms of suitably chosen equilibrium thermodynamic quantities.

As used here, a DC model is characterized entirely in terms of dielectric 'constants' (ε) of the pure solvent (ie, in the absence of the solute and its cavity) and the structure of the molecular cavity (size and shape) enclosing the solute. We confine ourselves to dipolar medium response, due either to the polarizability of the solvent molecules or their orientational polarization. [redacted] Within this framework, in its most general space and time-resolved form, one is dealing with the dielectric 'function' ε(k,ω), where k refers to fourier components of the spatial response of the medium, and ω, to the corresponding fourier components of the time domain. In the limit of spatially local response (the primary focus of the present chapter), in which the induced medium polarization (P) at a point r in the medium is specified entirely by the electric field (E) at the same point, only the 'long wavelength' component of ε is required (ie, k=0).

In general, ε(0,ω), or simply ε(ω), is a complex function, but real dielectric constants may be defined fir certain regions along the ω axis. In the low frequency limit, the static dielectric constant, $\varepsilon_0 \equiv \varepsilon\ (0)$ corresponds to a medium at full equilibrium with the solute electric field. When the solute charge density is changing (as in ET), only optical modes of the medium can remain in equilibrium, and the response is characterized by $\varepsilon_\infty \equiv \varepsilon\ (\infty)$, where 'infinity' simply denotes the fact that the electronic frequencies of the medium are well above those associated with the nuclear modes. The nuclear modes constitute an inertial drag which controls the solvent reorganization energy, the seat of the activation energy for thermal ET and the Stokes shift for optical ET, as discussed below.

Introduction of the solute (or solutes) into the medium obviously leads to complications relative to the homogeneous pure solvent. In simple models of the PCM type, the presence of the solute is accounted for by a suitable cavity (or cavities for multiple solute species) in the dielectric medium. Outside of the cavity (cavities), the medium maintains its homogeneous DC character, and the interface with the cavity is accommodated by suitable boundary conditions. Analogous use of boundary conditions can be used to treat an inhomogeneous medium in terms of piecewise homogeneous dielectric zones. Traditionally, for reasons of computational simplicity, molecular solutes have often been treated in terms of simple point-multipolar models, which are placed in idealized cavities (eg, spheres or ellipses), but modern computational implementation permits the use of cavities of very general shape, adapted to the structuaral details of complex molecular solutes. In general, the molecular cavity and its spatial extent may be considered to be a joint property of the solute and solvent. Much useful analysis concerning molecular cavities has been reported, but it is to be emphasized that in certain respects the specification of the cavity remains fundamentally empirical. While common ET models employ a fixed cavity (ie, the same for initial and final ET states), fluctuating cavity models have been proposed, with distinct equilibrium cavity structure for initial and final states.

Recent perspective concerning DC models of solvation has been provided by molecular-level theories and simulations. Such studies, for example, draw attention to the importance of departures from the homogeneous, spatially local models discussed above, and help to elucidate the nature of effective molecular cavities. Examples of these effects will be included in the specific results illustrated in Section VC.

II. CLASSIFICATION OF ET TYPES

Electron transfer (ET) processes can often be classified into three basic types: charge separation (CS), charge recombination (CR), and charge shift (CSh). In CS (CR), the initial (final) state is characterized by charge neutral D and A sites, while the final (initial) is dipolar (D^+/A^-). In CSh processes, an excess charge (positive or negative) is transferred between D and A sites. Eq. (1) has already introduced the CS case, and examples of CR and CSh ET are displayed, respectively, in Eqs. (2) and (3)

$$D^+A^- \rightarrow DA \tag{2}$$

$$DA^+ \rightarrow D^+A \tag{3}$$

In the cases considered below, D and A sites may be separated by bridging spacers (B, as in Figure 1), which mediate electronic tunneling between D and A without involving chemical intermediates in which the transferring electron resides on B. Hereafter, we will suppress the B notation, except as needed for clarity.

The CS, CR, and CSh processes in general may involve even or odd electron species (in the former case, the states may be either closed or open shell in character). Furthermore, the initial state can be either a ground (eg, DA) or an electronically excited state: eg, a locally excited (LE) state (D*A or DA*), as depicted for CS in Eq. (4).

$$D^{*}A \rightarrow D^{+}A^{-} \qquad (4a)$$

$$DA^{*} \rightarrow D^{+}A^{-} \qquad (4b)$$

Analogous excited state CSH processes are displayed in Eq. (5),

$$D(A^{+})^{*} \rightarrow D^{+}A \qquad (5a)$$

$$D^{*}A^{+} \rightarrow D^{+}A \qquad (5b)$$

When the initial states are created by photoexcitation, the ET process is denoted as photoinitiated ET (PIET), in constrast to the case of optical ET, in which the ET is achieved directly by a radiative process (eg, of the CS (Eq. (6)) or CSh (Eq. (7)) type.

$$DA \xrightarrow{hv} D^{+}A^{-} \qquad (6)$$

$$DA^{+} \xrightarrow{hv} D^{+}A \qquad (7)$$

It is clear that in detailed modeling studies, a flexible quantum chemical approach is required to accommodate the variety of electronic states which may be involved. Figure 2 displays free energy profiles along the ET reaction coordinate (η) for some examples of the CS and CR type. The definition of η and the formulation of the energy surfaces are discussed in Section IV.

The label 'thermal' can apply to any of the ET types just described and implies that the initial state is at thermal equilibrium (ie, all the molecular and medium modes are at thermal equilibrium with the given electronic state). Ultrafast PIET processes may be sufficiently fast (ultrafast) that the equilibrium assumption is no longer valid.

The ET processes under discussion here correspond by definition to 'pure' ET, in which molecular or medium coordinates may shift (the polaron response), but no overall bonding rearrangements occur. More complex ET processes accompanied by such rearrangements (eg, coupled electron/proton transfer and dissociative ET) are of great current interest, and many theoretical approaches have been formulated to deal with them, including quantum mechanical methods based on DC treatment of solvent.

III. KINETIC FRAMEWORK

A standard point of reference for thinking about the thermal ET rate constant (k_{ET}) is given by Eq. (8)

$$k_{\mathrm{ET}} = (2\pi H_{\mathrm{DA}}^2 / \hbar)/(4\pi\lambda k_{\mathrm{B}}T)^{1/2})(\exp-(\Delta G^{\dagger}/k_{\mathrm{B}}T)) \qquad (8)$$

where

$$\Delta G^{\dagger} = (\Delta G^{\circ} + \lambda)^2 / 4\lambda \qquad (9)$$

corresponding to the limiting situation characterized by :

- weak D/A coupling (the nonadiabatic limit, expressed in the Condon approximation, where the electronic coupling matrix element has been factored out of the full vibronic matrix element)
- harmonic profiles with respect to η (linear solute/solvent coupling)
- the classical (high temperature) limit for nuclear motion (no quantum tunneling)
- kinetics governed by transition state theory (TST).

In spite of these limitations, Eq. (8) serves in the present context to highlight the role of thee crucial energetic quantities in activated ET:

- the net free energy change (ΔG^{o})
- the reorganization free energy (λ)
- the electronic coupling matrix element (H_{DA})

The activation free energy ($\Delta G^{\dagger}$) is expressed as a quadratic function of ΔG^{o} and λ in Eq. (9), the well-known result of Marcus theory, which only displays a linear free energy relationship in the limit where $|\Delta G^{o}| << \lambda$. Dielectric continuum (DC) models have been of great value in modeling the solvent contribution to ΔG^{o} and λ, and hence also to $\Delta G^{\dagger}$. The activation energy is a manifestation of the Franck-Condon (FC) control of ET dynamics (as well as that for many other electronic processes): ie, in the classical limit represented by Eqs (8) and (9), the ET does not occur until a thermal fluctuation brings the system to the crossing point (the transition state (TS)), eg, as in Figure 2, where electron tunneling can occur between resonant D and A sites. The location of the TS along the η axis is entirely defined by λ, and it is of particular interest to understand the abilities (and limitations) of DC models in accounting for the solvent contribution to this nonequilibrium free energy quantity.

IV. ET ENERGETICS

A. Classical Expressions

The basic features of ET energetics are summarized here for the case of an ET system (solute) linearly coupled to a 'bath' (nuclear modes of the solute and medium). We further assume that the individual modes of the bath (whether localized or extended collective modes) are separable, harmonic, and classical (ie, $h\nu < k_BT$ for each mode, where ν is the harmonic frequency and k_B is the Boltzmann constant). Consistent with the overall linear model, the frequencies are taken as the same for initial and final ET states. According to the FC control discussed above, the nuclear modes are frozen on the timescale of the actual ET event, while the medium electrons respond instantaneously (further aspects of this response are dealt with in Section IV.D). The energetics introduced below correspond to free energies. Solvation free energies may have entropic contributions, as discussed elsewhere. Before turning to the DC representation of solvent energetics, we first display the somewhat more transparent expressions for a discrete set of modes.

1. Discrete Modes

The free energies of the initial (i) and final (f) states, the so-called diabatic states in the ET process (discussed in more detail in Section IV.D.2), are given by

$$G_a(\mathbf{x}) = G_a^o + \langle \mathbf{x}-\mathbf{x}_a | \mathbf{K} | \mathbf{x}-\mathbf{x}_a \rangle /2 \qquad (10)$$

where the discrete space of modes is represented by vector $|\mathbf{x}>$, $|\mathbf{x}_a>$ denotes the equilibrium coordinate values for state a (a = i, f) and **K** is the force constant matrix, taken as diagonal. The vector $|\Delta\mathbf{x}> \equiv |\mathbf{x}\text{-}\mathbf{x}_a>$ may be considered an arbitrary fluctuation of $|\mathbf{x}>$ from its minimum energy value $|\, \mathbf{x}_a >$.

We adopt as the reaction coordinate for the ET process, the vertical gap, η:

$$\eta(\mathbf{x}) = G_f(\{\mathbf{x}\} - G_i(\{\mathbf{x}\}) \qquad (11)$$

This gap is given by the following linear function of $\{\mathbf{x}\}$:

$$\eta(\mathbf{x}) \;=\; \Delta G^{o}_{if} \; - <\mathbf{x}\text{-}\mathbf{x}_i \,|\, \mathbf{K} \,|\Delta\mathbf{x}_{if}> + \lambda_{if} \qquad (12)$$

where $\Delta G^{o}_{if} \;=\; G^{o}_{f} - G^{o}_{i}$, $|\Delta\mathbf{x}_{if}>$ is the shift in equilibrium coordinate values ($|\mathbf{x}_f\text{-}\mathbf{x}_i>$), and λ_{if} is the reorganization energy

$$\lambda_{if} = <\Delta\mathbf{x}_{if} \,|\, \mathbf{K} |\, \Delta\mathbf{x}_{if}>/2 \qquad (13)$$

If we define the minimum energy value of G_i or G_f in **x**-space subject to the constraint of a particular value of η (at $|\,\mathbf{x}> = |\,\mathbf{x}_{min}(\eta)>$), a straight-line path lying along the $|\,\Delta\mathbf{x}_{if}>$ direction is obtained,

$$|\mathbf{x}_{min}(\eta)> \;=\; |\mathbf{x}_i> + ((\Delta G^{o}_{if} + \lambda_{if} - \eta)/2\lambda)|\, \Delta\mathbf{x}_{if}> \qquad (14)$$

Along this path, G_i and G_f may be re-expressed as harmonic functions of the single coordinate η:

$$G_i = G^{o}_{i} + (\lambda_{if} + \Delta G^{o}_{if} - \eta)^2/4\lambda_{if} \qquad (15)$$

$$G_f = G^{o}_{f} + (\lambda_{if} - \Delta G^{o}_{if} + \eta)^2/4\lambda_{if} \qquad (16)$$

Any linear function of η can serve equally well as a reaction coordinate as long as all the coordinates contributing to the collective coordinate η are globally harmonic (i.e., with the same force constant matrix for initial and final states, as in Eq. (10)). A familiar alternative to

η is the dimensionless progress parameter of Marcus, *m*, for the overall ET process, related to η (Eqs. (12) and (14)) by the following linear transformation

$$m = (\lambda_{if} + \Delta G^{o}_{if} - \eta)/2\,\lambda_{if} \qquad (17)$$

where the initial (i) and final (f) diabatic minima correspond to m=0 and m=1. The diabatic crossing point for thermal ET occurs at $\eta = 0$ (or $m^{\dagger} = (\lambda_{if} + \Delta G^{o}_{if})/2\,\lambda_{if}$), yielding the quadratic Marcus expression for $G^{\dagger}$ (Eq. (9), and the second term of Eq. (15) when $\eta = 0$), the free energy of the thermally activated TS relative to G^{o}_{i}.

The quantity $G_a(|\mathbf{x}>) - G^{o}_{a}$ (the second term in Eq. (10) is seen to have the form of a reorganization energy, $\lambda(|\Delta\mathbf{x}>)$, but with $|\Delta\mathbf{x}_{if}>$ in λ_{if} (Eq. (13)) replaced by the arbitrary coordinate fluctuation $|\Delta\mathbf{x}>$ (see definition following Eq. (10)). Letting state a be the initial state i, we note that along the reaction coordinate, $\lambda(|\Delta\mathbf{x}>)$ is scaled relative to λ_{if} by the square of the progress parameter m. In particular, $G^{\dagger}$ is seen to be $\lambda\,(m^{\dagger}|\Delta\mathbf{x}_{if}>) = (m^{\dagger})^2\,\lambda_{if}$.

Even in the non-harmonic case, one may still define η as the vertical energy gap $G_f - G_i$, but η will no longer be linear in $|\mathbf{x}>$, in contrast to Eq. (12). In this case, the relationship noted by Tachiya

$$G_f(\eta) = G_i(\eta) + \eta \qquad (18)$$

remains valid in general, indicating clearly that at a given value of η, G_i and G_f have the same curvature with respect to η, irrespective of the functional form of G_i and G_f. The relationships among the G, λ, and η quantities are displayed in Figure 3. When G_i and G_f depart from pure quadratic form, initial and final states have distinct λ values (λ_i and λ_f), in which case a mean value may be used to define λ_{if}.

2. Dielectric Continuum Solvent Model

When the density of bath modes becomes high, as in the case of a DC, counterparts of the discrete-mode expressions (Eqs. (6-13)) are readily available, based on the assumption that the solute-solvent coupling can be expressed as a linear functional of solute charge densities (ρ). Models for defining or calculating ρ are discussed in later Sections.

Corresponding to Eq. (10), we have for a general non-equilibrium situation, the following solvation free energy,

$$G_{\text{non-eq}}\,(\rho_a,\rho_{in}) = G_{eq}(\rho_a) + \lambda_s\,(\Delta\rho) \qquad (19)$$

where $G_{eq}(\rho_a)$ is the equilibrium free energy, when all continuum modes (slow (inertial) as well as fast (optical)) are at equilibrium with respect to ρ_a, $\lambda_s\,(\Delta\rho)$ is the solvent reorganization energy corresponding to $\Delta\rho = \rho_{in} - \rho_a$, and ρ_{in} is the hypothetical charge density with which (by construction) the inertial modes are in equilibrium (only for full equilibrium is $\rho_{in} = \rho_a$). The relationship between the continuous densities ρ_a and ρ_{in} and their discrete counterparts, $|\mathbf{x}_a>$ and $|\Delta\mathbf{x}>$, is discussed below and illustrated for specific ET situations.

For a homogeneous DC in the absence of dielectric image effects (associated with boundary conditions at the solute/solvent interface), $G_{eq}(\rho_a) + \lambda_s\,(\Delta\rho)$ may be represented as,

$$G_{eq} = G_{a,vac} + (1\ \varepsilon \quad 1\ 8\pi) \int_{V_s} |\vec{\boldsymbol{D}}(\rho_a)|^2 \, d\tau$$

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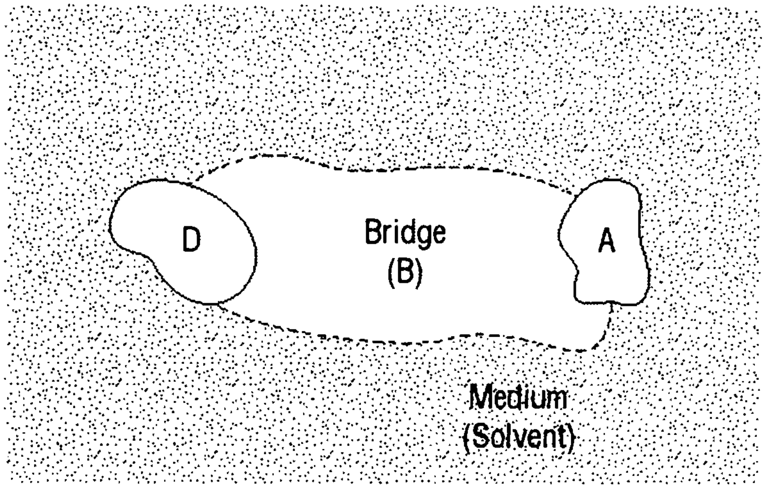
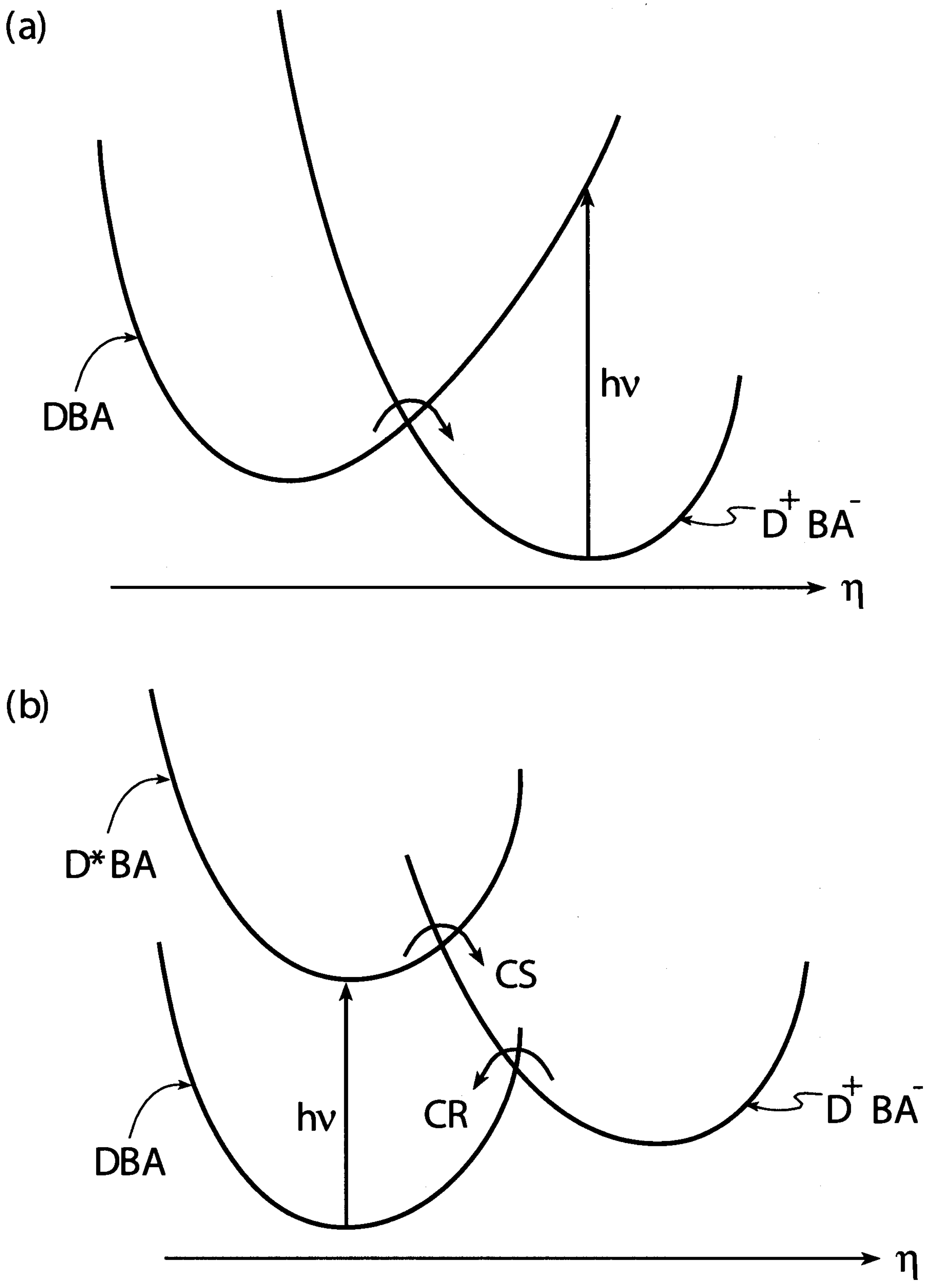
Long-range D/A Interaction

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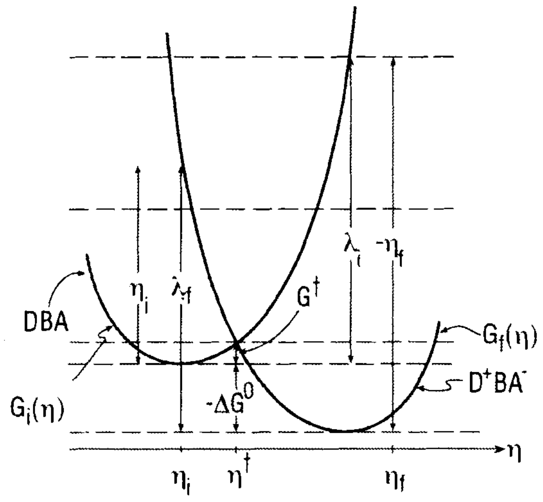
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η_i
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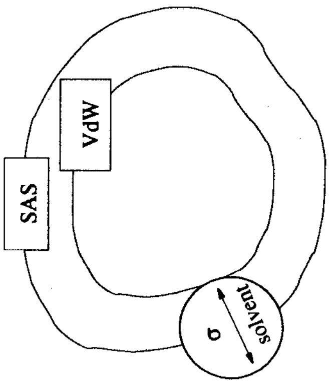
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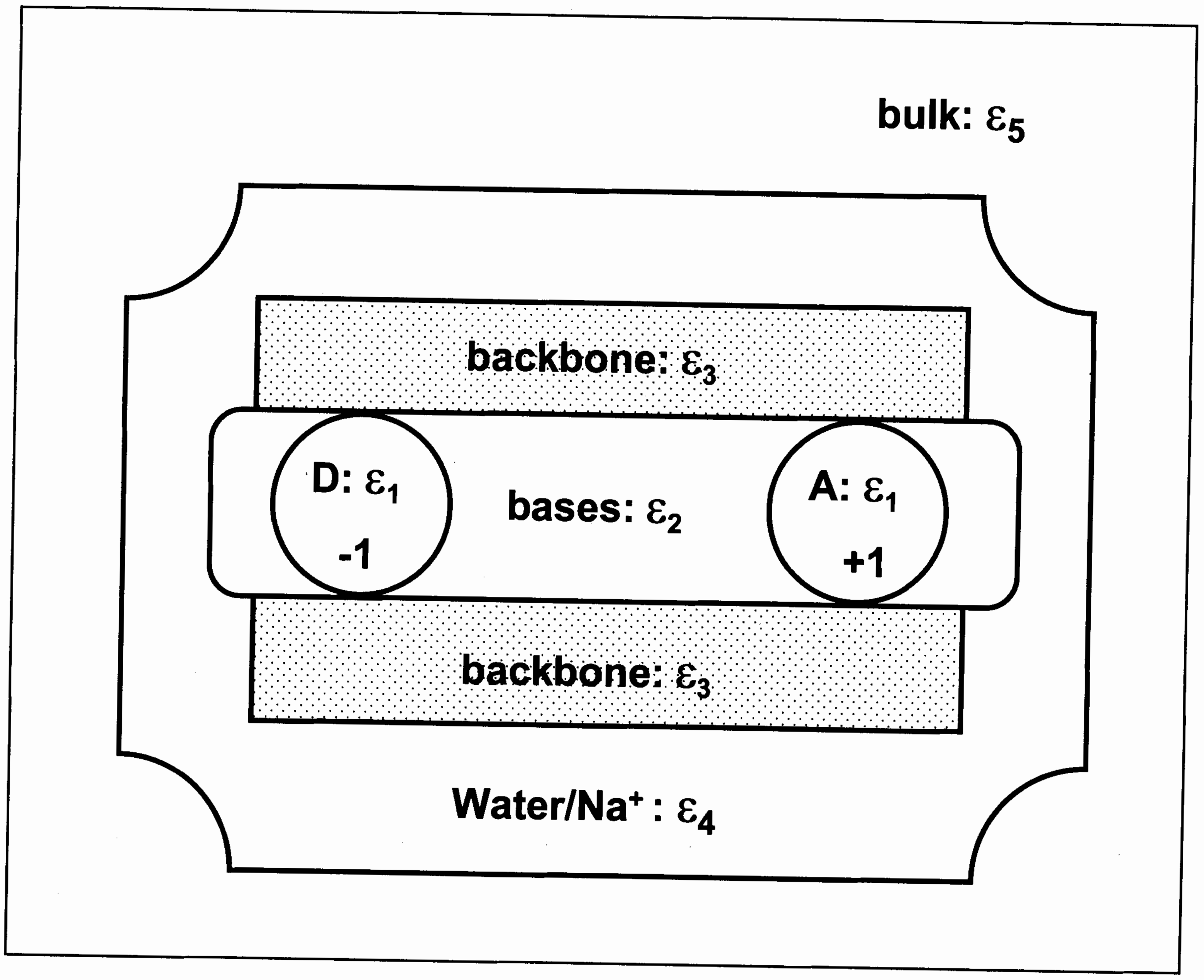
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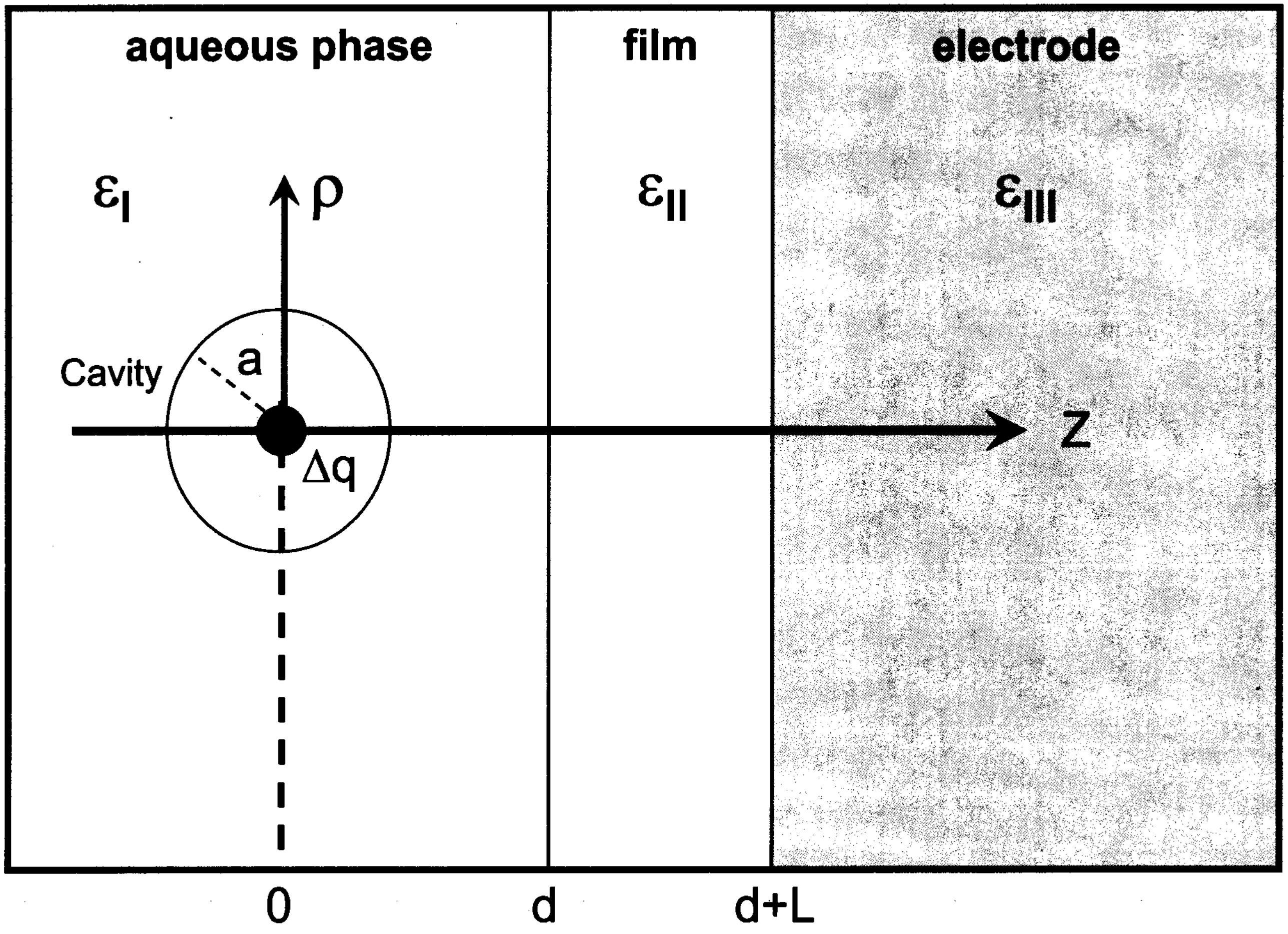
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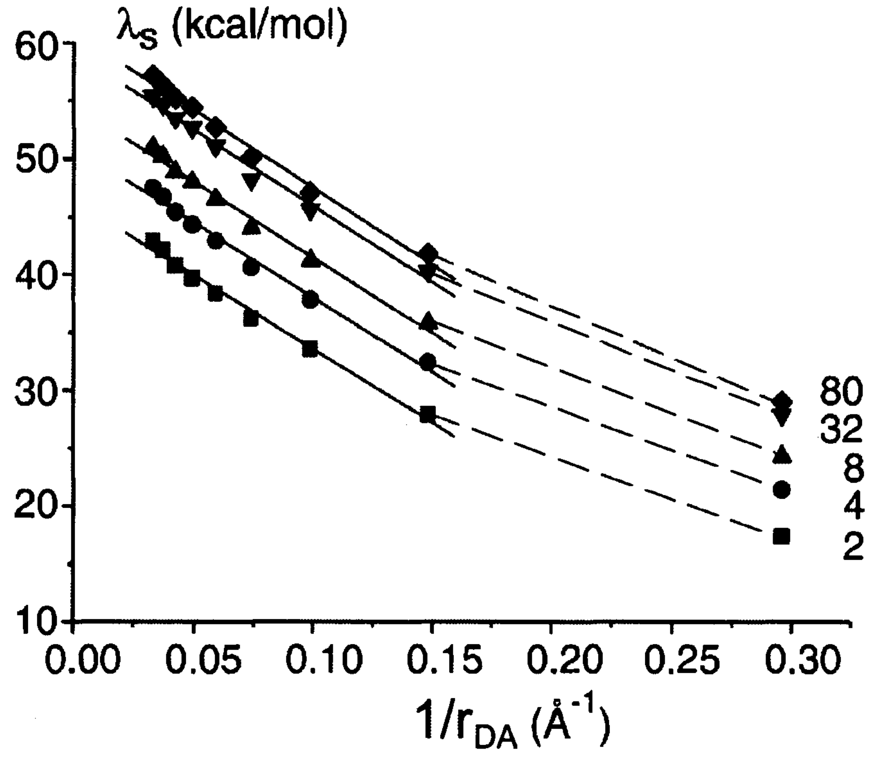
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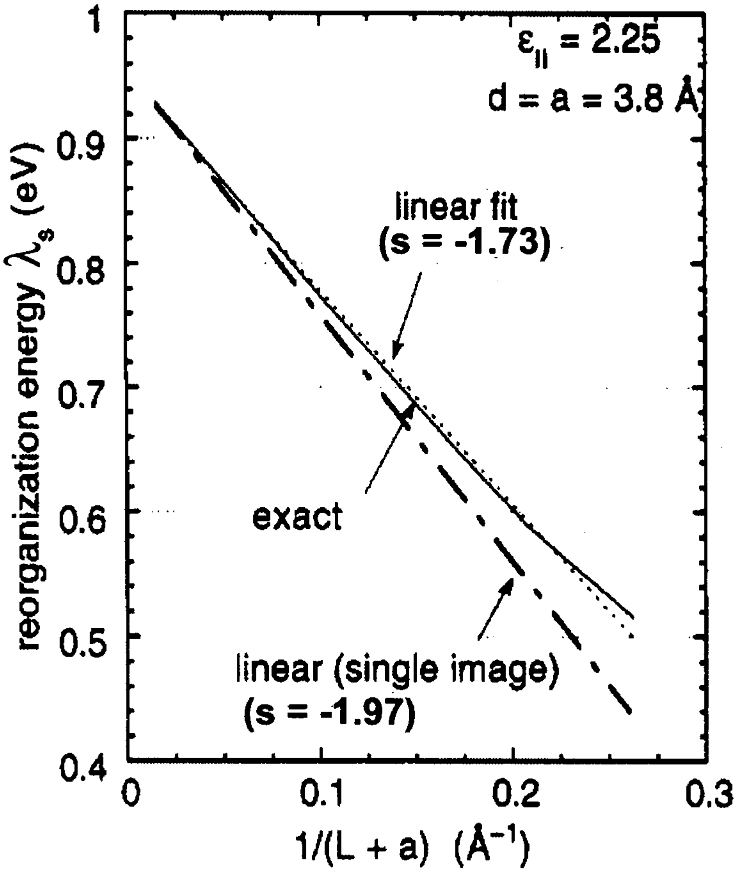

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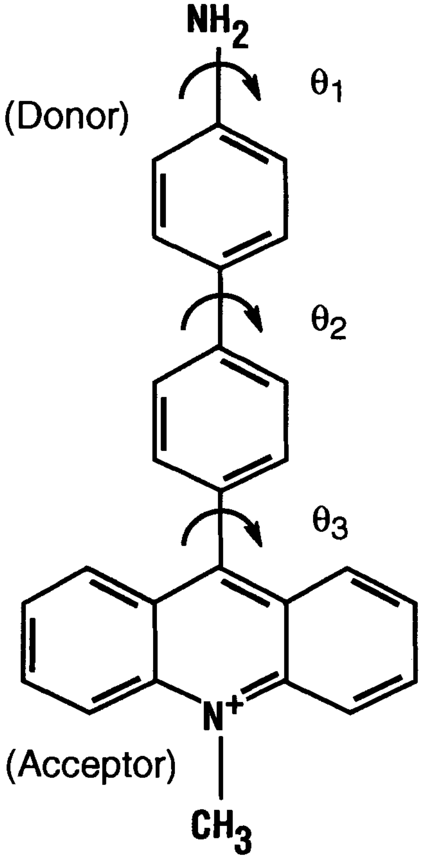

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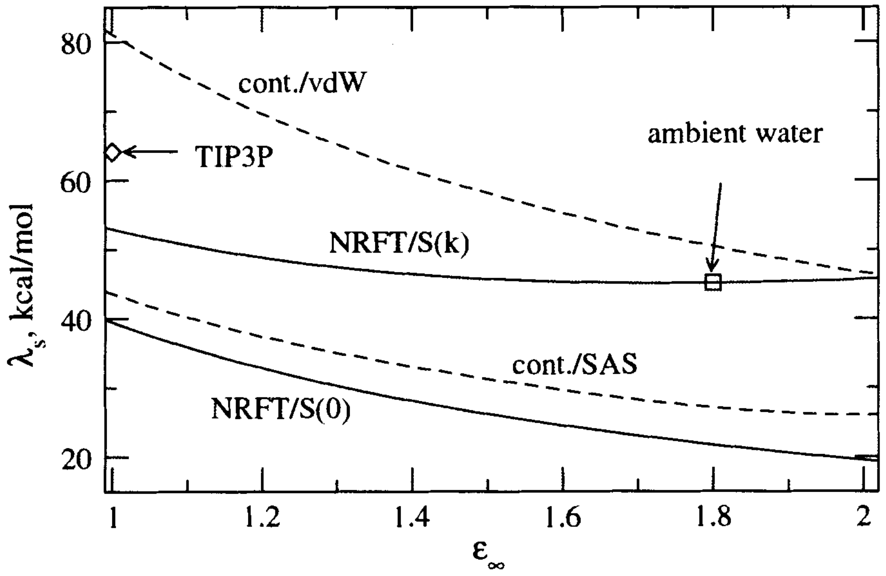

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