



Theoretical study on the ionization of aniline in aqueous solutions



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ABSTRACT

The ionization and excitation processes of aniline in aqueous solutions are investigated by the method of RISM-SCF-SEDD (reference interaction site model self-consistent field with the spatial electron density distribution). Four different models are employed to characterize the response of the solvation upon the ionization and excitation. A simple treatment for estimation of the spectral width is also proposed.

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1. Introduction

Ionization potential (IP) is one of the fundamental quantities to characterize the electronic structures of molecules. As precise IP values have recently become available for molecules in the solution phase [1–3], significant shifts have been observed for molecules in aqueous solutions from those in the gas phase. These results strongly indicate that the electronic structures of the molecules are significantly influenced by solvation.

The effects of solvation on ionization have been studied theoretically by means of the electronic structure theory combined with a variety of solvation theories [2–10]. The IPs of DNA and RNA bases were calculated in aqueous solutions using the polarizable continuum model (PCM) [2,3,9,10]. However, the role of local interaction such as hydrogen bonding is not sufficiently understood due to the simplification of the model. The IP and the spectral width of aqueous phenol were calculated using the quantum mechanics/molecular mechanics (QM/MM) simulation combined with the dielectric continuum treatment [11], but this theory requires a high cost of computation for the generation of the solvent configurations in thermodynamical equilibrium.

We wish to report here the effects of solvation on the electronic transition of aniline with particular focus on ionization. Aniline is the simplest aromatic amine, and its electronic structure has been studied in detail both experimentally and theoretically [12–15]. However, little is yet known on the interactions in solvated aniline despite the vital importance from the viewpoint of a biologically relevant model system.

The RISM-SCF-SEDD method [16–19] has been applied in the present Letter to investigate the solvation effects on the IP values

of aniline. The reference interaction site model self-consistent field (RISM-SCF) is the method that combines the statistical mechanics of molecular liquids (RISM) [20] and ab initio molecular orbital theory. Thanks to the analytical nature of RISM, the solvation structure can be computed in the thermodynamical equilibrium state with a reasonable computational cost. The RISM-SCF method has achieved clarification of the solvation effect on molecular electronic structures [4–8,21–25]; the ionization processes of dimethyl aniline [7,8] and the excitation of *p*-nitro aniline in water over a wide range of density condition [24] are examples. We have used RISM-SCF in the present study with the method of spatial electron density distribution (RISM-SCF-SEDD) [18,19]; this is an extended method of the original RISM-SCF by explicit inclusion of electron density distribution. In contrast to the original RISM-SCF, RISM-SCF-SEDD method is numerically stable in the convergence, even if the buried atoms are involved. Please refer Ref. [18] for more details. The method has been applied to a wide range of chemical processes. To our knowledge, this is the first theoretical study of the solvation effects on aniline.

2. Method

2.1. RISM-SCF-SEDD method

Let us first summarize the RISM-SCF-SEDD method, which combines the statistical mechanics of molecular liquids (RISM) with the ab initio molecular orbital theory. The equation of RISM is given as

$$\mathbf{h}^{UV} = \omega^U * \mathbf{c}^{UV} * \omega^V + \omega^U * \mathbf{c}^{UV} * \rho^V \mathbf{h}^{VV}, \quad (1)$$

Here ‘*’ denotes convolution integral. Symbols ω^U and ω^V are intramolecular correlation functions of solute and solvent, \mathbf{h}^{UV} and \mathbf{c}^{UV} are the total and direct correlation functions between solute and solvent, respectively, and \mathbf{h}^{VV} is the total correlation function for solvent with the number density ρ^V . Hyper-netted chain (HNC) closure is adopted in the present study to solve the equation,

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$$h_{zs}^{UV} = \exp\left(-\beta u_{zs}^{UV} + h_{zs}^{UV} - c_{zs}^{UV}\right) - 1 \quad (2)$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant and u_{zs}^{UV} is the interaction between site α and s . Under the HNC approximation, solvation free energy ($\Delta\mu$) is expressed as

$$\Delta\mu = \beta^{-1} \rho^V \sum_{\alpha,s} \int_0^\infty 4\pi r^2 dr \left[\frac{1}{2} \left(h_{zs}^{UV}\right)^2 - \frac{1}{2} c_{zs}^{UV} h_{zs}^{UV} - c_{zs}^{UV} \right]. \quad (3)$$

In RISM-SCF-SEDD, the solvated Fock operator is defined by

$$\widehat{F} = \widehat{F}^{\text{gas}} - \widehat{V} \quad (4)$$

where F^{gas} is the Fock operator of an isolated molecule, V is the solute–solvent electrostatic interaction operator. The electrostatic interaction energy between the solute and solvent is written as

$$\langle \Psi | \widehat{V} | \Psi \rangle = \sum_j D_j V_j = \mathbf{D} \cdot \mathbf{V}, \quad (5)$$

and Ψ is the wave function of the solute molecule in the solution phase. The expansion coefficients, D_j , of the charge density correspond to the net population of electrons in the j -th auxiliary basis set (ABS, f_j), and V_j is the electrostatic potential on this ABS (f_j) from the solvent,

$$\widehat{V}_j = \rho^V \sum_s q_s \int \frac{f_j(r)}{r} h_{zs}^{UV}(r) 4\pi r^2 dr. \quad (j \in \alpha) \quad (6)$$

2.2. Electronic transition energy

The electronic transition energy in the gas (ΔE_X^{gas}) is given as the difference in the total energy between the initial (E^i) and final (E^f) states,

$$\Delta E_X^{\text{gas}} = E_X^f - E_X^i. \quad (X = \text{I, II, III and IV}) \quad (7)$$

The transition energy in aqueous solution is expressed as a sum of Eq. (7) and the contribution from the solute–solvent interaction, but the former is changed due to the electronic distortion caused by the solvation. Based on Ref. [5], the following four approximated formulae are considered in the present study to investigate the contributions of electronic and geometric relaxations in the ionization process.

As the first model stage, the solvent and the geometry of solute molecule are assumed to be completely frozen at the initial equilibrated state upon the transition. While the electronic structure of the solute molecule is changed on the transition, the polarization of solvent is not allowed. Namely, the electrostatic field generated by solvent is fixed at the initial one, \mathbf{V}^i .

$$\Delta E_{\text{I}}^{\text{aq}} = \Delta E_{\text{I}}^{\text{gas}} + (\mathbf{D}_1^f - \mathbf{D}_1^i) \cdot \mathbf{V}^i. \quad (8)$$

This treatment is named “model I”. The second stage takes into account a part of the solvent polarization in an effective manner (model II).

$$\Delta E_{\text{II}}^{\text{aq}} = \Delta E_{\text{II}}^{\text{gas}} + k_{\text{slow}} (\mathbf{D}_{\text{II}}^f - \mathbf{D}_{\text{II}}^i) \cdot \mathbf{V}^i + \frac{1}{2} k_{\text{fast}} (\mathbf{D}_{\text{II}}^f \cdot \mathbf{V}_{\text{II}}^f - \mathbf{D}_{\text{II}}^i \cdot \mathbf{V}^i), \quad (9)$$

where \mathbf{V}_{II}^f is the electrostatic field from the solvent equilibrated to the final state. The second and third terms on the right-hand side correspond to slow and fast components of the solvent response, respectively. Symbols k_{slow} and k_{fast} are the constants (0.4426, 0.5574) calculated from the dielectric permittivity and the optical dielectric permittivity of water solvent. See Ref. [5] for more detailed discussion.

The third treatment allows the solvent to completely relax,

$$\Delta E_{\text{III}}^{\text{aq}} = \Delta E_{\text{III}}^{\text{gas}} + (\Delta\mu_{\text{III}}^f - \Delta\mu^i). \quad (10)$$

The second term on the right-hand side is simply a difference in the solvation free energy between the two equilibrium states under the

assumption that the solute molecular geometry remains unchanged (model III). Finally, the geometry relaxation of solute molecule is taken into account (model IV). ΔE_X^{gas} is replaced by $\Delta E_{\text{rlx}}^{\text{gas}}$, which is the energy difference between the two optimized geometries of the initial and final states.

$$\Delta E_{\text{IV}}^{\text{aq}} = \Delta E_{\text{rlx}}^{\text{gas}} + (\Delta\mu_{\text{IV}}^f - \Delta\mu^i). \quad (11)$$

This quantity is the adiabatic ionization potential corresponding to the difference in free energy. Namely, the initial and final states are both in their thermodynamic equilibrium states. Note that $\Delta\mu_{\text{IV}}^f$ is calculated at the optimized geometry of the final state, while $\Delta\mu_{\text{III}}^f$ and $\Delta\mu^i$ are calculated at the optimized geometry of the initial state.

3. Computational details

Geometry optimization and energy calculation were performed using the DFT (B3LYP functional) method with the cc-pVDZ basis set both in the gas and aqueous solution phases, respectively. For calculation of the cation, the unrestricted version with the same basis set was adopted. The low-lying excited states were also computed using MRMP2 with the same basis set at the CASSCF-optimized geometry of the ground state. The active spaces comprised a full set of the valence π -orbitals and the lone pair of N atom; eight electrons were distributed over seven orbitals for the neutral species.

Solvation effect was taken into account using the RISM-SCF-SEDD method coupled with HNC closure. Standard Lennard–Jones (LJ) parameters taken from the literature were employed (Table 1). All calculations were performed at 298.15 K and the density of 1.0 g/cm³. We utilized the GAMESS program package [26] modified by us to perform the RISM-SCF-SEDD calculation. PCM (polarizable continuum model) was also employed to calculate the ionization potential in aqueous solution, using Gaussian 03. Non-equilibrium PCM was employed for the calculations of models I and II.

4. Results and discussion

4.1. Ionization potential and excitation energy

Table 2 summarizes the calculated ionization potential and the excitation energies in the gas phase. The ionization potential (IP) with (U) B3LYP/cc-pVDZ calculation, 7.59 eV, agrees reasonably with the experimental value 7.72 eV [12], as well as with the SAC-CI value, 7.66 eV [14]. The computed excitation energies also agree with the reported values. This table lists the transition energies to the two low-lying excited states of the neutral aniline (S_1 and S_2) and those of the ionized species (D_1 and D_2).

The S_1 and S_2 states are both characterized by the $\pi \rightarrow \pi^*$ transition. The former is described as the excitation from HOMO (a') to LUMO (a'') in the Kohn–Sham orbitals of DFT. The latter transition is attributed to that from HOMO (a') to the next LUMO (a' , usually abbreviated as LUMO+1). The electronic structures of D_1 and D_2 are also described in terms of one-electron picture. D_1 corresponds to

Table 1
Lennard–Jones parameters of each atom [24].

Site	$\sigma/\text{\AA}$	$\epsilon/\text{kcal mol}^{-1}$
<i>Solute (aniline)</i>		
C	3.550	0.070
H	2.420	0.030
N	3.250	0.170
<i>Solvent (water)</i>		
H	1.000	0.056
O	3.166	0.155

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