



A new potential model for acetonitrile: Insight into the local structure organization



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ABSTRACT

Thorough understanding of the microscopic organization and dynamics of individual constituents is a crucial step in the description and the prediction the properties of electrolyte solutions based on dipolar aprotic solvents such as acetonitrile. For this aim, a new potential (force field) model for acetonitrile was developed on the basis of comprehensive approach comprising quantum chemical calculations, *ab initio* molecular dynamics simulations and empirical parameterization. The developed potential model is able to reproduce the experimental thermodynamic and dynamic properties of neat acetonitrile in the range of temperatures between 228.15 and 348.15 K. The local structure of neat liquid acetonitrile then was analyzed in a framework of the nearest neighbor approach. It was shown that the distance standard deviations relative to the average distance between the nearest neighbors have a non-linear behavior that was traced back to the changes in the mutual orientation between acetonitrile molecules. The closest neighbors have a dominant antiparallel dipoles orientation with respect to a reference acetonitrile molecule, while for the further nearest neighbors perpendicular and parallel mutual orientation is observed. The nearest neighbors approach in combination with angular distribution functions was used for the estimation of the Kirkwood factor. Our results show that in order to reproduce the corresponding experimental values derived in the framework of the Onsager–Kirkwood–Fröhlich theory, it is necessary to take into account the mutual orientation of the 5–6 nearest neighbors. Although the atomic charges, on N and the methyl group hydrogen atoms, are negative, the values of the N⋯H distance and the N⋯H–C (methyl group), are compatible with a weak hydrogen bond between the two atoms.

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1. Introduction

Acetonitrile (AN) is a polar aprotic solvent that finds ubiquitous usage in chemical industry, electrochemistry and research activity. Despite its intrinsic hazard of flammability and toxicity the wide use of AN arises from the unique combination of such advantageous properties as wide electrochemical window and low viscosity [1]. Furthermore, due to its relatively high dielectric constant, AN can easily dissolve electrolyte salts (e.g., quaternary ammonium salts) [2] and is fully miscible with ionic liquids (e.g., families of imidazolium- and pyrrolidinium-based ionic liquids) [3–5] achieving a considerably high ionic conductivity. This makes AN solutions a promising group of electrolytes for various electrochemical devices such as supercapacitors [6,7] or dye-sensitized solar cells (DSSCs) [8]. As a consequence, a thorough understanding of the microscopic organization of individual constituents

(particularly AN) is a crucial element in the predictive description of the properties of these electrolyte solutions.

Indeed, vibrational spectroscopic measurements were carried out to inspect the structure of AN in the pure liquid state and in solution [9–13]. The results of these measurements allowed the authors to assume that AN molecules tend to form dimeric structures due to the dipole interactions between the molecules. Considerable effort also has been devoted to the experimental studies of dielectric properties in the pure AN [1–7,14–23]. The latter is used frequently to elucidate the local structure (mutual orientation of dipoles) in terms of the so-called Kirkwood correlation factor, g_K . These studies converge to define the mutual orientation between AN molecules as antiparallel. Moreover, numerous X-ray and neutron-diffraction experiments have also confirmed that neighboring AN molecules are aligned in antiparallel manner due to the strong dipole-dipole interactions [24–27].

The issue of mutual arrangement of AN molecules also has been addressed using MD simulations by following the distribution of the angles between the molecular dipoles as a function of the distance between the molecular centers of mass [28–32]. However, the reliability of the simulations to reproduce a wide set of experimental properties

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and then to get a microscopic level insight largely depends on the accuracy of the force field model used. At present, numerous AN force fields models have been designed to reproduce various experimental properties. Their degree of detail commonly ranges from models with six interaction sites (all atom models) [29,31,33–40], to the more simplified three-site models (united atoms models) [30,32,41–45] where hydrogen atoms of the methyl group are not considered explicitly to reduce the computational cost and to allow for simulations of larger systems over longer time scales.

Most of the recent computational studies devoted to neat AN are directly connected to calibration of parameters for all-atom models. Rather successful AN potential models were implemented in terms of OPLS/AA [39] and AMBER [36] force fields. The thermodynamic and structural properties derived with these models show reasonable agreement with experimental measurements. Subsequently, their further usage undergone considerable revisions. Thus, Wu et al. [46] by calibration Lennard-Jones parameters has introduced a potential model able to reach an experimental value of diffusion coefficient, while the density was noticeably underestimated. A similar effort on the calculations of thermodynamic properties was reported in the study of Nikitin and Lyubartsev [37]. Despite the several advantages, a common drawback of these potential models is that some intramolecular parameters significantly vary and are not reproducible due to universality of available force fields. Typically such parameters are defined from quantum-chemical calculations. Nevertheless, based on DREIDING [47] force field Orhan has presented another approach that combines empirical tuning of both intra- and intramolecular parameters and leads to the good agreement of the studied dynamic and dielectric properties [31].

Considering the uncertainty in the empirical approaches of parameterization of AN as well as its wide relevance in different applications, particularly in electrochemistry, one can deduce about the demand for such potential model that is able *i)* to reproduce correctly the intramolecular vibrations along with considering the effects polarization in condensed phase; *ii)* to reproduce the greatest possible set of properties in wide temperature range.

Here we present a new fully flexible potential model for AN finely tuned to reproduce structural, thermodynamic and dynamic properties over a wide range of temperatures between 228.15 K and 348.15 K relevant for practical applications of AN-based systems. The atomic charges were derived in a framework of *ab initio* MD simulation while the Lennard-Jones parameters were tuned by fitting the experimental thermodynamic and transport properties for the new model. The determination of the intramolecular parameters (stretching and bending force constants) was derived using quantum chemical calculations. Using the new potential model of AN, the local radial and orientational structure has been studied within the nearest neighbor approach [48–50].

2. Methodology and validation

2.1. Intramolecular force field

A reliable representation of molecular geometry is important in terms of adequate parameterization of the intramolecular potentials, which in turn is essential for reproducing the vibrational spectra of AN. Toward this purpose, the quantum chemical calculations of one AN molecule (Fig. 1) in gas phase were carried out followed by harmonic vibrational analysis and determination of the force constants associated with the bond lengths and bond angles in a framework of relaxed potential energy surface (rPES) scanning concept. The latter were carried out using GAUSSIAN 09W program suite [51]. The second-order Møller-Plesset perturbation theory (MP2) [52] has been employed together with Dunning's correlation consistent polarized valence triple- ζ basis set with diffuse functions, aug-cc-pVTZ [53,54]. Optimal geometry was obtained under very tight optimization convergence criteria as implemented in the software and tested to be true minima by the absence of imaginary frequencies in the corresponding vibration spectra.

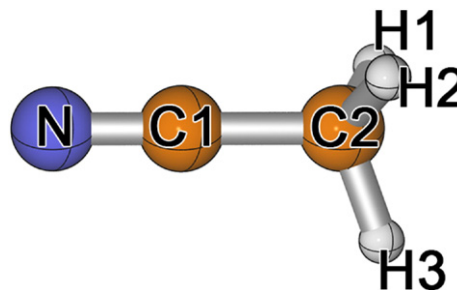


Fig. 1. Structure of AN molecule with atom labeling used in this work.

In order to evaluate the reliability of the level of theory and basis set used in this work, a series of calculations were carried out by using the additional hybrid meta-GGA exchange-correlated functional from Truhlar's group (M06-2X) [55,56] with six different basis sets (6-31++G(d,p), 6-31++G(2d,2p), 6-311++G(d,p), 6-311++G(2d,2p), aug-cc-pVDZ and aug-cc-pVTZ). Calculated geometry parameters and vibrational frequencies together with literature data [57] are listed in the Table S1 and S2 (see Supporting Information). The geometry parameters obtained by both methods are comparable to each other and are in good agreement with experimental data. Nevertheless, the value of C≡N bond length calculated with MP2 [58] is slightly overestimated and is closer to the experimental value in liquid phase [24] comparing with those obtained with M06-2X. On another hand, M06-2X significantly blue-shifts the CN-stretching band ($146\text{--}159\text{ cm}^{-1}$), which is reflected in the PES profiles (see Fig. 2 and Table S3).

Starting from the optimized structure rPES scans were performed for all internal coordinates simultaneously optimizing all the unconstrained degrees of freedom, so that the minimum total energy is obtained along the chosen internal coordinate. For each coordinates 18 scans configurations have been computed with a step of 0.0002 nm and 0.3° for bonds and angles, respectively. Fitting these curves to suitable polynomials reveals good description by second-order polynomial, *i.e.* in terms of a simple harmonic approximation. The following functional form has been used for the intramolecular potential, which is the typical expansion in terms of valence coordinates

$$U(r, \theta) = U_{\text{bond}} + U_{\text{angle}} = \sum_{\text{bond}} \frac{k_r}{2} (r - r_0)^2 + \sum_{\text{angle}} \frac{k_\theta}{2} (\theta - \theta_0)^2 \quad (1)$$

where $U(r, \theta)$ is a sum over the internal terms as a function of atomic coordinates represented by bond distances (r) and angles (θ). The

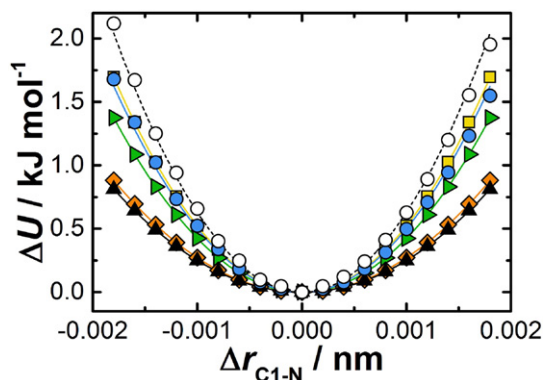


Fig. 2. Examples of rPES profiles for C1–N stretching from the gas phase *ab initio* calculations and plotted from the literature data: M06-2X/aug-cc-pVTZ (empty circles), MP2/aug-cc-pVTZ (blue circles), AMBER based models (black triangles) [36,37], Orhan (yellow squares) [31], OPLS/AA (orange diamonds) and GAFF (green triangles) adopted by Coleman et al. [81]. Lines represent the harmonic approximation function.

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