



## Topical Perspective

## Visualizing spatially decomposed intermolecular correlations in the infrared spectra of aprotic liquids



Maciej Śmiechowski

Department of Physical Chemistry, Chemical Faculty, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

## ARTICLE INFO

## Article history:

Received 2 May 2017

Received in revised form

25 September 2017

Accepted 26 September 2017

Available online 29 September 2017

## Keywords:

 $\gamma$ -Butyrolactone

Ab initio molecular dynamics

Infrared spectroscopy

Spatially resolved spectra

Spatial distribution functions

## ABSTRACT

Infrared (IR) spectroscopy is commonly used to study intermolecular interactions in the liquid phase, including solvation phenomena. On the other hand, ab initio molecular dynamics (AIMD) simulations offer the possibility to obtain IR spectra from first principles. Surpassing the experiment, AIMD simulations can deliver additional information on the spatial intermolecular correlations underlying the IR spectrum of the liquid. Although such correlations contribute significantly to the IR spectra of associated liquids, such as water, they are equally important in the case of aprotic solvents, where dipole–dipole interactions are dominant. Here, the extent and non-trivial character of the spatial correlations in the IR spectra are demonstrated on the example of  $\gamma$ -butyrolactone (GBL), an important solvent in the rechargeable cell industry.

© 2017 Elsevier Inc. All rights reserved.

## 1. Introduction

Vibrational spectroscopy is an established method in the studies of interactions in molecular liquids and their mixtures [1]. It continues to deliver invaluable structural and dynamical data on liquid water and aqueous solutions [2–5]. At the same time, both Raman and infrared (IR) spectroscopies are indispensable for providing a detailed picture of intermolecular interactions in non-aqueous systems [6–9], including electrochemically relevant solvents [10,11].

Polar aprotic solvents are universally used in the lithium-ion (Li-ion) battery industry due to numerous advantages they offer with respect to aqueous electrolyte systems [12–14]. Cyclic esters are especially promising candidates for non-aqueous systems containing  $\text{Li}^+$  and particularly  $\gamma$ -butyrolactone (GBL) fulfils most of the requirements posed for such solvents: high dielectric constant, moderate viscosity, broad liquid range and adequate solubility of lithium salts [14–17]. It has undergone extensive tests as a solvent or cosolvent component of Li-ion batteries [18–23]. Although vibrational spectroscopy was used in the studies of liquid GBL [24–29], the data analysis was often concerned with the band assignment of the fundamental vibrational transitions [26,27,30] and special emphasis was put on the GBL dimerization in the liquid phase as the process primarily responsible for the detected spectral changes [24,28,29]. However, aggregation of molecular dipoles in the liquid

phase is a complicated phenomenon, the precise interpretation of which is sensitive to the choice of treatment [31]. IR spectroscopy also found limited applications in the studies of electrolyte solvation in GBL-based systems [32,25,33].

Experimental measurements in the liquid phase can be successfully complemented with invaluable structural and dynamical data delivered by molecular dynamics (MD) simulations [34,35]. In particular, ab initio molecular dynamics (AIMD) combines quantum mechanical treatment of the electron density with the classical evolution of the nuclei trajectory [36]. However, in spite of the wide applicability of AIMD for condensed phase simulations, its hitherto usage in the studies of non-aqueous solvents has been quite limited, mainly due to the demand on computational resources. Therefore, the investigations of aprotic solvents and other liquid systems, e.g., molten salt mixtures with AIMD simulations are a relatively novel and emerging area of computational studies [32,37–42].

Using the maximally localized Wannier functions (MLWFs) formalism in AIMD simulations [43], it is possible to unambiguously partition the system's dipole moment into molecular dipole moments in the condensed phase [44] and further apply them in obtaining solute/solvent IR spectra based on first principles [45,46]. Nowadays, more advanced smooth decomposition schemes are available and have found tremendous success in deciphering the fully spatially resolved IR spectrum of liquid water [47], as well as radially resolved spectra of liquid water and aqueous solutions of simple ions [48–51]. For a more solute-specific analysis, the distance-dependent absorption coefficient provides a detailed pic-

E-mail address: [Maciej.Smiechowski@pg.gda.pl](mailto:Maciej.Smiechowski@pg.gda.pl)

ture of the modulations of the IR spectrum around a reference molecule [48]. This offers a direct insight into the solvent effect on IR spectra of the solution depending on the distance from the solute [32,50,51]. In parallel, studying velocity cross-correlations in liquids in real or reciprocal space offers a comprehensive view of the correlated particle motion in the system [47–49,52].

Recently, we reported AIMD simulations of LiBr solvation in liquid GBL in combination with experimental IR spectroscopic measurements [32]. Application of the distance-dependent spectra formalism allowed us to unambiguously relate the spectral features observed in LiBr solution to the separate influences exerted by cation and anion on the solvent. Here, we offer a complementary analysis in terms of the radially and spatially resolved IR spectra of bulk GBL, this approach being applied for the first time to a non-aqueous solvent with a highly anisotropic internal structure. We further aim to identify various contributions to the total IR spectrum of a moderately associated liquid that stem from intermolecular dipolar couplings.

## 2. Visualizing spatial correlations in the infrared spectra

The theory behind the computation of IR spectra from MD simulations is well known and routinely applied [47,53], so only a brief summary is given here. In linear response theory, the frequency-dependent IR spectrum of a system is obtained as a Fourier transform (FT) of the total dipole moment time (auto-)correlation function (TCF),

$$\alpha(\omega) = \mathcal{F}(\omega) \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \mathbf{M}(t_0 + t) \mathbf{M}(t_0) \rangle, \quad (1)$$

where the ensemble averaging ( $\dots$ ) runs over all time origins  $t_0$  and  $\mathcal{F}(\omega)$  denotes the quantum correction prefactor to the classical total dipole moment TCF that fails to fulfill the detailed balance condition obeyed by the exact quantum TCF [53]. In many cases it is preferable to work with the total dipole moment derivative instead which in the absence of true dipole velocities (e.g., when using the maximally localized Wannier function picture of the electron density) must be approximated by taking finite differences,  $\dot{\mathbf{M}} \approx \delta \mathbf{M} / \delta t$ , where  $\delta t$  is the time step of the dipole moment trajectory. The total dipole moment derivative is independent on the origin of the coordinate system and usually provides better quality spectra due to noise reduction [50,51]. In this case, the  $\mathcal{F}(\omega)$  prefactor (assuming the so-called harmonic approximation to quantum correction [53]) reads

$$\mathcal{F}(\omega) = \frac{1}{n(\omega)} \frac{1}{6\epsilon_0 k_B T V c} \text{sinc}^{-2}(\omega \delta t / 2) \quad (2)$$

for the system at temperature  $T$  and volume  $V$ , where  $n(\omega)$  is the refractive index,  $\epsilon_0$ ,  $k_B$ , and  $c$  denote the fundamental constants and the  $\text{sinc}^{-2}(\omega \delta t / 2)$  factor corrects for the time discretization of the dipole moment trajectory [50].

We begin the discussion of the intermolecular correlations in the IR spectra of liquids with a simple decomposition scheme that allows to separate the intra- and intermolecular contributions to the IR spectrum [45,46]. The total dipole moment can be formally decomposed into molecular dipole moments, i.e.,  $\mathbf{M} = \sum_{i=1}^N \boldsymbol{\mu}_i$ . In this case, the TCF from Eq. (1) can be rewritten as

$$\begin{aligned} \langle \mathbf{M}(t_0 + t) \mathbf{M}(t_0) \rangle &= \left\langle \sum_{i=1}^N \boldsymbol{\mu}_i(t_0 + t) \sum_{i=1}^N \boldsymbol{\mu}_i(t_0) \right\rangle \\ &= \sum_{i=1}^N \langle \boldsymbol{\mu}_i(t_0 + t) \boldsymbol{\mu}_i(t_0) \rangle + \sum_{i=1}^N \sum_{j \neq i} \langle \boldsymbol{\mu}_j(t_0 + t) \boldsymbol{\mu}_i(t_0) \rangle, \end{aligned} \quad (3)$$

and the IR spectrum can consequently be interpreted as

$$\begin{aligned} \alpha(\omega) &= \mathcal{F}(\omega) \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{i=1}^N \langle \boldsymbol{\mu}_i(t_0 + t) \boldsymbol{\mu}_i(t_0) \rangle \\ &\quad + \mathcal{F}(\omega) \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{i=1}^N \sum_{j \neq i} \langle \boldsymbol{\mu}_j(t_0 + t) \boldsymbol{\mu}_i(t_0) \rangle \\ &= \alpha_{\text{mol}}(\omega) + \alpha_{\times}(\omega), \end{aligned} \quad (4)$$

where the “self” and “cross” (i.e., intra- and intermolecular) terms in the spectrum are explicitly defined.

At variance to this approach, instead of a discrete partitioning according to Eq. (3) the total dipole moment can be smoothly decomposed on a regular spatial grid  $\mathbf{r}$  in the form of a continuous local dipole density,

$$\boldsymbol{\rho}_{\mu}(t, \mathbf{r}) = \sum_{i=1}^N \boldsymbol{\mu}_i(t) \frac{1}{(2\pi\sigma^2)^{3/2}} \exp \left[ -\frac{(\mathbf{R}_i(t) - \mathbf{r})^2}{2\sigma^2} \right], \quad (5)$$

where  $\mathbf{R}_i(t)$  is the center-of-mass (CoM) position of molecule  $i$  and  $\sigma$  is the regularization parameter that controls the Gaussian projection of the molecular dipoles on the grid [48,47]. The total dipole moment can be recovered by volume integration,  $\mathbf{M}(t) = \int d^3\mathbf{r} \boldsymbol{\rho}_{\mu}(t, \mathbf{r})$ . By choosing the origin of the grid to be the CoM of a reference molecule, fixing a local molecular reference frame, and summing over all equivalent solvent molecules, we may write by analogy to Eq. (3),

$$\begin{aligned} \langle \mathbf{M}(t_0 + t) \mathbf{M}(t_0) \rangle &= \left\langle \sum_{i=1}^N \boldsymbol{\mu}_i(t_0 + t) \sum_{i=1}^N \boldsymbol{\mu}_i(t_0) \right\rangle \\ &= N \left\langle \sum_{i=1}^N \boldsymbol{\mu}_i(t_0 + t) \boldsymbol{\mu}_{\text{ref}}(t_0) \right\rangle \\ &= N \left\langle \int d^3\mathbf{r} \boldsymbol{\rho}_{\mu}(t_0 + t, \mathbf{r}) \boldsymbol{\mu}_{\text{ref}}(t_0) \right\rangle. \end{aligned} \quad (6)$$

Using thus recast total dipole moment TCF in Eq. (1) leads to,

$$\begin{aligned} \alpha(\omega) &= \mathcal{F}(\omega) N \int_{-\infty}^{\infty} dt e^{-i\omega t} \left\langle \int d^3\mathbf{r} \boldsymbol{\rho}_{\mu}(t_0 + t, \mathbf{r}) \boldsymbol{\mu}_{\text{ref}}(t_0) \right\rangle \\ &= \int d^3\mathbf{r} \mathcal{F}(\omega) N \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \boldsymbol{\rho}_{\mu}(t_0 + t, \mathbf{r}) \boldsymbol{\mu}_{\text{ref}}(t_0) \rangle \\ &= \int d^3\mathbf{r} \alpha(\omega, \mathbf{r}), \end{aligned} \quad (7)$$

whereby the fully spatially resolved IR spectrum is introduced that enables detailed analysis of the individual contributions to the spectrum due to correlated oscillations of molecular dipoles in the anisotropic liquid as seen from the point of view of a reference molecule. The resulting spectral intensity at point  $\mathbf{r}$  might be positive, indicative of locally correlated oscillations of the molecular dipole density which lead to increased IR absorption by the sample, as well as negative, signifying locally out-of-phase oscillations which contribute to decreased IR absorption [47].

The discussed dipolar correlations might be contrasted with spatial correlations in the atomic density that can be visualized by the well-known spatial distribution functions (SDFs) [54],

$$N(\mathbf{r}) = \rho \int d^3\mathbf{r} g(\mathbf{r}), \quad (8)$$

that are likewise defined in the local molecular reference frame. Analysis in terms of SDFs provided valuable insight into the structure of liquid water [55,56], as well as other molecular liquids [54,57,58].

We further note that if the structure of the liquid is assumed to be isotropic, then it is in principle possible to factor out the angular

Download English Version:

<https://daneshyari.com/en/article/6877519>

Download Persian Version:

<https://daneshyari.com/article/6877519>

[Daneshyari.com](https://daneshyari.com)