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UDC 539

PICOSECOND DYNAMICS OF MOLECULAR ENTITIES IN LITHIUM SALT SOLUTIONS IN DIMETHYL SULFOXIDE, PROPYLENE CARBONATE, AND DIMETHYL CARBONATE

An analysis of the Raman spectra of solutions of lithium salts in dimethyl sulfoxide, propylene carbonate, and dimethyl carbonate in a concentration range from diluted solutions to the mixtures of molten solvates with salts has been performed in terms of the dynamics, specifically, dephasing (τ_V) and modulation (τ_ω) times of all molecular entities present in solutions are determined and analyzed. It has been found that, in the picosecond time domain, dephasing and modulation in solvent molecules hydrogen-bonded with an anion and/or solvating a cation are slower than in free solvent molecules. In solvent separated ion pairs, both τ_V and τ_ω are much longer than in solvated anions, thus indicating strong interactions between anions and their surrounding. In contact ion pairs, τ_V are great, whereas τ_ω appear close to those for free anions. This reflects that the structure of the liquid tends to the structure of molten salts.

K e y w o r d s: Raman spectra, solvation, ion pairs, dephasing, modulation.

1. Introduction

Vibrational spectroscopy is widely used for recognizing solvation and formation of solvent-separated (SSIP) and contact (CIP) ion pairs in ionic solutions [1]. In spite of the fact that vibrational spectroscopy approaches are considered a powerful tool for studying interparticle interactions and dynamics in ionic systems [2–4], not so much work has been done in the past so as to uncover the nature of solvates and ion pairs. The first studies of the dynamics of solvent molecules surrounding cations in lithium salt solutions in pyridine and acetone performed by means of line profile analysis have shown a decrease in characteristic times of vibrational dephasing upon the solvation [5, 6]. A similar observation follows for lithium salt solutions in dimethylsulfone [7]. The ion pair formation has been treated in terms of dynamics in nitrate and perchlorate solutions in water and non-aqueous solvents [8–11]. It has been found that, for the anions in SSIPs and CIPs, the dephasing process is more rapid as compared to the solvated anions. In studies of specific solvation of molecular anions via hydrogen bonding carried out in pump-probe experiments [12], the rapid vibrational energy relaxation has appeared characteristic of strong coupling between the anions and the solvents, while longer vibrational energy relaxation reveals weaker solvent interactions.

Nowadays, the interest in the study of dynamics of lithium salts in various solvents is renewed, especially due to a particular attention paid by electrochemists to concentrated solutions of lithium salts [13]. In recent years, dynamics in lithium salt solutions has been studied by various methods, including coherent two-dimensional infrared spectroscopy and pump-probe experiments [14–17]. In Ref. [14], investigations of dynamics of $LiPF_6$ solutions in butylene carbonate and dimethyl carbonate have been conducted, by using steady-state and two-dimensional infrared spectroscopies. It has been found that the addition of a salt induces a slowdown of the motions of solvent molecules, because the presence of ions imposes a strong ordering through ion dipole interactions (solvation shell) and Coulombic interactions between the charged species. Time resolved experiments reveal that the solvation shell formed by cyclic carbonates is more rigid than that formed by linear carbonates. The study of the ultrafast carbonate solvent exchange dynamics around lithium ions in carbonate solutions with coherent two-dimensional infrared spectroscopy [15] demonstrates that the time constants of the formation and dissociation of the lithium-ion – carbonate complex in solvation sheaths are on a picosecond time scale, and the vibrational lifetime of the Li diethyl carbonate complex is found to be much shorter than that of a free solvent. Molecular rotation measurements of lithium salts in solvents containing a C–N group [16, 17] show that the anisotropy decay of the solvent bound to Li^+ is much slower than that of a free solvent molecule, and the lifetime of the cation solvate was determined.

In spite of some progress in this field, the problem of dynamic criteria of the cation solvation and the ion pairing is far from being settled. Unlike the situation with a specific solvation via the hydrogen bonding, where clear dynamic signatures are established, the data on the dynamics in ionic solutions need to be specified and systematized. In order to make a step in this direction, this paper deals with the Raman data on the solvation and ion pairing in solutions of various lithium salts in dimethyl sulfoxide (DMSO), propylene carbonate (PC) and dimethyl carbonate (DMC) in a concentration range from 0.05 to 0.25 mole fractions of a salt, from diluted solutions to the mixtures of molten LiX×4S solvates with LiX, where X is the anion [18, 19], and treats this data from the point of view of dynamics.

One of the simplest and well-established methods of studying the dynamics in condensed media is the analysis of line profiles in terms of vibrational relaxation phenomena of probe molecules. The time correlation function (TCF) $G_V(t)$ is determined by the Fourier transformation of the isotropic $I_{\mathrm{iso}}(\nu)$ Raman spectrum [20–22],

$$G_V(t) = \int_{-\infty}^{+\infty} I_{\mathrm{iso}}(\nu) \exp(2\pi i c \nu t) d\nu, \tag{1}$$

where c is the speed of light, and ν is the frequency measured in wavenumbers. Among various mechanisms of vibrational relaxation, the main cause for the broadening of isotropic lines in Raman spectra is the vibrational dephasing [20–22] with a characteristic time $\tau_V = \int G_V(t)dt$. It arises due to the adiabatic perturbations of the probe molecule by its surrounding. These perturbations modulate the molecular vibrations and lead to phase shifts. The TCF of the vibrational dephasing is described by the Kubo equation [23],

$$G_V(t) = M_2 \tau_\omega^2 e^{-\exp(-t/\tau_\omega)-1+t/\tau_\omega}, \tag{2}$$

where τ_ω is the modulation (perturbation) time and $M_2 = \int \nu^2 I_{\mathrm{iso}}(\nu)d\nu / \int I_{\mathrm{iso}}(\nu)d\nu$ is the vibrational second moment. If $\tau_\omega \to 0$ (perturbations are weak and fast, interactions are nonspecific, the surrounding of a probe molecule is flexible), the TCFs are exponential, and the spectra have a Lorentzian shape. In this case, the modulation phenomenon is described in terms of collision concepts and is considered to be collision-driven, and τ_ω may be equated to the time between collisions τ_{BC} of the probe particle with neighboring particles. If $\tau_\omega \to \infty$ (perturbations are strong and slow, the interactions are specific and directed, the particle and its surrounding form a rigid quasilattice), the shape of the TCFs and the spectra become Gaussian. Just these principles are used in what follows.

2. Experimental

$LiBF_4$ (Novosibirsk, Russia, 99.98%), $LiClO_4$ (Novosibirsk, Russia, 99.98%), $LiCF_3SO_3$ (Fluka, 62621, 99.5%), $LiN(CF_3SO_2)_2$ (Fluka, 15224, 99.95%), and $LiB(C_2O_4)_2$ (Novolite, 99.9%) were dried in vacuum at 150 °C for 24 hours. DMSO (Aldrich, 276855, ≥99.9%, melting point 18.5 °C), PC (Aldrich, 310328, melting point –48.8 °C), and DMC (Aldrich, 517127, melting point 4.6 °C) were used without further treatment. Solutions containing 0.05, 0.1, 0.15, 0.2, and 0.25 mole fraction of the salt were prepared by mixing the proper amounts of salt and solvent in a dry glovebox. Remaining humidity in the glovebox was monitored with a digital hygrometer. All preparation procedures were described in more detail in Ref. [24]. For the investigation of Raman spectra, solutions were flame-sealed in Pyrex tubes with an inner diameter of 5 mm.

A method to obtain Raman spectra is described in Refs. [18, 25] in detail. Since all the lines studied are sharply polarized, only isotropic spectra are presented in what follows. The decomposition of overlap lines and calculations of TCFs have been performed in terms of an analytical method suggested in Ref. [26] and reviewed in Refs. [3, 4].

The Raman spectra of $LiBF_4$, $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, and $LiB(C_2O_4)_2$ in DMSO were recorded at 50 °C, and the $LiClO_4$-DMSO system

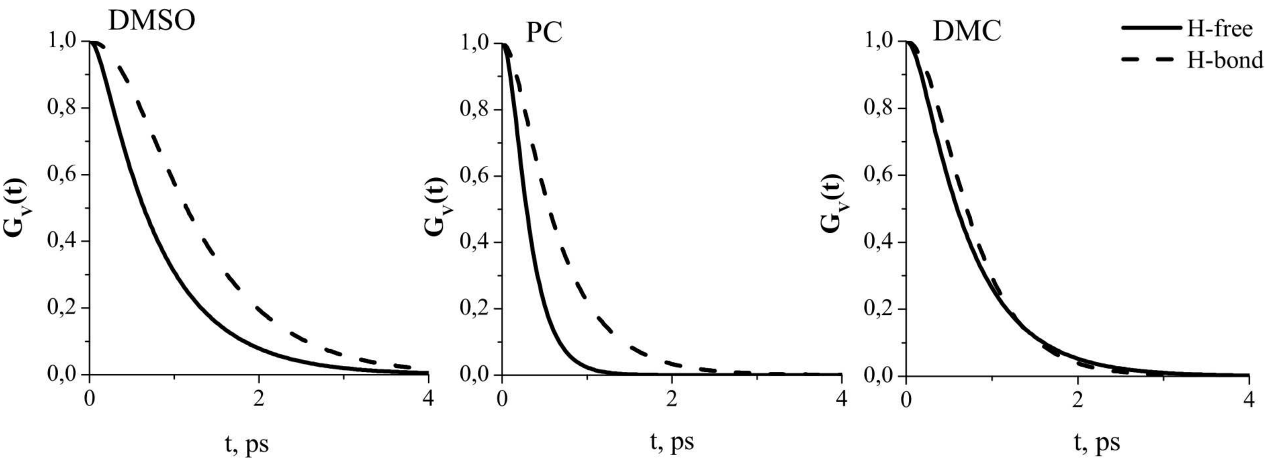

Fig. 1. TCFs of dephasing of hydrogen-bond-free solvent molecules and solvent molecules hydrogen-bonded with anion in $LiClO_4$ solutions in DMSO, PC, and DMC

at 90 °C, since these are the minimal possible temperatures for studying the whole concentration range of these systems in the liquid state. The $LiClO_4$ spectra in PC and DMC were registered at ambient temperature. For more detail regarding the assignment of vibrational lines and their choice for the solvation and ion pairing studies, the concentration dependences of solvation numbers of cations and anions and the content of solvated ions, SSIPs and CIPs in solutions, see Refs. [18, 19].

3. Results and Discussion

Aiming at understanding the dynamical signatures of solvation and ion pairing, it would be quite natural to begin with solvation of molecular anions via the hydrogen bonding and to compare the results obtained with conclusions drawn in pump-probe experiments [12]. In order to do so, vibrations involving the hydrogen atoms of CH_3-groups have been analyzed. In the CH_3-groups, the positive charge is localized on the hydrogen atoms. Hence, O or F atoms of an anion interact with the hydrogen of a methyl group of the solvent molecule, forming the so-called "blue-shifting" hydrogen bond [27–29].

As follows from our work [30], in the neat DMSO, the line at $\sim$2913 cm^{-1} corresponding to the CH_3 symmetric stretch ν_3 (A') is single, has a symmetric profile, and demonstrates no evidences of hydrogen bonding between DMSO molecules. From the point of view of dimerization processes, the absence of its splitting means that the perturbations of CH_3-groups in the monomers and dimers are of the same value, and, in this spectral region, the monomers and dimers are indistinguishable in Raman spectra. The analysis of the spectra of lithium salt solutions in DMSO in the region shows the presence of the non-bonded DMSO molecules ($\sim$2919 cm^{-1}) and the solvent molecules entering the solvation sphere of an anion and hydrogen-bonded to it ($\sim$2913 cm^{-1}) [25].

The line at $\sim$2930 cm^{-1} corresponding to the symmetric CH_3 stretch ν_{14} (A_1) in the neat PC is split into two components at 2930 and 2941 cm^{-1} corresponding to hydrogen-bond-free molecules and to molecules hydrogen-bonded to anions [31]. Upon adding the salt, the intensity of the component at $\sim$2941 cm^{-1} increases, and the intensity of the component at $\sim$2930 cm^{-1} decreases [25, 32].

Like in DMSO, the line at $\sim$2960 cm^{-1} corresponding to the symmetric CH_3 stretch ν_2 (A_1) of the cis-cis conformer of the neat DMC [29] shows no evidence of the hydrogen bonding . The behavior of the ν_2 (A_1) vibration in the salt solutions in DMC is similar to that of CH-vibrations in DMSO solutions [25]. The split lines can be assigned to the non-bonded DMC molecules ($\sim$2919 cm^{-1}) and the solvent molecules entering the solvation sphere of the anion and hydrogen-bonded to it ($\sim$2913 cm^{-1}) [25, 34, 35].

Respective TCFs are shown in Fig. 1. Calculations reveal that, as expected, in hydrogen-bond-free solvent molecules, dephasing and modulation are faster than in solvent molecules hydrogen-bonded with

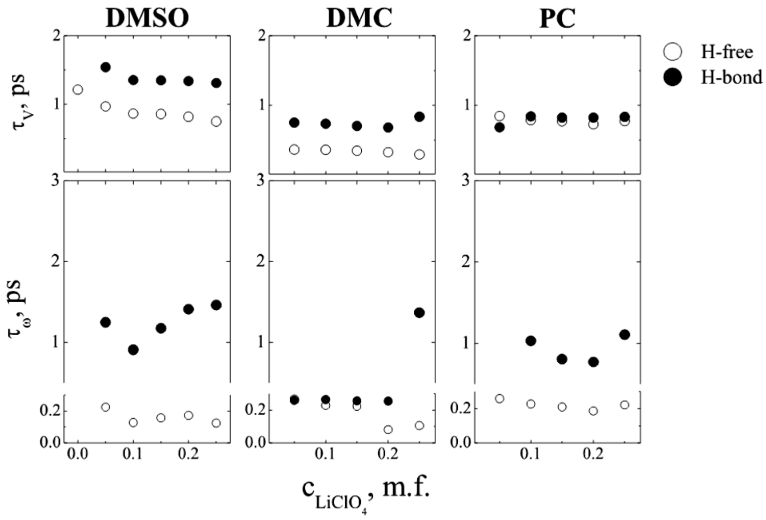

Fig. 2. Dephasing and modulation times for free solvent molecules and solvent molecules hydrogen-bonded with anions in $LiClO_4$ solutions in DMSO, PC, and DMC

anions (Fig. 2). It can also be noted that, for the hydrogen-bond-free solvent molecules, the TCFs are close to exponential, and the spectra have a more Lorentzian shape, as opposed to the solvent molecules hydrogen-bonded with anions, for which the shape of the TCFs and the spectra become more Gaussian.

Now, let us turn to cation solvation effects. In DMSO, these have been studied by the analysis of the isotropic line corresponding to the symmetric CS stretching ν_{10} (A') vibration. In the Raman spectra of pure liquid DMSO, this line is split into two components at ∼665 and ∼669 cm^{-1}, which reflects the presence of monomeric molecules and cyclic dimers [30]. When lithium salts are added, the Raman spectra of DMSO undergo changes. From our recent studies [25], a composite line in the region of the ν_{10} (A') vibration can be decomposed into three components, the first two corresponding to the vibrations of monomeric (ν = 663–670 cm^{-1}) DMSO molecules and DMSO dimers (ν = 667–669 cm^{-1}), and the new component at higher wavenumbers (ν = 674–676 cm^{-1}) corresponding to particles entering the solvation shell of cations [36–39].

The ordering in PC is also seen in the Raman spectra as splitting of the line corresponding to the ν_{10} (A_1) symmetric vibrations of a PC ring, ν ∼706 cm^{-1} for monomers, and ν ∼ 710 cm^{-1} for dimers [40, 41]. In the presence of lithium salts, the line of ν_{10} (A_1) vibrations can be decomposed into three components reflecting the presence of monomeric (ν = 706–707 cm^{-1}), dimeric (ν = 711–712 cm^{-1}), and solvating (ν = 716–717 cm^{-1}) PC molecules [25].

As to DMC, the presence of monomers ($\nu \sim$ ∼ 513 cm^{-1}) and cis-cis dimers (ν ∼ 516 cm^{-1}) is noticeable in the Raman spectrum in the region of ν_9 (A_1) O–C–O bond vibrations [33]. When lithium salts are added, the ν_9 (A_1) line can be decomposed into three components corresponding to monomeric (ν = 513–515 cm^{-1}), dimeric (ν = 516–517 cm^{-1}), and solvating (ν = 523 cm^{-1}) DMC molecules [25].

The time correlation functions of the vibrational dephasing of the monomeric, dimeric, and solvating molecules in DMSO, PC, and DMC are shown in Fig. 3. The analysis of characteristic times (Fig. 4) reveals that, for both associated (dimeric) and solvating molecules of the solvent in the systems studied, the vibrational dephasing is slow, and its speed is approximately equal to the modulation speed. This contrasts with the rapid modulation process for monomeric solvent molecules, which should be considered collision-driven. Such situation closely resembles relations between characteristic times in the case of anion solvation described above.

The "bonded" solvent molecules are located near their neighbors. When the bonds between them are disrupted (characteristic time τ_ω), phase shifts (characteristic time τ_V) take place. The relation $\tau_V \approx \tau_\omega$

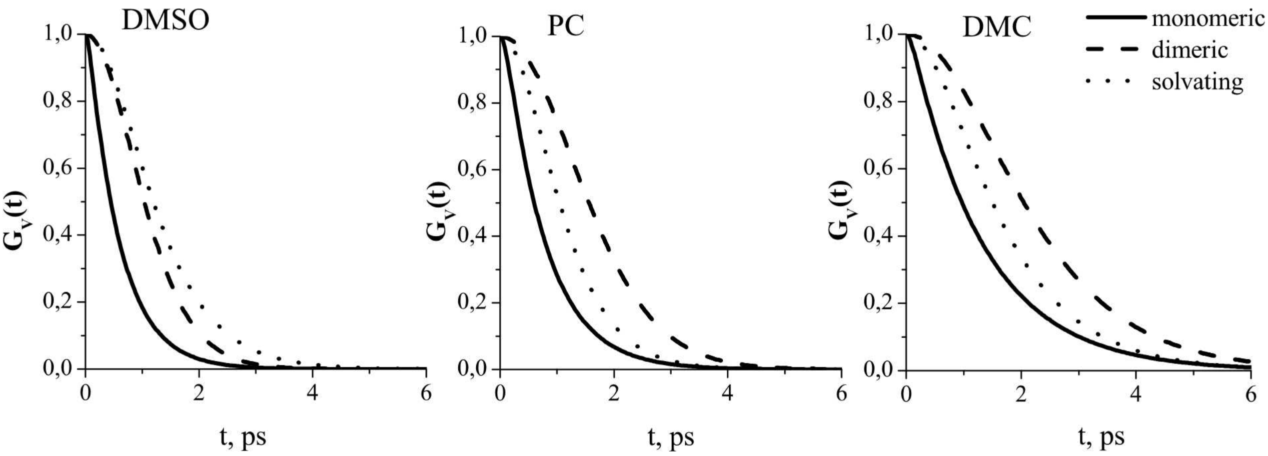

Fig. 3. TCFs of the dephasing of monomeric, dimeric, and solvating solvent molecules in $LiClO_4$ solutions in DMSO, PC, and DMC

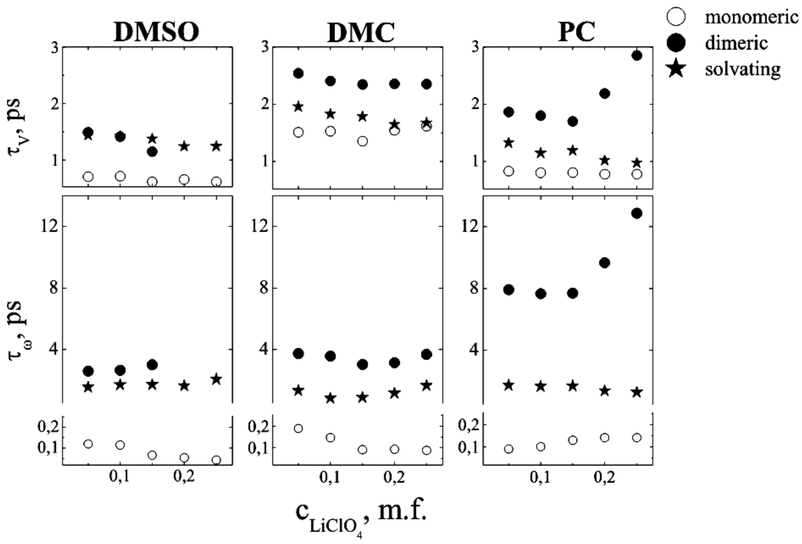

Fig. 4. Dephasing and modulation times for monomeric, dimeric, and solvating solvent molecules in $LiClO_4$ solutions in DMSO, PC, and DMC

may be considered as an evidence of the close stability of both associates and solvation complexes in the solutions studied. From the point of view of the dynamic criteria of complex formation [44, 45], the lower limit of the lifetime of solvation spheres surrounding Li^+ ions is equal to $\tau_\omega \approx \tau_V \sim 1.5$ ps, and the solvated complexes should be considered long-lived, at least, in the picosecond time domain. The TCFs for the "bonded" solvent molecules become more Gaussian, while the TCFs for monomeric solvent molecules are close to exponential, and the respective components have more Lorentzian shape.

Signatures of ion pairing in solutions are seen, first of all, as extra lines appearing in the vicinity of intense lines corresponding to non-degenerated vibrations of anions. Upon adding $LiBF_4$ to DMSO, the ν_1 line of BF_4^- splits into three components at 760, 763, and 768 cm^{-1}, which can be assigned to anions in the free state, in SSIPs, and in CIPs, respectively [25, 46, 47]. The integrated intensities of the component lines vary with the salt concentration. If the salt content is growing, the intensity of the component corresponding to free ions passes a maximum, and, at 0.25 mole fraction of the salt, becomes negligible. SSIPs

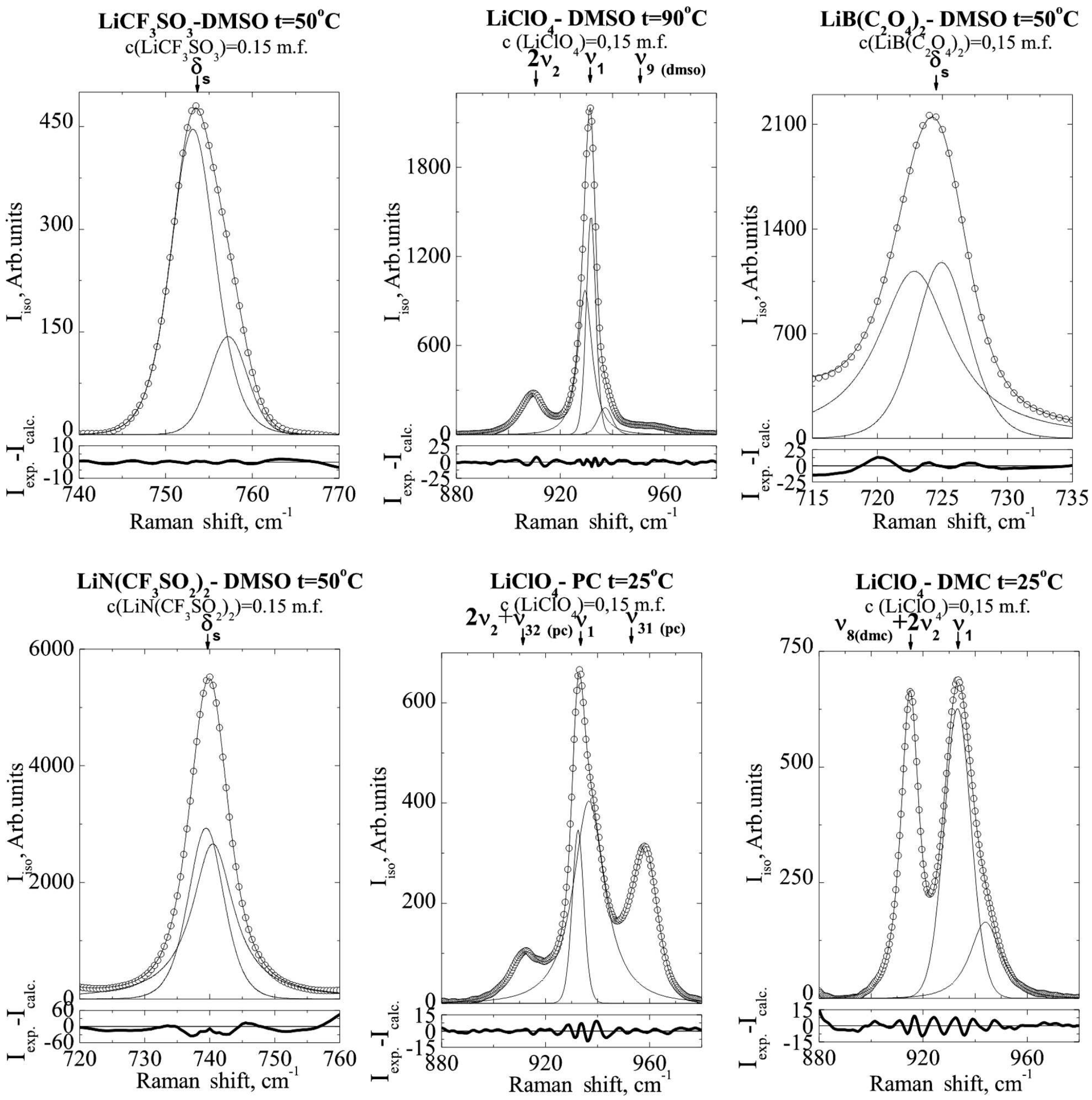

Fig. 5. Raman spectra of lithium salt solutions in DMSO, PC, and DMC in regions sensitive to the ion pairing

are present in solutions at all concentrations studied. CIPs become visible at 0.15 mole fraction of the salt [19].

In solutions of $LiCF_3SO_3$ in DMSO, the line corresponding to the δ_s (A_1) CF_3 vibrations of the anion is split into three components at 753, 758, and 762 cm^{-1} attributed to free anions, SSIPs, and CIPs, respectively (Fig. 5) [48, 49]. The intensity of the components attributed to free anions increases with the salt concentration, SSIPs become visible at 0.1 mole fraction of the salt, and CIPs appear in more concentrated solutions containing 0.2 mole fraction of $LiCF_3SO_3$. A similar behavior is characteristic of $LiClO_4$-DMSO solutions (Fig. 5). The ν_1 line of ClO_4^- splits into three components at 929, 932, and 937 cm^{-1} corresponding to anions in the free state, in SSIPs, and in CIPs, respectively [50–52]. In this system, free ions and SSIPs are present in all solutions, and CIPs exist in solutions containing more than 0.1 mole fraction of $LiClO_4$.

Unlike three previous systems, Raman spectra in the ion-pairing sensitive region of solutions of

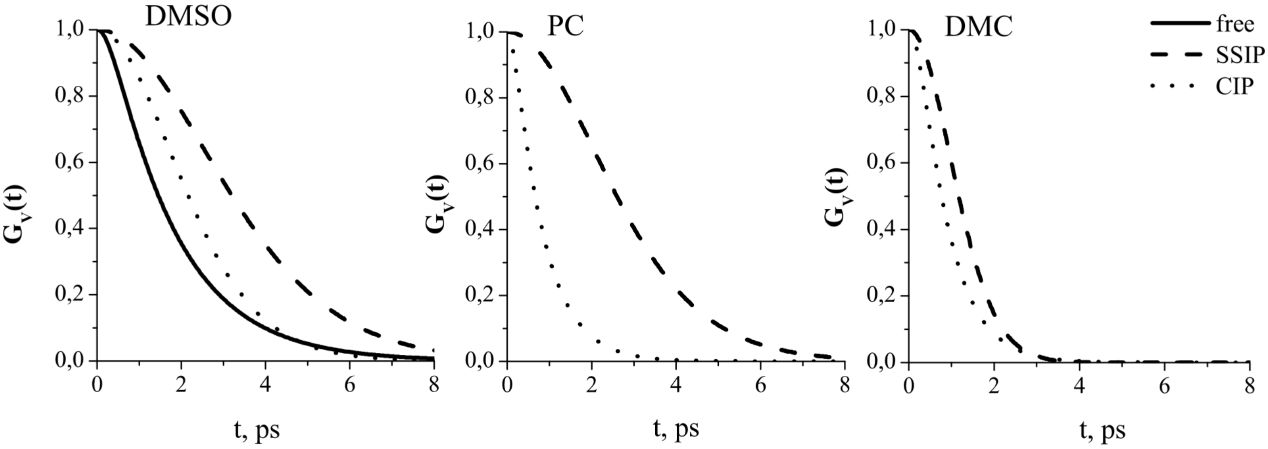

Fig. 6. TCFs of the dephasing of ClO_4^- anion in the free state, SSIPs, and CIPs in $LiClO_4$ solutions in DMSO, PC, and DMC

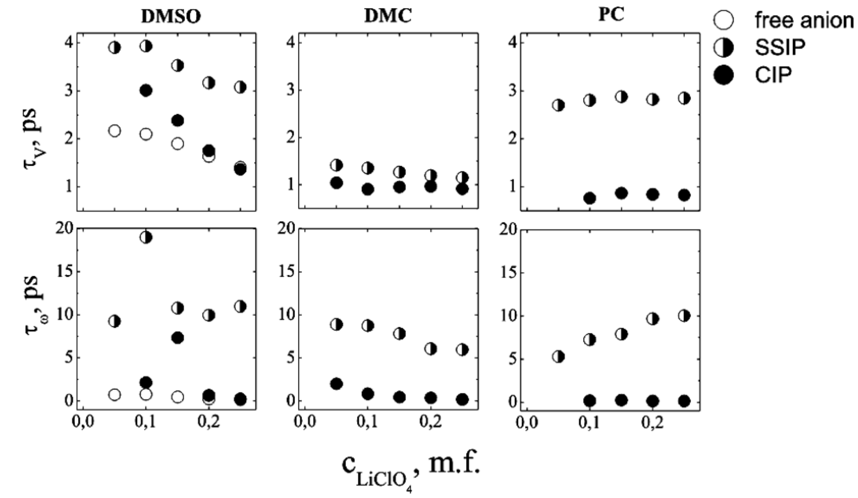

Fig. 7. Dephasing and modulation times for a ClO_4^- anion in the free state, SSIPs, and CIPs in $LiClO_4$ solutions in DMSO, PC, and DMC

$LiB(C_2O_4)_2$ and $LiN(SO_2CF_3)_2$ in DMSO are split into two components (Fig. 5) and do not demonstrate the presence of CIPs. The line corresponding to the δ_s (A_1) O–B–O vibrations of $B(C_2O_4)_2^-$ can be decomposed into components at 723 (free anions) and 725 cm^{-1} (SSIPs). The components of the line corresponding to δ_s (A_1) CF_3 vibrations of $N(SO_3CF_3)_2^-$ can be assigned to free anions (741 cm^{-1}) and SSIPs (739 cm^{-1}). In both systems, free ions are present in all solutions, and SSIPs are visible at the highest dilutions studied (Fig. 5).

The Raman spectra of solutions of $LiClO_4$ in PC and DMC and their fits clearly reveal the presence of two types of particles having the lines at ν = 932.5 and 937 cm^{-1} in PC and at ν = 933 and 942 cm^{-1} in DMC (Fig. 5). In PC, the intensity of the low-frequency component increases with the salt concentration, and the high-frequency component is absent in the most diluted solutions. In DMC, the intensity of both components grows upon adding the salt. The low-frequency components can be assigned to anions forming SSIPs and the high-frequency components – to anions in CIPs, respectively [32, 53].

The analysis of TCFs (Fig. 6) and characteristic times (Fig. 7) shows that, in free anions, τ_ω are short and evidence the weak interactions between anions and their environment. In SSIPs, τ_ω are an order of magnitude longer, by signifying strong interactions between anions and cations. In CIPs showing up in more concentrated solutions, τ_ω becomes shorter than in SSIPs, probably by demonstrating that the structure of concentrated solutions acquires the features of molten salts, for which short τ_ω are quite obvious [2]. Moreover, when passing from the solvated anion to the SSIP, the Raman profiles of anion lines are transformed from Lorentzian to Gaussian form, and passing from SSIP to the CIP – from Gaussian to Lorentzian form.

4. Conclusion

In this paper, the analysis of the Raman spectra of various lithium salt solutions in DMSO, PC, and DMC in a concentration range from diluted solutions to the mixtures of molten solvates with salts has been performed in terms of the dynamics. The TCFs of vibrational dephasing and respective dephasing and modulation times of all molecular entities present in solutions have been determined. It has been found that, in the picosecond time domain, dephasing and modulation in solvent molecules hydrogen-bonded with anions and/or solvating cations are slower than in free solvent molecules. In SSIPs, both dephasing and modulation times are much longer than in solvated anions. The slowing-down of dephasing and collisions indicates strong interactions between anions and their surrounding. At low concentrations of CIPs, the dephasing times are great, at high concentrations these get shorter, whereas modulation times become close to those for free anions. This reflects that the structure of the liquid tends to the structure of molten salts.

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ПІКОСЕКУНДНА ДИНАМІКА МОЛЕКУЛЯРНИХ ОБ'ЄКТІВ У РОЗЧИНАХ СОЛЕЙ ЛІТІЮ В ДИМЕТИЛСУЛЬФОКСИДІ, ПРОПІЛЕНКАРБОНАТІ ТА ДИМЕТИЛКАРБОНАТІ

Р е з ю м е

Проведено аналіз спектрів комбінаційного розсіювання розчинів солей літію в диметилсульфоксиді, пропіленкарбонаті та диметилкарбонаті в діапазоні концентрацій від розведених розчинів до сумішей розплавлених сольватів з солями з точки зору динаміки, зокрема визначено та проаналізовано часи дефазування (τ_V) та модуляції (τ_ω) всіх молекулярних об'єктів, присутніх у розчинах. Встановлено, що в пікосекундній часовій області процеси дефазування та модуляції в молекулах розчинника, зв'язаних водневим зв'язком з аніоном та/або сольватуючих катіон повільніші, ніж у молекулах вільного розчинника. В іонних парах, розділених розчинником, і τ_V, і τ_ω є значно довшими, ніж у сольватованих аніонах, що свідчить про сильні взаємодії між аніонами та їх оточенням. У контактних іонних парах τ_V є великими, тоді як τ_ω виявляються близькими до значень для вільних аніонів. Це відображає наближення структури рідини до структури розплавлених солей.