ULTRAFAST INFRARED STUDIES OF THE VIBRATIONAL RELAXATION DYNAMICS OF ANIONS IN IONIC LIQUIDS

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Fourier-transform infrared (FT-IR) and time-resolved IR pump - IR probe spectroscopy have been used to study the vibrational band positions, vibrational energy relaxation (VER) rates, and reorientation times of anions in several ionic liquid (IL) solutions. The ILs have alkyl imidazolium cations, especially 1-butyl-2,3-dimethylimidazolium ([BM_2IM]), with thiocyanate (NCS^-), dicyanamide ($N(CN)_2{}^-$), and tetrafluoroborate ($BF_4{}^-$) anions. Spectroscopic studies were carried out for the C≡N stretching bands of NCS^- and $N(CN)_2{}^-$ near 2000 cm^{-1} and for NCS^-, $N(CN)_2{}^-$, and azide ($N_3{}^-$) anions dissolved in the $BF_4{}^-$ IL. The static spectral shifts and VER rates of the anions in IL solution are quite similar to those in polar, weakly hydrogen bonding, conventional organic solvents. In order to establish that the solvation properties of the ILs are not primarily due to the absence of the hydrogen at the 2-carbon (C2) position in the [BM_2IM] ILs, similar studies were also carried out for these same anions in another IL with the C2 hydrogens intact. The band positions and vibrational relaxation times for the anions are similar, indicating that, based on the IR spectroscopy, substituting the C2 hydrogen with a methyl group does not substantially affect the degree of hydrogen bonding in the anion - IL solvation interaction.