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Optical Kerr Effect Spectroscopy of a Nonpolar Solute in Dicationic versus Monocationic Ionic Liquids¹ ESHAN GURUNG, LIANJIE XUE, GEORGE TAMAS, EDWARD QUITEVIS, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409 — A comparison of the intermolecular dynamics of small nonpolar solute molecules in monocationic and dicationic ionic liquids (ILs) was performed using optical heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES). The optical Kerr effect (OKE) spectrum of CS_2 in 1-methyl-3-propylimidazolium bis(trifluoromethane-sulfonyl)amide [C₃mim][NTf₂] and 1,6-bis(3-methylimidazolium-1-yl) hexane bis(trifluoromethanesulfonyl)amide $[C_6(\min)_2][NTf_2]_2$ was investigated as a function of concentration at 295 K. An additivity model with components from the subpicosecond dynamics of IL and CS_2 was used to interpret the OKE spectra of the mixtures. The spectrum of CS_2 in the two ILs is lower in frequency and narrower than that of neat CS_2 . The spectrum of CS_2 in the dicationic IL is higher in frequency than in the monocationic IL. This result shows that CS_2 molecule experiences a stiffer potential in dicationic ILs as compared to monocationic ILs. Higher stiffness in $C_6(\min)_2$ [NTf₂] might be due to a more ordered arrangement and lower mobility of the alkyl chains linking the imidazolium rings.

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