TRANSIENT RAMAN SPECTRA, STRUCTURE AND THERMOCHEMISTRY OF THE THIOCYANATE DIMER RADICAL ANION IN WATER

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Time-resolved resonance-enhanced Stokes and anti-Stokes Raman spectra of the thiocyanate dimer radical anion, (SCN)$_2{}^-$, prepared by pulse radiolysis in water, have been obtained and interpreted in conjunction with theoretical calculations to provide detailed information on the molecular geometry and bond properties of the species. The structural properties of the radical are used to develop a molecular perspective on its thermochemistry in aqueous solution. Twenty-nine Stokes Raman bands of the radical observed in the 120-4200 cm^{-1}region are assigned in terms of the strongly enhanced 220 cm^{-1}fundamental, weakly enhanced 721 cm^{-1}, and moderately enhanced 2073 cm^{-1}fundamentals, their overtones and combinations. Calculations by range-separated hybrid (RSH) density functionals (ωB97x and LC-ωPBE) support the spectroscopic assignments of the 220 cm^{-1}vibration to a predominantly SS stretching mode and the features at 721 $\mathrm{cm}^{-1}$and 2073 $\mathrm{cm}^{-1}$to CS and CN stretching modes, respectively. The corresponding bond lengths are 2.705 (+0.036) Å, 1.663 (+0.001) Åand 1.158 (+0.002) Å. A first order anharmonicity of 1 cm^{-1}determined for the SS stretching mode suggests a convergence of vibrational states at an energy 1.5 eV, using the Birch-Sponer extrapolation. This value, estimated for the radical confined in solvent cage, compares well with the calculated gas-phase energy required for the radical (1.22 eV) to dissociate into SCN and SCN$^-$ fragments. The enthalpy of dissociation drops to 0.63 eV in water when solvent dielectric effects on the radical and its dissociation products upon S-S bond scission are incorporated in the calculations. No frequency shift or spectral broadening was observed between light and heavy water solvents, indicating that the motion of solvent molecules in the hydration shell have no perceptible effect on the intramolecular dynamics of the radical. The Stokes and anti-Stokes Raman frequencies were found to be identical within the experimental uncertainty, suggesting that the frequency difference between the thermally relaxed and spontaneously created vibrational states of (SCN)$_2{}^-$ in water is too small to be observable.