

VIBRATIONAL CHARACTERIZATION OF HEMI-BONDED HALIDE-THIOCYANATE DIMER RADICAL ANIONS (XSCN) \cdot^- IN WATER

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Time resolved Raman studies of halide-thiocyanate dimer radical anions, (X-SCN) \cdot^- (for X=Cl, Br, I), were performed in resonance with their peak of light absorption wavelength at 415 nm. In two of the experiments (for X $^-$ =Br $^-$ or I $^-$) the apparent Raman spectrum contains signatures of three hemibonded intermediates present simultaneously in mutual equilibria with their precursor and successor hemibonded radical counterparts: X $_2\cdot^-$ + SCN $^-$ = (XSCN) \cdot^- + X $^-$ = (SCN) $_2\cdot^-$ + X $^-$. In order to extract (X-SCN) \cdot^- (for X=Br, I) from the composite spectrum additional experiments were performed to generate pre-resonance spectra of X $_2\cdot^-$ and (SCN) $_2\cdot^-$ at 415 nm in order to collect and then subtract their contributions from the composite spectrum. Ten Stokes Raman bands of the halide-thiocyanate radical anions (X-SCN) \cdot^- (for X=Br, I) were observed in the 60-2400cm $^{-1}$ region. They were assigned in terms of the strongly enhanced 198 and 174cm $^{-1}$, weakly enhanced 719.5 and 729cm $^{-1}$, and moderately enhanced 2069 and 2078cm $^{-1}$ fundamentals, their overtones, and combinations in BrSCN \cdot^- and ISCN \cdot^- , respectively. On attempt to record chloride intermediate only characteristic bands coming from the mixed contributions of Cl $_2\cdot^-$ and (SCN) $_2\cdot^-$ have been apparent. Quantum chemical calculations using a range-separated hybrid density functional (ω B97x) with flexible augmented correlation-consistent basis sets support the spectroscopic assignments of the strongest fundamental vibrations to a predominantly S-X (X = Br, I) stretching mode and the features around 720cm $^{-1}$ and 2070cm $^{-1}$ to CS and CN symmetric stretching modes, respectively. Interestingly, CS and CN bond stretching vibrational frequencies in asymmetrical (X-SCN) \cdot^- anion radicals are shifted a few wavenumbers down or up in comparison to the symmetrical (SCN) $_2\cdot^-$ molecule in BrSCN \cdot^- or ISCN \cdot^- , respectively. Considering that ClSCN \cdot^- seems to have vibrational frequencies almost identical to (SCN) $_2\cdot^-$ does not grant any systematic correlation between hemi-bond polarization in this array of molecules and vibrational frequencies of CS and CN bonds. A possible explanation of such an observation can relate to a counteracting induction and migration effects in σ and π bonds, respectively, upon charge migration across the molecule.