

## ANALYSIS OF COMPLEXATION REACTIONS THROUGH MULTISPECTRUM FITTING

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Chemical reactions having equilibrium constants in the range 0.01 – 100 generally have significant amounts of both reactants and products present at equilibrium. If the reaction components have spectral signatures in the UV-visible region, such processes can be analyzed with remarkable precision through nonlinear least-squares fitting of multiple absorption spectra recorded as a function of temperature and composition. As one example, the classic complexation of I<sub>2</sub> with mesitylene in solvents like heptane and CCl<sub>4</sub> yields a 1:1 complex with a well-defined charge-transfer band in the near-UV and also a weaker "molecular" band at longer wavelengths. The latter has long been attributed to absorption within the I<sub>2</sub> of the complex, but because of extensive overlap with the absorption by free I<sub>2</sub> in the solution, has never been well defined. The multispectrum fitting approach precisely characterizes this band. Even routine spectrophotometric data can yield 1% precision in the equilibrium constants  $K$ . In the case of the gas-phase reaction yielding BrCl from the parent halogens, this precision translates into a  $\sim 1\text{-cm}^{-1}$  uncertainty in the molecular dissociation energy, which is a factor of  $\sim 5$  better than the current best spectroscopic estimate. For reference, values of  $K^\circ$  for this reaction appearing in the recent literature range from 6 to 10.