THE NEGLECTED HALOGEN DIMER BANDS: DIMERIZATION EQUILIBRIUM CONSTANTS FROM SPECTROPHOTOMETRIC DATA

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The halogens exhibit concentration-dependent absorption bands in the UV that were long ago attributed to the formation of dimers. Although the spectral profiles of these bands have been moderately well characterized, the equilibrium constants K_c for their formation have mostly remained ill-defined. In particular, spectrophotometric data have been dismissed as inherently incapable of providing estimates of K_c. Here this presumption is shown to be incorrect in the cases of Br_2(g) dimer absorption near 205 nm and I_2(soln) absorption near 300 nm. The analysis is enabled by precise spectrophotometric data for 20 concentrations, analyzed via a multiwavelength global approach. The Br_2 dimerization constant is found to be K_c = 2.5(3) L/mol at 22C, giving less than 2 percent dimerization at the maximum studied pressure (119 Torr). The K_c value is more than a factor of 2 larger than a previous estimate from analysis of PVT data – an approach that can be shown to yield at best a lower limit.