Spectroscopy and Gibbs Energy of Bimolecular Complexes

Henrik G. Kjaergaard

Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark.

In atmospheric research, the formation of complexes affects among other radiative transfer, reaction mechanisms and nucleation. The formation of a molecular complex relies on the Gibbs energy of formation, ΔG, which is difficult to obtain accurately, from pure experimental or theoretical methods. We have developed a combined experimental and theoretical approach with which ΔG of bimolecular complex formation can be determined with an accuracy better than 1 kJ/mol.[1] This requires accurate calculation of the oscillator strengths of vibrational transitions associated the observable vibrational bands.

We have developed a reduced dimensionality vibrational model within the local mode framework, which can be combined with \textit{ab initio} methods to calculated oscillator strengths. In bimolecular complexes, it is important to consider the effect of the six intermolecular modes. For hydrated complexes (H$_2$O-X), our model includes the three intramolecular high frequency modes of the water molecule (OH-stretch & HOH bend) as well as selected low frequency intermolecular modes. For the water-trimethyl amine complex, we use this approach for several observed vibrational transitions (see figure) to improve the ΔG determination.[2] We are currently extending our approach to the weaker bound water-dimethyl ether complex. The OH-O hydrogen bond of this complex is similar to that in water dimer (H$_2$O-H$_2$O), which is a key compound to the radiative transfer in our atmosphere. We continue our efforts to improve the calculation of water dimer spectra,[3] and have found that frequencies of OH stretching transitions can be well described from reduced dimensional models.

References: