

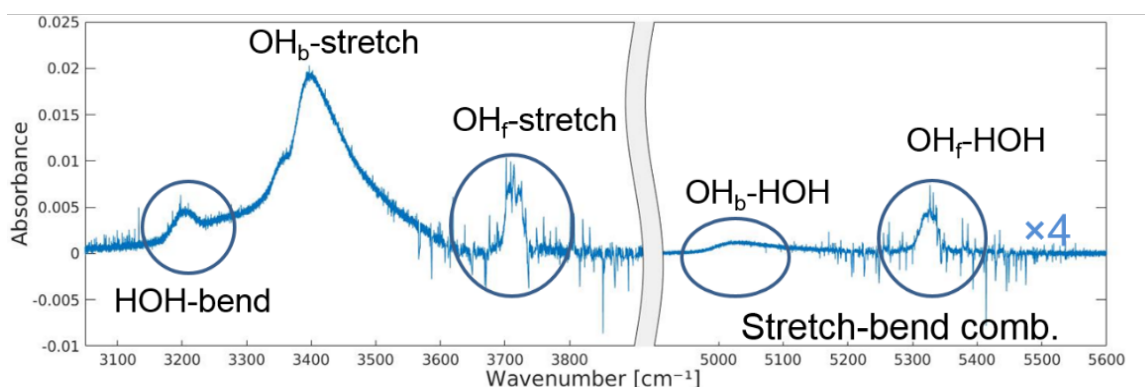
# Spectroscopy and Gibbs Energy of Bimolecular Complexes

Henrik G. Kjaergaard<sup>1</sup>

<sup>1</sup>*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,  $\Delta G$ , which is difficult to obtain accurately, from pure experimental or theoretical methods. We have developed a combined experimental and theoretical approach with which  $\Delta G$  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 *ab initio* methods to calculate oscillator strengths. In bimolecular complexes, it is important to consider the effect of the six intermolecular modes. For hydrated complexes ( $H_2O-X$ ), 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  $\Delta G$  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 ( $H_2O-H_2O$ ), 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.



*Gas phase spectrum of the water-trimethyl amine complex.[2]*

## References:

- [1] A.S. Hansen, E. Vogt, H.G. Kjaergaard, *Int. Rev. Phys. Chem.* **38**, 115 (2019).
- [2] A. Kjaergaard, E. Vogt, A.S. Hansen, H.G. Kjaergaard, *J. Phys. Chem. A.* **124**, 7113 (2020).
- [3] E. Vogt, H.G. Kjaergaard, *Annu. Rev. Phys. Chem.* **73**, (2022).