

Project Description:

Local Mode Van Vleck Perturbation Theory

This project aims to improve the theoretical modeling of vibrations in hydrogen-bonded bimolecular complexes. Hydrogen-bonded bimolecular complexes are believed to be precursors to secondary aerosols i.e. aerosols that are formed in the atmosphere through nucleation processes. Secondary aerosols play a central role in current climate models, but are associated with the largest uncertainty. Therefore, one goal in our group (the Kjaergaard group) is to determine the thermodynamic stability of atmospheric complexes, to help limit these uncertainties. Nevertheless, experimental determination of the thermodynamic stability of bimolecular complexes is not trivial as the pressure of each species involved in the equilibrium (monomers and complex) needs to be determined accurately, yet often span several orders of magnitude.

A combination of vibrational spectroscopy and theory is an alternative approach to address the task of accurate pressure determination of both monomers and the complex. With this approach, the pressure of the monomers are determined directly in the experiment, but the pressure of the complex is determined by associating the intensity of a measured vibration, unique to the complex, and the corresponding calculated intensity. A trademark of hydrogen-bonded bimolecular complexes is that the fundamental transition of the bonded XH-stretching (XH_b-stretching) vibration red-shifts and gains intensity relative to that of the XH-stretching fundamental transition in the monomer. Therefore, the intensity of the fundamental XH_b-stretching transition is experimentally accessible, even for low complex pressures, and the accuracy of this alternative approach relies on the calculated intensity.

The intensity of a XH_b-stretching transition is challenging to calculate, partly due to strong perturbations from the low frequency vibrations that arise upon complex formation (intermolecular vibrations). One approach is to use second-order vibrational perturbation theory (VPT2), a full 3N-6 dimensional model, where all vibrations are coupled. VPT2 is however only computationally feasible for small complexes and therefore not applicable for many atmospheric relevant complexes. Kasper Mackeprang, a former PhD student in our group, developed the Local Mode Perturbation Theory (LMPT) model to address these challenges. In LMPT, only specific local vibrations are considered, and only relevant couplings are included in the perturbation treatment. Although this model has proven to be accurate for a range of hydrogen-bonded bimolecular complexes, slow convergence of the perturbation series limits the reliability for XH_b-stretching overtone transitions. Furthermore, the model assumes a localized description of the intermolecular vibrations and the significance of this approximation is often unclear. As a part of my Master's project I seek to develop an alternative approach, Local Mode Van Vleck Perturbation Theory (LMVVPT), in order to address both of these issues. The hope is that a non-local description of the intermolecular modes may improve the accuracy of the calculated intensities, and therefore the accuracy of the determined thermodynamic stability of bimolecular complexes. Furthermore, the LMVVPT approach may result in better convergence of the perturbation series and therefore a more accurate description of overtone transitions.

To start up this project I plan to visit professor Lauri Halonen and his group at the University of Helsinki, Finland, from the 2nd to the 11'th of May. Professor Lauri Halonen has previously contributed to developing the LMPT model and his group specializes in molecular spectroscopy and theoretical chemistry, and other research areas closely related to the subject of this project. I seek financial support to help cover my expenses.

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