

SHORT TERM SCIENTIFIC MISSION (STSM) – SCIENTIFIC REPORT

The STSM applicant submits this report for approval to the STSM coordinator

Action number: CM1405

STSM title: Van Vleck Perturbation Theory

STSM start and end date: 02/05/2018 to 11/05/2018

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PURPOSE OF THE STSM/

Hydrogen-bonded bimolecular complexes play an important role in atmospheric reactions, radiative transfer processes and nucleation. Furthermore, these complexes are believed to be precursors to secondary aerosols. Aerosols play a central role in current climate models but are associated with large uncertainties. In our group we are interested in calculating thermodynamic properties of hydrogen-bonded bimolecular complexes, to help limit these uncertainties. A pure experimental approach is challenging because the pressure of the donor unit, the acceptor unit and the complex must be determined accurately, but often span several orders of magnitude. We therefore apply a combined experimental and theoretical approach which require precise modelling of selected vibrations unique to the complex.

The purpose of this STSM was to develop a local mode van Vleck perturbation theory model (LMVPT) to improve calculations of vibrational frequencies for water dimethylamine and water trimethylamine. The project is a response to challenges recently encountered when using the model we usually apply to calculate vibrational properties of hydrogen-bonded bimolecular complexes, the local mode perturbation theory model (LMPT). For water dimethylamine and water trimethylamine, the challenge is that the first HOH-bending overtone couples to the bound OH-stretching fundamental transition, which affect transition frequencies and intensities for these transitions. In the LMPT model, this coupling becomes artificially large because the intramolecular vibrations, the vibrations of the water donor unit, are coupled prior to coupling to the intermolecular modes (the modes that arise upon complex formation).

Professor Lauri Halonen and his group have experience in the interaction between small and large amplitude motion and helped with developing the LMPT model. We therefore believed that the group of professor Lauri Halonen could help us develop the LMVPT model.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

The work carried out during the STSM can be divided into three main categories.

1. Understanding the formulation of van Vleck perturbation theory
2. Deriving the necessary equations
3. Writing a Matlab code to calculate transition frequencies

1) The first part of the project involved becoming familiar with the formulation of van Vleck perturbation theory. Although van Vleck perturbation theory has been applied for various purposes, there is not much literature on the general theory. Lauri Halonen helped me connect van Vleck perturbation theory and point contact transformations. Point contact transformations is a much more common tool in theoretical spectroscopy, and by reading and discussing selected articles, we were able to identify the limitations of van Vleck perturbation theory. One of these limitations involved convergence criteria for the perturbation series generated in van Vleck perturbation theory (related to the size of matrix elements in the transformation matrices). We found that by avoiding combination states between inter- and intramolecular modes, convergence of the perturbation series could be ensured, at least theoretically. The idea is to then reintroduce these combination states, again using van Vleck transformations.

2) Deriving the necessary equations was probably the most time consuming part of the STSM. The greatest challenge encountered arose when trying to generalize the van Vleck transformation to any order. In the literature, the transformation is often written to second (or third) perturbation order in a simple manner. Proceeding to higher order, using the same mathematical course of action, turned out to be non-trivial. Nevertheless, we did eventually generalize the transformation scheme by changing the starting point for the transformation. This meant that the first transformations were slightly less intuitive (probably the reason we did not encounter this approach in the literature), but generalizing the transformation to any order became much easier.

3) Obtaining results by writing a Matlab code was the final goal. Because LMPT and LMVPT uses the same potential energy surfaces, coupling constants and coordinates, much of the code written for LMPT could be directly transferred to the LMVPT code. This meant that the duration of the STSM was just sufficient to obtain transition frequencies with the LMVPT model.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

As we are currently working on reintroducing combination states between intra- and intermolecular modes, we regard the calculated transition frequencies as preliminary results. The table below shows the transition frequencies obtained with the LM, LMPT and LMVPT model, as well as the corresponding experimental values. The experimental values are obtained with Fourier transform infrared spectroscopy and has not been published yet. The transitions of interest are denoted by their final intramolecular (local mode) state.

Table 1: Calculated and experimental transition frequencies (in cm^{-1}) for selected intramolecular transition of the water donor unit in the water dimethylamine complex.

HOH·DMA			
VV-order	$ 0\rangle_f 0\rangle_b 2\rangle_\theta$	$ 0\rangle_f 1\rangle_b 0\rangle_\theta$	$ 1\rangle_f 0\rangle_b 0\rangle_\theta$
LMVVPT ^a			
0	3323	3291	3731
1	3209	3377	3715
2	3215	3386	3721
3	3214	3385	3719
4	3214	3386	3720
⋮	⋮	⋮	⋮
10	3214	3386	3720
LM ^a			
-	3211	3302	3715
LMPT ^a			
-	3219	3337	3714
Experimental			
-	3204	3399	3714

a) Calculated at the CCSD(T)-F12a/VDZ-F12 level of theory.

Table 2: Calculated and experimental transition frequencies (in cm^{-1}) for selected intramolecular transition of the water donor unit in the water trimethylamine complex.

HOH·TMA			
VV-order	$ 0\rangle_f 0\rangle_b 2\rangle_\theta$	$ 0\rangle_f 1\rangle_b 0\rangle_\theta$	$ 1\rangle_f 0\rangle_b 0\rangle_\theta$
LMVVPT ^a			
0	3324	3252	3731
1	3206	3351	3715
2	3213	3361	3721
3	3211	3359	3720
4	3212	3360	3720
⋮	⋮	⋮	⋮
10	3212	3360	3720
LM ^a			
-	3193	3283	3715
LMPT ^a			
-	3222	3297	3713
Experimental			
-	3199	3375	3715

a) Calculated at the CCSD(T)-F12a/VDZ-F12 level of theory.

Where f, b, theta stands for the free OH-stretch, the bound OH-stretch and the HOH-bend, respectively. As seen from the tables, the LMVPT model significantly improves the transition frequency of the bonded OH-stretching fundamental transition, relative to the LM and LMPT model. Furthermore, the free OH-

stretching fundamental transition and the first HOH-bending overtone are still in decent agreement with the corresponding experimental value. We believe that these preliminary results strongly indicate that the LMVPT model circumvents the problem encountered in the LMPT model.

FUTURE COLLABORATIONS (if applicable)

As stated earlier, we are currently working on reintroducing the combination states between intra- and intermolecular modes. The final goal is to obtain both transition frequencies and transition intensities, and this project is therefore far from complete. I hope to extend the collaboration with Lauri Halonen and his group, not only with this project, but also regarding future research.