SHORT TERM SCIENTIFIC MISSION (STSM)
SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CM1405 - Molecules in motion (MOLIM)
STSM title: Theory and implementation of rovibrational Raman intensities
STSM start and end date: 11/11/2018 to 20/11/2018
Grantee name: Sebastian Erfort

PURPOSE OF THE STSM:

The STSM took place at the UCL in London, in the group of Dr. Sergey Yurchenko. The topic concerned the theory and implementation of rovibrational Raman intensities which is part of my PhD. To our knowledge there are no published implementations of this. The aim was to develop a theoretical basis, setting up working equations and making first steps towards an implementation. In our group we are working within the MOLPRO system of programs while Dr. Yurchenko is working mostly within the TROVE program. His extensive experience with rovibrational spectra and the fact that my supervisor, Prof. Guntram Rauhut, has known him for years made him the perfect colleague for a collaboration.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

During my stay in London we started by having a look at a problem within our implementation of rovibrational infrared intensities. This is the first major topic of my PhD and the base for rovibrational Raman intensities which were the motivation for this STSM. We encountered symmetry forbidden transitions in selected parts of the spectrum, likely due to an error in the equations or a bug in the code. Although we were not able to pin it down exactly, Dr. Yurchenko nonetheless gave me excellent ideas on how to trace this problem systematically.

We then went on to have a look at a different basis set for the rotational part of the wavefunctions, namely so-called Wang functions. Shortly before the STSM I started working with these because of the prospect of eliminating the aforementioned problem and due to several advantages. Most of all there is an enormous reduction of the size of the eigenvalue problem to be solved for rovibrational energies. Dr. Yurchenko made clear to me why it is imparative to use these for transition moments in intensities. He also explained to me a slightly modified version of these basis functions he uses,

$$|JKm\tau\rangle = \frac{i^{\sigma}}{\sqrt{2}}\left(|JKm\rangle + (-1)^{J+K+\tau}|J{-K}m\rangle\right)$$

which has additional benefits such as purely real matrix elements and a desirable behavior under symmetry operations. We went on to discuss how to avoid significantly more complicated expressions resulting from this basis by transforming back to the primitive rigid rotor basis $|J\,k\,m\rangle$ such that the crucial Wang combinations occur simply as a further expansion. With this we will be able to reuse the major part of the equations I derived and used so far while making use of the advantages of this more sophisticated approach. Dr. Yurchenko has given me notes such that I have a comparison for my derivations and can check for errors.

The topics we discussed up to this point are an important basis for the Raman intensities which were the main reason for this collaboration. This is due to the fact that the operator, for which matrix elements or integrals

have to be computed, has the same structure but is only of higher order comparing infrared to Raman intensities. This gives rise to additional terms, but the basic treatment is the same. Again we discussed how to set up equations that are in a form well suited for an implementation. That is, the final expressions contain the cartesian components α_{ab} of the polarizability tensor as well as rotational matrix elements in the primitive rigid rotor basis functions. The reason behind this is that the first are available within the MOLPRO system and the latter are more manageable and less error-prone. The expression for the line strengths then becomes

$$R_{\mathrm{if}}^{(\omega)} = \left| \sum_{ab} \sum_{\sigma=-\omega}^{\omega} \sum_{v''v'} d_{ab}^{(\sigma)} \langle v'' | \alpha_{ab} | v' \rangle \right.$$
$$\left. \times \sum_{K''K'} \sum_{\substack{\tau''\tau' \\ \bar{\tau}''\bar{\tau}'}} (-1)^{K'} \left(c_{vK\tau}^{v_i J_i r_i} \right)''^{*} \left(c_{vK\bar{\tau}}^{v_i J_i r_i} \right)' \left(t_{\tau\bar{\tau}}^{JK} \right)''^{*} \left(t_{\tau\bar{\tau}}^{JK} \right)' \left\langle J''(-1)^{\bar{\tau}''} K'' \middle| D^{(\sigma)*}_{(-1)^{\bar{\tau}''}K''(-1)^{\bar{\tau}'}K'} \middle| J'(-1)^{\bar{\tau}'} K' \right\rangle \right|^2$$

with transformation coefficients *d* and *t*, wavefunction coefficients *c* and *ω=0 (ω=2)* for the so-called (an-)isotropic part. The vibrational part involving the polarizability tensor is computed numerically while the rotational part can be solved analytically. Having obtained this form I started finishing the development of the working equations and will soon proceed by implementing them within our program code.

Beyond this Dr. Yurchenko helped me developing a basis on how to proceed from the VSCF method I mostly worked with so far to the VCI method. This will give more accurate results for rovibrational energies and is essential for spectra where features are not well separated.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

We are certain that we will now be able to trace down the reason for the occurrence of some forbidden transitions in the rovibrational infrared spectra.

Dr. Yurchenko helped me a lot in understanding the more sophisticated approach for the rotational basis functions and how to employ it effectively. With this I am close to finishing the working equations for rovibrational energies and infrared intensities with only a slight modification compared to our previous approach. We also discussed how to proceed from the VSCF method to the VCI method which is important for accurate results.

The previous steps are important for Raman intensities as the treatment is very similar to infrared intensities. Regarding this main reason for the STSM, we optimized the way of setting up the working equations. To this end the components of the polarizability tensor are represented in Cartesian components and the rotational transition moments are expressed in primitive rotational wave functions. Connection to the quantities used in the derivations can be achieved by simple transformations. Effectively these are merely further expansions in the overall transition moments.

FUTURE COLLABORATIONS (if applicable)

Dr. Yurchenko and one of his PhD students are currently preparing an application for a STSM to our group in Stuttgart scheduled for February. This will be on a different topic, but we look forward to this further collaboration.

In spring we will likely meet Dr. Yurchenko at the MOLIM general meeting in Bologna were we hope to have further fruitful discussions.