SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

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

Action number: CM1405
STSM title: Using deMonNano as a tool for the calculation of reaction rate constants and cross sections.
STSM start and end date: 21/10/2018 to 27/10/2018
Grantee name: Victoria Clark

PURPOSE OF THE STSM:

The purpose of this short term scientific mission (STSM) was to gain further understanding and insight into using deMonNano for the calculation of rate constants and cross sections for molecular reactions of interest to the plasma physics community. These reactions will be between two neutral molecules, and at conditions of 600-1000 K and 10-100mTorr. We hoped that a visit to Université Paul Sabatier to work with Dr Rapacioli, a developer of the deMonNano code, could help fix some of the problems we had encountered. The issues faced were a mix of user issues (we the user not knowing the best practices for when using deMonNano), and code limitations (the code had not been written to be used as we were using it, hence the results were variable).

DESCRIPTION OF WORK CARRIED OUT DURING THE STSM

A mixture of theoretical and computational work was carried out during this STSM. The theoretical work involved deriving new equations for the statistical calculation of rate constant and cross sections from many molecular dynamics (MD) event simulations; and consideration of the reliability of the experimental data. The computational work included rewriting deMonNano parameter files to allow for the description of halogen bonds and permit some halogen reactions to be able to be simulated with the code; changing

parameters in the input files to allow for periodic boundary conditions and hence specification of pressure conditions; and adding new key words to deMonNano to allow the molecules to thermally equilibrate before any collision simulations took place.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

The most unexpected acheivements were the integration of halogen parameters into deMonNano, and the coding for new key words which allowed for thermal equilibration of the molecules which were added into deMonNano. Before heading to Toulouse for the STSM, we had not even thought it possible to have either of these features, but the time spent with Dr Rapacioli at Université Paul Sabatier has been crucial to making both possible.

The halogens were incorporated by editing a parameter file which deMonNano reads for bonding information. The bond information for halogens were available for DFTB, however had not been incorporated into deMonNano owing to the lack of need until now. The thermal equilibration of the molecules was a larger edit to the Fortran code, and required several new key words to be added and coded for in order to specify the temperature desired, the amount of energy to give the molecules and the number of iterations to wait before giving the molecules a velocity and allowing the event simuations to begin.

In addition to the aforementioned results, we also learnt how to use the pressure command in deMonNano. Periodic boundary conditions (PBC) are required in order for the code to alter the pressure of the system to the value stated by the user. However, until now, we had been setting a pressure without implementing PBC. We learnt that this resulted in the pressure command not doing anything, and we were taught the correct procedure for turning PBC on in the deMonNano input file.

A critical theoretical result was the analysis of the equations we had previously used to calculate the cross-sections and rate constants from the statistical analysis of many MD simulations. Previously, we had been sampling the impact parameter as if it was a long thin line (a French fry), when the correct method to sample is by taking a more triangular shape (a pizza slice). This is shown below in Figure 1.

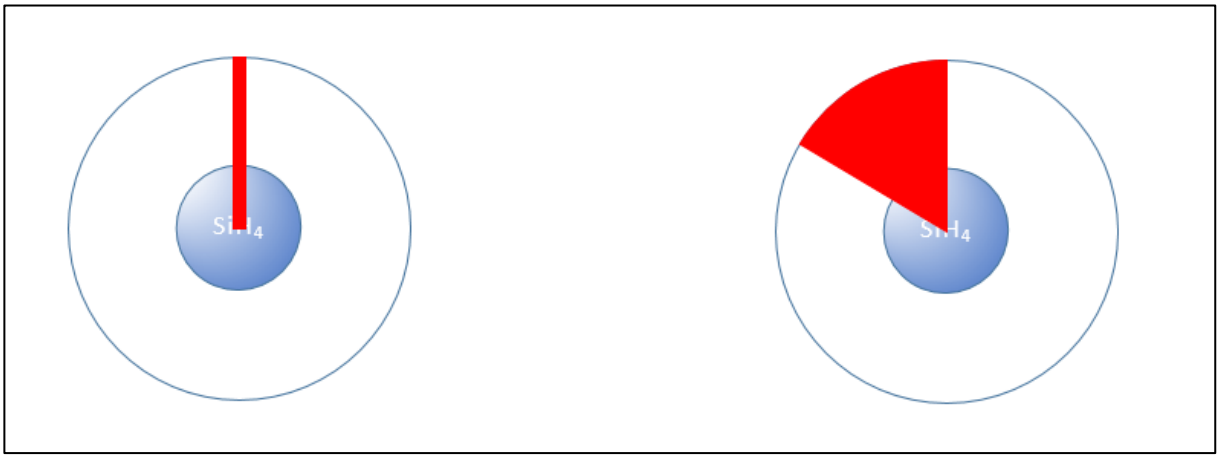

Figure 1: *Schematics illustrating the impact parameter we had previously been sampling, shown in red on the left, compared to the impact parameters we should be sampling, shown in red on the right.*

The reason for this is that the larger impact parameters, eg. 9-10 angstrom, have a larger area and therefore a larger probability than the smaller impact parameters, eg. 1-2 angstrom. Owing to this, the larger impact parameters needed a greater weighting in the statistical analysis, whereas previously we had been giving all impact parameters the same statistical probability.

Lunch times provided oppourtunity for many interesting conversations, and one of the topics discussed was the reliability and comparitability of the experimental data. We learnt that rate constants calculated experimentally can vary vastly depending whether they are calculated with cross-beam experiments, or in a large gas chamber. As we were unsure which technique our comparisons were being made against, we now know to go back and check which technique has been used in the literature we're comparing our results against.

FUTURE COLLABORATIONS (if applicable)

The overwhelming success of this week long STSM has resulted in many exciting future directions for our project, including calculations and simulations with halogen atoms; comparison of mathematical approaches fro statistical analysis of the MD results; comparison of computational methods; and investigation of pressure dependence on rate constant and cross section values obtained. We are keen to involve Dr Rapacioli and Université Paul Sabatier involved and up to date with all our new findings, and are eager to keep him involved in the publications we hope will come from this work.