SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

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

Action number: CM1404
STSM title: Studies of the kinetics and dynamics of the OH + HBr --> H_2O + Br and CH_3 + HBr --> CH_4 + Br reactions

STSM start and end date: 14/03/2019 to 20/03/2019
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PURPOSE OF THE STSM:

In the Budapest laboratory, theoretical reaction kinetics and dynamics studies are in progress on the OH + HBr --> H_2O + Br and CH_3 + HBr --> CH_4 + Br reactions, motivated by their relevance to the operation of fire extinguishers (the most efficient of which contain bromine).

The two title reactions have been studied by using the quasiclassical trajectory (QCT) method, which provides reliable rate coefficients in many cases, but cannot handle accurately some important quantum effects: the quantization of vibrational energy and tunneling. The Ring Polymer Molecular Dynamics (RPMD) method offers an efficient way to handle both kinds of quantum effects. Prof. Suleymanov of the host institute has developed an RPMD computer code, which has been installed and used in the Budapest laboratory.

The reactions studied are challenging for the RPMD method, because the reactants can form a weakly bound complex. Serious difficulties were encountered during the calculations. The purposes of the visit were 1) to learn how one can set the parameters of the calculations to avoid these difficulties; 2) get a deeper insight into the operation of the computer program; 3) summarize the existing results in a draft manuscript.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

1. During the STSM the parties overviewed the results obtained on the OH + HBr reaction in Budapest, and a deep analysis was performed. The rate coefficients obtained at high temperatures proved to be reliable, but at lower temperatures more accurate calculations will be needed. It turned out that reactions involving a poorly structured potential energy surface (a slightly attractive potential, a weakly bound complex and a submerged potential barrier simultaneously) cannot be handled with the parameters that proved to be applicable in other kinds of reaction and are routinely used in calculations involving less "soft" potential energy surfaces.

The actual calculations require substantial computation time, as long as several months. During the STSM several such calculations have been started and many new input files have been prepared. Preparations were made to perform calculations on the CH_3 + HBr -> CH_4 + Br reaction (compilation and testing of the code; preparation of input files)

Collecting the high-temperature rate coefficients on the OH + HBr reaction that proved to be reliable, and assuming that the lower-temperature rate coefficients will change in the expected manner, a draft for a joint paper has been prepared, keeping in mind that some parts of the paper may need to be subjected to major revisions depending on the final results of the calculations that are to be finished a few months from now.

2. The applicability of the direct RPMD method was discussed and the possible ways of coding were analyzed.
3. The possible ways of speeding up the calculations via code parallelization were explored.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

1.a. Determination of parameters necessary to get converged RPMD results.

Based on the analysis of the existing data, two kinds of parameters have been identified, setting of both requiring extreme care. One of them concerns the first step of the calculation, the determination of the potential of mean force along the reaction coordinate. The distance range covered in this step has to be set to multiple times larger than the routinely used value. The other parameter to be set very carefully concerns the second step of the RPMD calculation, the search of the so-called re-crossing trajectories. We found that the time period needed to get converged results is generally enormous as compared with the values used routinely. In addition, especially at lower temperatures much larger numbers of trajectories are needed to achieve convergence.

1.b. New calculations were started on the OH + HBr reaction.

1.c. The code and input files were prepared for calculations on the CH_3 + HBr reaction.

1.d. A draft manuscript has been prepared on the OH + HBr reaction.

2. The direct RPMD method

The conditions when this method can be advantageous have been analyzed. In this version the RPMD calculation is done similar to the quasiclassical trajectory methodology. Namely, the thermodynamical equilibration involved in the calculation of potentials of mean force would be performed once, to describe the thermal average states of the reactants only. The obtained ensembles of phase space points can be used as initial conditions of the internal states of the two reactants to be used in some classical-like trajectory calculations. The intermolecular initial conditions would be set in the way routinely done in quasiclassical trajectory calculations. The integration of the trajectories, however, would differ significantly from regular trajectory calculations, because they involve ring polymer dynamics, which is computationally much more intensive. By analyzing various scenarios, we found that the sketched method can be more efficient than the regular RMPD calculation when the potential energy surface involves an attractive potential between the reactants *such as the title reactions). An advantage of the direct RPMD method is that some dynamical information can also be extracted from the results. The preliminary version of such a code has already been used by the host, and another version will be developed and streamlined in Budapest.

3. Parallelization of RPMD calculations

The RPMD code is set up so that it is able to use all available processors of a computing node. The computational resources available in Budapest include a cluster of nodes equipped with 64 processor cores, but no fast cross-node parallelization is available. On such machines the calculations take several months. The current version of the RPMD code has been modified to make possible that batches of 64-core calculations be run simultaneously on different nodes, and the results merged, so that de facto several nodes can be involved in the parallelization, allowing the possibility of reducing the computation time by a factor of four.

FUTURE COLLABORATIONS (if applicable)

We plan to finish the calculations on the reaction of OH and HBr, and complete the paper whose draft has been put together.

On a longer term, we study together two reactions whose potential energy surfaces are characterized by a shallow van der Waals well and a submerged barrier: the reaction of methyl radicals with HBr, and that of OH radicals with HI. For the former, RPMD calculations are planned, and the results compared with the existing QCT results, while for the latter we develop a potential energy surface and perform both QCT and RPMD calculations.