Focal issues of the panel discussion on the GKIAC workshop

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The international workshop on Gas-phase Kinetics in Interstellar, Atmospheric and Combustion (GKIAC) was successfully held on Mar. 6-9, 2019 at the University of Science and Technology of China, Hefei. Many thanks to all participants, scientific and local committee members and student volunteers! In addition to many fascinating oral presentations, we also spent a whole afternoon to have a fruitful discussion chaired by Prof. Michael J. Pilling. Special appreciation should be given to Dr. Stephen Klippenstein for sharing many stimulating thoughts on the panel discussion through e-mail. We tried to list some focal issues from the discussion section. I hope that it will bring some inspiration to all participants and other scientists who might be interested in the discussion topics. I would also welcome any further comments on these issues.

1. *Demands and challenges in developing new experimental methods in the area of chemical kinetics, including those demands from potential users of the coming Hefei advanced light source.*

High resolution mass spectrometry with high sensitivity provides an excellent technique for the detection of reactive intermediates involved in the relevant reaction systems. A realistic detection limit of this technique is ~10 ppb and the technique is not appropriate for species with lower concentrations. Every technique has its inherent advantages and disadvantages. For example, mass spectrometry is not the ideal tool for detecting OH radical or O atom quantitatively; existing optical techniques are better. High resolution mass spectrometry, on the other hand, provides an excellent tool for detecting larger species and especially for distinguishing isomers. It is recommended that benchmark experiments are performed to validate the experimental technique.

Before performing precise measurements or developing new experimental tools, one must have a clear idea of the target – which reaction system is important, and which species are key to the study. If the research target is only to identify a species using those advanced experimental tools, it might not make much contribution to the community. For kinetic modellers, quantitative information on species concentrations is required and cross-sections of the detected species become the key to enable quantification. Thus acquiring the cross section data will need a substantial and concerted effort from the community. (*Nils Hansen, Katharina Kohse-Höinghaus, Xiaofeng Tang, Jiuzhong Yang, Zhandong Wang, Yuyang Li, Yiguang Ju, Guillaume Dayma*)

In terms of reactor design, uncertainties implicit in the jet-stirred reactor (JSR) were discussed. Sometimes the fuel concentration has to be increased to increase intermediate concentrations, which may lead to unrepresentative kinetics. Is it feasible to improve the design of JSR to assure that it provides a more “ideal” system? Wall reactions of some species such as H_2O_2 and HONO are also an issue for both experiments and for kinetic modeling. In addition to thinking hard about how to “improve” the reactor to avoid the wall effect, another angle might be addressed by kinetic modelers – how to compare the reactor studies with the real system which actually doesn’t have the wall effect? (*Yiguang Ju, Guillaume Dayma, Christa Fittschen, Zhandong Wang, Nils Hansen*)

2. *Challenges in measuring or calculating rate constants for elementary reactions*

The measurement of gas phase rate constants has a long history and is well developed. The measurement of surface reactions is less mature. The big challenge in measuring rate constants of surface reactions lies in the ambiguous and sometimes obscure representation of a surface reaction and the definition of the surface. (*Yiguang Ju, Christa Fittschen, Michael Pilling, Katharina Kohse-Höinghaus*)

3. *Re-analysing data in the literature as new understanding, data and modelling methods emerge*

In order to make it easy for researchers to re-analyse published experimental data, should we require authors to supply their raw data somewhere? The interpretation of experimental data to obtain rate constants often requires the use of literature data. If those data should change, then it is often difficult to reanalyze the experiments and generate revised rate constants without the raw experimental data. Researchers involved in atmospheric field measurements have done a quite successful job on the issue of data storage and documentation standards. However, raw experimental data for combustion diagnostics, and rate constant measurements are usually unavailable, which has been a limitation for the chemical kinetics community. There are some arguments on who should be responsible for this, where is the proper place for the data storage and how (i.e. format issues) to store these data. Concerns were also raised on the drawbacks of providing the raw data. Interpreting experimental data usually requires expertise, which is also a great challenge. The improper interpretation of raw data from those who are not experienced in the specific experimental technique might lead to confusing or even misleading results. It was acknowledged that experimental data need to be well documented either in the required supplementary materials or on other websites which are designed for data storage. (*Michael Pilling, Katharina Kohse-Höinghaus, Michael P. Burke, Nicole Labbe, Nils Hansen, Christa Fittschen*)

4. *Challenges in theoretical kinetic studies*

It seems that we have reached a situation where theoretically calculated rate constants can be as good as experimental measurements. Should we move beyond the basic rate parameters themselves? With the good calculations, we may be able to check the basic physics of a specific reaction or even a complex reaction network. It's strongly suggested that experimentalists, theoreticians and modellers should have closer and deeper interactions to figure out which reactions are important (and under what conditions) and what are the underlying origins of parameter uncertainties.

There were also arguments on how to improve the kinetic theories. In addition to putting lots of efforts into developing 2D master equation (ME) methods, one also need to look at the uncertainties in the use of 1D master equations. For example, the collisional energy transfer model is always an issue of RRKM/ME theory and we need to move towards a deeper understanding and agreed methods of parameterization. Error cancellation in RRKM/ME simulations is common but poorly understood and should be addressed. With a better understanding of uncertainty origins and error cancellation, one may not need to put as much effort into defining every single parameter to get good, reproducible rate constants.

In terms of the "automatic" rate constant calculations, there is a need to train graduate students with well-documented manuals with examples and background theory. It might also be encouraging if some training lessons either online or in person were available. (*Stephen J. Klippenstein, Michael J. Pilling, Michael P. Burke, Struan H. Robertson, Katharina Kohse-Höinghaus, Nicole Labbe, Feng Zhang, Carlo Cavallotti*)

5. *Multi-scale informatics*

It's widely acknowledged that the methodology of multi-scale informatics will be a useful tool to link theory, experiment and kinetic modeling. The standard of the data format could be a problem for users, but it should not be a limiting issue. The introduction of such concepts in a more efficient and systematic way to the whole community is encouraged, especially for graduate students, e.g. via summer schools. (*Michael P. Burke, Michael J. Pilling, Katharina Kohse-Höinghaus, Nicole Labbe, Carlo Cavallotti*))

6. *Experiment/theory design*

With newly developed methodologies, experiment/theory design has been acknowledged by the community. Which reactions are desired to be carefully studied? What conditions are ideal for accurate measurement of target parameters? It's expected that these important questions can already be addressed. It's suggested that one should clearly understand the scientific question, in order to "design" an ideal experiment. In addition to traditional combustion features such as flame speed or ignition delay time, there are also some other key features derived from experiments which can be used to constrain the uncertainty of combustion kinetic models. (*Bin Yang, Michael P. Burke, Nils Hansen*)

7. *Chemical kinetic databases/websites*

Not only experimental data and but also theoretical data will contribute to chemical kinetic databases. As for the calculated rate constants, it might be valuable to upload input files for specific codes used in the kinetic calculations. Besides focusing on how to build the database, e.g. the data format issues, everyone should ask why we need a chemical kinetic database. The motivation should go beyond simple data storage. The biggest advantage of a good chemical kinetic database is that it helps to digitize data in figures in the literature and makes them easy to be utilized by others. Another advantage could be that it can provide tools to convert experimental or theoretical data to any other format needed. There is also a concern on the reliability or accuracy of the data if someone uploads their raw data which are extracted from non-peer-reviewed materials. One should also be cautious on the copyright issues. (*Tamás Turányi, Alexander M. Mebel, Nils Hansen, Katharina Kohse-Höinghaus, Nicole Labbe, Michael J. Pilling, Michael P. Burke, Ruben Van de Vijver, Carlo Cavallotti*)

8. Working across environmental (combustion, atmospheric and interstellar) boundaries

As indicated by the title of this workshop (Gas-phase Kinetics in Interstellar, Atmospheric and Combustion Chemistry, GKIAC), scientists from these different areas were invited to encourage extensive interdisciplinary discussion. The chemistry of highly oxidized molecules (HOM) in the atmosphere is an example where understanding of low temperature oxidation chemistry in combustion has been transferred to atmospheric chemistry. Other developed methodologies of kinetic modeling in combustion may be valuable to some extent in atmospheric studies. Chemical kinetics of reactions involving van der Waals interactions is important in atmospheric and especially interstellar chemistry and is recognized as a big challenge for both experiment and theory. *(Michael J. Pilling, Katharina Kohse-Höinghaus, Stephen J. Klippenstein, Carlo Cavallotti*)