Theoretical determination of rate constants for the reaction of various positive ions with selected short chain neutral organic iodide molecules

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The ultimate aim of the proposed project is to determine a cost-effective method of theoretically predicting chemical ionization rate constants for the reaction of various positive chemical ionization (CI) reagent ions with selected short chain neutral organic iodide molecules. That is, the charge-transfer-reaction between the common CI reagents and selected neutral organic iodide (RI) molecules is studied to investigate if consistent environmental quantification of the gas phase RI is possible without prior calibration. The chosen positive ion CI reagents include molecular oxygen ions ($O_2{}^+$), hydronium ions (H_3O^+), hydronium ion complexes (proton hydrates) ($H_2O(H_3O^+)_{1-3}$), and nitrous oxide ions (NO^+). These CI reagent ions are readily employed in commercial field mass spectrometry instruments to detect gas-phase neutral molecules.[1] In this proposal, neutral RI molecules (RI = $CH_3I, CH_2I_2, CHI_3, C_2H_5I, \ldots$) were

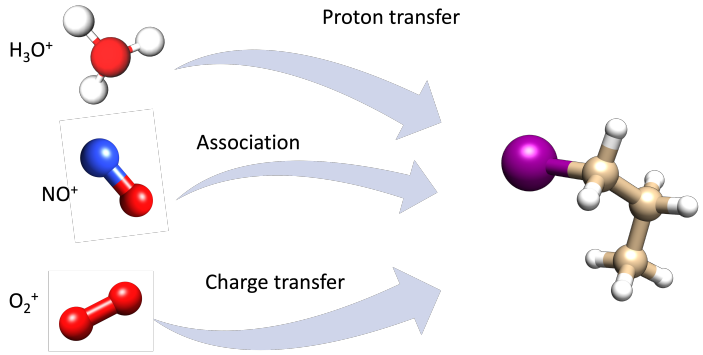

Figure 1: These chemical ionization reagent ions are often employed in commercial field mass spectrometry measurement of gas-phase trace molecules; here, C_3H_7I.

chosen because these compounds are of atmospheric and marine environment interest and of environmental importance in the field of nuclear power plant safety. As a result, the proposed project is of value to the academic community and of industrial/commercial interest.

The CI reagents are used within the drift-tube of a Chemical-Ionization-Reaction Mass Spectrometer (CIMS) to produce reagent ions. These protonated neutrals react with sampled gas-phase RI molecules by three mechanisms: dissociative proton transfer, non-dissociative proton transfer, and association.

The use of CI reagent ions allows for fast, sensitive, and specific detection of gas phase RI. The analytic success of CIMS instruments results from selectively and sensitively detecting many atmospheric neutrals. The key to the CIMS technique is finding readily generated primary CI ions that react rapidly with the agents and yield product ions with unique mass signatures.

[1]Examples include http://www.ptrms.com, http://www.syft.com, and http://www.transpectra.com.

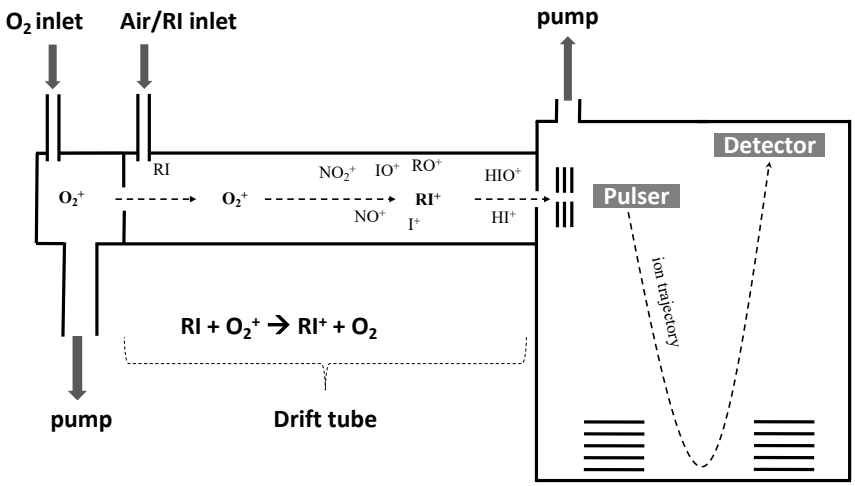

Figure 2: In this schematic representation of a chemical ionization mass spectrometer, molecular oxygen (O_2) is used as a chemical ionization reagent to detect gas-phase RI neutral molecules.

Little is known about the kinetics, mechanisms, thermochemistry, and various ion affinities of neutral RI compounds. As a result, the rate constants and product ion branching ratios will be calculated for a variety of positive CI reagent ions reacting with a selected RI molecule.[2] This series of calculations is designed to elucidate ion-molecule reactions that produce unique product ions to guide the development of CIMS detection methods for research and industrial applications. Comparison between the calculated collision rate constants and the experimentally determined rate constants will be assessed to understand chemical ionization kinetic processes better.

The majority of the internship will involve using quantum chemistry software such as Gaussian[3] and TopChem[4] to thoroughly examine the various reaction pathways of the CI + RI reaction, identify the most stable products, and characterize the nature of chemical bonds. These pathways will likely be studied using the Density Functional Theory (DFT) calculations. Once the reaction pathways are established, it will be possible to calculate the reaction rate constants for the identified elementary reactions and compare them with experimental measurements available in the literature.

Validation pour mise en ligne ECM :

[2]Badr R'Mili, Brice Temime-Roussel, Anne Monod, Henri Wortham, Rafal S. Strekowski, Quantification of the gas phase methyl iodide using O_2^+ as the reagent ion in the PTR-ToF-MS technique, International Journal of Mass Spectrometry, 431, 43-49, 2018. https://doi.org/10.1016/j.ijms.2018.06.003.

[3]https://gaussian.com/

[4]http://topchemweb.sorbonne-universite.fr/