

Modeling the Sensitivities and Intra-Instrument Kinetics of an Iodide-based Chemical Ionization Mass Spectrometer for a set of Organic and Inorganic Compounds

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Chemical ionization mass spectrometry (CIMS) using iodide-molecule adduct formation has become an important approach for quantifying carboxylic acids, HNO_x species, and halogen molecules in the atmosphere (Lee and Lopez-Hilfiker *et al.*, 2014). In this study, we model the University of Washington iodide-based CIMS (UW-CIMS) instrument by comparing the experimentally determined sensitivities of a number of organic and inorganic molecules to the quantum chemically calculated molecule-iodide complex binding enthalpies. The model is then used to predict the sensitivity of the instrument towards a set of isoprene and monoterpene oxidation products. We also perform a kinetic study of the effect of humidity in the instrument on sensitivity by including instrument specific attributes, such as ion-molecule reaction time, temperature, and pressure in Rice-Ramsperger-Kassel-Marcus (RRKM) calculations of three HNO_x molecules.

The molecules were built using the Spartan '14 program. All possible conformers from different combinations of torsional angles were generated and optimized to obtain minimum energy geometries. Molecular energies were calculated using the Gaussian 09 program with the PBE density functional and the SDD and aug-cc-pVTZ-PP basis sets. Coupled-cluster corrections were performed using the ORCA program with the def2-QZVPP basis set. Binding enthalpies of molecule-I⁻ clusters were calculated, and compared to the corresponding sensitivities of the UW-CIMS instrument.

The RRKM calculations were carried out using the Master Equation solver for Multi-Energy well Reactions (MESMER) software at instrument temperature/pressure.

Binding enthalpies calculated with relatively simple quantum chemical methods predict the sensitivity of molecules with an iodide-based CIMS instrument reasonably well. This indicates that quantum chemical data can be used to convert CIMS signals into order-of-magnitude estimates of the concentrations of neutral precursor species. This may be useful in future studies of e.g. Extremely low volatility organic compounds (ELVOCs). Lopez-Hilfiker *et al.* (2015) observed that the UW-CIMS detected at a maximum sensitivity (19-21 cps/pp) molecules with binding enthalpies to I⁻ close to that of malonic acid. Our quantum chemical study on three such maximum sensitivity molecules showed that there is indeed a threshold molecule-I⁻ binding enthalpy (~26 kcal/mol at the PBE/SDD level), above which the molecules are detected at maximum sensitivity by the

UW-CIMS instrument. In addition, we used our model to predict the UW-CIMS instrument sensitivities towards a set of isoprene and monoterpene oxidation products.

Preliminary kinetic modeling of the effect of humidity inside the instrument on the sensitivity using MESMER program (Glowacki, *et al.*, 2012) showed that water increased the formation rate of non-hydrated HNO_x-I⁻ clusters (x=2,3,4), which should, in principle, enhance the sensitivity of the instrument towards these molecules. This is in partial agreement with the experiments. A more detailed study that incorporates the effects of instrument voltages and guiding optics on the stability of the cluster is ongoing.

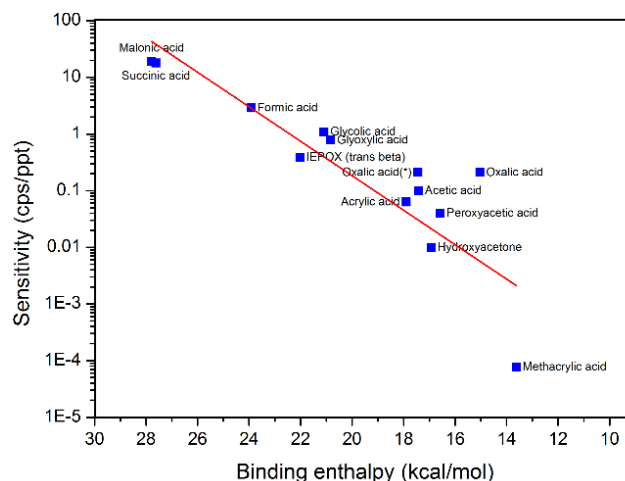


Figure 1. Comparison between the binding enthalpies calculated at the DLPNO-CCSD(T)/def2-QZVPP//PBE/aug-cc-pVTZ-PP level and the UW-CIMS sensitivities (Iyer *et al.* 2016).

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