Collision Cross Section Calculation and Differential Mobility Analysis-Mass Spectrometry (DMA-MS) of Po-210 and Electrospray Generated Ions

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In the free molecular regime, the collision cross section of charged particles and ions, Ω, can be related to electrical mobility, Z_p, via the relationship:

$$Z_p = \frac{3ze}{4\rho_{gas}\bar{c}\Omega} \quad (1)$$

where z is the integer charge on the particle/ion, e is the unit electron charge, ρ_{gas} is the background gas mass density, and $\bar{c}$ is the mean thermal speed of the particle/gas molecule reduced mass. The collision cross section in turn, can be calculated from polyatomic (all-atom) model structures for particles via gas molecule scattering simulations, and with proper calculation techniques, mobility measurements can be used to distinguish possible particle candidate structures from one another.

However, such gas molecule scattering simulations require an input model for the manner in which gas molecules scatter from a particle surface (both in terms of the scattering angle and reemission speed), when particles are modeled as fixed polyatomic structures. Here, we present new, efficient computational approaches for collision cross section calculation from polyatomic models, which can invoke any set of predefined gas molecule scattering rules. In the results presented, two specific scattering models are examined: (1) elastic hard sphere scattering (EHSS) which has been frequently invoked for comparison to collision cross section measurements made on ~1.0 nm ions in Helium background gas, and (2) diffuse hard sphere scattering (DHSS), which, when applied to a spherical particles, leads to results in excellent agreement with the free molecular limit of the semi-empirical Stokes-Millikan equation. With both scattering models, the influence of gas molecule polarization (the ion-induced dipole potential) is accounted for in calculations.

The described calculation procedures are applied to determine the collision cross sections of singly and doubly charged Sodium, Potassium, Rubidium, and Cesium Iodide cluster ions (positively charged). These ions are selected for examination because they have reasonably well-defined local-minima structures which can be determined via ab initio and density functional theory calculations. EHSS and DHSS predicted collision cross sections for these ions are compared to the measured collision cross sections in dry air for these ions, measured with a high resolution parallel-plate differential mobility analyzer coupled to a time of flight mass spectrometer (DMA-MS). Salt cluster ions are produced via electrospray ionization of salt solutions in methanol, and mass measurement subsequent to mobility analysis enables clear identification of the atomic composition and charge state of each examined cluster. Figure 1 plots the ratio of the DMA-MS measured collision cross sections to the calculated collision cross sections for these salt ions, as a function of the number of neutral ion pairs per cluster ion. In general, DHSS predictions are found in better agreement with measurements than are EHSS predictions, though the measurement agreement with DHSS predictions and disagreement with EHSS predictions both decrease with increasing cation mass in cluster ions.

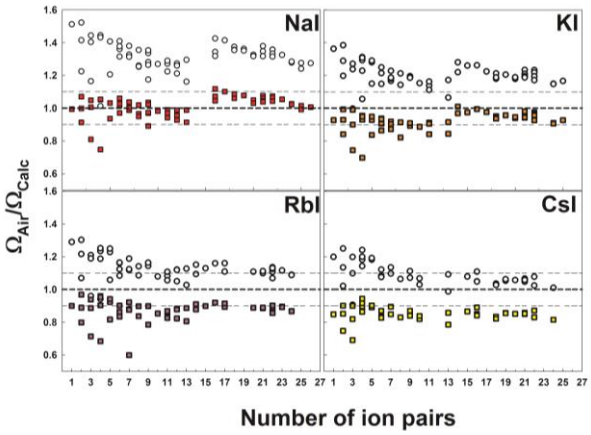

Figure 1. Comparison of measured (Ω_{air}) to calculated (Ω_{calc}) collision cross sections for positively charged salt cluster ions. Open symbols: EHSS calculations. Closed symbols: DHSS calculations.

DMA-MS measurements, density functional theory structure calculations, and collision cross section calculations are also performed on Po-210 generated positive and negative ions. Ions are generated in water-free "zero" air with clean metal tubing connecting the ion source to the DMA-MS (though the Po-210 is housed with plastic). Generally, Po-210 ions are found to be 50-300 Da organic ions, formed via protonation/deprototation or electron loss/gain. Similar to salt cluster ions. The predicted collision cross sections with DHSS calculations are found to be in better agreement with measurements for Po-210 ions. Overall, the presented work suggests that mobility-mass measurement in combination with structural modeling and collision cross section calculation from gas molecule scattering is a promising route to the examination of particles in the nanometer size range.