

Supplementary Material for

Ion Mobility Spectrometry: A Personal View of Its Development at UCSB

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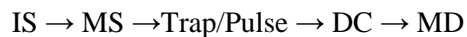
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THE ION MOBILITY METHOD

For those not familiar with ion mobility, a very brief functional synopsis is given here. A much fuller description can be found in many of the references cited in the main text. I will only consider drift cell based ion mobility as that is the form used in our group. There have been two different types. The original version was of the form:



where IS = ion source, MS = mass selection, DC = drift cell and MD = mass detection. A variety of ion sources have been used including electron impact, laser desorption/cluster formation, MALDI, and ESI. While in principle it can be useful to mass select the species before entering the drift cell, as shown in the transition metal ion and carbon cluster examples in the main text, at times this process can energize the ions and either lead to dissociation (of weakly bound clusters, for example) or isomerization (of solution structures being sampled by ESI). Hence for many applications it is actually preferable to gently pulse them into the drift cell, and mass analyze following the drift cell.

So how does ion mobility work? A short pulse of ions is injected into the drift cell where it encounters a weak electric field, E , that draws the ions through the cell. Collisions with the buffer gas (He, N₂, others) provide a frictional drag on the pulse of ions and very rapidly they obtain a constant velocity, v_D , proportional to the electric field:

$$v_D = KE.$$

The proportionality constant, K , is termed the ion mobility and is inversely proportional to the size of the ion. For convenience the “reduced” mobility, K_0 , is used because K is proportional to the temperature and inversely proportional to the pressure:

$$K_0 = K \frac{p}{p_0} \cdot \frac{T_0}{T}$$

where pressure and temperature are normalized to their standard states values, p_0 (760 Torr) and T_0 (273.15 K). The actual measurement made is an arrival time distribution (ATD) at the detector, where the pulse injection starts the clock and arrival at the detector stops it. Since the drift cell length, ℓ , is accurately known and since $E = V/\ell$, where V is the applied voltage, then it follows the arrival time is given by

$$t_A = \frac{\ell^2}{K_0} \frac{T_0}{p_0 T} \frac{p}{V} + t_0$$

and

$$t_A = t_D + t_0$$

where $t_D = \ell/v_D$ and t_0 is the time from the cell exit to the detector. In practice t_A is plotted versus p/V with K_0 obtained from the slope and t_0 from the intercept. In these measurements p is kept constant and V varied, which can be done extremely accurately. It is straightforward using kinetic theory to relate K_0 to the collision cross section of the ion of interest with the buffer gas.

In order to get structural information from the measured cross sections, model structures of the ion have to be determined and then cross sections determined from them. this process is briefly discussed near the end of the main text and won't be repeated here. In order to interpret the structures obtained, information about the source of the ions and its treatment until reaching the drift cell are required. Both factors are important. While the first is generally appreciated, the second is often unfortunately ignored. Both factors are points of emphasis in all measurements made in our group. Examples are given in the main text.

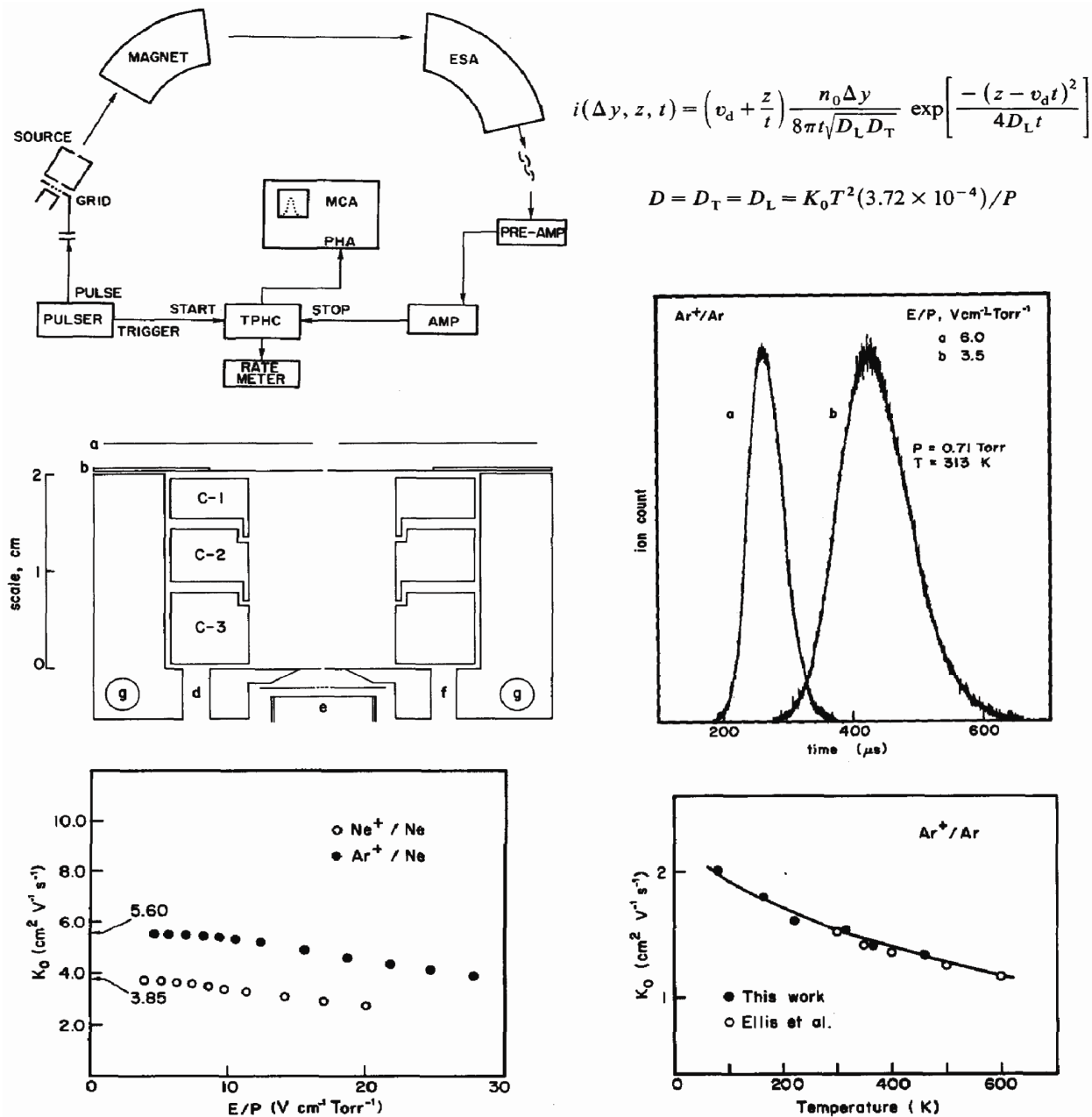


Figure S1. The top left panel gives an overall functional schematic of the experiment. The equations at top right give an expression for the time dependence of the signal arriving at the detector. The center left panel is a schematic of the ion source where the electron beam is coaxial with the ion exit hole. The center right panel shows two typical ATDs for different source voltages. The bottom panels give plots of K_0 vs. E/P and temperature for the systems noted. Figure adapted from: P.A.M. van Koppen, P.R. Kemper, A.J. Illies, M.T. Bowers, An Improved High-Pressure, Temperature-Variable Ion Source with Coaxial Electron Beam/Ion Exit Slit, *International Journal of Mass Spectrometry and Ion Processes*, 54 (1983) 263-282.

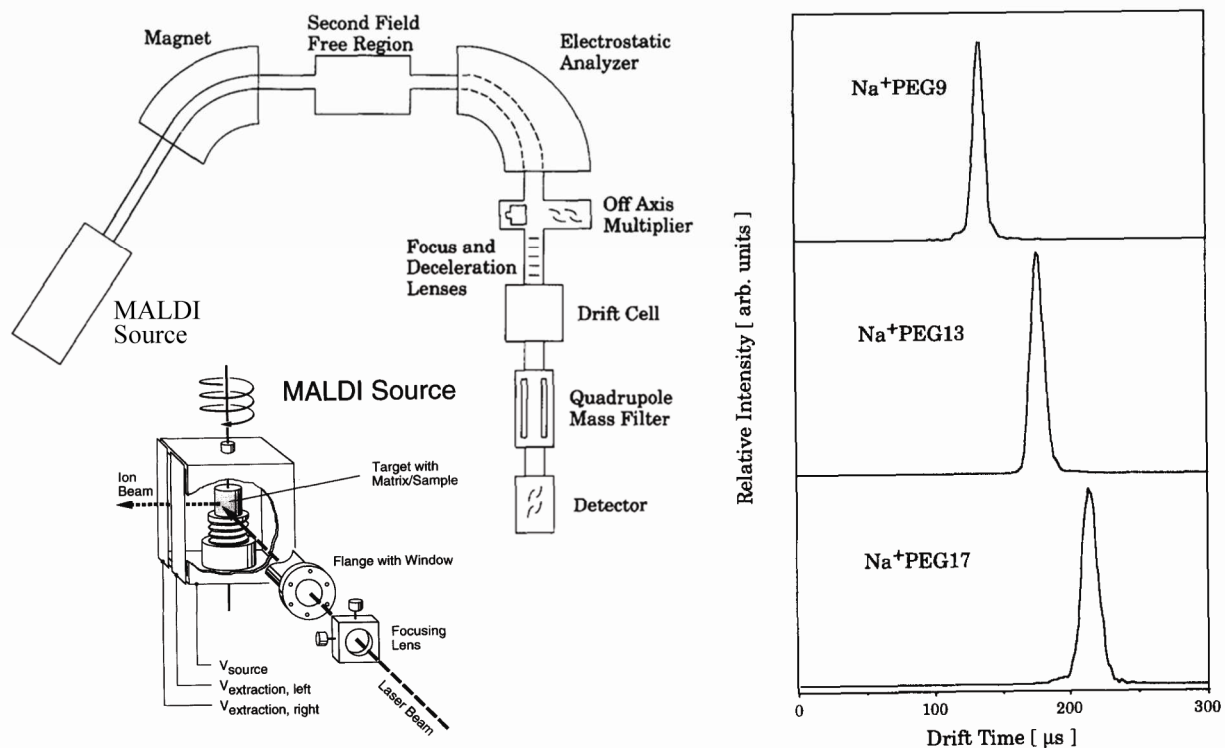


Figure S2. The top left panel gives a schematic of the instrument while the bottom left panel, a schematic of the MALDI source. By rotating and translating the center cylinder the source could produce signal for several hours as needed for IMS studies. The right panel gives ATDs for the systems noted. Figure adapted from: G. von Helden, T. Wytttenbach, M.T. Bowers, Inclusion of a MALDI Ion Source in the Ion Chromatography Technique: Conformational Information on Polymer and Biomolecular Ions, *International Journal of Mass Spectrometry and Ion Processes*, 146 (1995) 349-364.

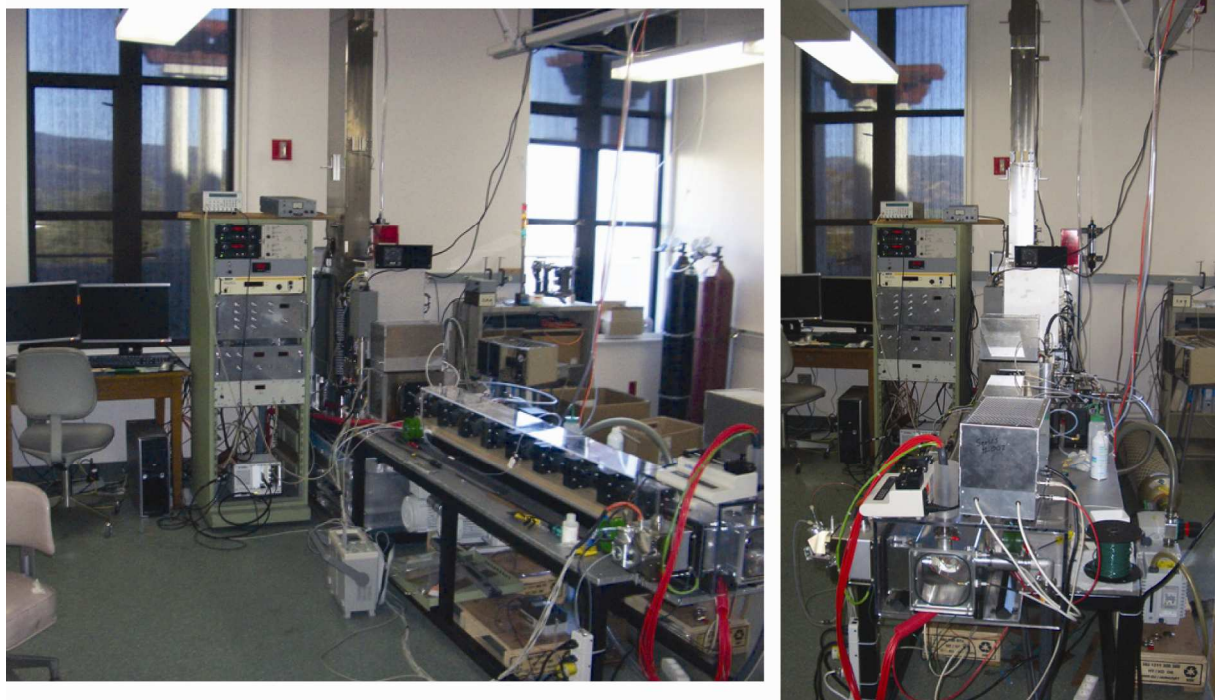


Figure S3. Photographs of a new high resolution IMS-MS system under development at UCSB. The two meter drift tube is made of resistive glass. The mass spectrometer is a high resolution maXis Q-TOF provided by Bruker Corp.