

## 2. PRELIMINARY RESULTS

As described in section 2.1 below, instrumentation to explore chemical orthogonality already exists and includes the valuable components of software and control electronics for a tandem DMS instrument. Additionally, other essentials including DMS/MS configurations exist with TOF MS and triple quadrupole MS instruments. Infra-structure for research in IMS and MS exists and systematic discovery of chemical orthogonality and refinement of drift tube technology can occur without delays.

### 2.1. Tandem DMS/DMS instrument

Our research group has been investigating the tandem ion mobility spectrometry resulting in an instrument with two sequential differential mobility spectrometry (DMS) drift tubes, with Faraday detectors.<sup>36</sup> Separate but coordinated electronic control for each drift tube allowed several modes of operation including: all ions passing; compensation voltage (CV) scanning; and ion selection over a narrow CV range. Any of these modes can be applied to each drift tube allowing multiple combinations of analytical measurements, analogous to tandem mass spectrometry, with ions entered into a gas atmosphere containing reagents between the mobility regions.

*Flows*- A central facet of the DMS/DMS experiment at ambient pressure is mixing of gas flows in region between two separation regions. Flow velocities, calculated using flow rates and analyzer dimensions, are 12.5 m/s for sample flow and 1 m/s for the dopant gas flow. Computational flow modeling (COMSOL Multiphysics) shows turbulence is not disrupting the mixing of ions and vapors (Fig. 3). Pressure values show even gradations in length and width once the mixing has occurred. The findings here suggest that intended ion motion or chemistry will not be complicated by excessive turbulence in the region of mixing and that DMS1 will be free from influx of reagents (or dopants). A rectangular or slit geometry should be explored in a future design

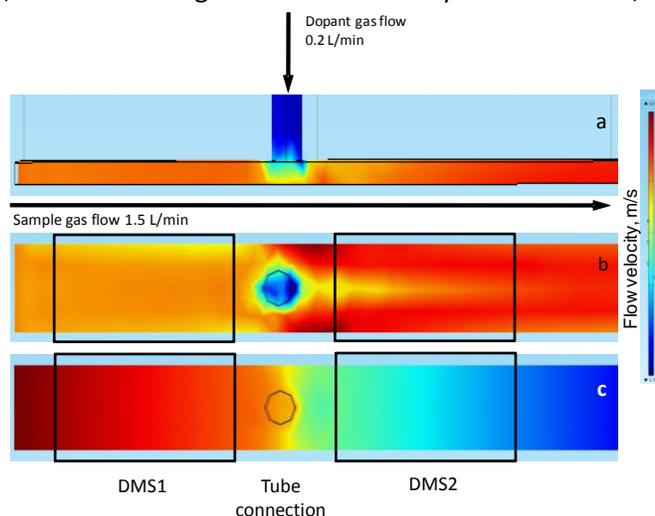


Figure 3. Heat maps from computational flow modeling of DMS/DMS instrument with a) flow velocity at side flow; b) flow velocity from top view, and c) pressure values from top view of analyzer.

*The tandem DMS experiment*- Results from DMS/DMS characterization of methyl salicylate in negative polarity are shown as a topographic plot (Fig. 4) of ion intensity,  $CV_{DMS1}$ , and  $CV_{DMS2}$ . The product ion for methyl salicylate,  $MO_2^-(H_2O)_n$ , is a single product ion peak at a  $CV_{DMS1}$  of -3.0 V and  $CV_{DMS2}$  of -3.0 V. Residual reactant ion peak intensity,  $O_2^-(H_2O)_n$ , is evident at  $CV_{DMS1}$  of -10.0 V and  $CV_{DMS2}$  of -10.0 V.

When isopropanol vapors were introduced at a level of 1% (v/v) between DMS1 and DMS2, the methyl salicylate peak is displaced to -3.0 V,  $CV_{DMS1}$  and -16.0V,  $CV_{DMS2}$ . A change in location on  $CV_{DMS2}$  is attributed to ion molecule reactions with isopropanol. *Ab initio* modeling (Spartan) has shown that Equation 1 with  $m=1$  is endothermic at 44 kJ/mol while at  $m=2$ ,  $\Delta H$  becomes -23kJ/mol. Since the concentration ratio for isopropanol methyl salicylate was  $\sim 10^6$ , it is very likely that  $m>1$  and thus reaction (Eq. 1) is exothermic.

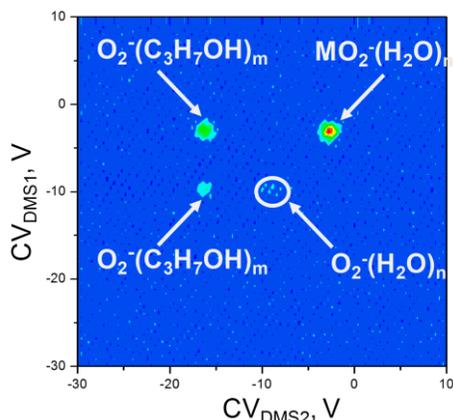
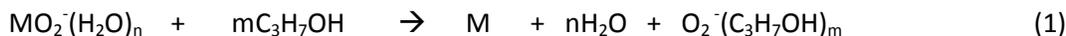
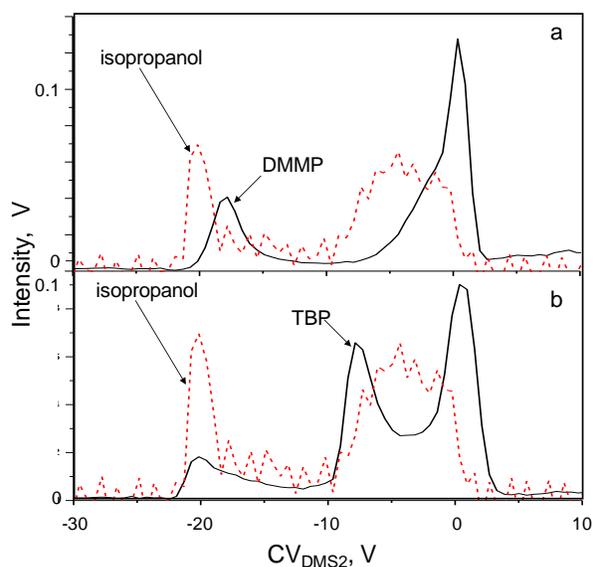


Figure 4. Topographic plot of ion intensity,  $CV_{DMS1}$ , and  $CV_{DMS2}$ , from DMS/DMS analysis of vapors of methyl salicylate with dopant gas of isopropanol introduced between the DMS analyzers. The transposition of ion charge for  $MO_2^-(H_2O)_n$  from -3V to -16V is the result of chemical orthogonality in the mobility measurement.



## 2.2. Ion reactions or formation of clusters in DMS with reagent gases

We reported the use of reagent gases to modify atmospheres in DMS in 2002 for separation of ion peaks of explosives<sup>33</sup> and this concept was extensively developed by Nazarov at Sionex Corp,<sup>35</sup> Yost at Univ. of Florida<sup>37</sup> and a DMS/MS team at AB Sciex Inc.<sup>34</sup> A reagent gas affects alpha functions in DMS and this was described as an increased  $\Delta K$  by increases in ion-neutral clustering when the core ion is “cooled” during the low field portion of the asymmetric waveform. We also clarified that moisture also alters compensation voltages through cluster formation.<sup>38</sup> In a tandem DMS, we demonstrated that an ion, which as a proton bound dimer appears near compensation voltage of 0V (Fig. 5) for dimethylmethyl



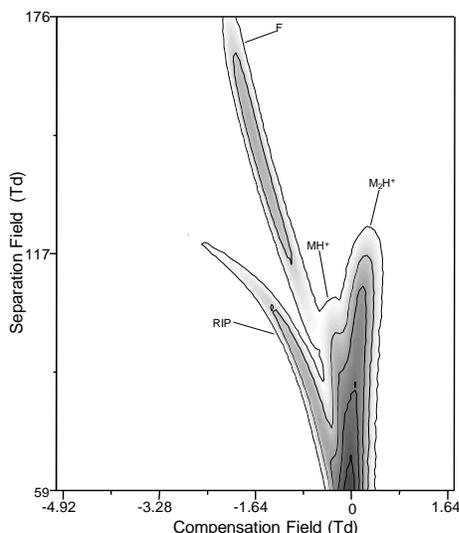
-phosphonate (DMMP) and tributylphosphate (TBP), can be transformed in the second DMS to a new and distinctive CV by adding isopropanol into the DMS/DMS. The product ion for DMMP was placed at -18V (shifted from 0V) and TBP at -8V (shifted from 0V). We have not confirmed the molecular basis of this change by mass analysis: either influence of modified alpha function or transformation of the ion. In either instance, this is another demonstration of chemical orthogonality in DMS/DMS

Figure 5. DMS/DMS study of proton bound dimers which appear at 0V in purified air atmosphere and which are shifted in DMS2 in an isopropanol atmosphere.

### 2.3. Dissociation and Fragmentation of ions at ambient pressure using strong electric fields

We have explored also the fragmentation of gas ions at ambient pressure using strong electric fields. Two fragmentation processes have been studied including:

- the fragmentation of alkyl esters to carboxylic acid ions,<sup>22</sup> and
- the dissociation of proton bound dimers of ketones to protonated monomers<sup>39</sup>

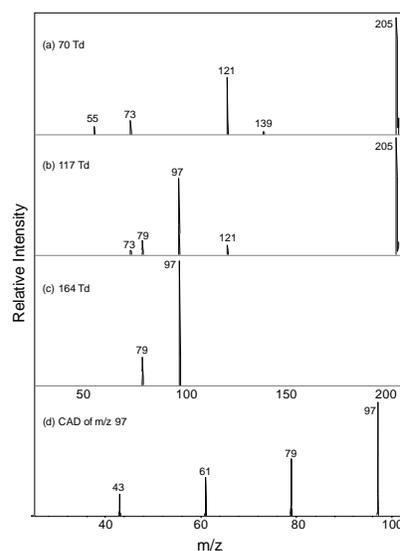


Fragmentation of ions occurs with ions in strong electric fields (30,000 V/cm) for short periods of 300 ns. At characteristic energies, the ions fragment proton bound dimers then to protonated monomer and finally to fragment ions. The plot of Fig. 6 is called a dispersion plot. The dimension of Td derives from field normalized to number density,  $E/N$ . In the separation volts scale, values of 50, 100, and 200 Td in a 0.5 mm gap correspond to ~570, 930, and 1660 V at ambient pressure.  $1 \text{ Td} = 10^{-21} \text{ V}\cdot\text{m}^2$ .

Figure 6. A dispersion plot (mobility spectra scans over a range of separation for propyl acetate at a DMS analyzer temperature of 100°C. The  $M_2H^+$  is  $(CH_3COOC_3H_7)_2H^+$ ,  $MH^+$  is  $(CH_3COOC_3H_7)H^+$ ;  $F^+$  is  $(CH_3COOH)H^+$ ; and RIP is  $(H_2O)_nH^+$ .

Studies in our laboratory are supported by mass identification of ions using DMS/MS and in our instance we have three versions of mass spectrometers: single quadrupole Shimadzu 2010 or 2020s analyzers; an API-III triple quadrupole instrument, and a Hexin time of flight MS, recently installed. Mass spectra from the fragmentation of an alkyl acetate, from DMS/MS measurements are shown in Fig. 7. Mass spectra in Fig. 7 illustrate how a ion ( $M_2H^+$ ) derived from a molecule (M) is, under the heating effect of applied RF electric field strength, dissociated to  $MH^+$  and then fragmented a carboxylic acid. This occurs in air at ambient pressure providing the electric field is strong, here 164 Td is roughly 30,000 V/cm and gas temperature was 120°C.

Figure 7. DMS/MS spectra for propyl acetate with separation fields of (a) 70 Td, (b) 117 Td and (c) 164 Td. The peaks are:  $m/z$  205,  $M_2H^+$ ;  $m/z$  103, 121 and 139,  $MH^+$ ,  $MH^+(H_2O)_1$  and  $MH^+(H_2O)_2$ ;  $m/z$  55 and 73,  $H^+(H_2O)_3$ ,  $H^+(H_2O)_4$ ;  $m/z$  61, 79, 97,  $CH_3CO_2H_2^+$ ,  $CH_3CO_2H_2^+(H_2O)_1$ ,  $CH_3CO_2H_2^+(H_2O)_2$ ;  $m/z$  43,  $CH_3CO^+$ . The CAD spectrum of hydrate of protonated acetic acid with  $m/z$  of 97 DMS analyzer temperature 100°C.



Summary: The individual components to introduce chemical orthogonality in mobility methods at ambient pressure suggest that ions can be manipulated chemically between DMS stages, both in ion clustering and ion fragmentation. Refined DMS/DMS drift tubes and an experimental framework for chemical orthogonality are needed to develop and assess the contributions to specificity of response and plausibility of DMS/DMS as a broad measurement concept.