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Temperature-dependent sensitivity of iodide chemical ionization mass spectrometers

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1 Ion molecule reactor cluster ratio closed loop control system

The NOAA I^- chemical ionization mass spectrometer (CIMS) utilizes a closed loop control system to achieve fixed cluster ratio ($I^-•H_2O:I^-$) (CR) in the ion molecule reactor (IMR) with varying sample gas humidity. This closed loop control system is comprised of a water bubbler, N_2 mass flow controller (MFC), saturated gas transfer line and computer control software. This system is outlined in supplemental figure 1. Real time signal measured at nominal mass 127 (I^-) and 145 ($I^-•H_2O$) is transferred from TofDAQ to the National Instruments Labview instrument control software. The apparent CR is determined at 0.2 Hz and compared to the user defined reference CR set point (typically 0.5), an error is determined and the saturated N_2 flow (0 – 100 sccm) MFC set point is adjusted accordingly. This system dynamically adjusts the amount of saturated N_2 flow delivered to the IMR as inlet sample gas humidity changes with altitude (on an aircraft) or time of day (at a ground site).

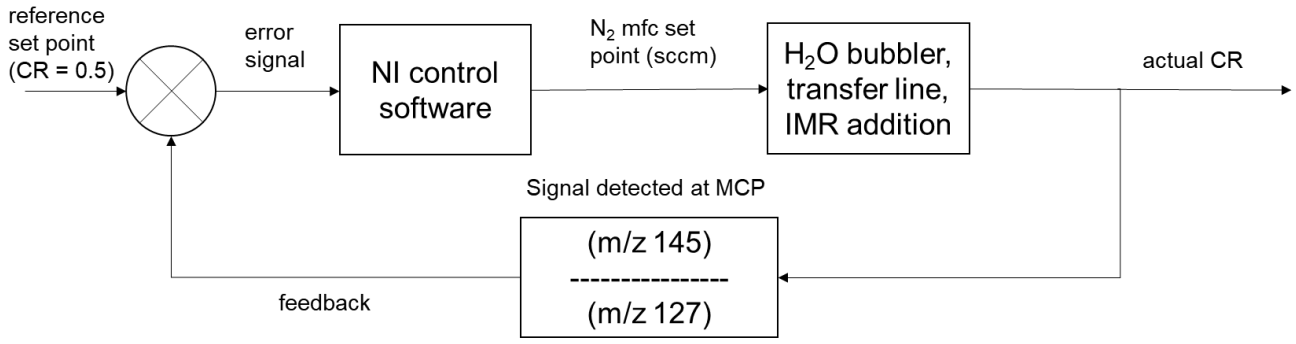
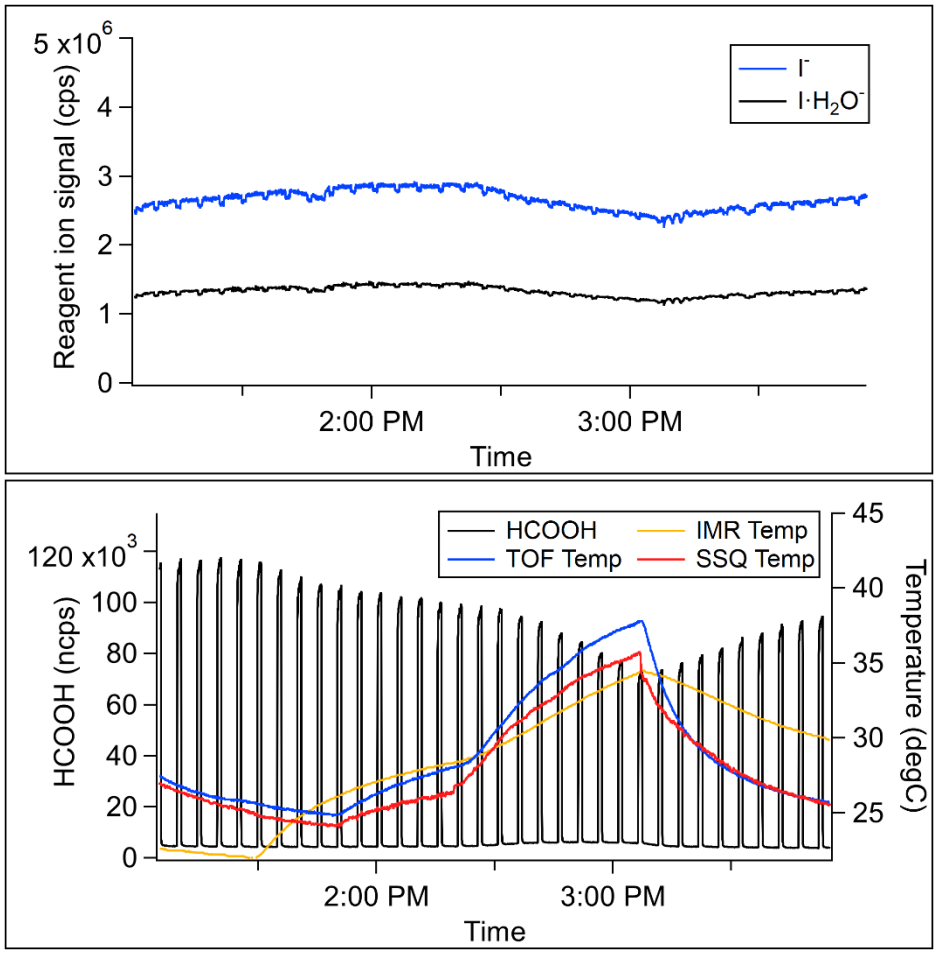


Figure S1: Block diagram of closed looped control of IMR cluster ratio.



15 **Figure S2: Typical time series for a ToF Body temperature experiment.**

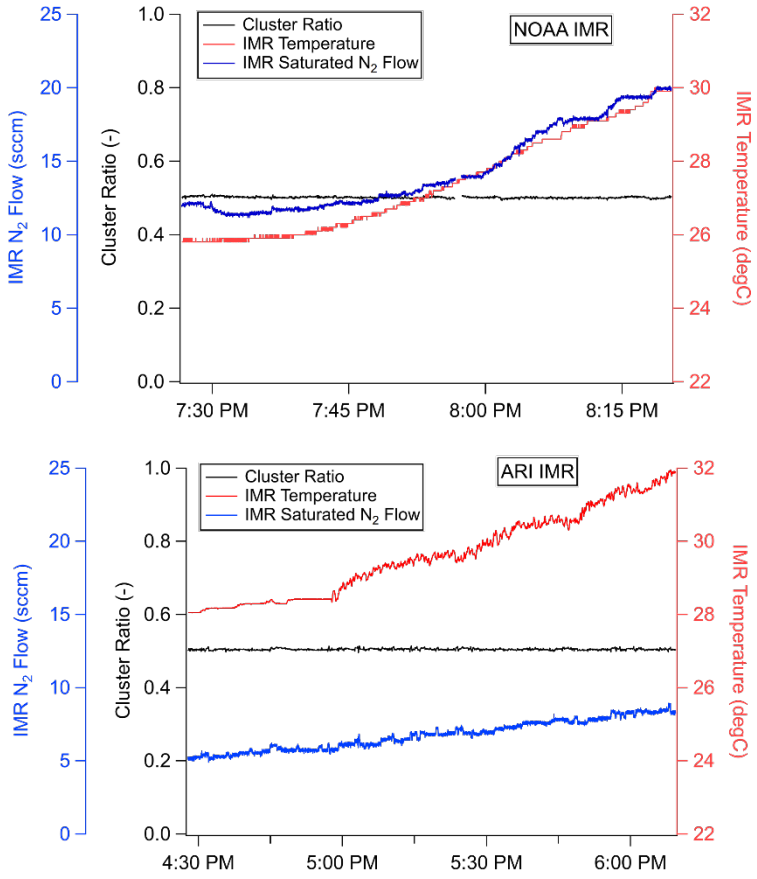


Figure S3: Comparison of NOAA IMR and ARI IMR during ToF body temperature experiments.

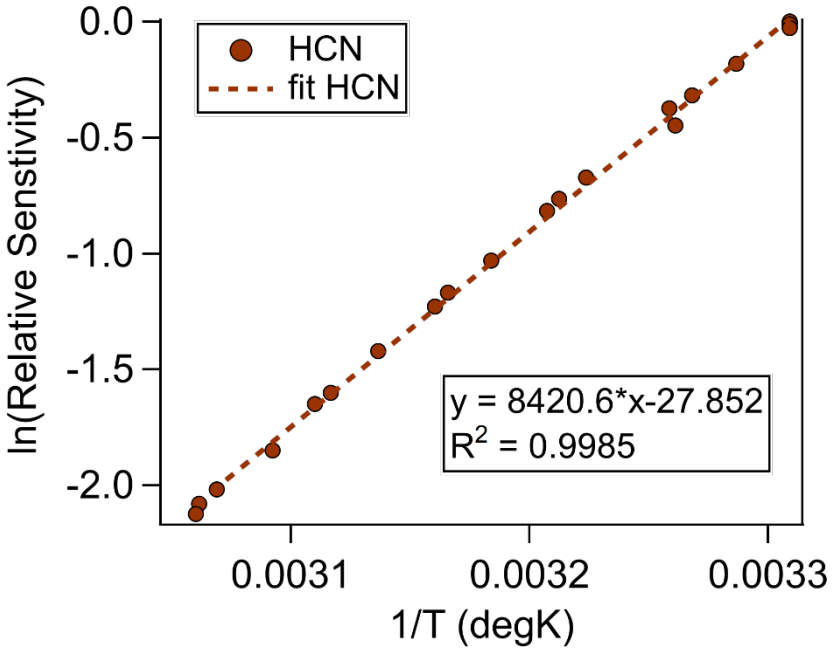


Figure S4: Example Van't Hoff relationship fit for HCN. The slope of this fit represents $-\frac{\Delta_r H^0}{RT}$ and is a measure of net reaction enthalpy under the conditions of the IMR.

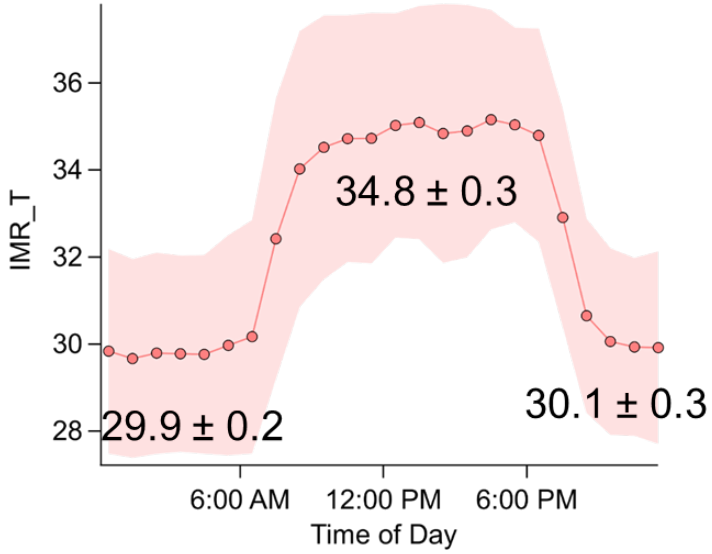


Figure S5: SUNVEx campaign IMR temperature average diurnal cycle, shading represents ± 1 standard deviation.

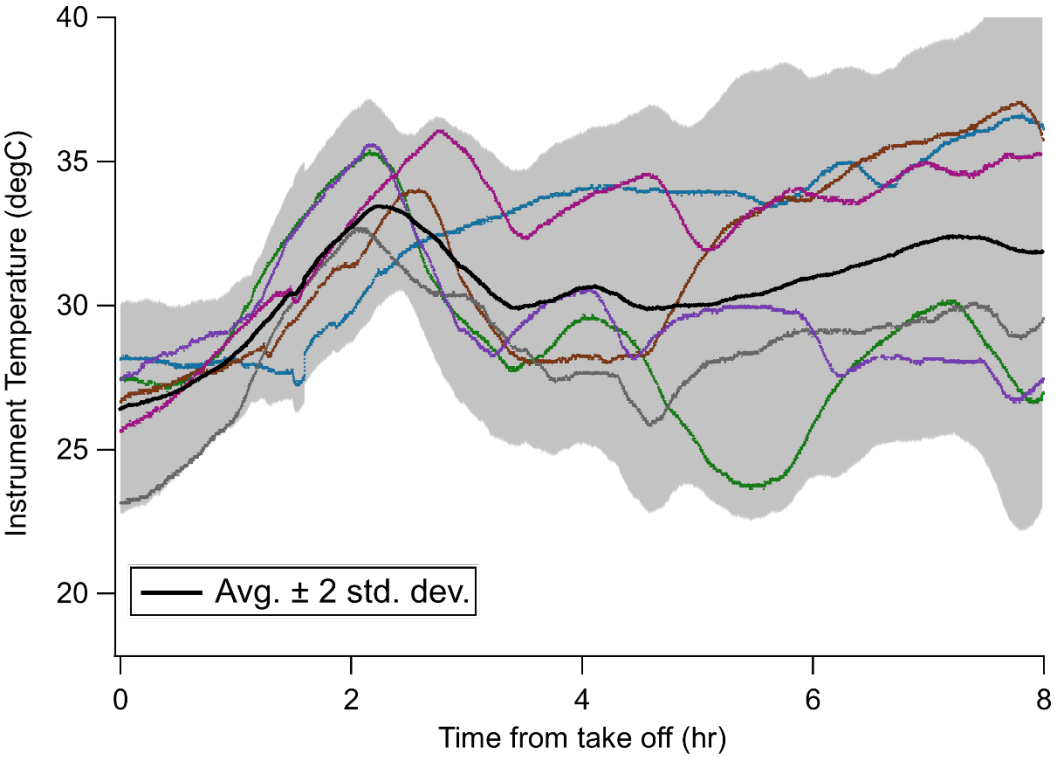


Figure S6: Example NOAA CIMS instrument temperature (ToF body temperature) from six research flights (color traces) during the FIREX-AQ research aircraft deployment in 2019. Black trace and shading represent the average ± 2 standard deviations.

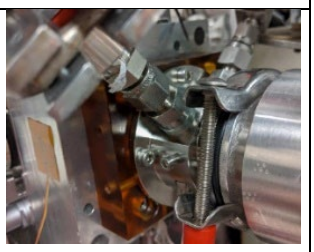
IMR Design	Materials	Temperature control range (°C)	Residence Time (40 mbar) (ms)	Volume (cm^3)	Image
ARI	Stainless Steel + PEEK (non-wetted)	30 – 50	46	47	
NOAA	Stainless Steel and Nylon	Ambient temperature	42	39	

Table S1: IMR designs investigated in this study.