

# Ion-molecule reaction rate coefficients studied in a multipole RF ion trap

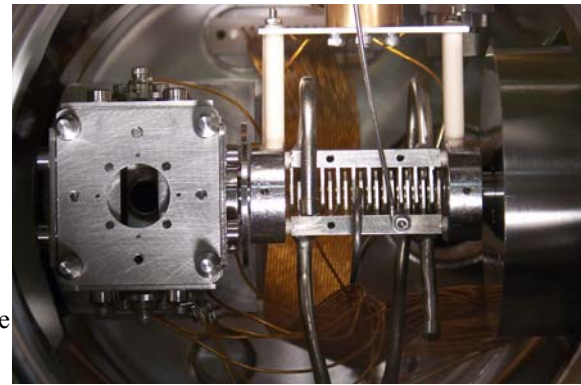
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## Multipole trap kinetics studies

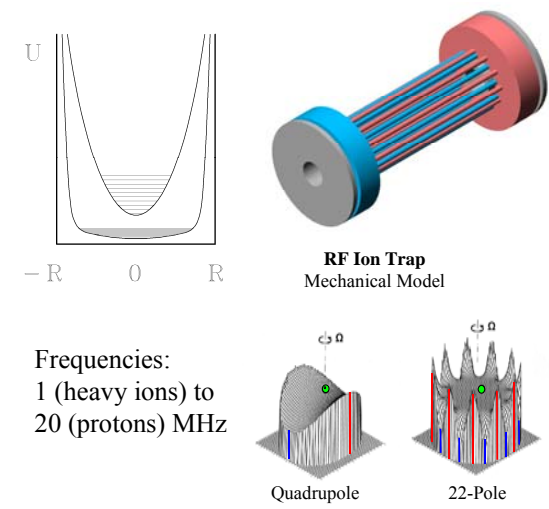
- Excellent temporal control, > 10+ seconds trapping times
- Large dynamic density regime,  $10^8 - 10^{14} \text{ cm}^{-3}$
- Versatile gas control - high pressure source, pulsed effusive and supersonic molecular beams
- Broad thermal window available (4-1000 K)
- Detection choices
  - Destructive MS
  - Chemical probing

## Methods: the basic trap kinetics experiment

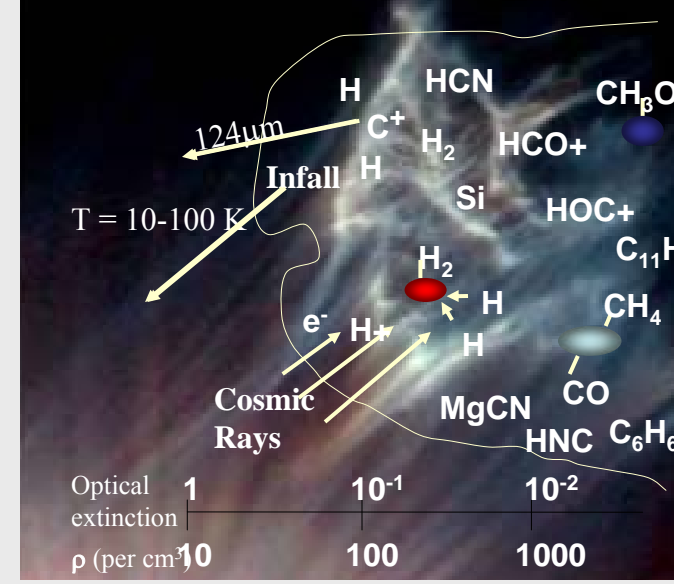


- Ion production
- Mass selection, trap loading
- He buffer cooling,  $\tau_{\text{cool}} \ll \tau_{\text{react}}$
- Expose to neutral species
  - Effusive neutral inlet
  - External neutral source
- Residence time 10 ms - 10 s
- Unload at different times after exposure
- Product/Reactant ion detection
  - Measure concentrations - measure  $k_f$
- Or add forward and reverse neutral species
  - Measure approach to equilibrium

## 22-pole RF ion trap



## Interstellar medium chemistry



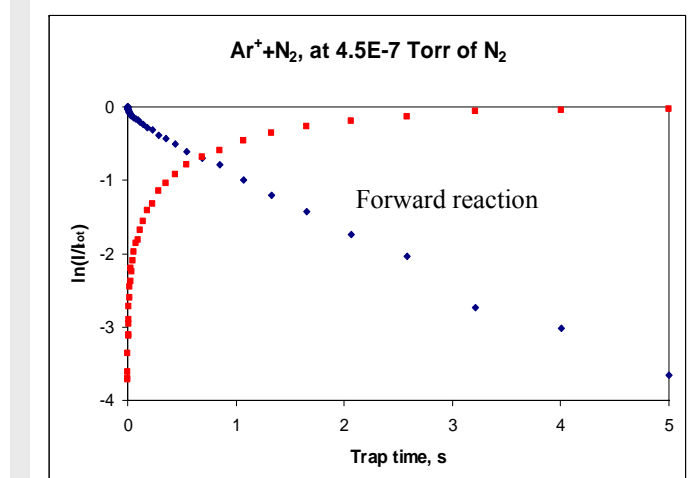
## Future Measurements

- Formaldehyde chemistry:**  
 $\text{H}_2\text{CO}^+ + \text{H}_2\text{CO} \rightarrow \text{CH}_2\text{COH}^+ + \text{H}_2\text{O}$
- Relevant to C growth in ISM
  - $k_f$  at 300K consistent with  $\Delta H$  below 5kJ/mol
  - Can monitor equilibrium vs. T using thermal ions and mixed effusive (or supersonic) beam of neutrals.
  - Compare technique with mixed direct entry at high T
- Alkyl transfer chemistry:**  
 $\text{CH}_3\text{OH}_2^+ + \text{HCN} \rightarrow \text{CH}_3\text{NCH}^+ + \text{H}_2\text{O}$
- Relevant to N fixation/C growth in ISM
  - $k_f$  at 300K consistent with  $\Delta H$  at or above 5kJ/mol
  - Modest negative temperature dependence inconsistent with barrier free reaction of this level of exothermicity

## Argon-Nitrogen ion exchange

- Reversible reaction used here as a test case for accuracy and dynamic range
- Noncondensing gases used here as a test case for accuracy and dynamic range
- Sensitized to spin-orbit ( $\text{Ar}^+$ ) and vibrational ( $\text{N}_2^+$ ) non-thermal effects

## Observations

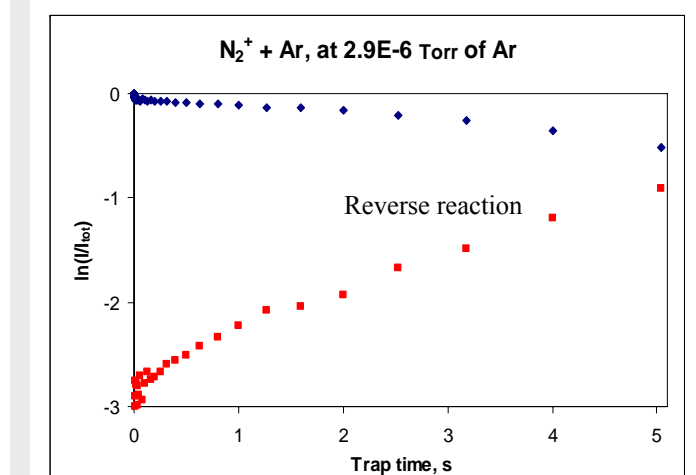


$\text{Ar}^+ + \text{N}_2 \rightarrow \text{Ar} + \text{N}_2^+$

$k_f = 4.9 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$   
at  $1.8 \cdot 10^{-7}$  Torr  $\text{N}_2$

$k_r = 5.1 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$   
at  $4.5 \cdot 10^{-7}$  Torr  $\text{N}_2$

$T = 298 \text{ K}$



$\text{N}_2^+ + \text{Ar} \rightarrow \text{N}_2 + \text{Ar}^+$

$k_r = 7.8 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$   
at  $1.5 \cdot 10^{-6}$  Torr  $\text{Ar}$

$k_f = 9.9 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$   
at  $2.9 \cdot 10^{-6}$  Torr  $\text{Ar}$

$T = 298 \text{ K}$

$K_{\text{eq}} = 57, \Delta G = -10 \text{ kJ/mol}$

- The results obtained compare favorably to available literature. According to the most recent evaluation,  $k_f = 1.10 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  and  $k_r = 2.00 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  at  $T = 300 \text{ K}$ , which yields
- $K_{\text{eq}} = 55$
- This demonstrates the RF ion trap method capabilities for a dynamic range in excess of  $10^6$  in reaction rate coefficients. The sensitivity of the instrument towards slow reactions will be further improved by modifications of the RF ion trap to allow higher neutral densities and lower temperatures.

Reference: V. G. Anicich, "Evaluated Bimolecular Ion-Molecule Gas Phase Kinetics of Positive Ions for Use in Modeling Planetary Atmospheres Cometary Comae/Interstellar Clouds", *J. Phys. Chem. Ref. Data*, **22**, 1469(1993).

## Further development goals for our apparatus

- Cryogenic cooling and 1000 K heating of the RF ion trap
- Pulsed buffer gas inlets for the ion trap
- 22-pole trap installation
- Atomic, radical beams
  - Accommodator (with cryostat) 10-100K for thermal beam
  - Delivery of clean & intense thermal sources
  - Thermal dissociation nozzle
  - Determination of  $\mu_{\text{radical}}$
- Velocity control
- Fast trap shuttering to explore maximal densities
- Chemical/spectral probing of products

## Conclusions

- Multipole RF ion trap as a part of a molecular/ion beam ultra-high vacuum apparatus is a unique and versatile instrument for kinetics studies
- Its pumping, temperature and temporal control characteristics are optimized for studying processes relevant to interstellar medium
- Argon - nitrogen ion exchange as a test system has already been studied using the instrument, now the research efforts may be focused on interstellar medium-related reactions

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