



Raman spectroscopy measurements of Polar Stratospheric Cloud (PSC) mimics



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**Environment
Research
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Background

- In the stratosphere (25km) species such as NO_x can lock “active” chlorine (Cl , ClO) as inactive forms (ClONO_2 , HCl) that cannot destroy O_3 .
- Discovery of Antarctic ozone “hole” (17km) blamed on catalysed release of photolytically active chlorine from reservoir species.

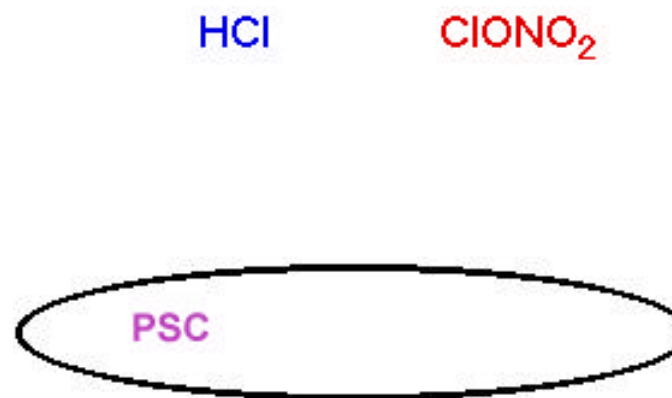




Reaction Mechanism



Reaction (1) is **very slow** in the gas phase and so the idea of heterogeneous processing on PSC surfaces to release the active chlorine *via* ionic intermediates (**fast**) was proposed.





Polar Stratospheric Clouds over Kiruna, Sweden.



Composition Theories



Early (laboratory-based) theories favoured three-phase concept for PSC composition:

- Sulfuric acid/sulfate core
- Condensation of NO_x as nitric acid trihydrate ($\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ called NAT)
- Condensation of water onto the particle ($\sim 189\text{K}$)



Solids, liquids or slushes?



Recent work has centred on the existence of liquid “particles”

- Theoretical models favour stability of liquid ternary solutions under stratospheric conditions
- Lidar measurements suggest (some) liquid droplets exist
- Measurements of Schreiner et al. show $\text{H}_2\text{O}:\text{HNO}_3$ to be above 10:1 in PSC particles (balloon-borne particle analysers)

The “state” of the PSC would be expected to exert a key control on the chemical pathways and their efficiency



Formation Mechanism



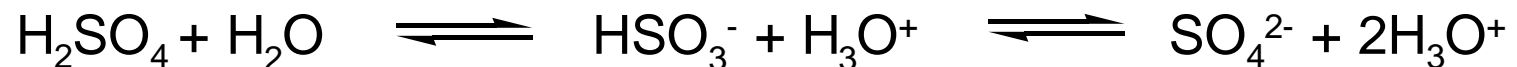
- Stratospheric sulfate aerosol exists (Junge layer)
- It deliquesces water and nitric acid vapour (liquid-solid equilibrium)
- A rapid uptake and size increase occurs from 192-190K
- Result is an NSW ternary solution. Whether it exists as a solid, liquid or slush will depend upon temperature and concentrations



UCC Project



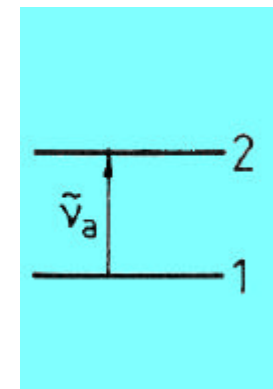
- Aim of this work is to measure solution/solid/slush equilibria in PSC-mimics (e.g. N:S:W 1:1:10) as a function of ionic composition and temperature
- Raman Spectroscopy used as a probe of the ionic speciation:



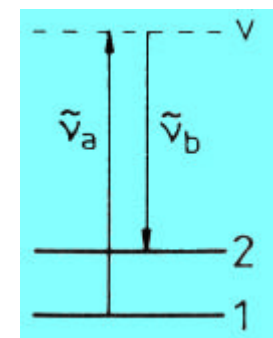
The Raman Experiment



- Need qualitative and quantitative analysis of ions such as nitrate in aqueous solutions and water-ice
- Water is a very strong IR absorber but a poor Raman scatterer
- Hence use Raman Spectroscopy to distinguish guest ion from solvent



IR absorption



Raman scattering

UCC Methodology

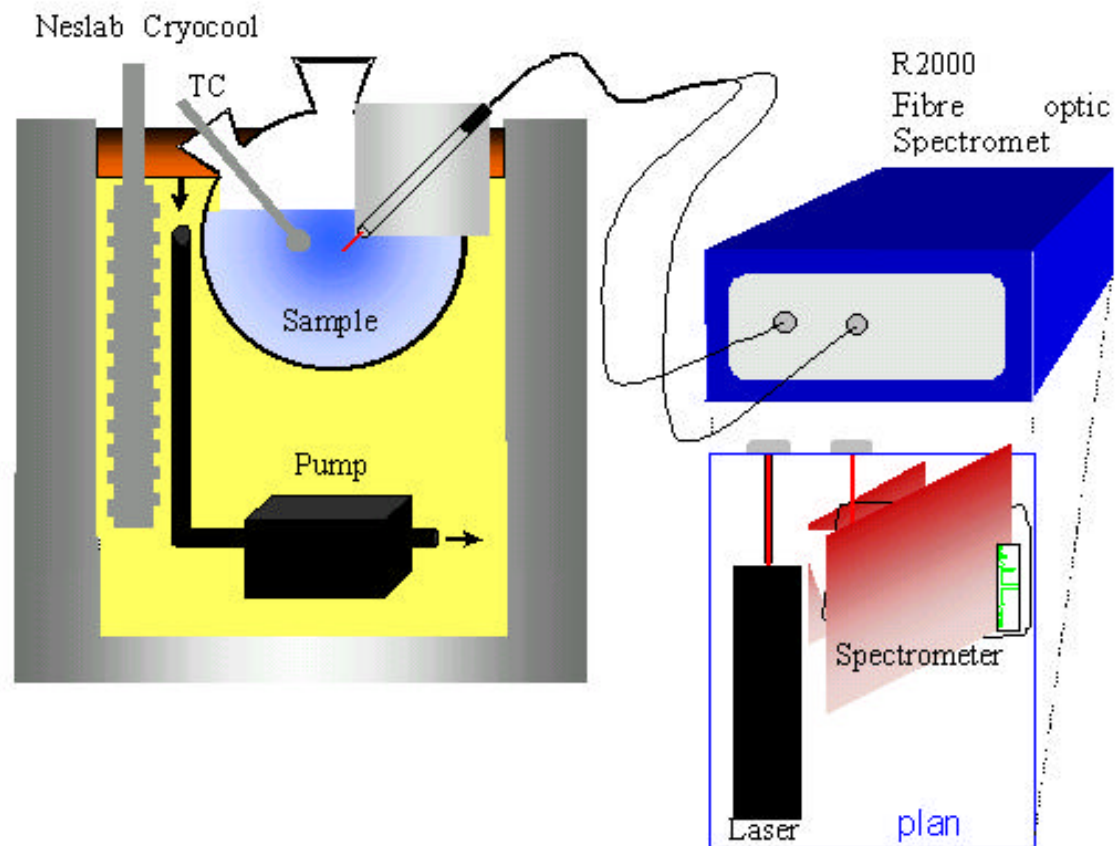


- Ocean Optics R2000 Raman Spectrometer
- 500mW 785nm (red) diode laser
- 1200mm^{-1} blazed grating
- 2048 element CCD array
- 400nm diameter silica fibre-optic probe lends flexibility for *situ* analysis
- Cheap!

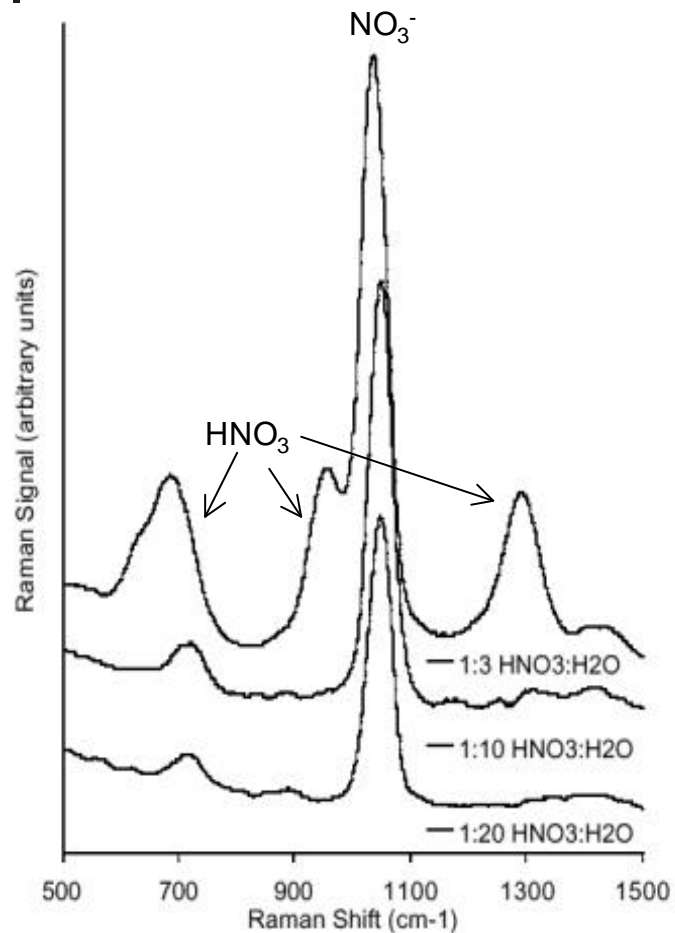




Experimental Setup



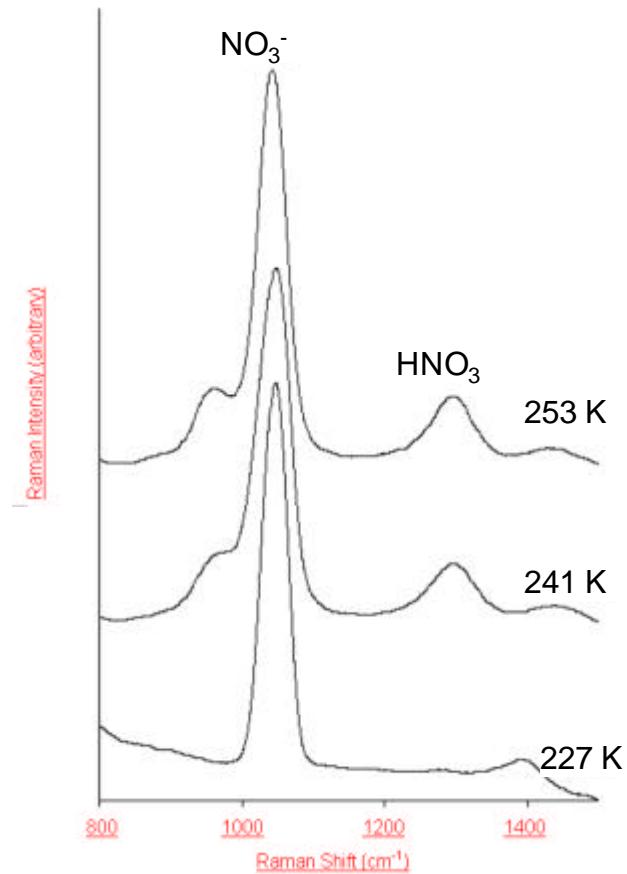
Nitric Acid solutions



- Increase in solute:solvent ratios (label)
- Equilibrium data (ion:molecule) can be obtained
- Non-ionic form prevails as solvent becomes scarce

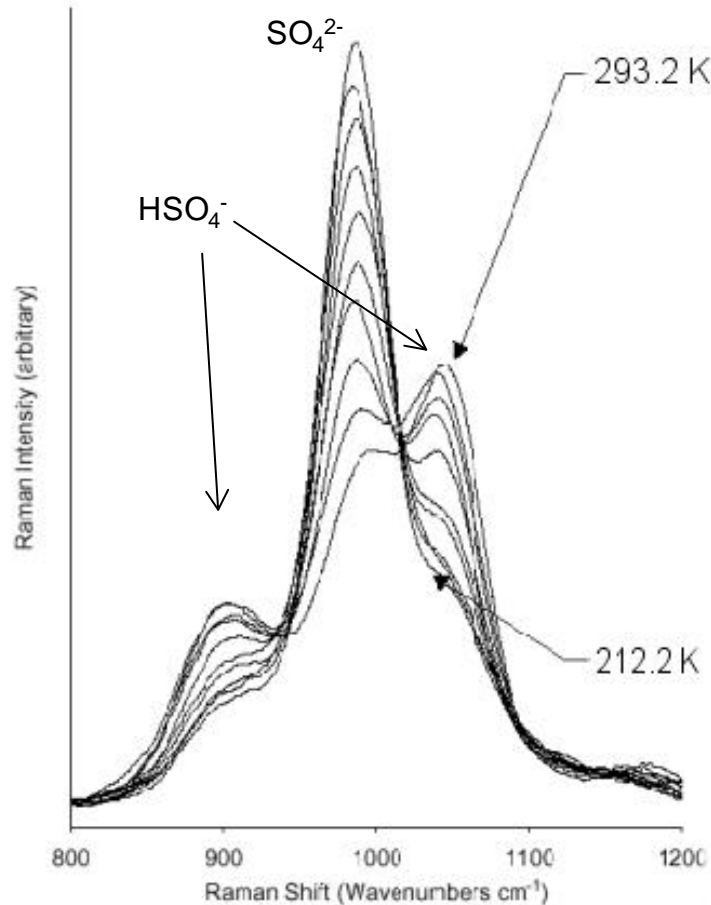


Temperature effect



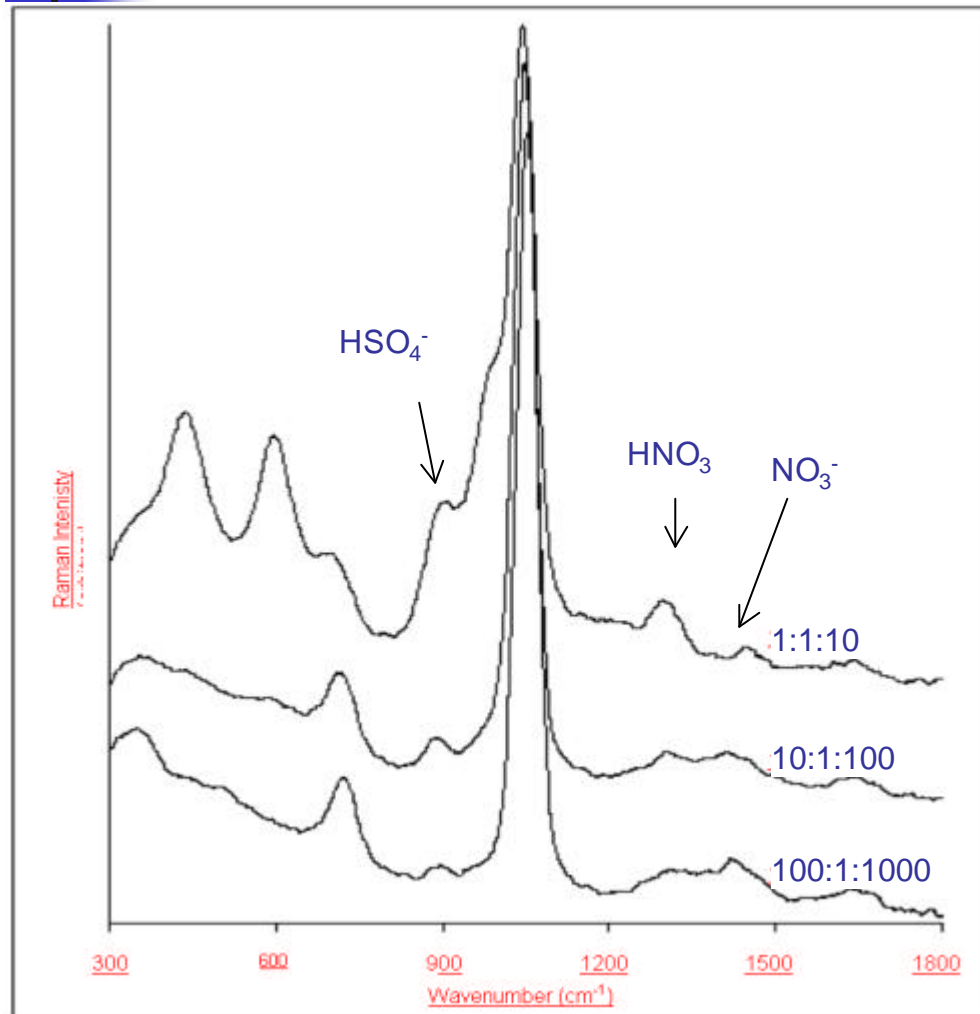
- 1:3 HNO₃ - H₂O solution
- Dissociation is exothermic
⇒ aided by cooling
- When ionisation is total THEN
freezing occurs

Sulfuric acid solutions



- Similar effects to Nitric acid
- Speciation change from acid to bisulfate to sulfate ions
- Freezes after total disappearance of bisulfate ions

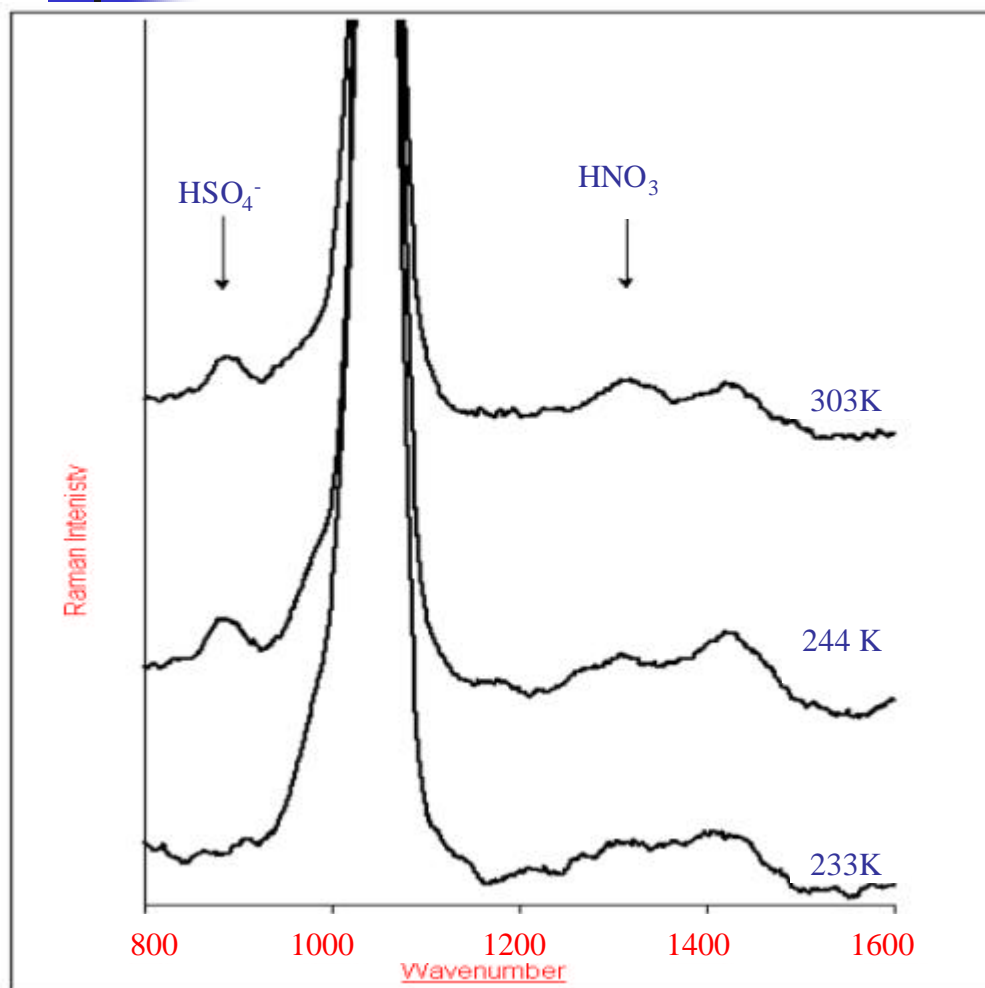
Ternary Solutions (NSW)



- Bisulfate ion always present even in dilute solutions
- As [H₂SO₄] decreases, Nitric acid equilibrium shifts toward ionic species



Ternary Freezing



- 1:1:10 NSW solution
- Freezing begins at 233K after ionisation of sulfate system
- (1:10 NW freezes at 248K)



Conclusions



- Associated forms (HNO_3 , HSO_4^-) prevail as concentration is increased
- Decreasing temperature drives equilibrium toward ionic species
- Solid phase forms only after complete ionisation has occurred
- HNO_3 ionises before H_2SO_4 , *i.e.* trace amounts of H_2SO_4 hinder formation of solid phase in HNO_3 solutions
- Cooling of stratosphere due to greenhouse effect may aid formation of solid phases