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New cross sections, indices of refraction, and reflectance spectra of atmospheric interest

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Abstract

A brief review is presented of the indices of refraction and cross sections that are on the HITRAN 2004 compilation. New measurements of the refractive indices of ternary ($H_2O/H_2SO4/HNO_3$) droplets by Myhre [2003,2005] and the indices of supercooled water by Wagner [2005] are presented and compared to previous data. New infrared cross sections of species of atmospheric interest (e.g., the measurements of HFC-125 and HFC-143a of Lonardo and Masciarelli [2000]) are also discussed.

We finally propose to link to the "other listings" portion of the HITRAN web site several established reflectance data bases, since many current and future remote sensing experiments are influenced by ground emission and reflectance contributions.

Outline of Presentation

Discussion of new

Indices of Refraction

Cross sections

Links to
Digital surface reflectance atlases

HITRAN 2004 Refractive Indices

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Water, ice

Sulfuric acid (stratospheric sulfate)

Nitric acid

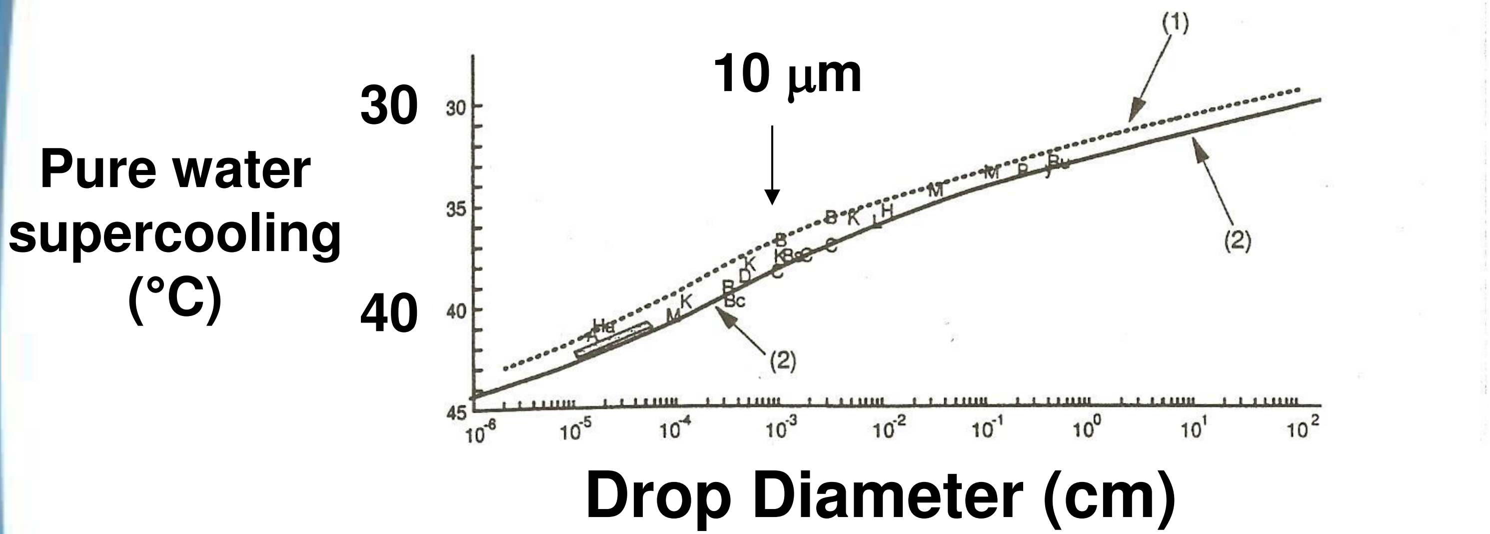
Solid hydrates (NAM, NAD, NAT)
nitric acid mono, di, tri hydrate

Ternary solution droplets
(H_2SO_4, H_2O, HNO_3)

Tropospheric (sodium chloride,
sea salt, ammonium sulfate, organic soot,
quartz, sand)

Supercooled Water - Motivation

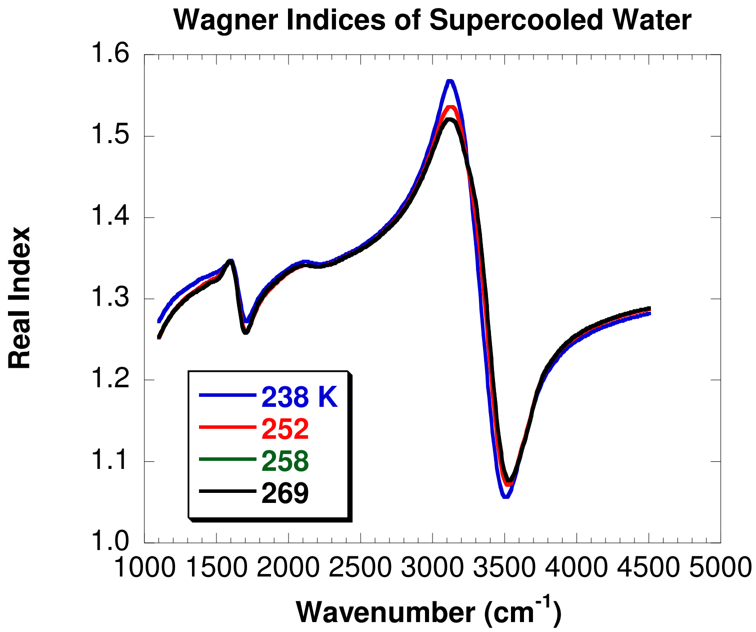
Pure water – 10 μm drop nucleates at -38° C

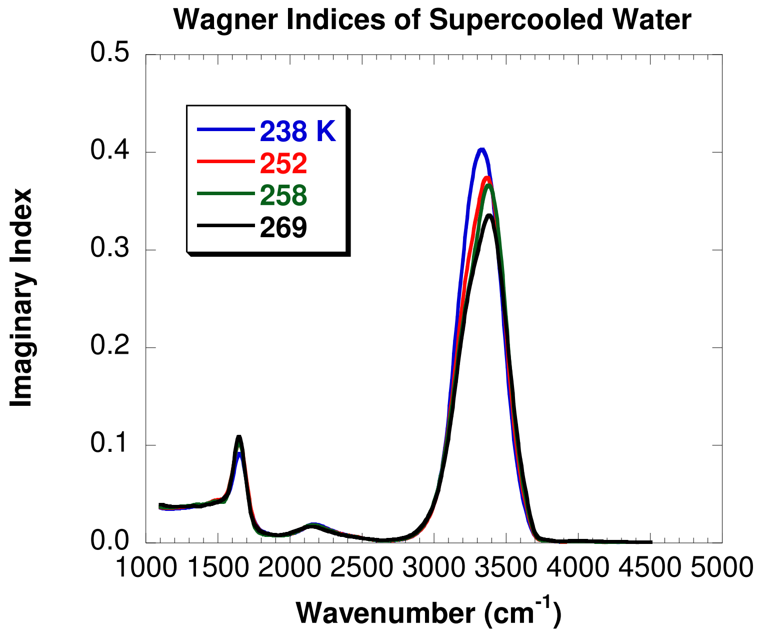


Pruppacher and Klett, Microphysics of Clouds and Precipitation, p213, 1998

Water droplet + desert dust nucleates at -15° C
(Sassen, *Nature*, *434*, p456, 2005)

Supercooled Water Indices

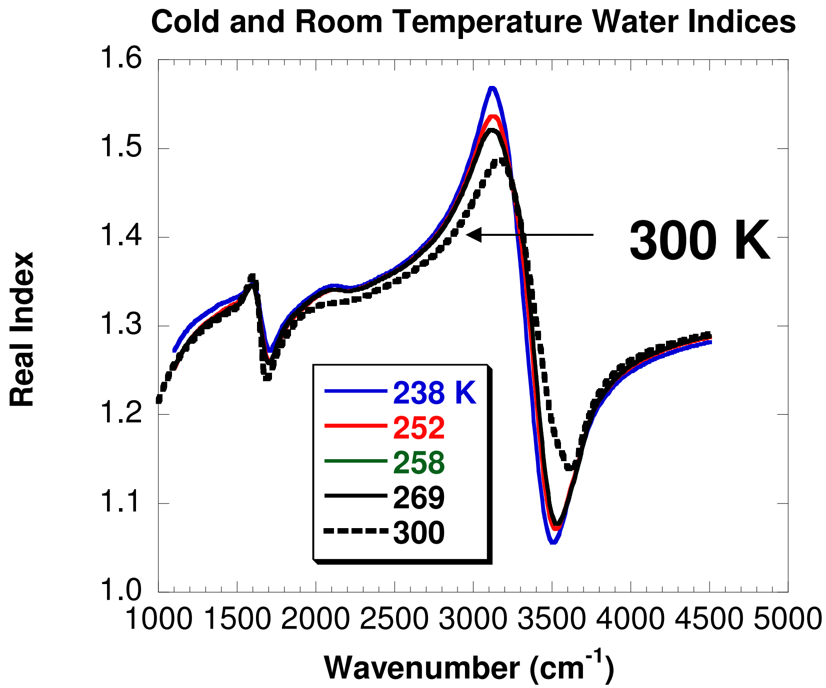


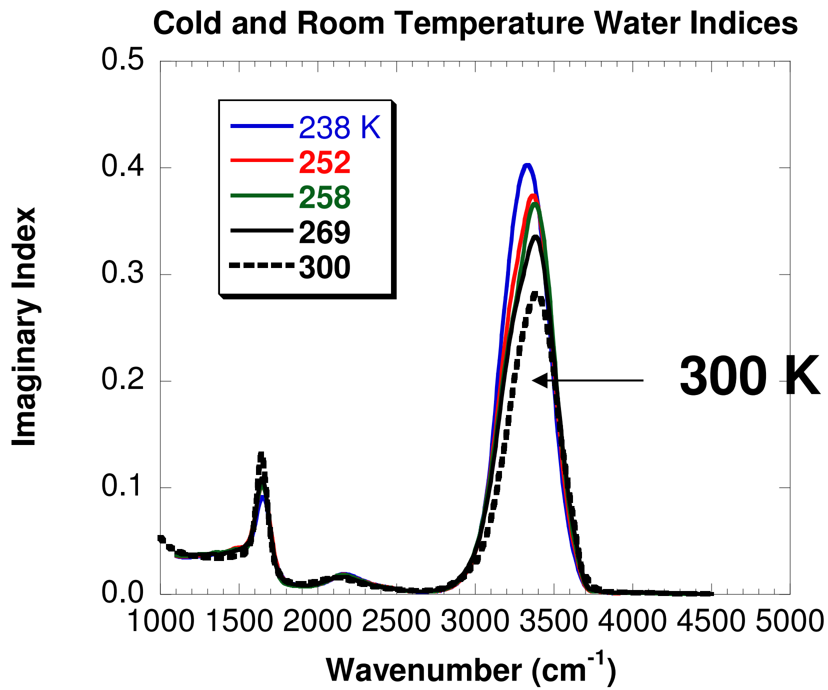


Real Index **Imaginary Index**

Wagner et al., Mid-infrared Extinction Spectra and Optical Constants of Supercooled Water Droplets, *J. Phys. Chem.*, *109*, p7099, 2005.

Comparison to Room Temperature Data





Real Index

Imaginary Index

Downing and Williams, Optical constants of water in the infrared, *J. Geophys. Res.*, *80*, 1656-1661, 1975.

Ternary Indices - Motivation

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Polar Stratospheric Clouds (PSCs)

Need to know PSC composition and size

Composition: Liquid droplets (ternary),

Solid hydrates (e.g. NAT, NAD)

Heterogeneous chemistry rates of reaction:

γ = reaction probability (unitless)

A = PSC surface area ($\mu m^2\ cm^{-3}$)

v = mean molecular speed ($cm\ sec^{-1}$)

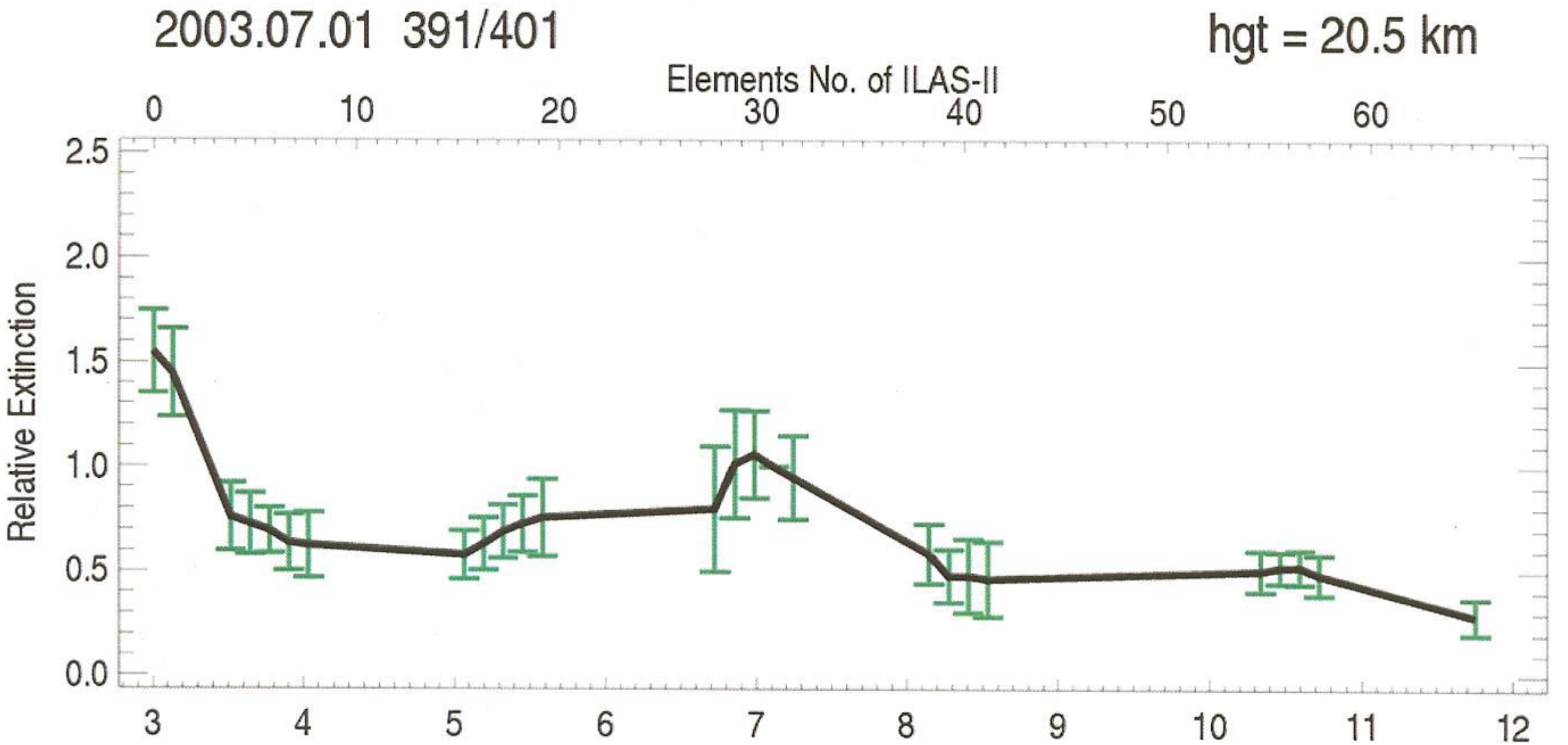
r = rate constant (sec^{-1})

$r = 10^{-8}\ \gamma\ A\ v/4$

γ is a function of PSC composition type

Denitrification: depends upon particle size

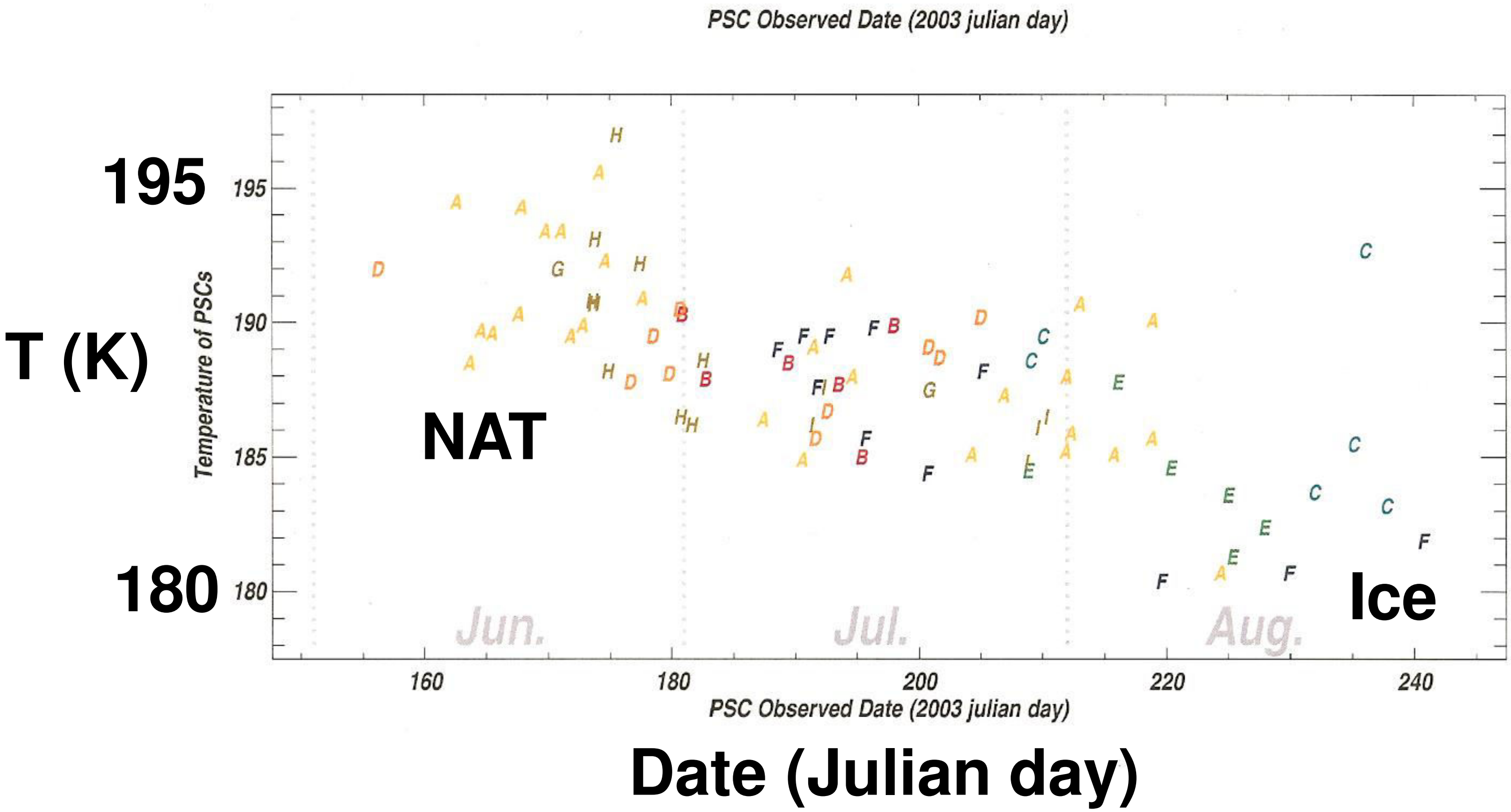
Example: observed PSC spectrum



Wavelength (micron)

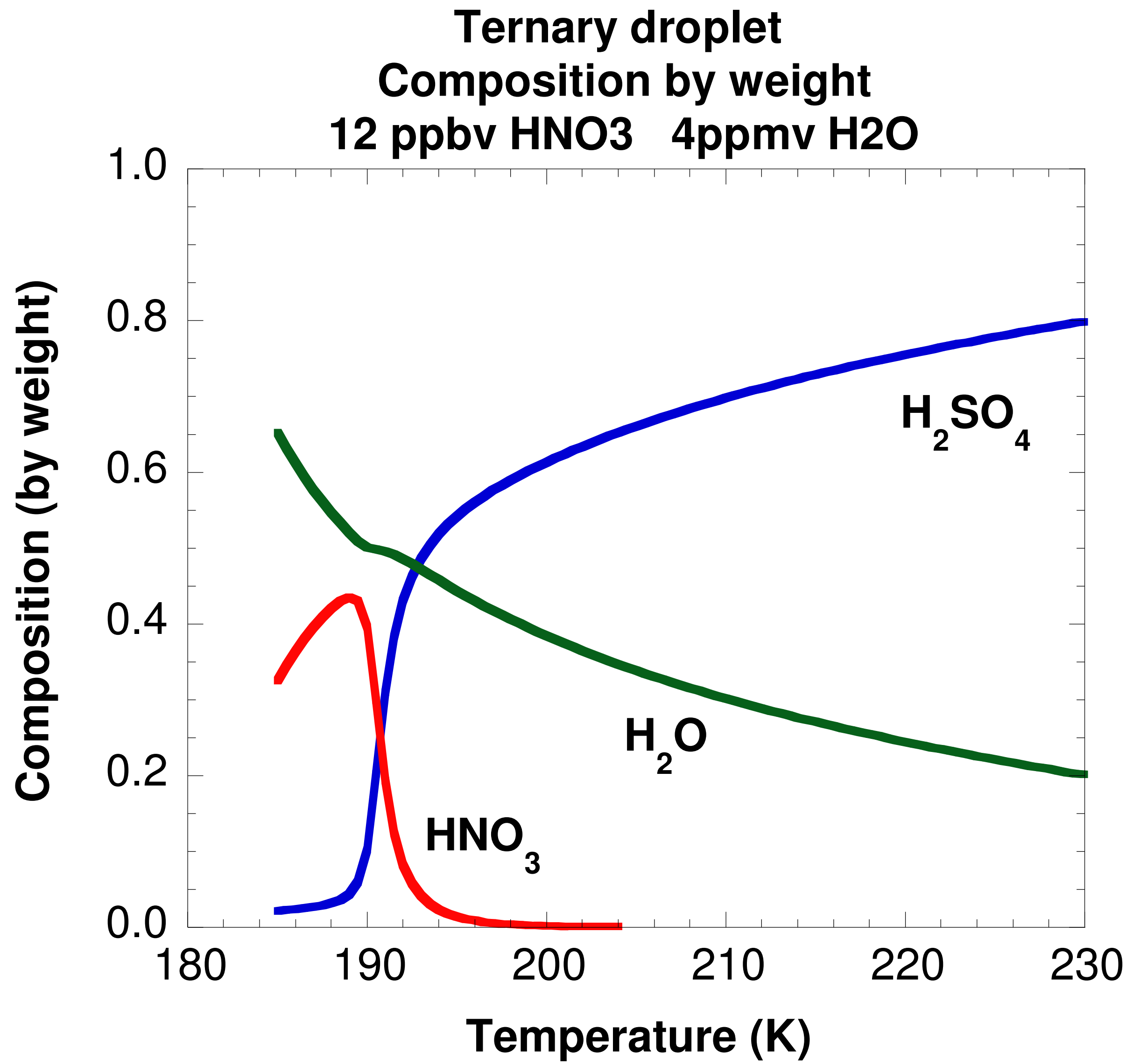
Kim et al., PSCs Observed by the ILAS-II in the Antarctic Region: Dual Compositions and Variation of Compositions during June-August of 2003, *JGR*, in press, 2006.

Example: PSC composition determination



Kim et al., PSCs Observed by the ILAS-II in the Antarctic Region: Dual Compositions and Variation of Compositions during June-August of 2003, *JGR*, in press, 2006.

Different letters denote different composition types.



Carslaw, Luo, Peter, *Geo Res Lett*, *22*, p1877, 1995

New Binary and Ternary Indices

C. E. Lund Myhre, D. H. Christensen, F. M. Nicolaisen, and C. J. Nielsen, Spectroscopic Study of Aqueous H_2SO_4 at Different Temperatures and Compositions: Variations in Dissociation and Optical Properties, *J. Phys. Chem. A*., *107*, 1979-1991, 2003.

C.E. Lund Myhre, H. Grothe, A. A. Gola, and C. J. Nielsen, Optical Constants of HNO_3/H_2O and $H_2SO_4/HNO_3/H_2O$ at Low Temperatures in the Infrared Region, *J. Phys. Chem. A*, *109*, 7166-7171, 2005.

Myhre (2003, 2005) measurements

Binary (H_2SO_4/H_2O) – 32 cases

Weight % H_2SO_4 = 81, 81, 81, 76, 76, 76, 76, 76, 72, 72
72, 72, 72, 72, 72, 65, 65, 65, 65, 58,
58, 58, 48, 48, 48, 48, 38, 38, 38, 38,
38, 38

Temperature(k) = 298, 273, 267, 298, 273, 233, 213, 203, 298, 253,
245, 233, 223, 213, 203, 298, 263, 243, 223, 298,
243, 233, 298, 273, 234, 213, 298, 277, 257, 243,
223, 213

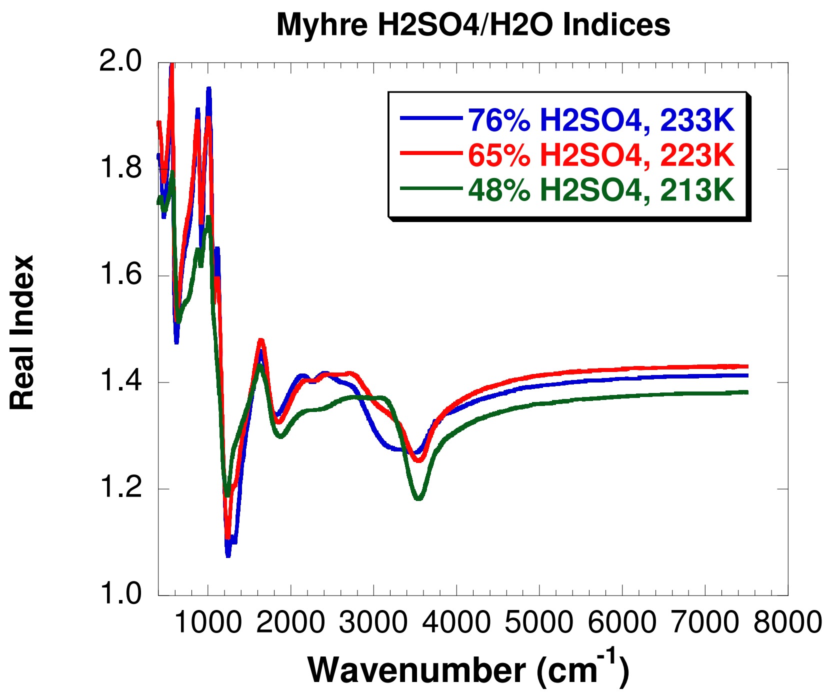
Binary (HNO_3/H_2O)

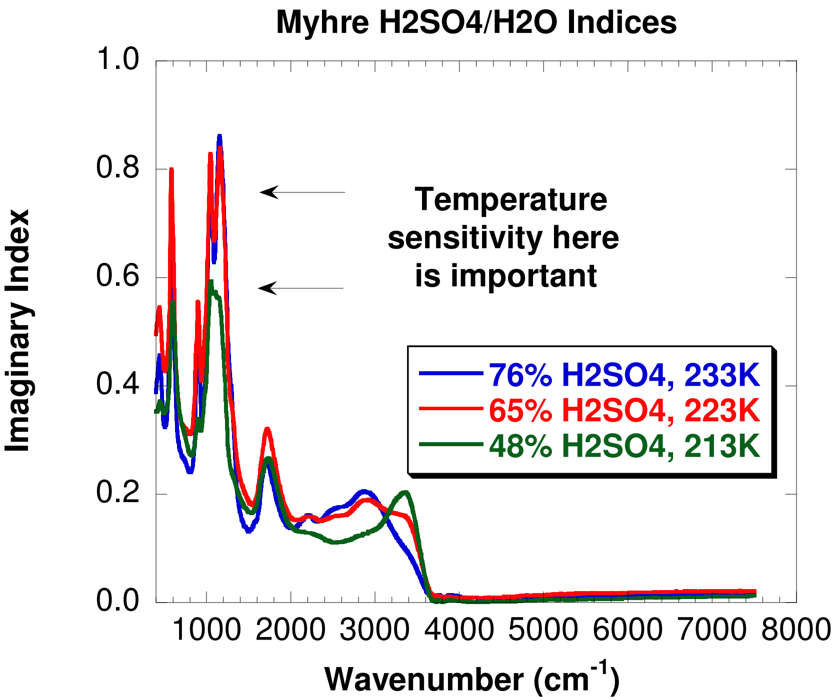
30% HNO_3, 70 % H_2O T= 223, 233, 243, 253, 273, 293 K
54% HNO_3, 46 % H_2O T= 243, 248, 253, 273, 293 K
64% HNO_3, 36% H_2O T= 238, 243, 253, 273, 293 K

Ternary ($HNO_3/H_2SO_4/H_2O$)

17% HNO_3, 25% H_2SO_4 T=183, 193, 203, 213, 223, 253, 273, 293 K
23% HNO_3, 21% H_2SO_4 T=203, 213, 223, 253, 273 K
46% HNO_3, 4% H_2SO_4 T=223, 253, 273, 293 K

Examples of Myhre H_2SO_4/H_2O Indices

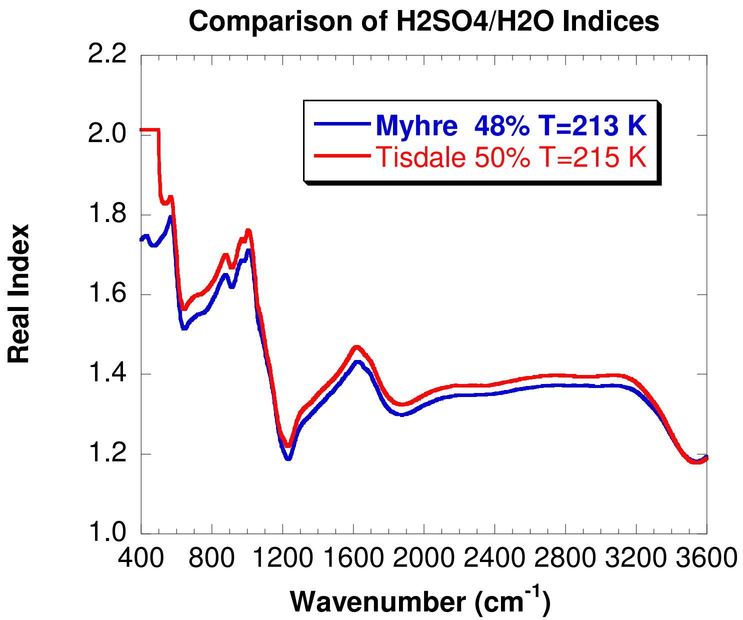


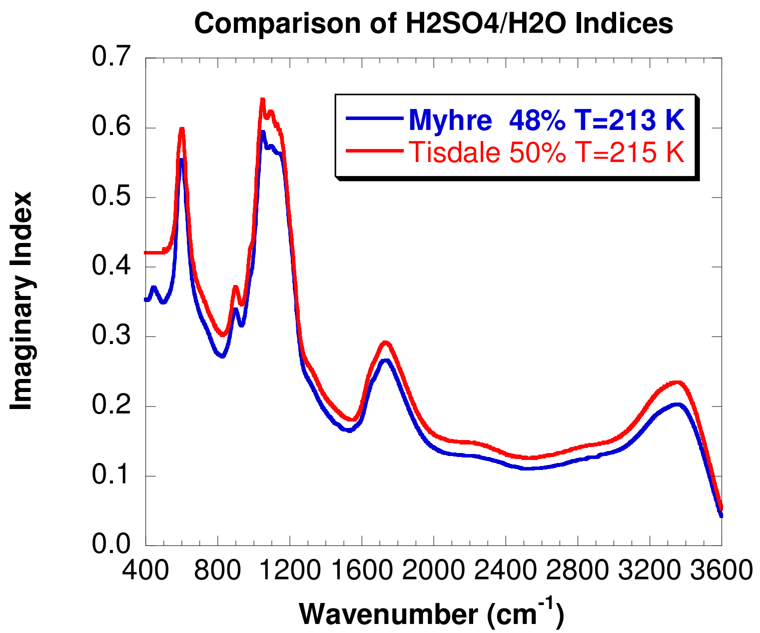


Real Index

Imaginary Index

Comparison of H_2SO_4/H_2O Indices

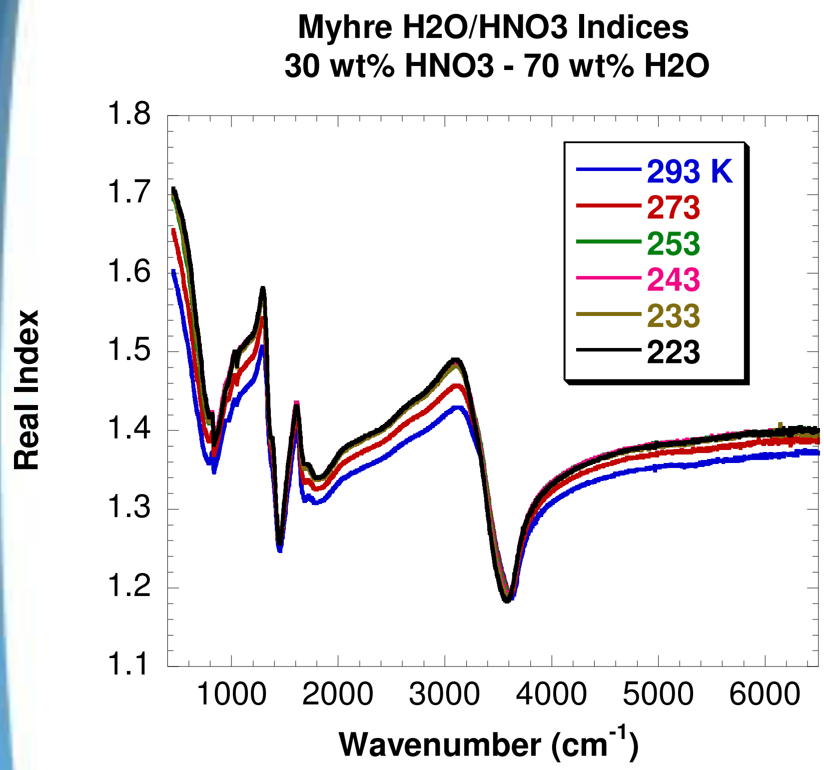


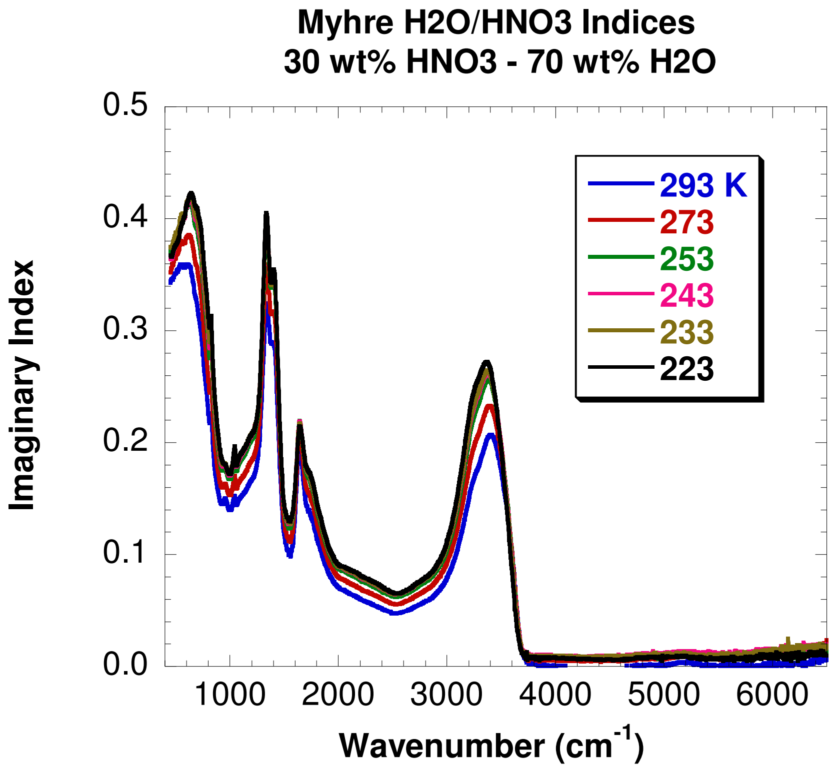


Real Index

Imaginary Index

Examples of Myhre HNO_3/H_2O Indices Small Temperature Dependence

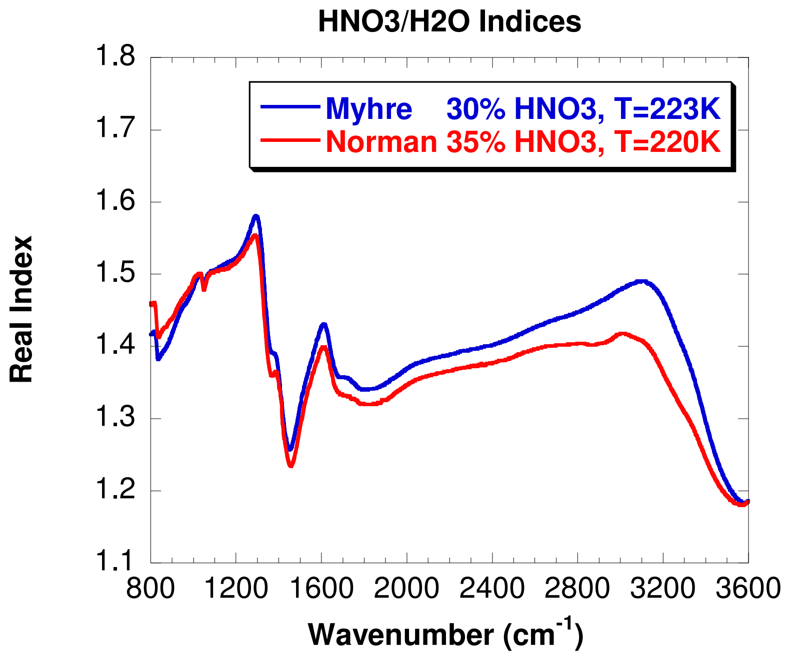


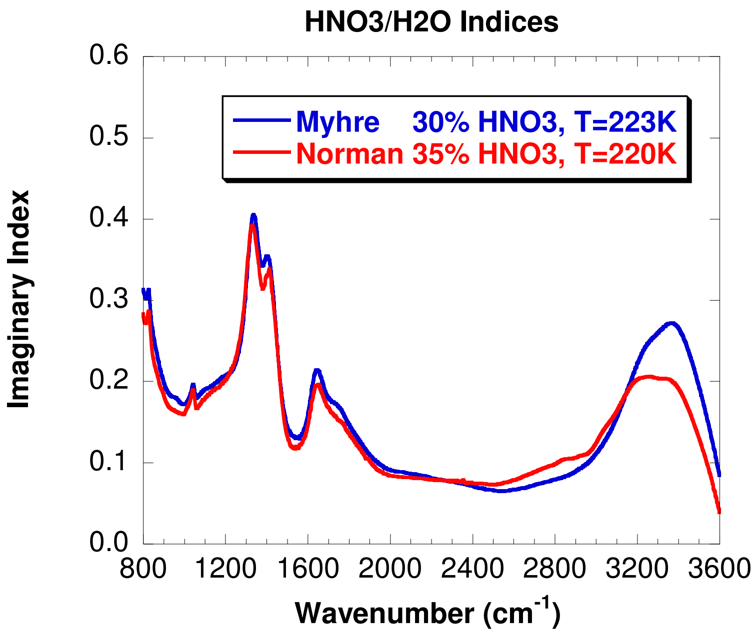


Real Index

Imaginary Index

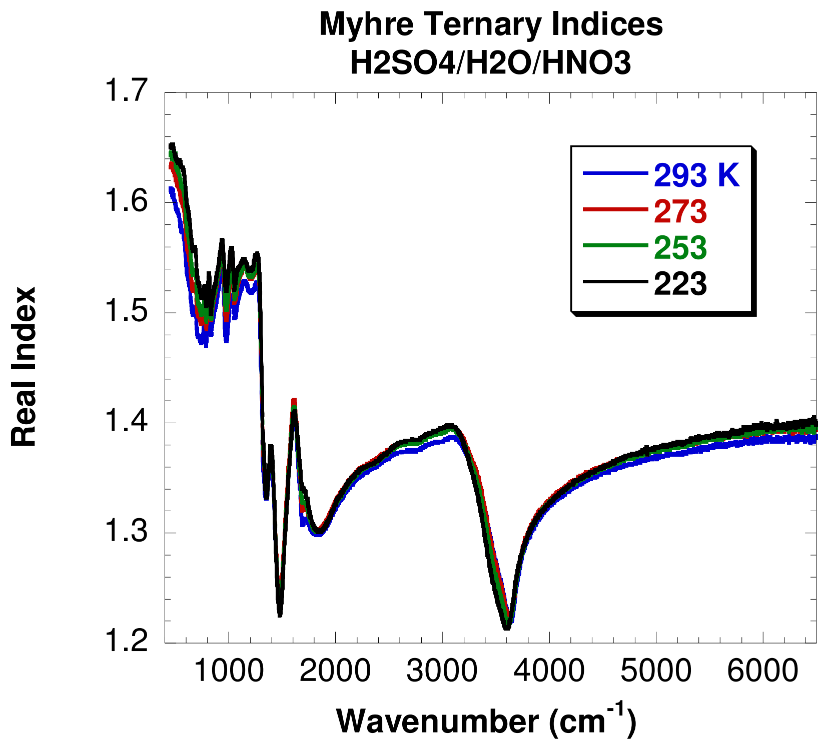
Comparisons of HNO_3/H_2O Indices



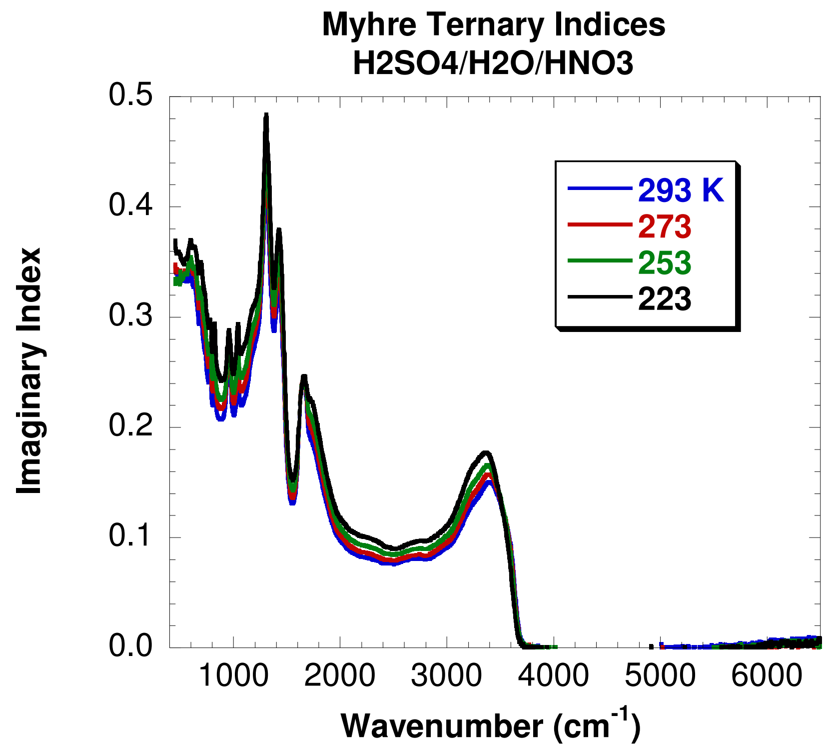


Real Index **Imaginary Index**

Examples of Myhre Ternary Indices
Small Temperature Dependence



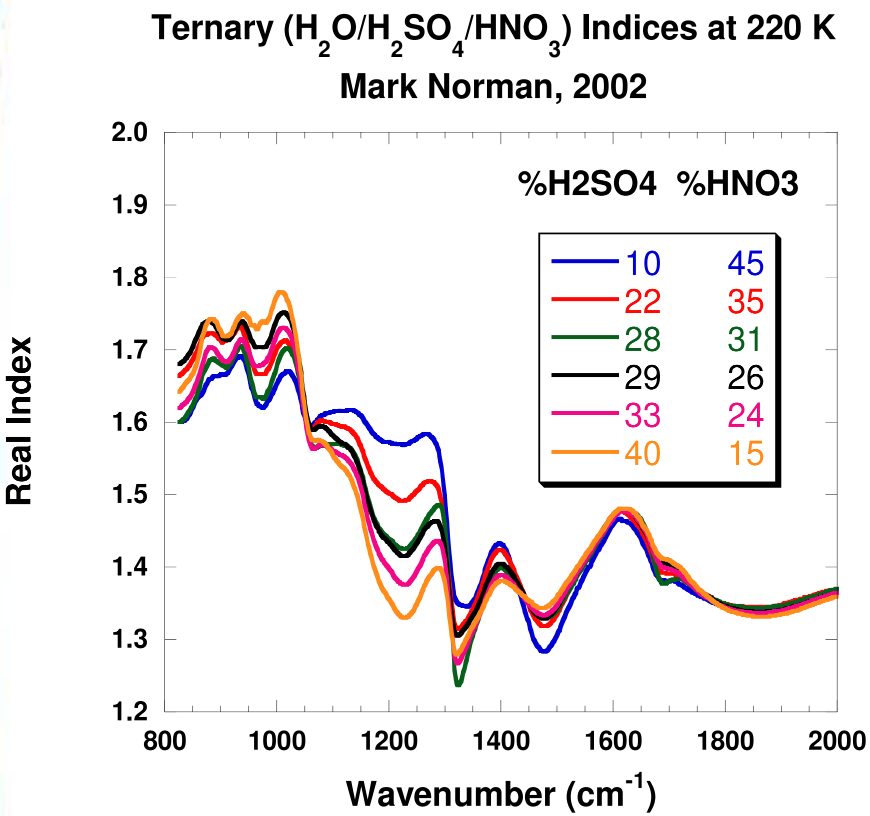
Real Index



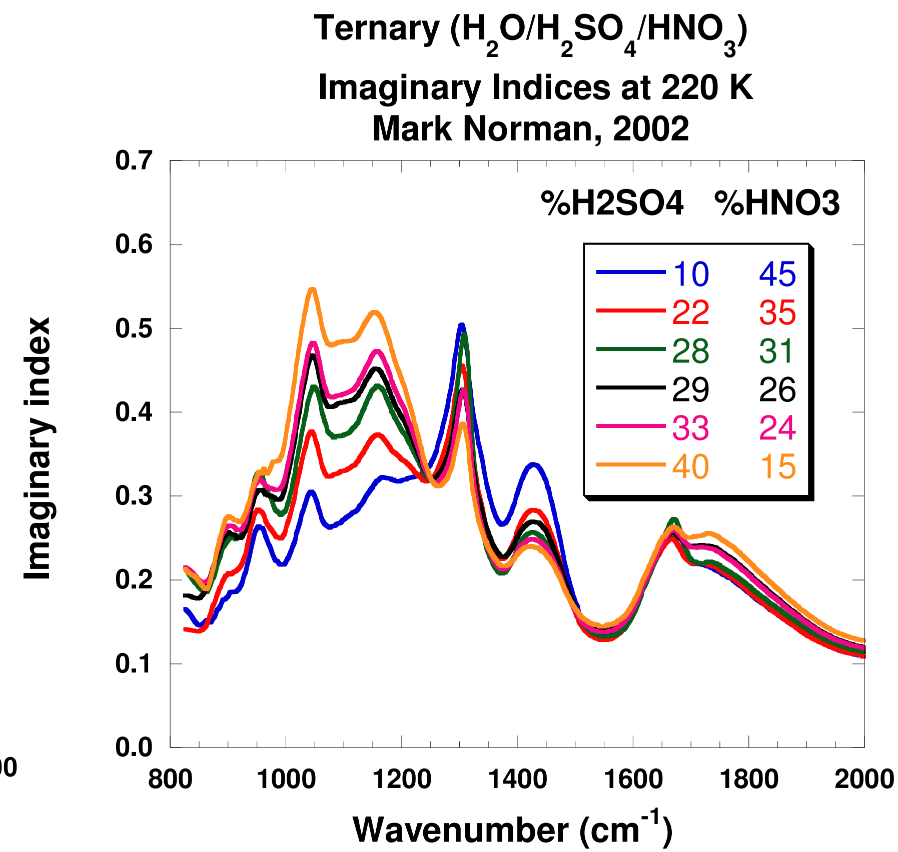
Imaginary Index

46 % HNO_3, 4% H_2SO_4

HITRAN 2004 Included Norman's Ternary Indices at 220 K



Real



Imaginary

Comparisons of Myhre data to other data sets

Percent differences in H_2SO_4/H_2O indices

Data set	Real Index	Imaginary Index
Niedziela	2%	10-20%
Biermann		
1000-3500 cm^{-1}	10%	10-20%
$v < 1000\ cm^{-1}$	problematic	
Tisdale	3%	10%

Which data sets to use?

Wagner et al., A quantitative test of infrared optical constants for supercooled sulphuric and nitric acid droplet aerosols, *Atmos. Chem. Phys., 3*, 1147-1164, 2003.

Compared cloud chamber measurements of H_2SO_4/H_2O and H_2SO_4/HNO_3 extinction spectra with spectra calculated using published indices.

Good agreement

Niedziela (1999)	H_2SO_4/H_2O
Norman (1999)	H_2SO_4/HNO_3

How to use the data?

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Mixing rule for the complex index has been proposed:

$$k(\nu, T, W_s, W_n) = (W_s/W_s+W_n)\, k_s + (W_n/W_s+W_n)\, k_n$$

complex indices k_s and k_n, weight percents W_s and W_n of H_2SO_4/H_2O (s) and HNO_3/H_2O (n) components

This mixing rule is likely not adequate.

Myhre et al. (2005) state that:
"a reliable model of the optical constants of ternary $H_2SO_4/HNO_3/H_2O$ solutions requires a thorough understanding of ionic speciation in the system"

Cross Sections

HITRAN 2004 - 28 molecules

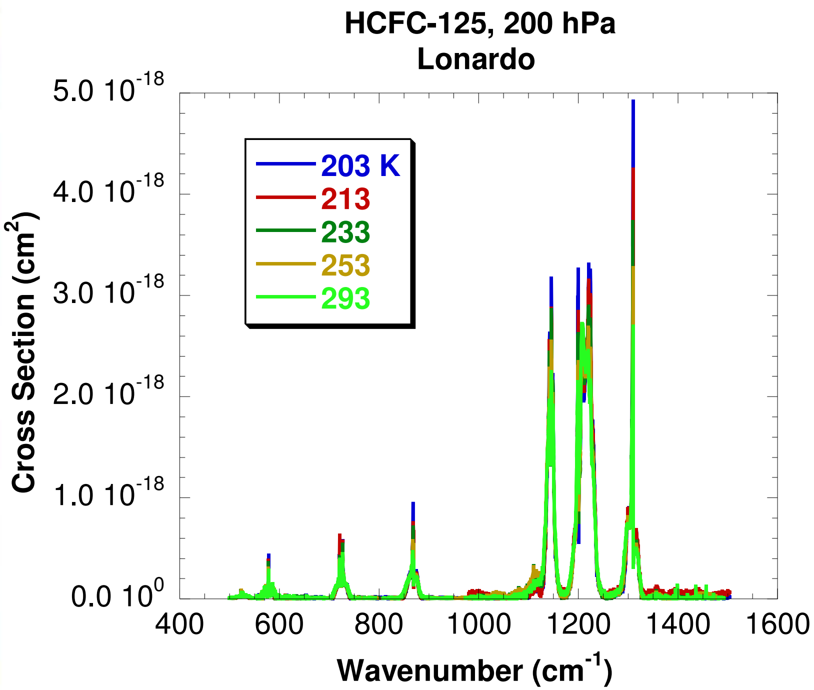
Rothman et al., The HITRAN 2004 molecular spectroscopic database, J. Quant. Spect. and Radiat. Transfer, 96, 139-204, 2005.

Data to be added to HITRAN:

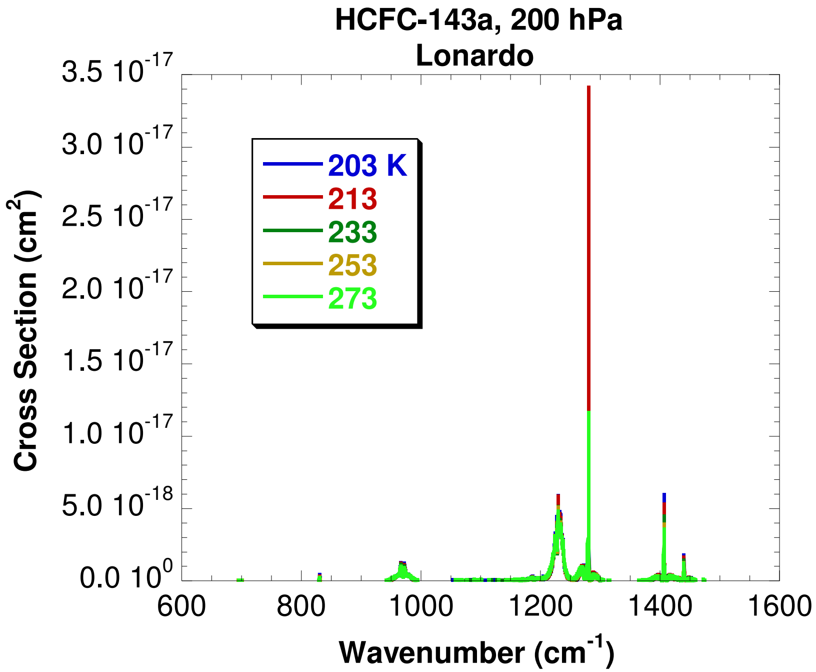
Lonardo and Masciarelli, Infrared absorption cross-sections and integrated absorption intensities of HFC-125 and HFC-143a, *J. Quant. Spect. and Radiat. Transf.*, *66*, p129-142, 2000.

16 HFC 125 and 19 HFC 143a sets
Temperature range: 203 – 293 K
Pressure: pure vapor, 50, 200, 800 hPa
Spectral resolution: 0.03 cm-1

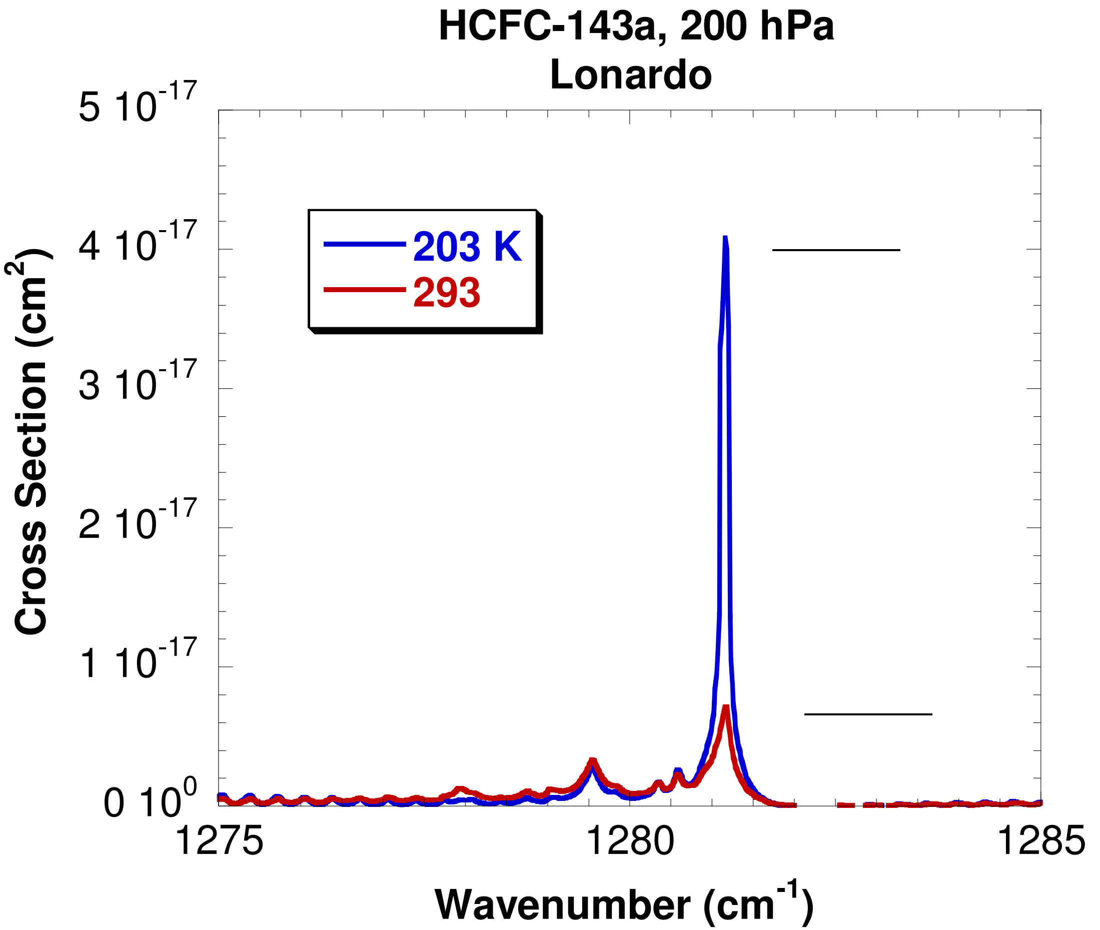
HFC-125



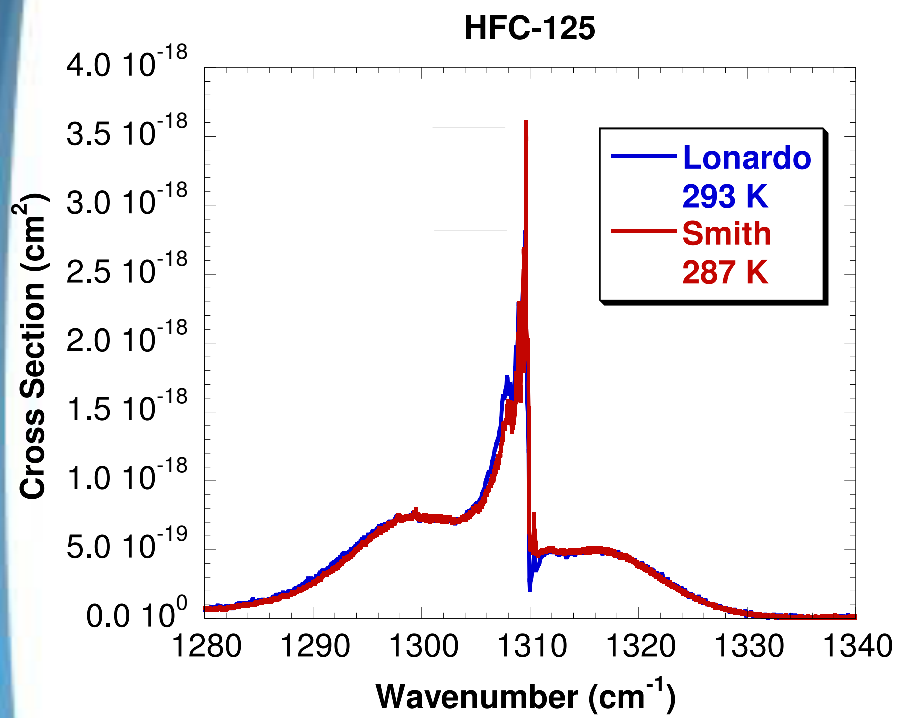
HFC-143a

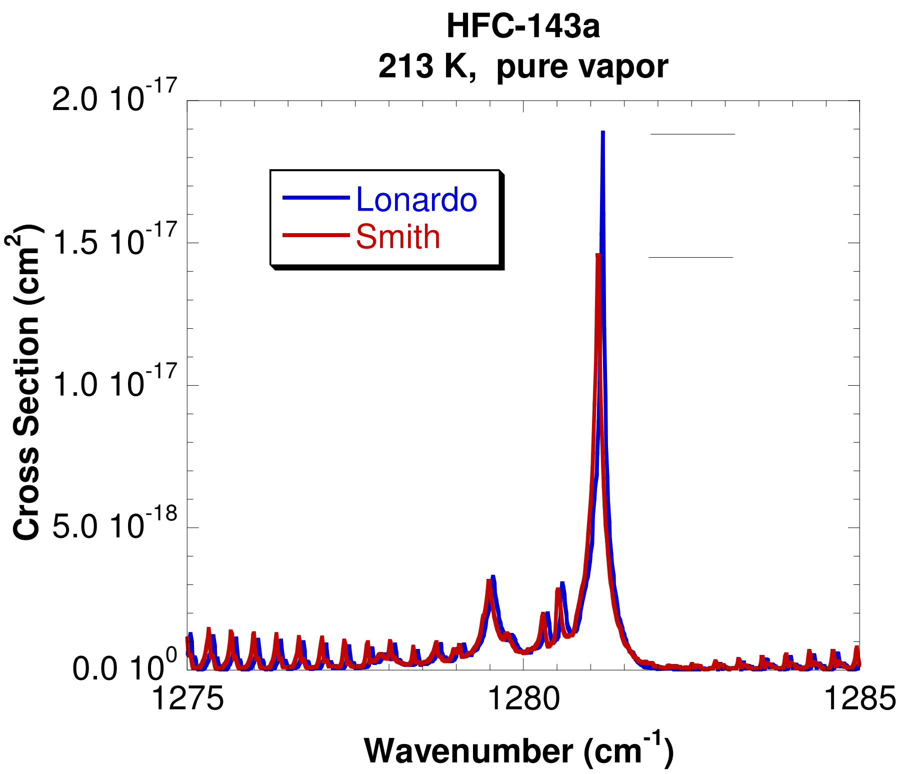


HFC-143a Temperature Dependence



Comparisons to Other Data





Reflectance Spectra - <u>Motivation</u>

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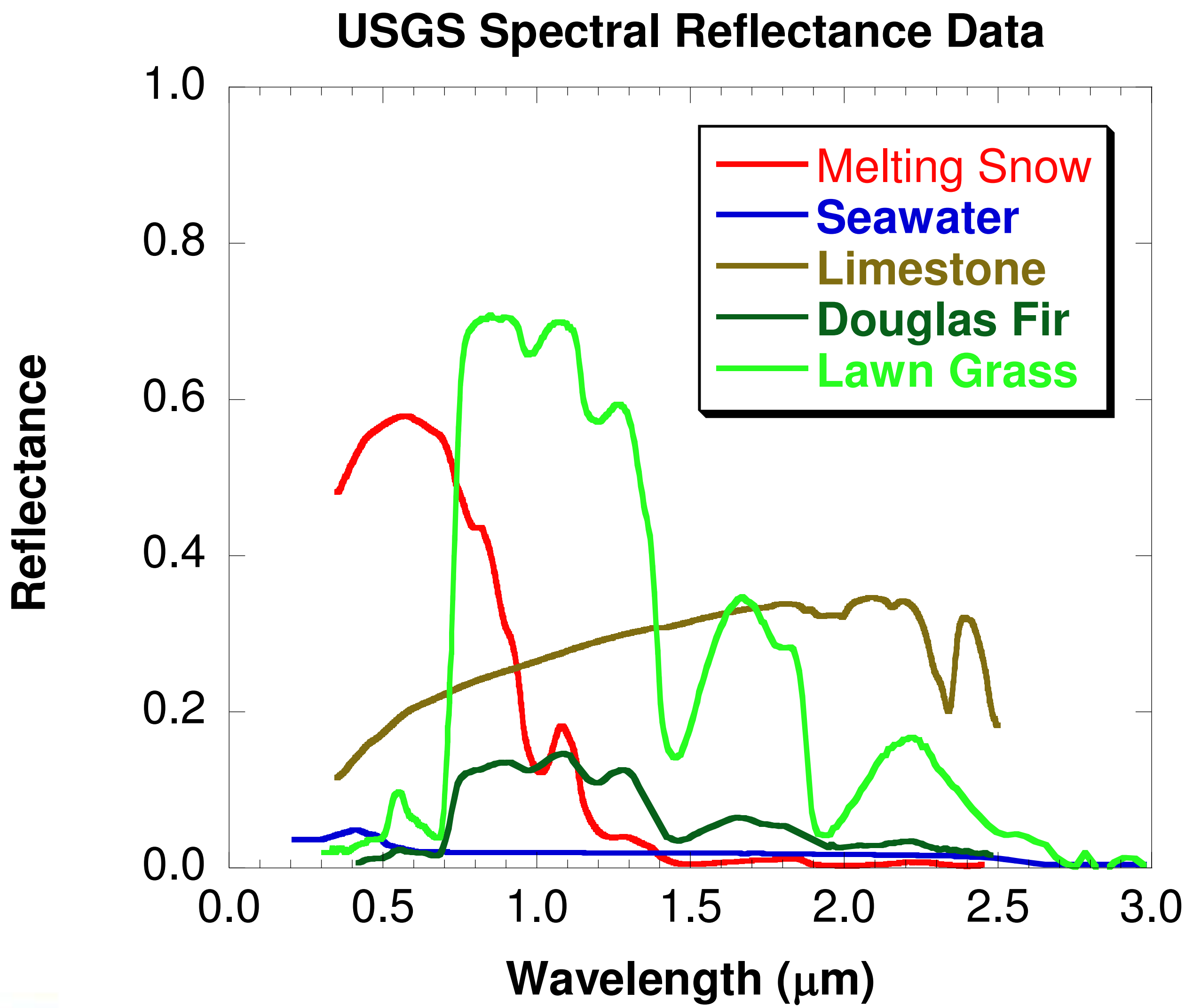
Recent interest focuses on the troposphere

To probe into the troposphere, one frequently encounters radiative transfer physics that is influenced by the surface

Nadir retrievals over bright surfaces are difficult

- MODIS experiment can not detect desert dust over bright deserts

Reflectance Spectra



Reflectance Spectra

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USGS Digital Spectral Library

http://pubs.usgs.gov/of/2003/ofr-03-395/ofr-03-395.html

Over 800 spectra, including:

13 mineral classes

borate, carbonate, chloride, element, halide,..

7 series

olivine, garnet, scapolite,..

Representative spectra of

H_2O ice, kerogen, desert varnish, evaporite,..

Vegetation

treees, shrubs, grasses, flowers,..

Man-made materials

roofing material, plastics, paint,..

Spectral range: 0.2 to 5.2 μm

Reflectance Spectra

ASTER spectral library
Simon.J. Hook@jpl.nasa.gov

http://speclib.jpl.nasa.gov/

The ASTER spectral library includes data from three other spectral libraries: the Johns Hopkins University (JHU) Spectral Library, the Jet Propulsion Laboratory (JPL) Spectral Library, and the United States Geological Survey (USGS - Reston) Spectral Library

~2000 spectra of natural and man-made materials

Conclusions

Refractive Indices

There's still work to be done with the ternary indices!

Cross sections

Tropospheric species will drive interest

Surface reflectance data

Link to existing libraries