

The Matrix Isolation Spectroscopy and Optical Constants of Ices Facility at NASA-Ames

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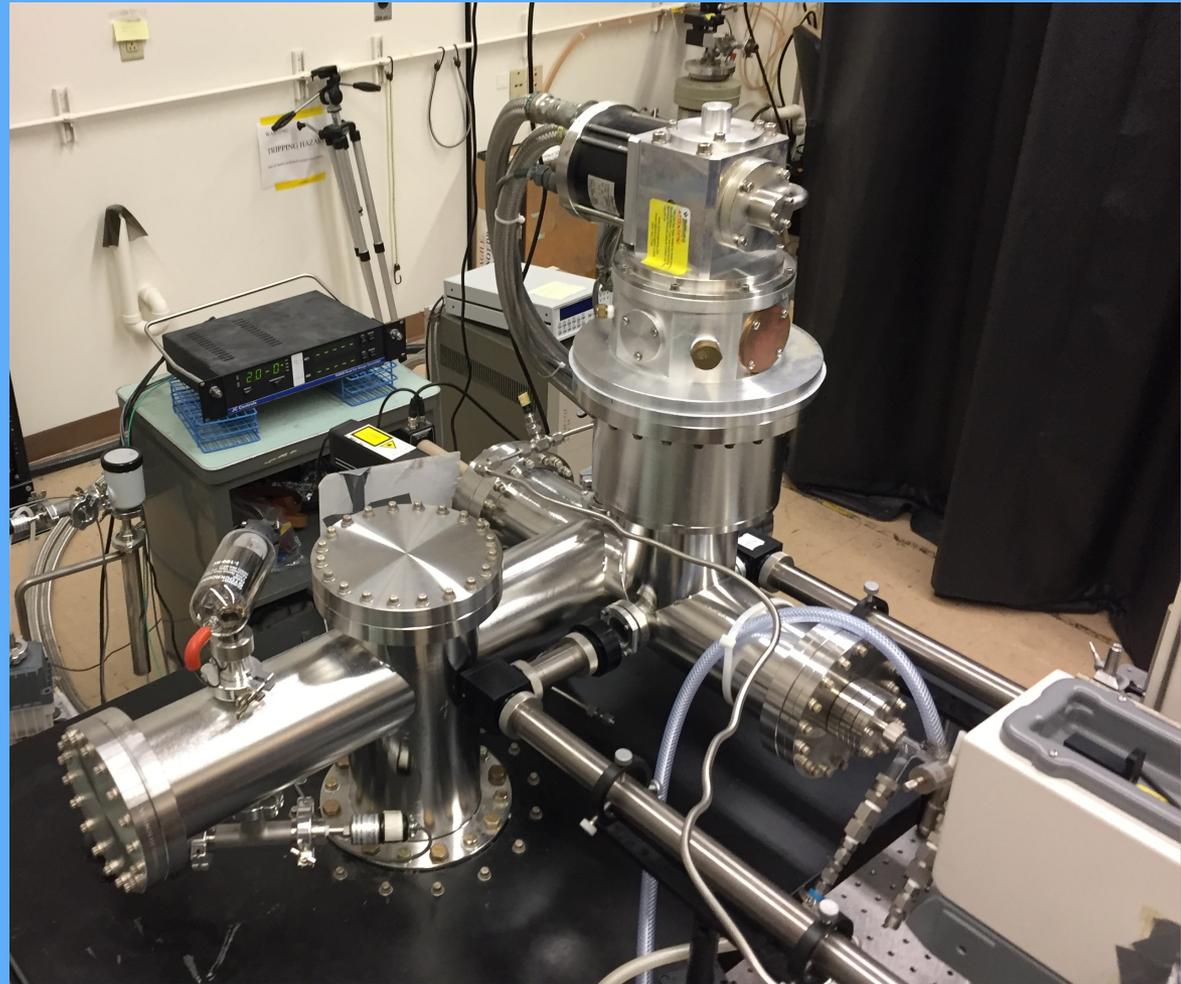
Diffusion-pumped vacuum chamber (10^{-8} torr pressure)

Rotatable, high cooling capacity cryogenic stage for substrate temperatures of 5K or less (can condense solid neon ice)

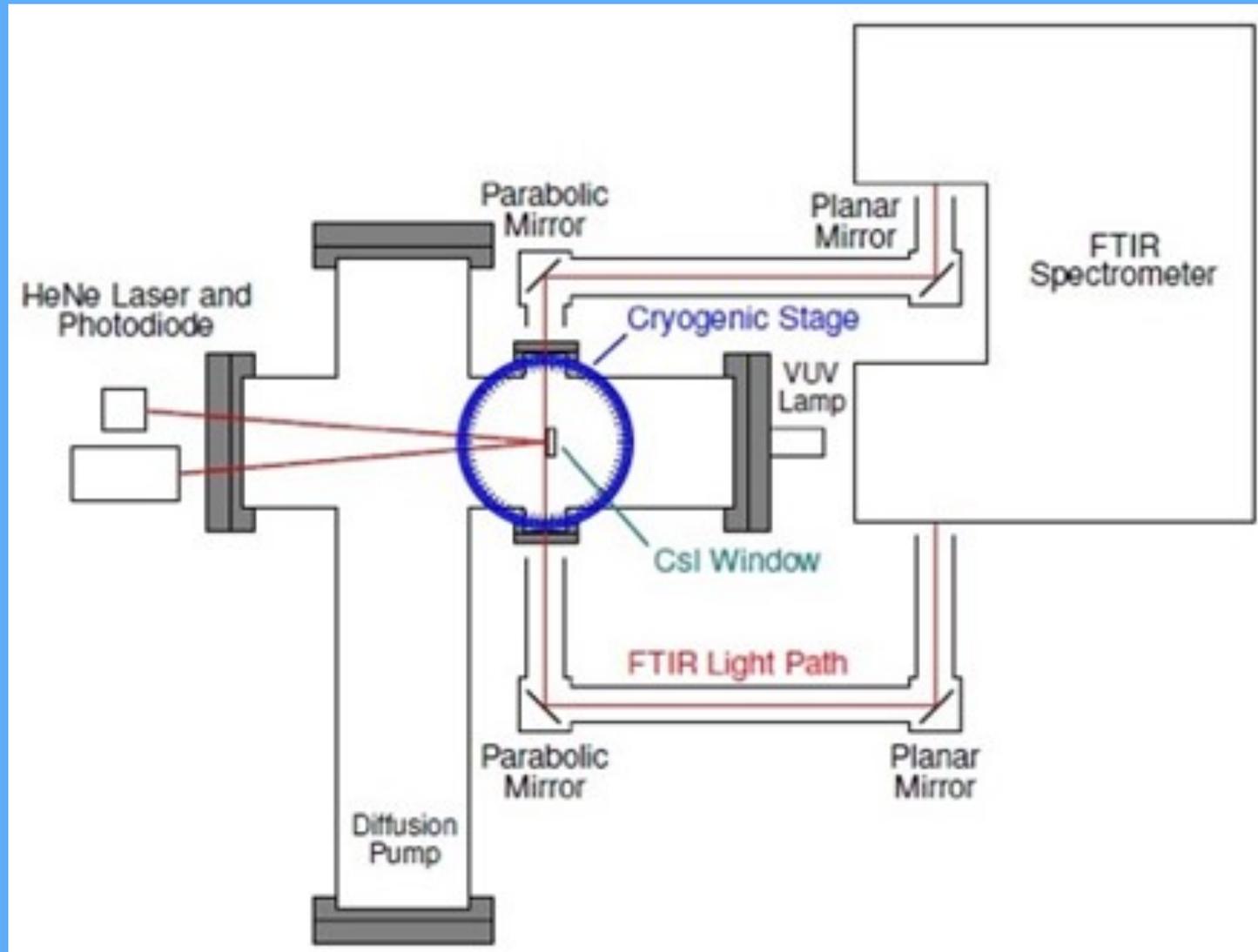
FTIR spectrometer for NIR to MIR transmission measurements ($14,500\text{ cm}^{-1}$ to 450 cm^{-1} effective wavenumber range)

Flowing-hydrogen VUV lamp

HeNe laser/photodiode for measuring reflected HeNe power



MIOC Facility Schematic Diagram



Matrix Isolation Spectroscopy

Matrix Isolation Spectroscopy of PAH Molecules

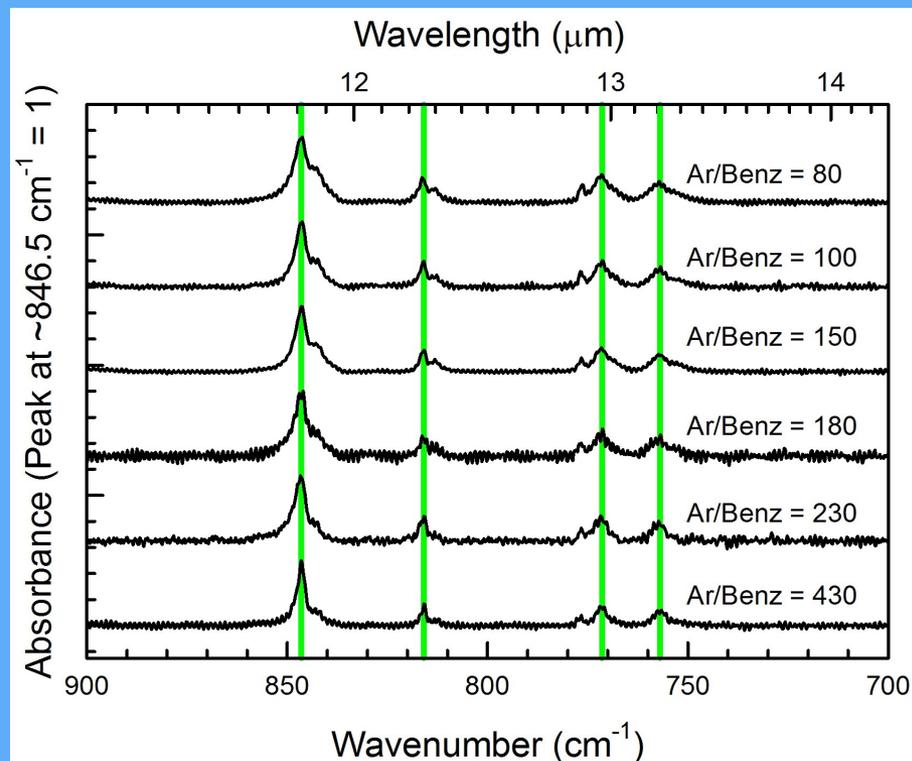
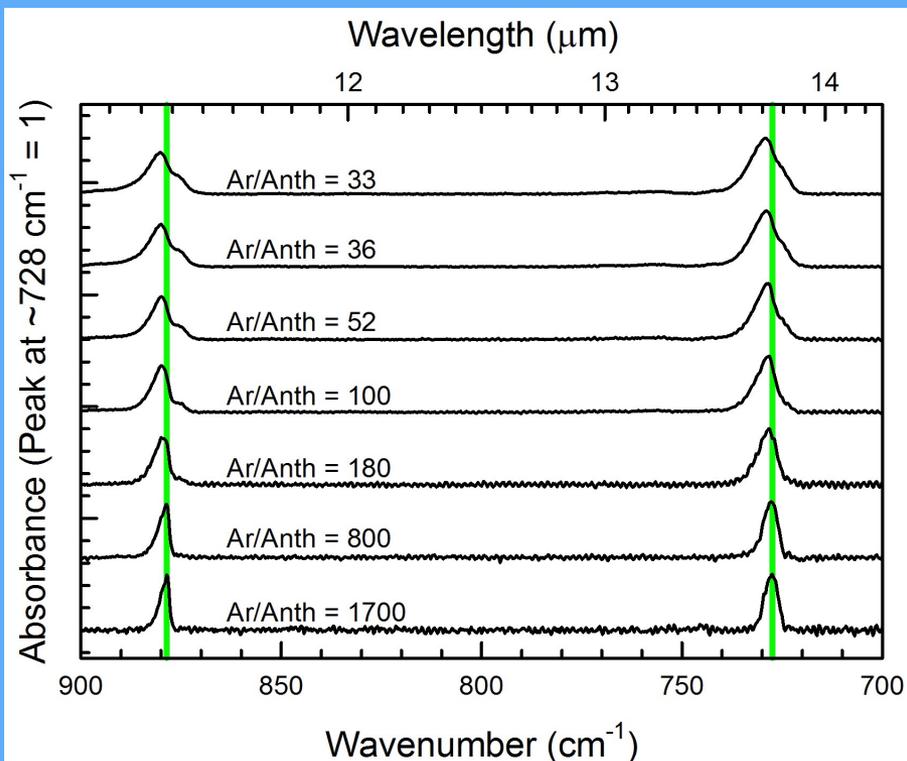
One experimental interest is spectroscopy of polycyclic aromatic hydrocarbons (PAHs).

Why study PAHs?

- These are molecules that are found throughout the interstellar medium but also in haze-forming atmospheres of bodies such as Jupiter and Titan.
- The interstellar aromatic infrared emission bands (AIBs) believed to originate in PAH molecules are seen throughout the Galaxy and in other galaxies as well.
- Van der Waals clusters of PAH molecules are also of interest because their contribution to the AIBs is unknown.
- In particular, the clusters of PAH molecules might contribute to broad emission “plateaus” that seem to underly the AIBs.
- Matrix isolation spectroscopy gives us a way of investigating the IR spectroscopy of PAH clusters without using an expensive gas-phase experimental measurement.

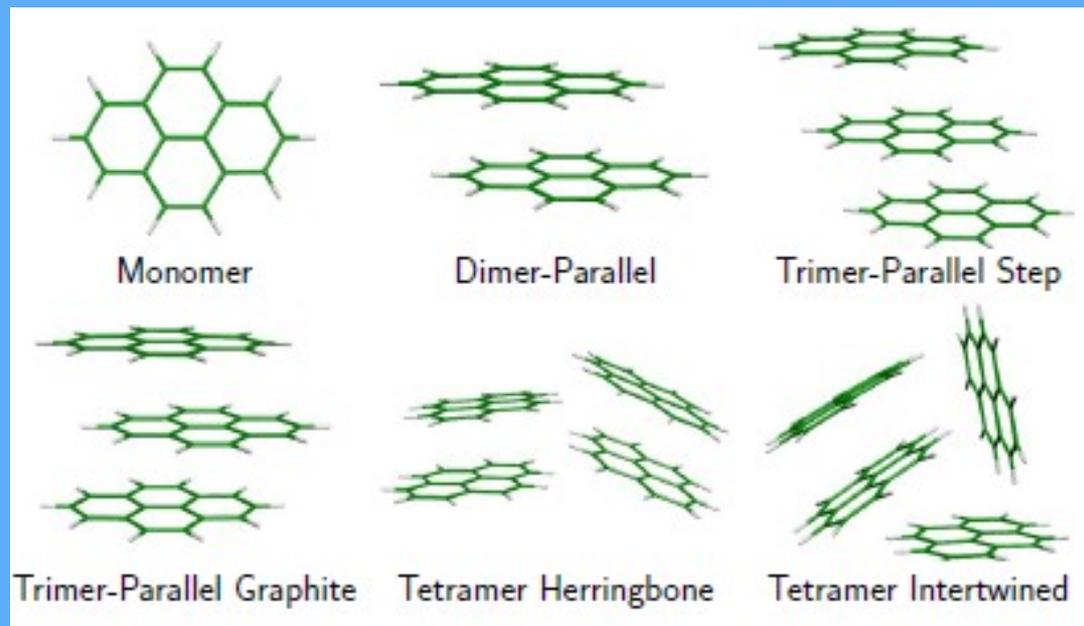
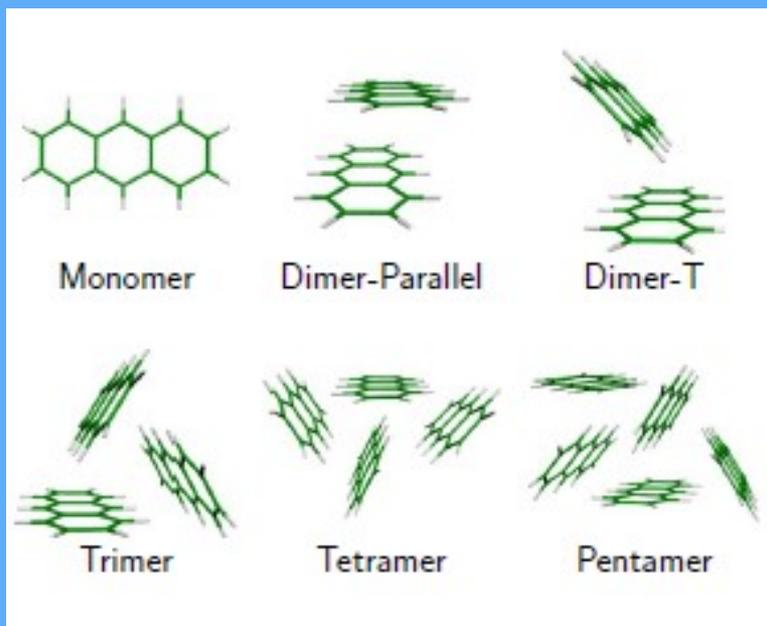
Two Patterns in the C–H out-of-plane bending region

We generally see two patterns of spectral features due to clustering in the C–H out-of-plane bending region. For linear (naphthalene, anthracene) or bent-linear (phenanthrene, chrysene), the strong bands tend to blueshift with increasing concentration of PAH in the matrix. For compact molecules (pyrene, benzo[ghi]perylene, coronene, hexabenzocoronene), the strong bands tend to develop a redshifted component.



Two Patterns in the C–H out-of-plane bending region

Theoretical spectra for homogenous PAH clusters predict that T-oriented clusters should have strong C–H out-of-plane bending modes that are blueshifted relative to the monomer band position while parallel-oriented clusters should have strong C–H out-of-plane bending modes that are redshifted relative to the monomer bands.



The “Periodic Table” of Polycyclic Aromatic Hydrocarbons

$d_s = \text{number of rings minus } N_{ic} \text{ minus } 2$

		0	1	2	3
N _{ic} = number of internal carbon atoms	0	Naphthalene (C ₁₀ H ₈)	Anthracene Phenanthrene (C ₁₄ H ₁₀)	Chrysene (C ₁₈ H ₁₂)	C ₂₂ H ₁₄
	2	Pyrene (C ₁₆ H ₁₀)	Perylene (C ₂₀ H ₁₂)	C ₂₄ H ₁₄	C ₂₈ H ₁₆
	4	Benzo[g,h,i]perylene (C ₂₂ H ₁₂)	C ₂₆ H ₁₄	C ₃₀ H ₁₆	C ₃₄ H ₁₈
	6	C ₂₈ H ₁₄	C ₃₂ H ₁₆	C ₃₆ H ₁₈	C ₄₀ H ₂₀

Full table originated in Dias, J. R. 1985, Acc. Chem. Res., 18, 241

Conclusions

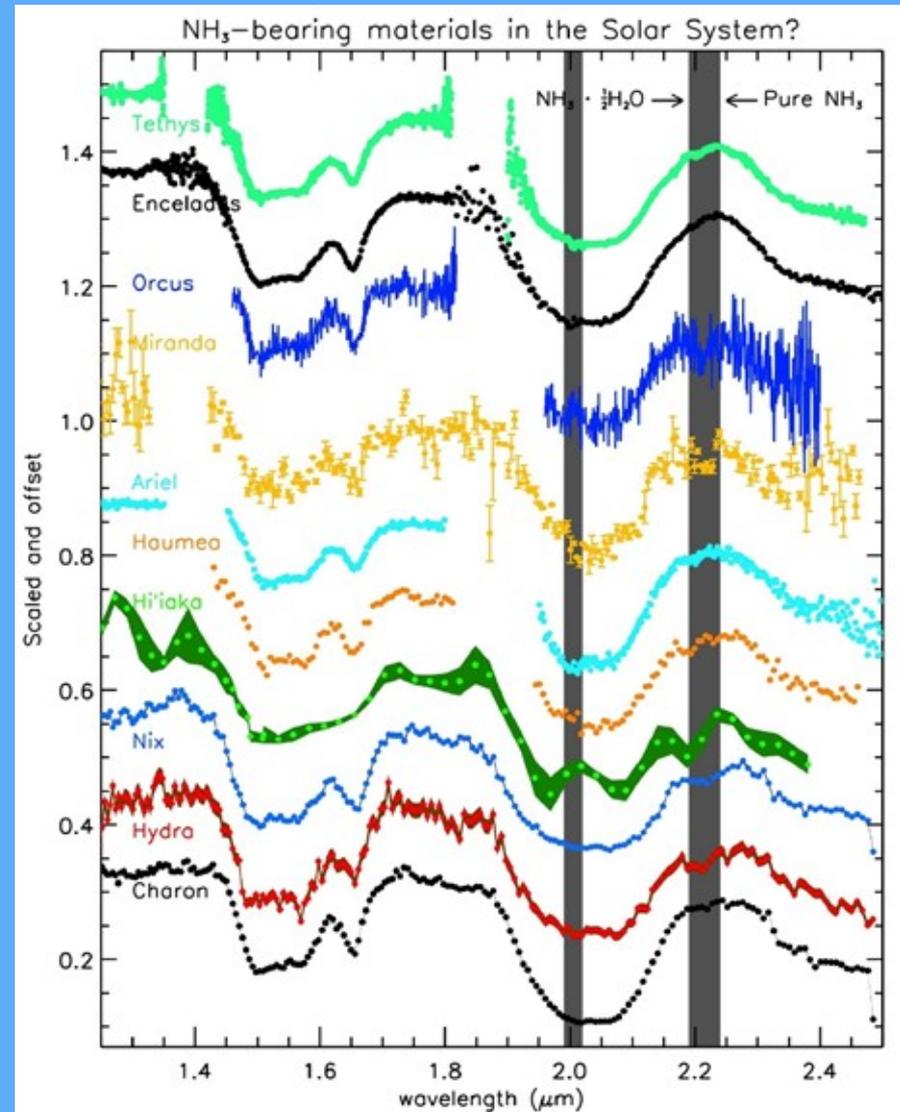
- The 11.2 μm band is a diagnostic of the cluster structures.
- The PAH molecules that are found in the interstellar medium are believed to be much larger than the ones typically studied in the lab. Assuming that compact PAH structures are favored, a redshifted feature appearing in the interstellar 11.2 μm would be expected.
- The degree of redshift due to PAH clustering would seem to be too small ($\sim 4 \text{ cm}^{-1}$) to explain broad ($100\text{--}200 \text{ cm}^{-1}$) emission plateaus.
- However, this degree of redshift is consistent with the hypothesis that PAH clusters are **evaporating very small grains** contributing to the AIBs.

Optical Constants of Ices

Ammonia Ice in the Outer Solar System

A 2.21 μm band found throughout the outer solar system is believed to be due to ammonia. It is not entirely clear whether this is due to ammonia, ammonia hydrates, or ammonium compounds of some kind.

The original goal of this optical constants research is to provide optical constants of ammonia and ammonia/water mixtures in order to better understand the 2.21 μm band.



Source: Cook, J. C., Dalle Ore, C. M., Protopapa, S., et al. 2018, Icarus, 315, 30

Why is ammonia important in the outer Solar System?

- Space environments are likely to destroy ammonia on fast time scales, so surface ammonia implies that some kind of resurfacing process is taking place (Dalle Ore et al. 2018).
- Cryovolcanism due to sub-surface reservoirs of $\text{H}_2\text{O}/\text{NH}_3$ is one obvious possibility (for example, Cruikshank et al. 2019).
- There might be other possibilities, such as ammonia diffusion from below the surface, other mechanisms for revealing subsurface ammonia, or perhaps ammonia is reacting to form compounds with a greater lifetime near the surface.
- Reduced nitrogen is also important in origin of life scenarios (remember that nitrogen fixation to produce fertilizers through the Haber-Bosch process is a major driver of human population growth).

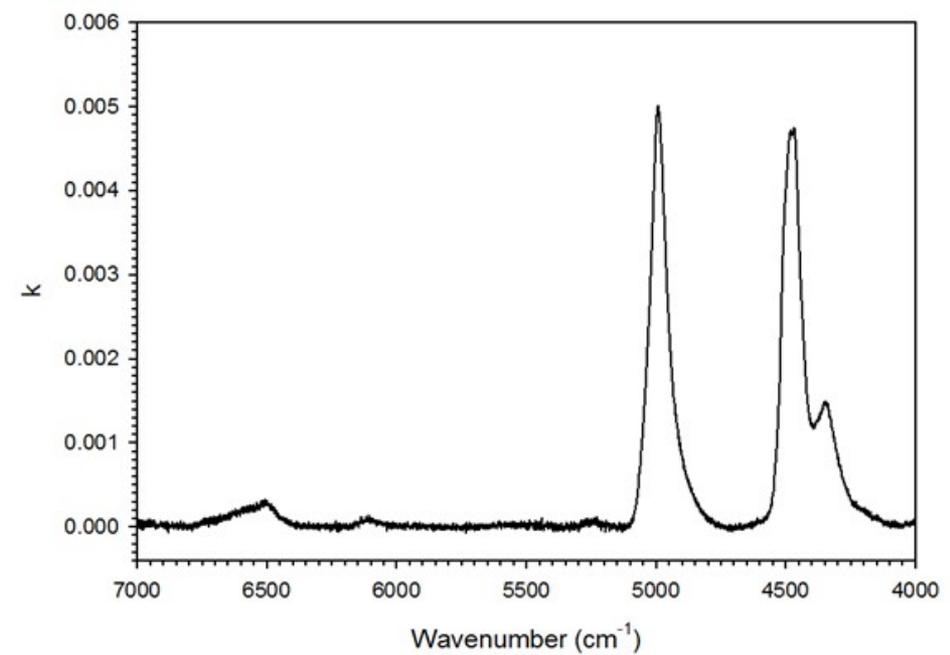
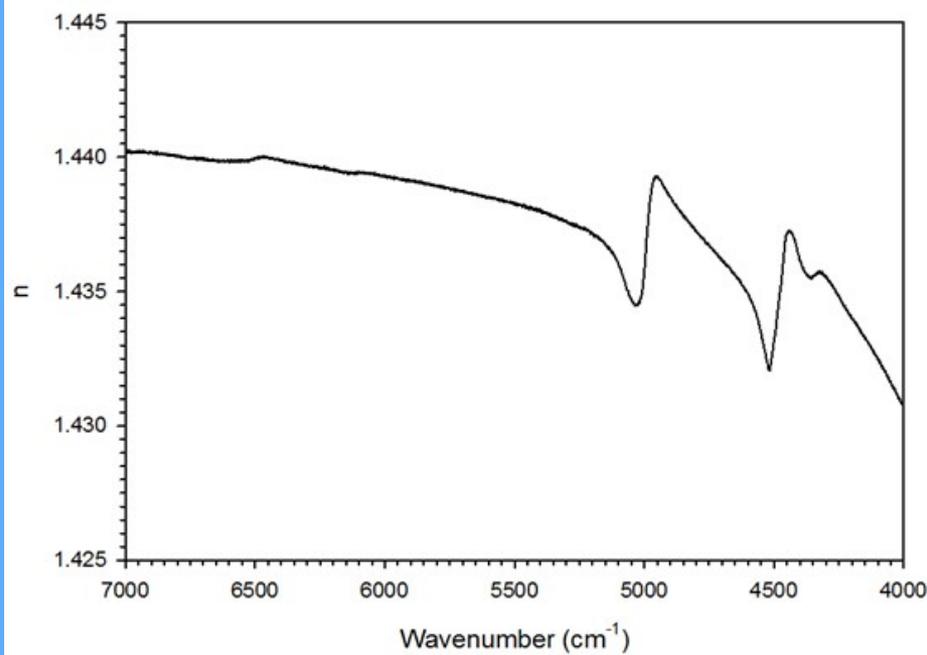
Optical Constants Strategy

1. The first step is depositing the ammonia ice and making the IR transmission measurements.
2. The second step is estimating the ice thickness. Since the ammonia ice index of refraction in the transparent optical region is known, the ice thickness can be determined from the interference fringes in the IR transmission spectrum. Interference fringes in the HeNe laser reflected power can also be used to estimate this.
3. A model of the deposited ice is required. **This needs to take into account ice deposited onto the reverse side of the substrate due to molecular effusion through the vacuum chamber.**
4. Optical depths of the IR bands and the ice thickness are used to calculate the extinction coefficient k .
5. The extinction coefficient k is used to calculate the index of refraction n using the Kramers-Kronig relation:

$$n(\nu) = n_0 + \frac{2}{\pi} \mathbf{P} \int_{\nu_1}^{\nu_2} \frac{\nu' k(\nu')}{\nu'^2 - \nu^2} d\nu'$$

A Python script automating the calculations uses an iterative procedure to refine final values of the optical constants.

Optical Constants of Amorphous Ammonia at 40K



- “Best so far” optical constants in the *New Horizons* observation range for amorphous ammonia deposited at 40 K
- Very thick (10+ μm total thickness) ice layers are required to see extremely tiny bands at 1.640 μm and 1.535 μm

Perspectives

- Matrix isolation spectroscopy of PAH clusters and associated theoretical work is in accord with the understanding that PAH clusters are evaporating very small grains in the interstellar medium.
- Optical constants determinations for ammonia/water mixtures are in progress.
- Future directions are to work with larger PAH molecules and ionized PAHs and to expand optical constants measurements and capabilities
- Experimental improvements to better measure the thickness of deposited ices are also in progress.

Acknowledgements

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