Chapter 3. Infrared Reflectance Spectra of Tholins at Cryogenic Temperatures

3.1. Introduction

Infrared spectroscopy is one of the cornerstone techniques for molecular structure determination. Because of the relation between infrared absorption and structure, the infrared is a preferred region for use in remote sensing applications, in order to acquire compositional information on the surfaces of astronomical bodies. Prior to remote sensing, though, careful laboratory work is required in order for the results to be interpretable. Remote detection of solar system bodies is necessarily a reflectance technique in the near and mid-infrared, and so for laboratory studies to be relevant to remote sensing applications, spectra should be taken in the reflectance mode. It is also important to obtain comparison spectra at a temperature as close as possible to that of the body being studied, since infrared spectra may change as a function of temperature.

Infrared spectra of tholins are useful not just as a means of broadly characterizing the material. They also serve as a proxy for organic material on many Solar System bodies, in addition to being the closest available analog to Titan atmospheric aerosols. The infrared spectral features of tholins have been used to model the reflectance spectrum of asteroids (Roush and Dalton, 2004), and explain absorption features seen on Iapetus and the rings of Uranus (Cruikshank*, et al.*, 1991). While most workers obtain mid-infrared spectra of their tholins as a matter of course (Khare*, et al.*, 2002; Sarker*, et al.*, 2003), few engage in a detailed examination and assignment of the spectra, and even fewer studies in the near infrared have been published. Imanaka et al. (Imanaka*, et al.*, 2004) made a detailed study of the variation in the mid-infrared spectrum of tholins as a function of pressure in the discharge reactor, and thoroughly studied the complex nitrile band. Only two papers containing the near-infrared spectrum of tholins have been published. Cruikshank (Cruikshank*, et al.*, 1991) published spectra of the near- and mid-infrared spectra of tholins, with a special emphasis on the first nitrile overtone band. Roush and Dalton (Roush and Dalton, 2004) have also published a near-infrared spectrum, using a "hydrated" tholin sample to examine the effect of added water on the spectrum. A near-infrared transmittance spectrum has also been published (Coll*, et al.*, 2001), but no interpretation of the features is offered.

In order to assist future studies of the surface of Titan, we have obtained the near and mid-IR reflectance spectra of tholins at cryogenic temperatures. A number of strong features are seen in the near-IR, resulting from overtone bands of nitriles, methyl and methylene groups. No significant temperature dependence is seen. The spectra are consistent with previously published work.

3.2. Experimental

Tholin samples were produced by Mark Smith at the University of Arizona, using a plasma discharge reactor, the details of which are given elsewhere (Sarker*, et al.*, 2003). The gas mixture used was 2% CH_4 in nitrogen, at a pressure of approximately 10^2 bar. The reactor was not cooled, and so remained at room temperature. Tholin was recovered by scraping from the reactor walls in a dry, oxygen-free glove box, and stored in dry, oxygen-free environment until needed. Polyacrylonitrile was purchased from Aldrich and used as received.

For these experiments, it was necessary to use tholins produced at room temperature, even though this is not representative of the temperature in the upper reaches of Titan's atmosphere (195 K) where photochemistry occurs. Tholins produced at low temperatures are sticky and difficult to handle, while room temperature tholins are a flaky, harder material that can easily be powdered. A powdery material was necessary to load into the sample cell for these experiments, and so room temperature tholins were chosen. We do not expect that the infrared reflectance spectra will be greatly influenced by the temperature at which the tholins are produced, since mass spectral data of room temperature and 195 K tholins are similar.

The sample was mounted in a small aluminum cup, approximately 2 cm in diameter and 0.5 cm deep, fitted with a sapphire window sealed to the cup with a gasket. The sample was loaded into the cup in a nitrogen-purged glove bag. The sample cup was mounted to a liquid nitrogen cooled cryostat, and the temperature of the sample was measured with a thermocouple in close mechanical contact to the cup. The cryostat head and sample were mounted in a chamber pumped to 10^{-6} torr by a turbomechanical pump. The chamber was fitted with quartz windows for optical access, and two CaF_2 lenses were arranged within the chamber to focus the light onto the sample, and to focus the light scattered from the sample onto the detector. The geometry of the sample and detector were arranged so that diffuse reflectance, and not specular reflectance spectra were obtained. The angle between the detector and spectrometer was approximately 105°.

Spectra were acquired with an Analect Diamond-20 Fourier transform infrared spectrometer, equipped with a separate EG&G BXK-625 detector. The region from 0.5

to 5 microns was scanned. Reference spectra using a gold diffuse reflectance standard were periodically taken during each experimental run, and typically were composed of 5000 averaged scans. Spectra were taken of the tholin sample as the sample was cooled, and at room temperature. Each spectrum was made up of 1000 co-added scans.

Spectra of tholins taken in transmission mode in a KBr pellet were prepared by grinding a few milligrams tholin with dry KBr, and pelletizing with a hand press. The spectrometer used was a BioRad Excalibur FTS 3000.

3.3. Near infrared reflectance spectra of tholins

Figure 3.1 compares the spectra of tholin at room temperature (303 K) and at cryogenic temperatures (123 K), and the mid-infrared region, between 2000 and 4000 cm^{-1} is shown in an expanded form in Figure 3.2. Table 1 summarizes the band positions and their assignments. A number of features are worth noting. The mid-infrared region is dominated by nitrile and amine stretches, as expected from a polymeric CHN material like tholin. This region is compared to a spectrum obtained by transmission with the tholin prepared in a KBr pellet. The spectra are identical. The nitrile band is complex, with at least four distinct peaks. Imanaka et al. (Imanaka*, et al.*, 2004) extensively studied the infrared spectrum of tholin, and thoroughly assigned peaks in the nitrile region. The spectra obtained here are very similar to Imanaka's and we can assign peaks according to the type of CN bond as he did. The peaks are assigned as aliphatic nitriles (2241 cm^{-1}), conjugated nitriles, i.e., a nitrile on a carbon that is doubly bonded to another carbon (2174 cm^{-1}), isocyanides (2139 cm^{-1}), and ketene imines (R-C=C=N-R) and diazo compounds (2100 cm^{-1}).

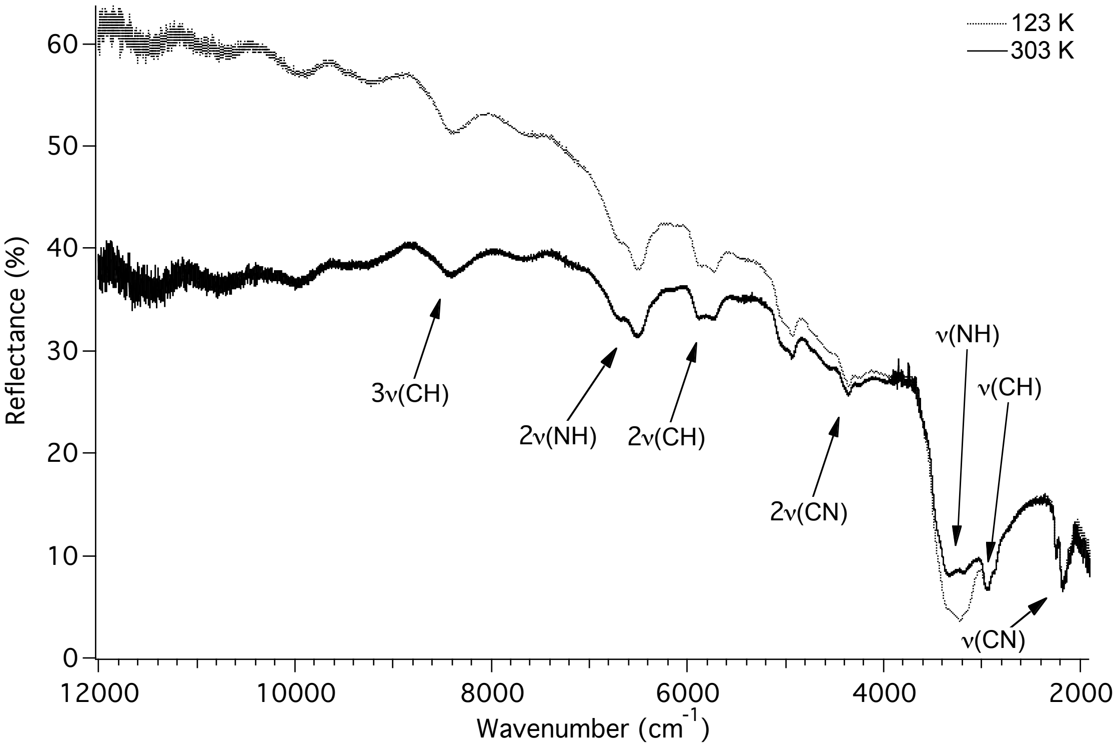

Figure 3.1. Near and mid infrared reflectance spectra of tholins at room temperature (303 K) and at 123 K.

At 10,000 cm^{-1} and above, a sinusoidal ripple in the spectrum is apparent. This is an artifact caused by a small amount of specular reflection in the signal. Between 4000 and 10,000 cm^{-1} is the near infrared region, useful to planetary science since it is amenable to remote detection. Several overtone bands of the CH, CN, and NH stretches are clearly identifiable, along with some as yet unidentified bands. The splitting in the CH bands is assigned to the methyl (-CH_3) and methylene (-CH_2) stretching modes, with the methyl stretches at higher frequencies (Hildrum*, et al.*, 1992).

We can compare the spectra shown here with those obtained by Cruikshank (Cruikshank*, et al.*, 1991). In the mid-infrared region, the nitrile fundamental is seen at

2169 cm^{-1}, but exhibits no structure. Cruikshank's spectra appear to have a lower resolution than ours, but detailed experimental procedures were not given, so we cannot be certain. A very broad peak centered at 3 μm (3333 cm^{-1}) can be assigned to NH and CH stretches. In the near-infrared, Cruikshank's spectra show the first nitrile overtone to occur at about 4545 cm^{-1}, almost 100 cm^{-1} higher in frequency than in the spectra we obtained. This is an odd finding. Since the nitrile fundamental is at 2169 cm^{-1}, its overtone should occur at slightly less than twice this frequency (due to anharmonicity), i.e., around 4338 cm^{-1}, consistent with the nitrile overtone we observe. The reason for

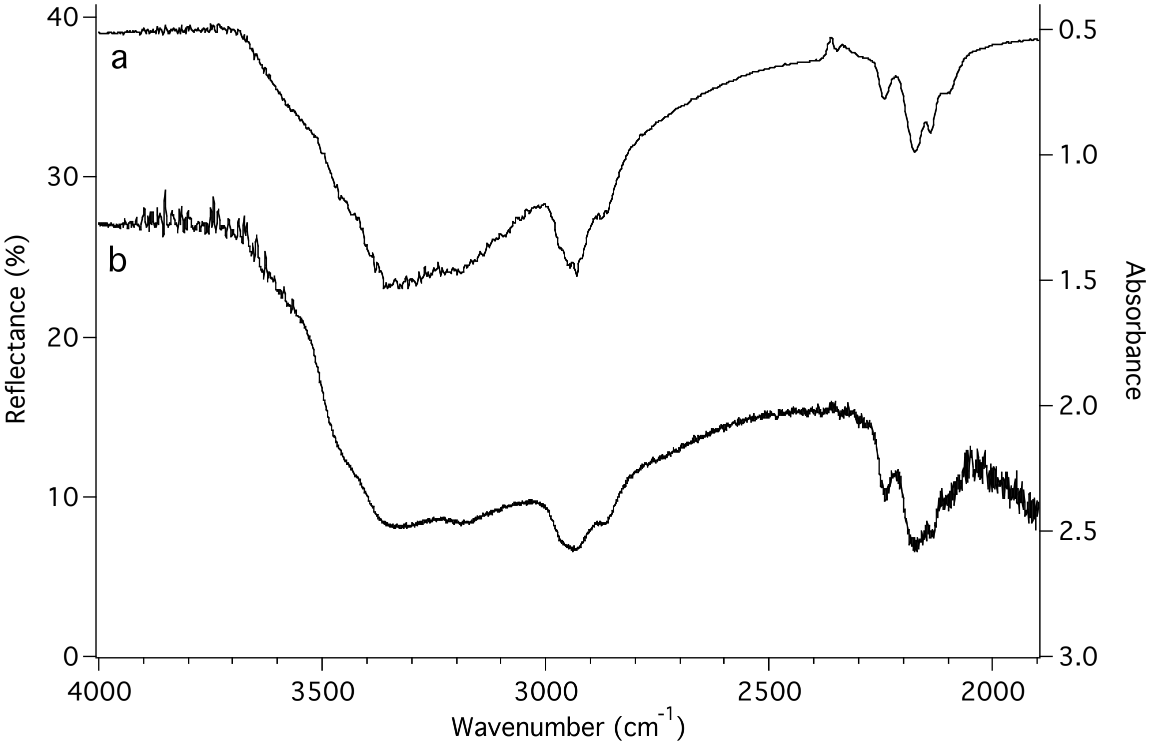

Figure 3.2. Expanded view of the mid-IR region of the reflectance spectrum of tholins (b) compared to a spectrum obtained by transmission in a KBr pellet (a).

this discrepancy is unknown. The other major features seen in our spectra are also visible in Cruikshank's spectra, although the CH overtones are far less pronounced.

Roush and Dalton (Roush and Dalton, 2004) examined the near infrared spectra of "hydrated" tholins, old material that had been exposed to atmosphere and absorbed some water vapor. Not surprisingly, the spectrum is dominated by water features. However, the first nitrile overtone is clearly visible at around 4445 cm^{-1}, and the first CH stretch overtone is at about 5880 cm^{-1}, consistent with the spectra we obtained, although the nitrile overtone frequency is a bit high.

There are two significant differences between the spectrum obtained at room temperature and the spectrum obtained at 123 K. The difference between the two spectra is shown in Figure 3.3. The broad band at 3229 cm^{-1}, corresponding to an increase in absorbance in the low temperature spectrum, is the most notable feature. This band is due to water ice (Baratta*, et al.*, 1991), which condensed from residual water in the vacuum chamber onto the cold window of the sample cup. Some smaller features, corresponding to CH overtones, are also apparent. Also, the low temperature spectrum appears to be generally brighter at shorter wavelength than the room temperature spectrum. In the current experimental set-up, the slope of the baseline at shorter wavelengths is not reproducible, and no significance should be ascribed to this feature. The IR spectrum of tholins does not appear have a large temperature dependence.

For comparison, the near IR reflectance spectrum of polyacrylonitrile is shown in Figure 3.4. Easily identifiable are the nitrile stretch (2243 cm^{-1}), the CH stretch (2943 cm^{-1}), and the first overtone of the CH stretch, 2ν(CH), (5925 cm^{-1}, 5763 cm^{-1}). The first overtone of the nitrile stretch, 2ν(CN), is visible at 4407 cm^{-1}, and a nearby peak, 4296 cm^{-1}, can be attributed to a methylene combination band, formed from the combination of the symmetric stretch and scissoring modes. The features at 3526 cm^{-1}, 3621 cm^{-1}, and 5235 cm^{-1} can be assigned to residual water adsorbed on the polyacrylonitrile sample. Since this sample was not loaded into the cell under nitrogen, but in ambient air, some adsorption of water is not unexpected.

Table 3.1 Frequencies and assignments of spectral features of tholins in the IR

Assignment	Frequency (cm^{-1})
ν(CN)	2100 2139 2174 2241
ν(CH)	2865 2940
ν(NH)	3196 3330 3461
2ν(CN)	4355
unassigned	4930
2ν(CH)	5735 5883
2ν(NH)	6511 6692
3ν(CH)	8403

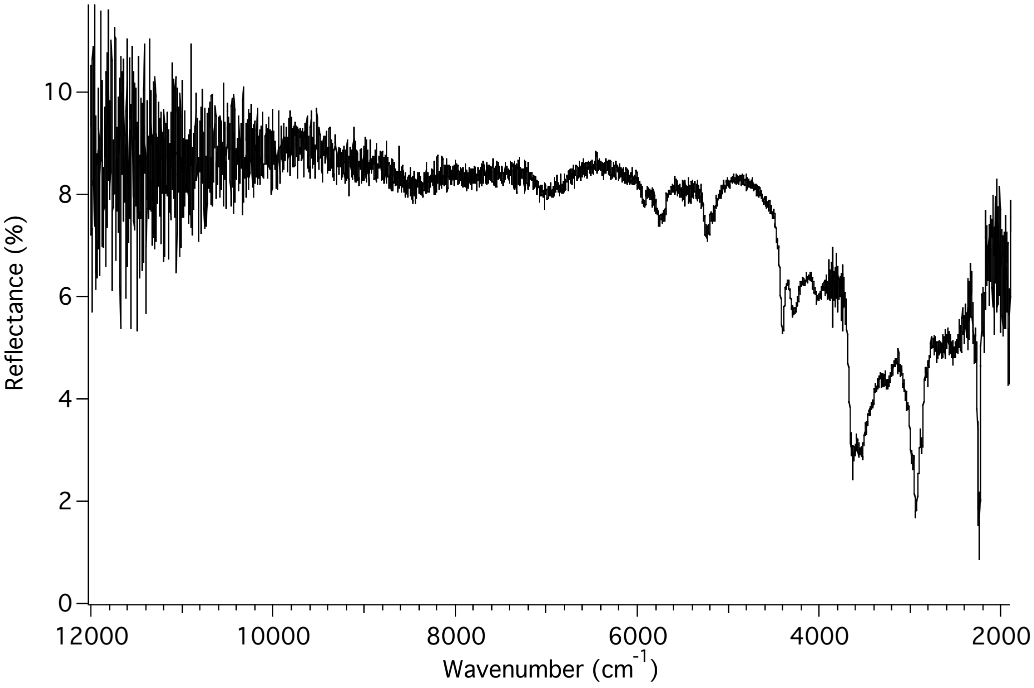

Figure 3.3. Infrared reflectance spectrum of polyacrylonitrile.

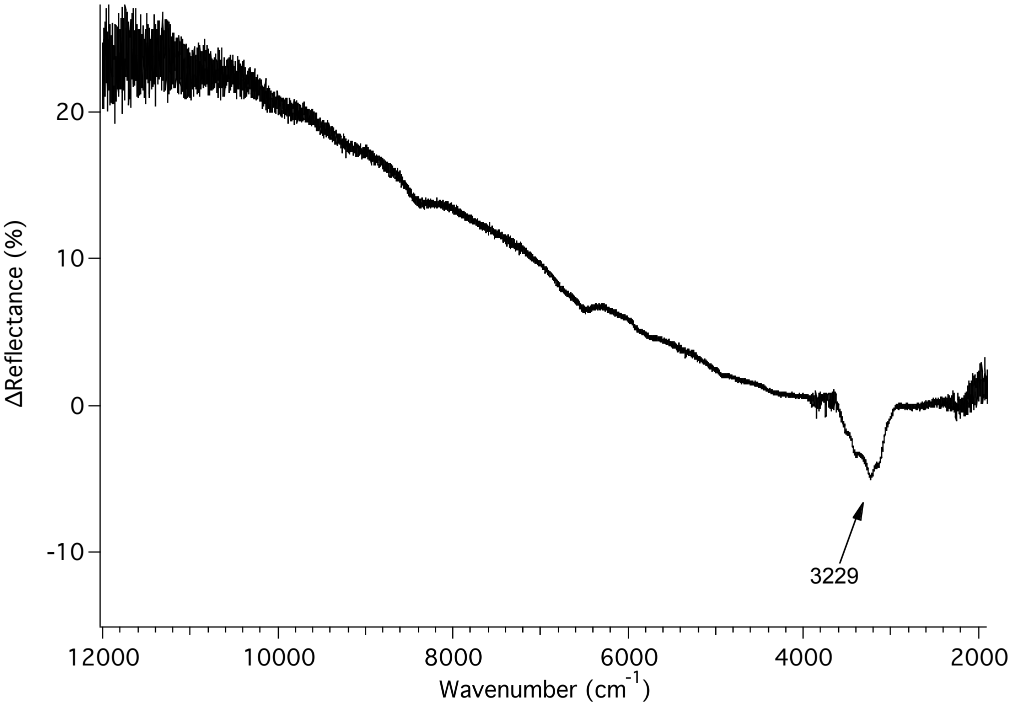

Figure 3.4. Difference between the reflectance spectrum obtained at 123 K and the spectrum obtained at 303 K.

3.4. Conclusions

The near infrared spectrum of tholins is complex, consisting of a number of overtone bands attributable to nitrile, methyl, and methylene functional groups. The mid infrared reflectance spectrum is identical to that obtained by transmission, down to approximately 2000 cm^{-1}. No temperature dependence between room temperature and 123 K is observed. The near infrared spectrum of polyacrylonitrile is an interesting comparison, and possesses a simple structure that allows easy assignment of all the spectral features.

The near infrared spectrum presented here should be useful for the modeling of the reflectance spectra of outer Solar System bodies, as well as for future studies of the surface of Titan. Further work should involve obtaining the near infrared reflectance spectrum of tholins mixed with water ice, and mixed with water-ammonia ices, which should be prevalent on the surface of Titan. Also, careful examination of the near infrared spectrum of tholins may be able to provide insight on the structure of the tholins themselves. For instance, the first CH stretch overtone can be used to determine relative concentrations of primary CH_3, secondary CH_2 and aromatic CH groups, and is more useful than the fundamental CH stretch region, since it does not overlap with the amine stretches, as the fundamental does. These experiments would require higher resolution spectra of the overtone region than those obtained here, and careful calibration experiments, but could provide additional functional group information for tholins.

3.5. References

Baratta, G. A., et al. (1991), The 3.1 Mu-M Feature in Ion-Irradiated Water Ice, *Astronomy and Astrophysics*, *252*, 421-424.

Coll, P., et al. (2001), Chemical and optical behaviour of tholins, laboratory analogues of Titan aerosols, *Space Life Sciences: Life in the Solar System: Prebiotic Chemistry, Chirality and Space Biology*, *27*, 289-297.

Cruikshank, D. P., et al. (1991), Solid Cn Bearing Material on Outer Solar-System Bodies, *Icarus*, *94*, 345-353.

Hildrum, K. I., et al., eds. (1992), *Near Infra-Red Spectroscopy*, Ellis Horwood, New York.

Imanaka, H., et al. (2004), Laboratory experiments of Titan tholin formed in cold plasma at various pressures: implications for nitrogen-containing polycyclic aromatic compounds in Titan haze, *Icarus*, *168*, 344-366.

Khare, B. N., et al. (2002), Analysis of the time-dependent chemical evolution of Titan haze tholin, *Icarus*, *160*, 172-182.

Roush, T. L., and J. B. Dalton (2004), Reflectance spectra of hydrated Titan tholins at cryogenic temperatures and implications for compositional interpretation of red objects in the outer Solar System, *Icarus*, *168*, 158-162.

Sarker, N., et al. (2003), Titan aerosol analogues: Analysis of the nonvolatile tholins, *Astrobiology*, *3*, 719-726.