SMC-TR-06-06

AEROSPACE REPORT NO.
TR-2006(8570)-1

The Infrared Spectral Signature of Water Ice in the Vacuum Cryogenic AI&T Environment

31 December 2005

20060309 072

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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. FA8802-04-C-0001 with the Space and Missile Systems Center, 2430 E. El Segundo Blvd., Los Angeles Air Force Base, CA 90245. It was reviewed and approved for The Aerospace Corporation by J. A. Hackwell, Principal Director, Space Science Applications Laboratory. Michael Zambrana was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Michael Zambrana

Michael Zambrana
SMC/AXE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE (*DD-MM-YYYY*) 31-12-2005

2. REPORT TYPE

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

The Infrared Spectral Signature of Water Ice in the Vacuum Cryogenic AI&T Enviuronment

5a. CONTRACT NUMBER FA8802-04-C-0001

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

D. K. Lynch

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

The Aerospace Corporation
Laboratory Operations
El Segundo, CA 90245-4691

8. PERFORMING ORGANIZATION REPORT NUMBER

TR-2006(8570)-1

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Space and Missile Systems Center
Air Force Space Command
2450 E. El Segundo Blvd.
Los Angeles Air Force Base, CA 90245

10. SPONSOR/MONITOR'S ACRONYM(S)

SMC

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

SMC-TR-06-06

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

In a thermal vacuum testing of spacecraft sensors, water ice can condense on optical surfaces. The most common source of water vapor is out-gassing from multilayer insulation (MLI). In the infrared, such ice films can significantly absorb radiation leading to lower performance of the sensor system. If chamber ice is heated, it normally sublimes (vaporizes directly from the solid state) at a temperature of around 150K. In an earlier paper aimed at the assembly, integration and test (AI&T) environment,[1] we outlined the behavior of ice using "warm ice," i.e., ice not far below its melting temperature. In this report, we extend our previous report to include cryogenic ice deposits by presenting low-temperature ice transmission spectra in the 2–14 μm region as a function of thickness and temperature.

15. SUBJECT TERMS

Ice, Infrared, Cryogenic, Vacuum, AI&T sensor

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Dave Lynch
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED		19	19b. TELEPHONE NUMBER *(include area code)* (310)336-6686

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

Acknowledgments

We thank Ray W. Russell, James D. Barrie, and Stephan Mazuk for useful discussions about ice's optical properties.

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1. Introduction

Ice is the most well-studied mineral.[2–5] The water molecule by itself is capable of many electronic, vibrational, and rotational absorption features. In liquid and solid form, the rotational transitions are modified by interactions with nearby molecules, and the vibrational bands are shifted in wavelength. In solid form, ice shows additional structure due to lattice effects in all crystalline and amorphous states. All transitions are functions of temperature.

Figure 1 shows the absorption coefficient (defined in Section 2) of ice and water near water's freezing temperature (273K) from the ultraviolet to the far infrared.[6,7] Both are generally similar because they are dominated by electronic and vibrational absorptions of the water molecule itself. Only longward of about 8 μm do the two curves differ significantly. These differences are the result of solid-state lattice vibrations in ice that do not occur in water. Water and ice are most transparent in the visible portion of the spectrum, where the absorption coefficients reach a minimum around 0.45 μm. This is the region where so much attention has been focused on "blue-green" lasers for underwater communication.

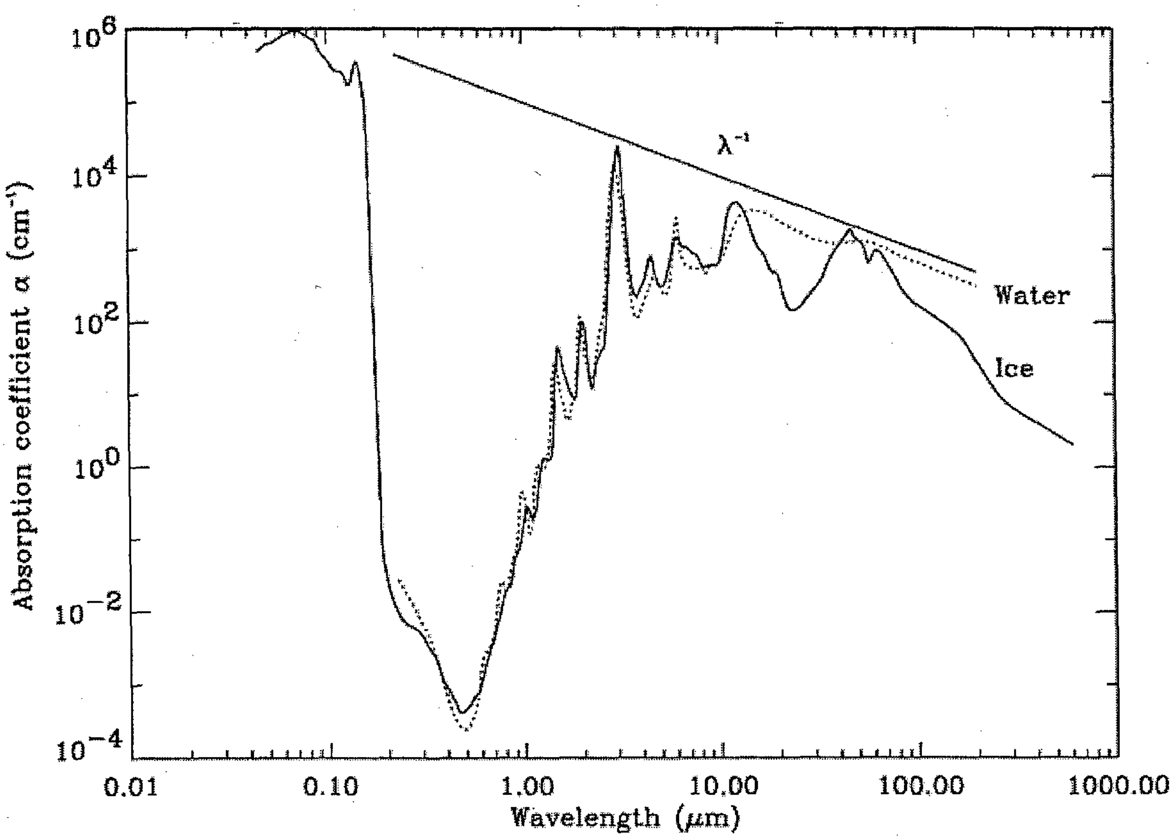

Figure1. Absorption coefficient $\alpha(\lambda)$ of water and ice from the ultraviolet to the far IR. Ice data are from Warren,[6] and water data are from Hale and Querry.[7]

At temperatures below about 137K in a vacuum, ice's lattice structure is amorphous. Between 137 and 197K, ice is cubic, and above 197K it is hexagonal. Any feature that originates in the water molecule (like the OH stretch at 3.16 μm) will also occur in the spectrum of ice, though there will be minor differences as a result of lattice interactions. Any feature that originates within the ice lattice itself (like the 13- and 45-μm features) will be absent from water's spectrum.

In general, the colder the ice, the lower the absorption coefficient. Figure 2 shows the absorption coefficients for warm[6] and cold ice[8] (250 and 80K, respectively). Although the overall structures are the same, there are significant differences in the spectra, and, in all cases, cold ice is less absorbing than warm ice.

In the 2–20 μm range, the spectra are dominated by the four features, and no others are possible for pure ice. The large, narrow peak at 3.16 μm is due to O-H-O symmetric stretch vibration (ν_1). The 6.1-μm feature is due to the ν_2 bending mode, and the feature at 4.6 μm is a combination of ν_2 and a weak libration mode. The broad peak centered at 13 μm is a lattice absorption. There are additional weak absorption features shortward of 2.5 μm (Figure 1), but they normally are not important in the AI&T environment.

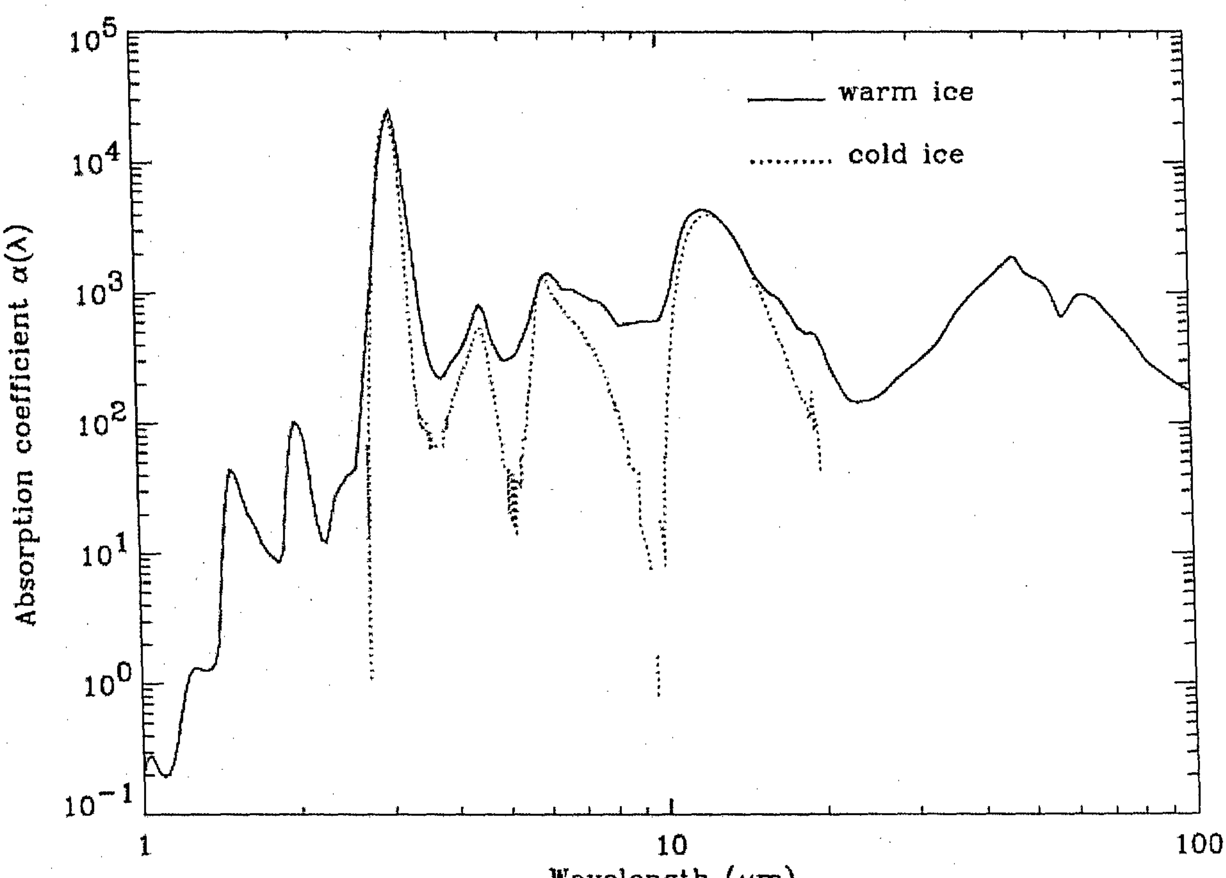

Figure 2. Absorption coefficient $\alpha(\lambda)$ of warm (250K)[6] and cold (80K)[8] ice based on tabulations of Warren[6] and Hudgins et al.[8]

2. Transmission, Absorption Coefficient, and Thickness

To compute transmission, t, the absorption coefficient, $\alpha(\lambda)$, and the thickness, D, must be known:

$$t = \exp(-D\alpha) = \exp(-\tau) \quad (1)$$

where the product $D\alpha$ is called the optical depth or optical thickness τ. D has units of distance, and α has units of 1/distance, typically cm and cm^{-1}, respectively. Clearly, τ is unitless. Here, as in all subsequent calculations, we will assume normal incidence and ignore the effects of reflections from the free surfaces of the ice layer (a few percent according to Fresnel's equations). The subject of surface reflections is discussed in Section 8.

The transmitted irradiance I (colloquially "brightness," "intensity," "power," etc.) is given by

$$I = Io\, t = Io \exp(-D\alpha) = Io \exp(-\tau) \quad (2)$$

where Io is the incident irradiance. According to Lambert's Law, the absorption coefficient is related to the imaginary part of the complex index of refraction, $N = n + ik$, by

$$\alpha = 4\pi k/\lambda \quad (3)$$

The presence of λ in Eq. (3) means that $\alpha(\lambda)$ decreases with increasing wavelength, other things being equal. Note that water's absorption coefficient (Figure 1) drops off roughly as $1/\lambda$ longward of about 10 μm as Eq. (3) suggests because there are no discrete absorptions in water at longer wavelengths. Note that Eqs. (1), (2), and (3) are generic,and apply to virtually any solid or liquid.

Equation (1) can be used in a number of ways. If $\alpha(\lambda)$ is known—say from the optical constants—then D can be determined from the transmission. Similarly, the transmission can be computed for any given thickness. If D and t are known, $\alpha(\lambda)$ can be retrieved and used for future predictions.

The quantity $1/\alpha$ is called the *skin depth, $\mathcal{D}$,* and corresponds to an optical depth, τ, of unity. To quickly estimate how thick a layer of ice is necessary to produce significant absorption, one need only consider the skin depth (Figure 3). For example, in the blue-green region, an optical depth of 1 occurs in a slab that is about 3300 cm thick. At the 3.1-μm absorption peak, however, only about 0.3 μm of material is needed.

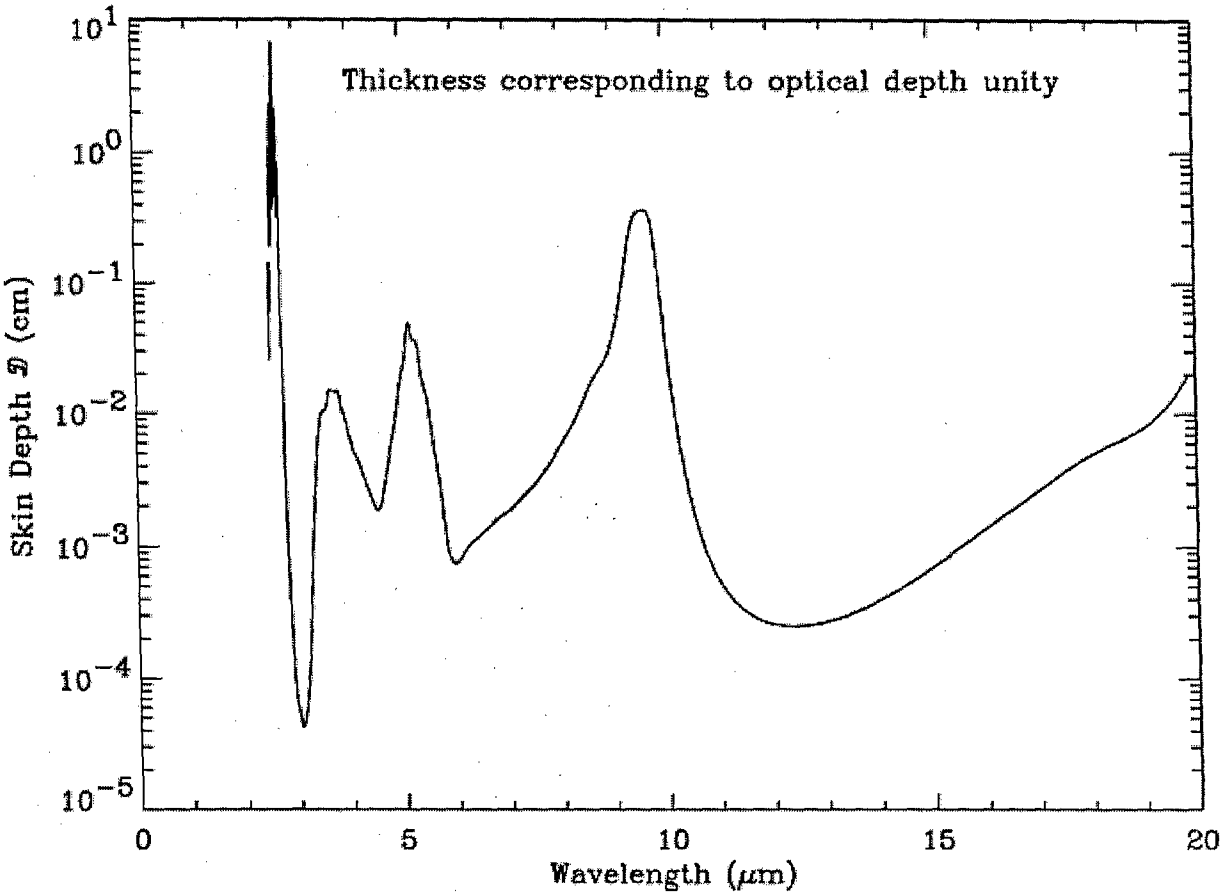

Figure 3. Skin Depth $\mathcal{D}$ ($1/\alpha$) of cryogenic(80K) ice based on tabulations of Hudgins et al.[8] The skin depth corresponds to an absorption optical depth of unity.

3. Determining the Absorption Coefficient, $\alpha(\lambda)$

The absorption coefficient is usually computed from the known optical constants (Eq. 3), or the measured transmission (Eq. 1).

The term "optical constants" refers to the spectrum of complex indices of refraction $N(\lambda) = n(\lambda) + ik(\lambda)$, though it is sometimes applied to (and compiled as) the complex dielectric function $\varepsilon = \varepsilon' + i\varepsilon''$. The two quantities are related:

$$(n + ik)^2 = \varepsilon' + i\varepsilon'', \tag{4}$$

which is easily solved for

$$\varepsilon' = n^2 - k^2 \quad \text{and} \quad \varepsilon'' = 2nk \tag{5}$$

or equivalently

$$n = (1/\sqrt{2})\,[(\varepsilon'^2 + \varepsilon''^2)^{1/2} + \varepsilon']^{1/2} \quad \& \quad k = (1/\sqrt{2})\,[(\varepsilon'^2 + \varepsilon''^2)^{1/2} - \varepsilon']^{1/2} \tag{6}$$

Broadly speaking, n controls reflection, refraction, and scattering, and k controls absorption.

In the discussion that follows, we will concentrate on ice's spectrum in the 1–20 μm region where many space sensors operate.

4. Cryogenic Ice

Ice formed at extremely low temperatures is usually amorphous and probably does not occur naturally on Earth. The coldest temperatures on Earth occur at the summer polar mesopause (~150K), where rare ice clouds called noctilucent clouds form.[9] The clouds are thought to be composed of hexagonal ice or mixtures of water and sulfuric acid. Amorphous ice may have formed naturally in the outer solar system or in the cores of dense molecular clouds in space. Naturally occurring ice clouds such as cirrus are composed of hexagonal ice.[10]

Cryogenic ice is amorphous,[8,11] and its absorption coefficient is temperature dependent.[8] Figure 4 shows the transmission spectrum of a 0.13-μm-thick film of ice deposited at 10K in a vacuum.

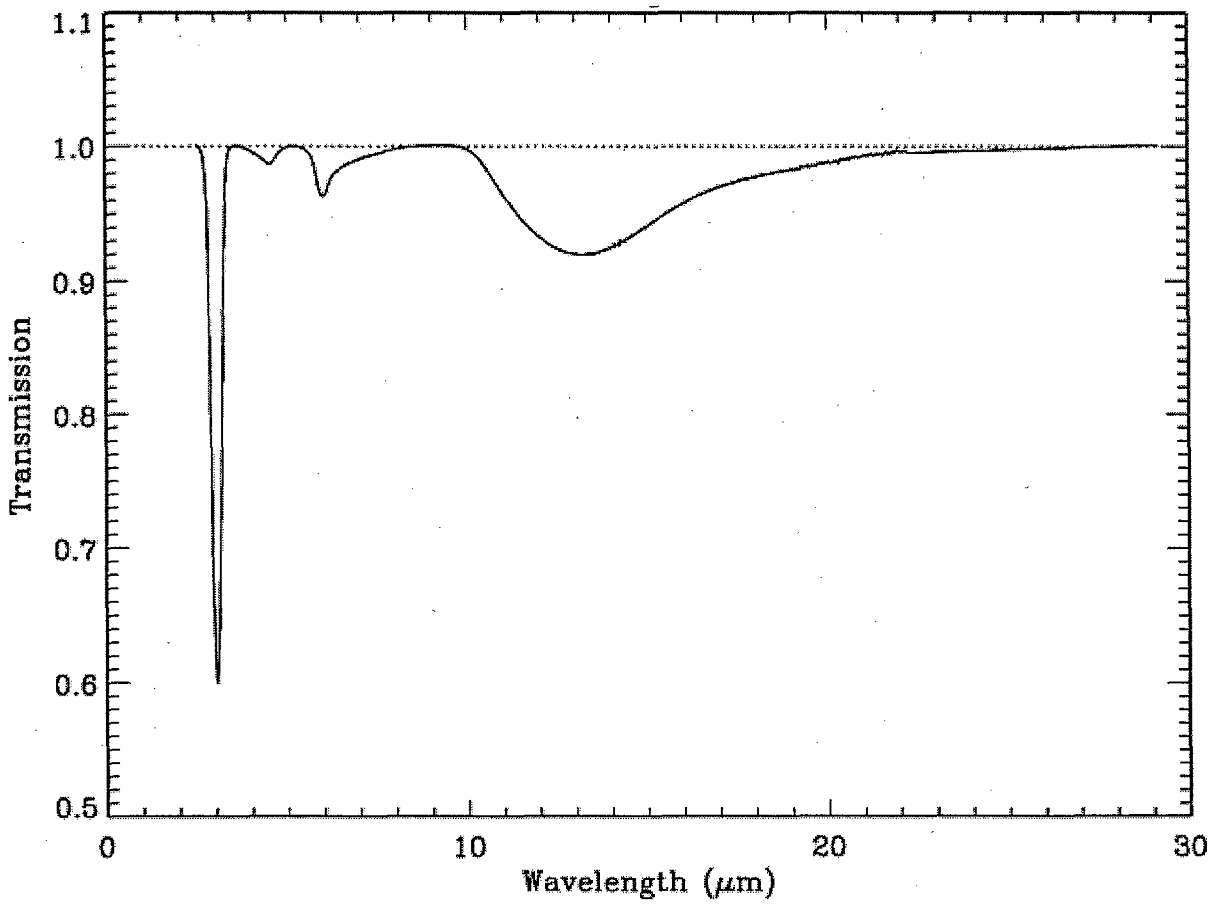

Figure 4. Transmission spectrum of a 0.13-μm-thick film of ice deposited in vacuum onto a 10K surface based on tabulations of the Jena group (www.astro.uni-jena.de).

The temperature dependence of amorphous ice's absorption characteristics have been well studied. The results generally agree; though, perhaps owing to different experimental conditions and different types of amorphous structure, there are some variations. Shortward of about 4 μm, the absorption coefficient increases with increasing temperature, typically by about 25% between 10K and 140K.

Figure 5 shows transmission spectra of 80K amorphous ice for a variety of thicknesses in the 2.5–12 μm region based on the work of Hudgins et al.[8]

Figure 6 shows the behavior of the O-H stretch band as a function of temperature based on data from Hudgins et al.[8] As the deposition temperature increases from 10K to 140K, the wavelength of peak absorption shifts from 3.02 to 3.06 μm, a change that has been documented by many groups. The absorption coefficient increases by about 28%. A similar transformation takes place when ice is deposited at 25K and then warmed to 120K (Raut et al.[11]), although there are slight variations.

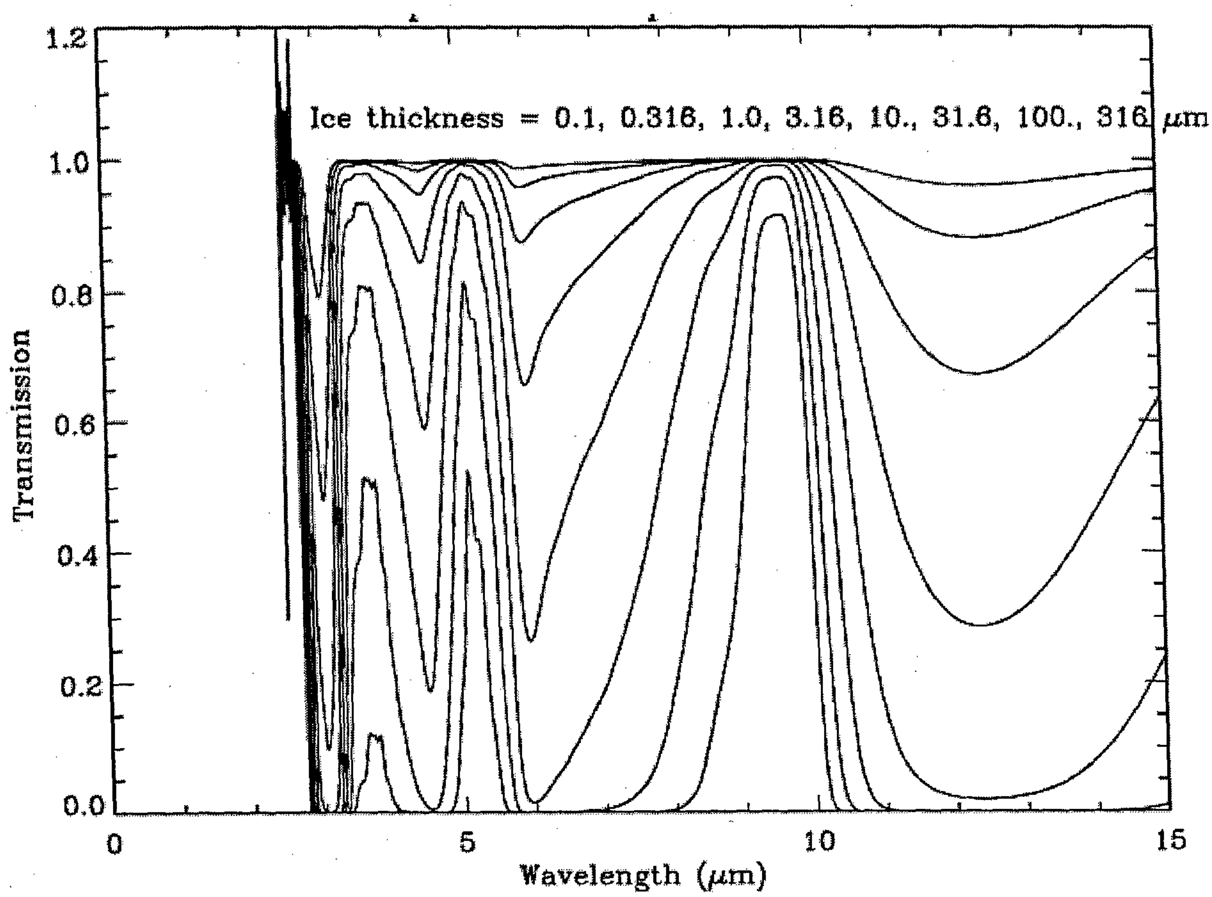

Figure 5. Transmission spectra for a variety of thicknesses for ice deposited at 80K. The transmissions greater than 1.0 shortward of 2.5 μm are numerical artifacts.

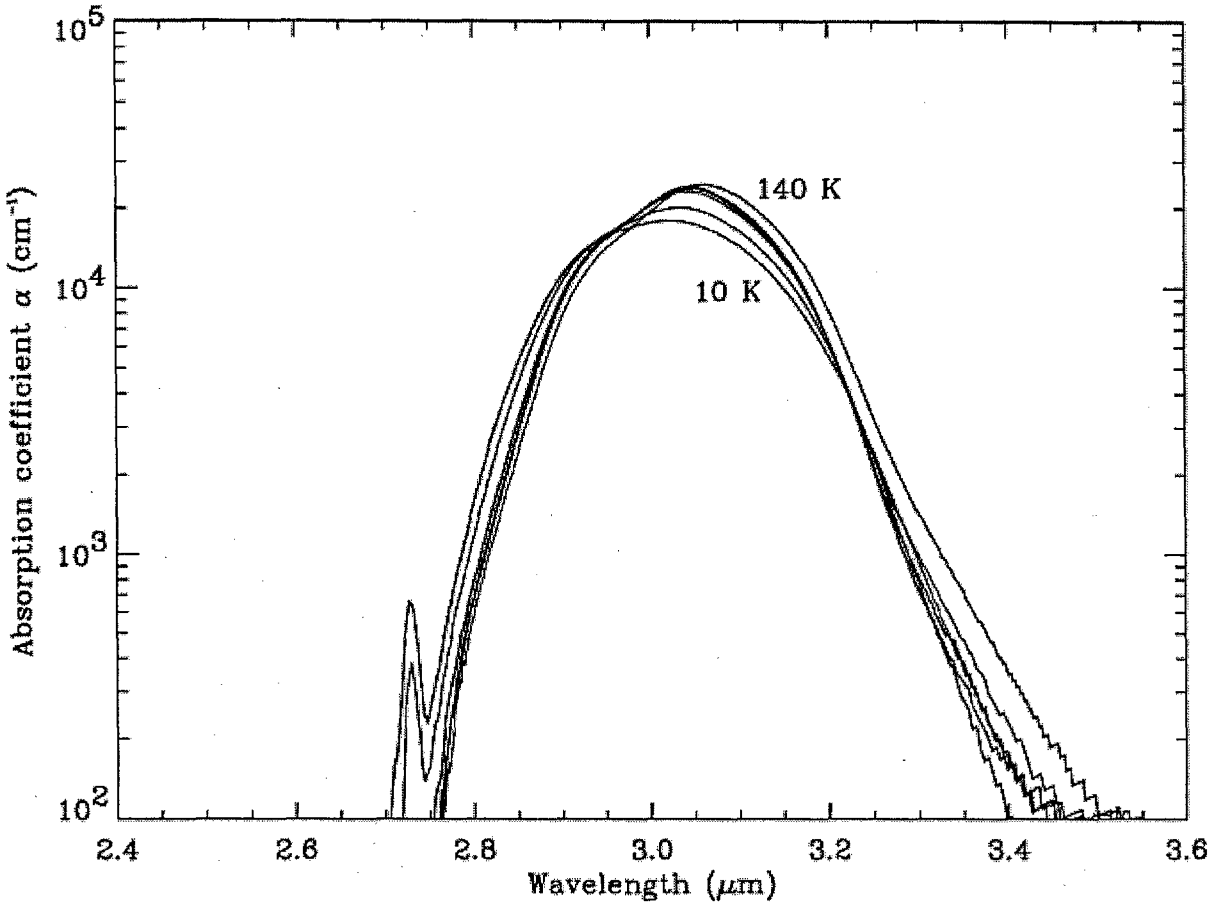

Figure 6. Temperature-dependent structure of the 3-μm OH stretch feature based on tabulations of Hudgins et al.[8]

5. Cubic Ice

Cubic ice can form at between 137 and 197K, but its optical constants are poorly known. Raut et al.[11] report a transmission spectrum that shows that the OH stretch feature splits into three distinct peaks (Figure 7). They increase in strength toward longer wavelengths and lie at 3.06, 3.14, and 3.22 μm.

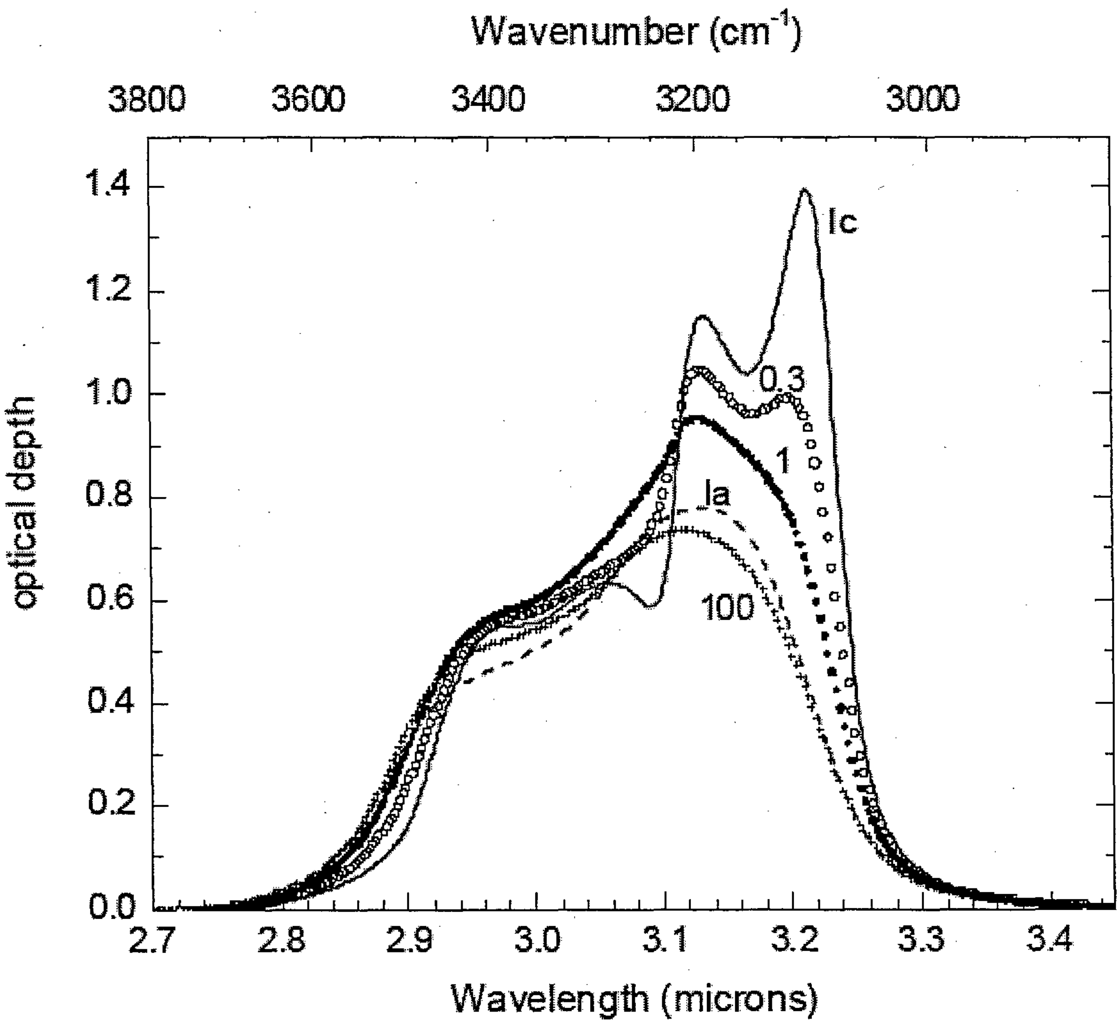

Figure 7. Structure in the 3-μm band of cubic ice from Raut et al.[11]

6. Evaluating Signal in Arbitrary Filter Bands

The signal S produced by a sensor can be written in the following simplified form:

$$S = G(\lambda) \int P(\lambda)\, I(\lambda)\, t(\lambda)\, d\lambda, \tag{7}$$

where the integral is carried out over the band of interest. G is a gain function, P is the source of radiation, I is the relative instrumental response that includes filter transmission and detector response, and t is the transmission of the ice film. In the absence of ice (t = 1.0), S represents the nominal signal from the sensor. While Eq. (7) can be considerably more complicated, what we seek here is not an absolute response, but rather a relative one: What is the signal in the absence of ice relative to what it is in the presence of ice?

By calculating the ratio $\mathcal{R}$ = S(with ice)/S(without ice), which is equal to the *relative signal*, we have a good measure of the loss: When $\mathcal{R}$ = 1.0, there is no loss. When $\mathcal{R}$ = 0.9, the signal is 90% of what it should be. When $\mathcal{R}$ = 0.33, the signal is one third of what it should be. Figure 8 shows some values of $\mathcal{R}$ as a function of ice thickness D in three bands: 3.0–3.1 μm, 2.8–4.0 μm and 11–14 μm.

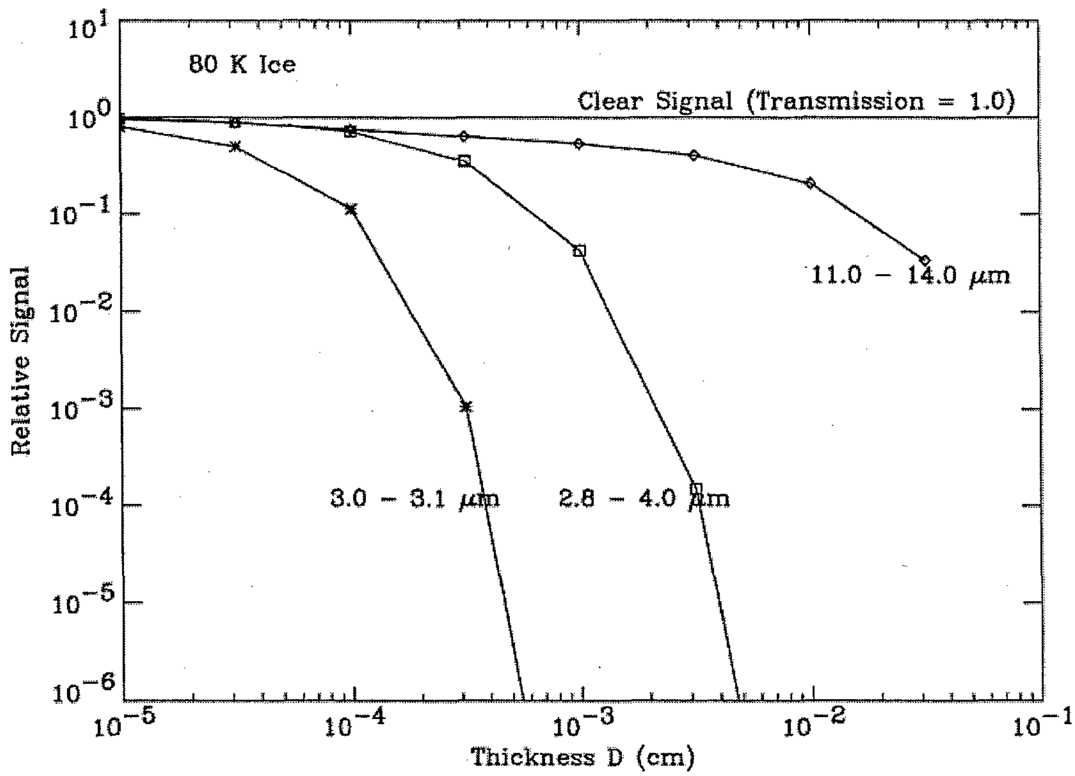

Figure 8. Relative signals $\mathcal{R}$ as a function of ice thickness for 80K ice.

7. Nuts and Bolts of Computing Transmission Spectra

Care must be taken when using wavelength units that are not expressed in cm, such as we do here, i.e. μm. Tabulations of $\alpha(\lambda)$ are typically given in $\alpha(\mathrm{cm}^{-1})$ vs λ (nm). Regardless of the wavelength units used, D must be in inverse units of α; i.e. , if α is in cm^{-1}, then D must be in cm. When the optical constants are given, then α can only be correctly obtained by having D and λ in the same units. Most absorption coefficients or optical constants are presented in frequency (wavenumber units) or do not have equal intervals of wavelength. For convenience, it is a good idea to regrid the spectra into equal wavelength intervals before doing an integration over a band.

When trying to assess the relative signal in a given band, the spectrum of the light source must be specified. This has important consequences because a source whose radiance increases rapidly at longer wavelengths will give a different result than one that decreases at longer wavelengths. This is also true of instrumental response, which includes any filters in the system. Care must also be taken when applying transmission curves to radiance. The two spectra can be multiplied together without worry. However, should there be a desire to convert the spectra from wavelength to frequency units, the shape of the spectrum and, in particular, its peak wavelength can change.[12]

The amount of absorption $(1 - t)$ is not a linear function of thickness D (Eq. 1). Therefore, one cannot simply interpolate between two transmission curves in Figure 4 to get the resulting thickness. The actually computation must be done. This is especially true when there is significant absorption, such as near the peak of an absorption feature. The only exception occurs when the optical depth is much less than unity everywhere within the band. In this case, $(1 - t) \sim \tau$, which is proportional to D because

$$t = \exp(-\tau) = 1 - \tau + \tau^2/2! - \tau^3/3! \ldots\ldots \approx 1 - \tau \quad \text{when} \quad \tau << 1. \qquad (8)$$

With the absorption coefficient or optical constants in hand, it is a simple matter to compute t directly.

8. Surface Reflections

The reflectivity, R, of a layer of ice is given by Fresnel's Equations, which reduce to a single equation for normal incidence

$$R= [(m-1)^2 + k^2]/[(m+1)^2 + k^2] \tag{9}$$

Figure 9 shows the reflectivity, R, of ice in a vacuum as a function of wavelength. The total irradiance of a signal passing through a layer of ice is then

$$I = Io\,(1-R)\exp(-\alpha D) \tag{10}$$

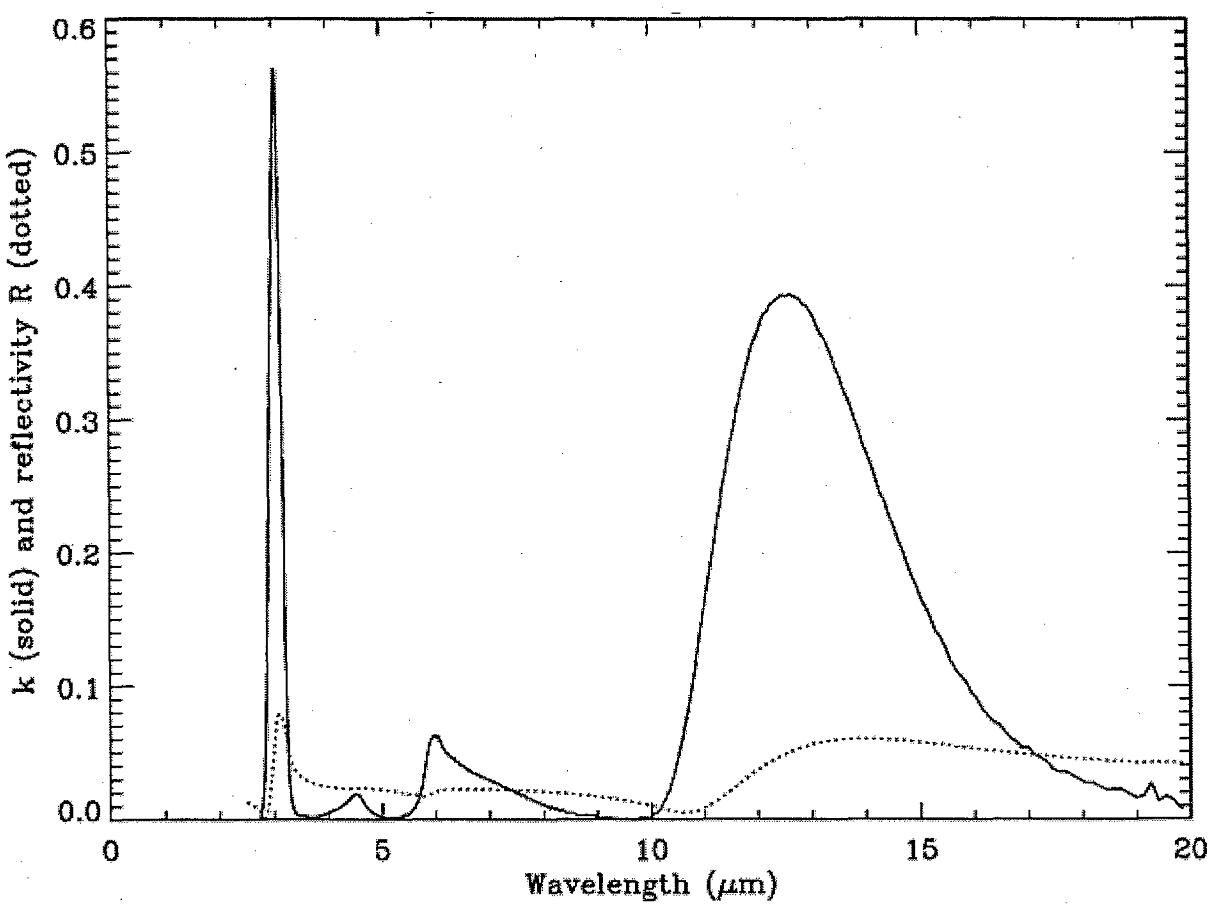

Figure 9. Amorphous Ice reflectivity, R, in a vacuum (at 80K) and imaginary part of the index of refraction as a function of wavelength.

For very thin layers of ice, reflective losses can be of the same order or greater than the absorptive losses. And, of course, there are reflective losses at the interface between the ice and the underlying substrate. These can be calculated from Fresnel's Equations as well.

A somewhat more troublesome effect occurs when the ice thickness is less than the skin depth ,$\mathcal{D}$. In this case, the electric and magnetic fields of the vacuum-ice and ice-substrate couple with each other, and the resulting amplitudes are more difficult to predict. And it obviously depends on index of refraction, which is a function of wavelength. A thin layer of ice may act as an anti-reflective coating, or a pro-reflective coating. If the ice thickness is much less than 1/4 of the wavelength of the incident light, such effects are minimal. Dealing with thin coatings like ice is well studied in the field of multilayer dielectric interference filters, but that is beyond the scope of this report, primarily because the underlying substrates can have a wide variety of optical constants. As a general rule, however, the transmission of ice on a substrate is independent of the substrate material.

8. Conclusions

We have presented an overview of ice's absorption properties with an emphasis on cryogenic ice ($T < 137K$) in the infrared. Absorption coefficients and transmission spectra are shown along with numerical examples of signal strength within several bands. We also discuss some practical aspects of computing transmission spectra including reflective losses and the influence of extremely thin layers of ice.

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