The optical constants of water ice have been determined in the near infrared from 4000 to 7000 cm\(^{-1}\). Polycrystalline ice films with thickness as great as \(1.164 \mu\text{m}\) were formed by condensation of water vapor on a cold silicon substrate at temperatures of 166, 176, 186, and 196 K. The transmission of light through the ice films was measured during their growth from 0 to 1.164 \(\mu\text{m}\) over the frequency range of approximately 500–7000 cm\(^{-1}\). The optical constants were extracted by means of simultaneously fitting the calculated transmission spectra of films of varying thickness to their respective measured transmission spectra with an iterative Kramers–Kronig technique. Equations are presented to account for reflection losses at the interfaces when the sample is held in a cell. These equations are used to reanalyze the transmission spectrum of water ice \(\sim 358\text{-}\mu\text{m}\) sample at 247 K recorded by Ockman in 1957 [Philos. Mag. Suppl. 7, 199 (1958)]. Our imaginary indices for water ice are compared with those of Gosse et al. [Appl. Opt. 34, 6582 (1995)], Kou et al. [Appl. Opt. 32, 3531 (1993)], Grundy and Schmitt [J. Geophys. Res. 103, 25809 (1998)], and Warren [Appl. Opt. 23, 1206 (1984)], and with the new indices from Ockman’s spectrum. The temperature dependence in the imaginary index of refraction observed by us between 166 and 196 K and that between our data at 196 K and the data of Gosse et al. at 250 K are compared with that predicted by the model of Grundy and Schmitt. On the basis of this comparison a linear interpolation of the imaginary indices of refraction between 196 and 250 K is proposed. We believe that the accuracy of this interpolation is better than 20%. © 2001 Optical Society of America

1. Introduction

Water ice is of great interest to climate and remote sensing studies because it is found in type II polar stratospheric clouds (PSCs), cirrus clouds, contrails, and surface snow. Type II PSCs form at \(\sim 188 \text{ K}\) in the polar stratospheres during the winter and play an important role in polar ozone depletion. Cirrus clouds occur primarily in the upper troposphere and are found at all latitudes and seasons. They have a global coverage as high as 30–40%\(^{1}\). Cirrus clouds form at temperatures between 190 and \(\sim 250 \text{ K}\) and are composed almost exclusively of ice crystals. Contrails are formed from aircraft emissions mainly at temperatures below a threshold of the order of 233 K\(^{2}\).

Cirrus clouds and contrails have been identified as two of the most uncertain components in regulating the Earth’s climate and variability\(^{3,4}\). Cirrus clouds reflect solar radiation back to space but also contribute to the greenhouse effect by absorbing and radiating terrestrial infrared. Whether these clouds tend to cool or heat the Earth depends in part on their radiative properties, which in turn depend on their microphysical properties (for example, ice particle shape, size distribution, ice-water content, and optical thickness).

Satellite observations provide the opportunity to derive these microphysical properties on scales required by general circulation models, but accurate optical constants are needed for proper retrieval.
Solar radiation reaching the top of the atmosphere has approximately 49% of its energy at wavelengths below 0.7 μm and ~51% in the longer-wavelength region up to 5.0 μm (near-infrared region), making the latter frequency region an important one. Since the optical constants of ice vary appreciably across the near infrared, ice crystals of sizes found in cirrus predominantly scatter light at some wavelengths, whereas they absorb appreciable amounts of light at other wavelengths. Figure 1 shows some of the channels used by satellite instruments in the near-infrared region along with a typical absorbance spectrum of water ice for a film whose thickness, 100 μm, is typical of cirrus particle sizes. Also summarized are the principal applications of these instruments. More information about these instruments can be obtained from the following website: http://spsoosun.gsfc.nasa.gov/cgi-bin/eos-ksh/eos.instru.ksh/.

Almost all the calculations of the single-scattering properties of cirrus clouds6–10 and microphysical property retrievals of cirrus clouds or contrails11–15 at near-infrared wavelengths used the refractive indices of water ice from Warren’s compilation16 based on measurements made during the 1950s and 1970s17–19 or the refractive indices from the research of Kou et al.20 and Gosse et al.21 Warren’s compilation used imaginary indices calculated from the spectrum of Reding.18 These imaginary indices corresponding to 195 K were shifted to shorter wavelength to make them appropriate for use at 266 K. Further, although both Ockman17 and Reding18 measured the transmission of their water ice samples sandwiched between windows, the reflection losses at the air–window and the window–ice interfaces were not taken into account in the calculation of the imaginary indices. As shown in Appendix A, this neglect can result in errors as high as 25%. Ockman’s17 transmission spectra were considered by Warren to be more reliable than Reding’s18 since the sample thicknesses were better known and also because there was some ambiguity in Reding’s data that was due to his mislabeling the ordinate on his spectra. Warren,16 however, believed that because of the possibility of diffuse scattering from the imperfect ice surfaces in this frequency region of small absorption, it is always better to choose the lowest values available for the imaginary indices. Since the imaginary indices from Reding’s data18 were lower in the valleys, they were used in his compilation.16

The optical constant measurements of Kou et al.20 and Gosse et al.21 correspond to temperatures close to 250 K. This temperature is at the higher end of what is relevant for cirrus clouds and much too high for PSCs. Recently, temperature-dependent absorption coefficients of water ice from 20 to 270 K in the near infrared were published by Grundy and Schmitt.22 The data presented in the paper by Grundy and Schmitt22 are the result of fitting the absorption coefficient spectrum with a set of 17 Gaussian functions. The Gaussian functions were chosen such that the same set, with frequencies, widths, and intensities smoothly varying with temperature, were able to fit the absorption coefficient spectrum at all the temperatures considered (20–270 K). The fitted parameters corresponding to the Gaussian functions were then used to parameterize the temperature-dependent water ice absorption coefficient spectrum. To our knowledge the results of Grundy and Schmitt22 are the only data available to date that cover the entire temperature range relevant to PSCs and cirrus clouds. Table 1 summarizes the various experimental measurements of the opti-
cal constants and absorption coefficients of water ice in the near infrared from each of these groups.

Figure 2(a) compares the imaginary indices of Grundy and Schmitt22 at 270 K and the values in Warren’s compilation16 at 266 K. Figure 2(b) shows the percentage difference between the two data sets relative to the values of Grundy and Schmitt.22 It can be seen that the agreement is within 20% around the 5000-cm\(^{-1}\) band and in the two valleys on either side of it, but the difference is more than 20% almost everywhere else. As shown in the following paragraphs, the values in Warren’s compilation16 and those of Grundy and Schmitt22 differ from all the other results in the valleys around the 5000-cm\(^{-1}\) band by more than 35%.

The data of Gosse et al.21 and of Kou et al.20 agree well with each other but do not agree well with Warren’s compilation. The former authors did account for reflection losses at the interfaces by using the ratio of spectra corresponding to different path lengths to derive optical constants. Although not exact, our data have confirmed that the error in this approach is less than 10%. Since Warren based some of his values on an incomplete analysis of Ockman’s data, we felt it would be significant if Kou et al.20 and Gosse et al.21 also agreed with the results of the reanalysis of Ockman’s spectrum.23 Thus we obtained Ockman’s transmission spectrum of a 358-μm sample23 of water ice247 K and extracted imaginary indices of refraction from it by properly taking into account the reflections at the air–glass and the glass–ice interfaces predicted by the theory of the optical properties of thin solid films24 see Appendix A.24 An important reason for doing this is that both the temperature and the sample thickness are comparable with what Gosse et al.21 and Kou et al.20 used. The model used to extract the imaginary indices is described in detail in Appendix A.

Figure 3(a) compares the new results from Ockman’s 358-μm transmission spectrum23 with those of Grundy and Schmitt22 at 250 K, Gosse et al.21 at 251 K, and Kou et al.20 at 248 K. Figure 3(b) shows the percentage difference between each of these three data sets (relative to Ockman’s data), plotted as a

<table>
<thead>
<tr>
<th>Table 1. Summary of Recent Experimental Measurements of the Optical Constants of Water Ice in the Near Infrared(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author</strong></td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>Current study</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Grundy and Schmitt, 1998(^b)</td>
</tr>
<tr>
<td>Gosse et al., 1995(^c)</td>
</tr>
<tr>
<td>Toon et al., 1994(^d)</td>
</tr>
<tr>
<td>Kou et al., 1993(^e)</td>
</tr>
<tr>
<td>Ockman, 1957(^f)</td>
</tr>
</tbody>
</table>

\(^a\)All these experiments measured transmission.
\(^b\)Ref. 22.
\(^c\)Ref. 21.
\(^d\)Ref. 28.
\(^e\)Ref. 20
\(^f\)Refs. 17 and 23.
function of frequency. Figure 3(c) shows the frequency regions where the agreement with the new Ockman result is within 10% and where it is within 20%, overlaid on the new Ockman imaginary index spectrum. On the whole the agreement between the imaginary indices of Gosse et al., Kou et al., and the new results from Ockman’s spectrum are within 10%. Although it is not too surprising that the results of Gosse et al. and those of Kou et al. agree this well with each other (both measurements were done in the same research group and in a similar manner), it is noteworthy that the results obtained from Ockman’s spectrum recorded ~35 yr prior to these results (at around the same temperature and of a sample of thickness comparable with the one used by Gosse et al.) agree as well as they do. The values of Grundy and Schmitt agree to within ~5% in the band maxima around 5000 and ~6700 cm⁻¹, but in the two valleys around 4450 and 5440 cm⁻¹ their imaginary indices differ by as much as 35%.

Given these appreciable differences between the results of Grundy and Schmitt and those of the others mentioned in the previous paragraph, we felt that further data were needed at lower temperatures (especially around 186 K) since the only data in the 3700–7000-cm⁻¹ region at such temperatures available to date are the absorption coefficients of Grundy and Schmitt. As pointed out by Arnott et al., it is important to assess the accuracy of the currently

Fig. 2. (a) Comparison of the frequency-dependent imaginary indices of refraction of Grundy and Schmitt at 270 K with those in the compilation of Warren at 266 K (1984). (b) Variation of the percentage difference (relative to the values of Grundy and Schmitt) between the two data sets, plotted as a function of frequency.

Fig. 3. (a) Comparison of the frequency-dependent imaginary indices of refraction of Grundy and Schmitt at 250 K with those obtained by Kou et al., Gosse et al., and the reanalyzed Ockman result. (b) Variation of the percentage difference (relative to Ockman) of the data sets mentioned in (a), plotted as a function of frequency. (c) Frequency regions where the agreement with the new Ockman result is within 10% (black diamonds) and where it is within 20% (gray diamonds), overlaid on the new Ockman imaginary index spectrum (solid curve).
available measurements of the refractive indices of water ice in the near-infrared region at various temperatures and under various growth conditions for proper interpretation of the observed radiation signatures of ice clouds.

2. Experiment

The apparatus used to measure infrared spectra has been described in detail previously.\textsuperscript{26} Briefly, polycrystalline ice films with total thickness of up to \( \sim 1164 \ \mu \text{m} \) were formed by condensation of water vapor on a cold 10-mm-diameter silicon wafer (transparent at these frequencies) mounted in a vacuum chamber and cooled by a liquid-nitrogen-cooled cryostat. Water vapor was introduced into the chamber through leak valves positioned to backfill vapors into the chamber. With backfilled vapors the films grew almost equally on both sides of the wafer. The temperature of the silicon wafer was measured with several type T thermocouples. The thermocouple junctions were attached to a copper heating plate in close thermal contact with the silicon. The silicon wafer was maintained at constant temperatures of 166, 176, 186, or 196 K to within \( \pm 1 \) K. At these temperatures the hexagonal form of ice is expected to be most stable. In the near-infrared spectral region, however, the spectra of the hexagonal and the cubic forms of ice are identical. The measured temperatures were calibrated with the frost point of ice. The temperature-dependent vapor pressures of Marti and Mauersberger\textsuperscript{27} were used for this.

The infrared absorbances of the films were measured in transmission with a Nicolet Magna 550 Fourier-transform infrared spectrometer equipped with a liquid-nitrogen-cooled MCT-B (mercury cadmium telluride, type B) detector. The absorbance, \( A \), is defined as the base 10 logarithm of the ratio, \( I/I_0 \), where \( I \) in our experiment, refers to the light intensity after passage through the vacuum–ice–substrate–ice–vacuum system and \( I_0 \) refers to the light intensity after passage through the vacuum–substrate–vacuum system. Data were collected at 4-cm\(^{-1}\) resolution with 12 scans added per spectrum. In our experimental geometry, infrared light incident normal to the surface undergoes multiple reflections within the substrate and within the films.\textsuperscript{28} The theory used to extract the optical constants from the measured transmission of infrared light through the film system has been described in detail previously\textsuperscript{28} and is discussed only briefly here. Determination of the optical constants is an iterative process with two steps that are repeated until a converging solution is reached. In the first step the thicknesses of the films are calculated by minimization of the squared difference between the calculated and the measured absorbances of the infrared spectra at a given temperature. The first time through the iterative loop, previously measured refractive indices\textsuperscript{28} are used to calculate the thickness. In the subsequent iterations the newly calculated refractive indices are used. In the second step the refractive indices are adjusted as follows: The imaginary index at each frequency is determined to minimize the squared difference between the calculated and the measured absorbance spectra for all the chosen films at that temperature simultaneously. Then the value of the real index at each frequency is calculated with the Kramers-Kronig relationship.

Ice crystals, being uniaxial, are slightly birefringent. They have been shown, however, to be isotropic within experimental uncertainties.\textsuperscript{29,30} Hence measurements can be made on bulk polycrystalline samples as was done in this study. The variations in refractive indices due to birefringence are expected to be less than the uncertainty in our derived values.

3. Data Analysis

In the near infrared (3700–7000-cm\(^{-1}\) region) the absorption by ice is weak compared with the absorption in the 500–3700-cm\(^{-1}\) region, and hence thick films (at least 300 \( \mu \text{m} \)) are essential for accurate determination of the imaginary refractive index. In the case of such thick films the strong absorbance, however, leaves only very narrow frequency windows (approximately 4449 and 5436 cm\(^{-1}\) ) where the absorbance is small enough for the detection of any interference fringes predicted by the model for this film system. Hence a method of finding film thickness based on interference fringes cannot be successfully used to determine an initial guess for the film thickness. To overcome this difficulty, the absorbances at the frequency \( v_0 = 3960 \) cm\(^{-1}\) [see Fig. 4(a)] measured relative to a baseline drawn through the points \( v_1 = 3825 \) and \( v_2 = 4438 \) cm\(^{-1}\) [Fig. 4(a)] were used to determine the film thicknesses. In other words, with reference to Fig. 4(a), the absorbance \( \left[ A\left( v_0 \right) - A\left( v_0 \right) \right] \) was used as a measure of the film thickness. The points \( v_1 \) and \( v_2 \) were chosen to coincide with the two nearest local minima on either side of the chosen absorption feature [Fig. 4(a)]. For the purpose of calibration, imaginary indices, \( k \), at the various frequencies, \( v \), were calculated from the absorption coefficients, \( \alpha \), of Grundy and Schmitt\textsuperscript{22} by use of the relationship \( k = \alpha/4\pi v \) at each of the temperatures. Grundy and Schmitt\textsuperscript{22} calculated \( k \) by dividing the natural logarithm of the “calculated intrinsic transmission” (p. 25812) by the thickness of the film. These \( k \) values were used along with the real refractive indices from Toon \textit{et al.} at 166 K,\textsuperscript{28} and the film model to calculate the absorbance, \( \left[ A\left( v_0 \right) - A\left( v_0 \right) \right] \), at the chosen frequency, \( v_0 \), for a set of input ice film thicknesses, \( d \). The calculated absorbance versus the film thickness is shown in Fig. 4(b). As shown in Fig. 4(b), a plot of \( \left[ A\left( v_0 \right) - A\left( v_0 \right) \right] \) versus the film thickness, \( d \), is found to be linear. The result of a linear fit to these lines was used along with the \( \left[ A\left( v_0 \right) - A\left( v_0 \right) \right] \) values for the experimental spectra to arrive at an initial estimate of the thicknesses of the chosen films at that temperature.

A second experimental difficulty had to do with diffuse light scattering from the imperfect ice surfaces in frequency regions of relatively weak absorption such as near 5500 cm\(^{-1}\), resulting in spurious baselines for the spectra. Typically, experiments
could be done at only one temperature on any given day because of the time required for growing films with a broad range of thickness. The chamber would then have to be completely pumped out before another set of experiments could be performed. Since the amount of light scatter depends on factors such as the surface roughness of the films, which is hard to control during the course of an experiment, the losses due to light scattering varied from day to day. This variability made it necessary to treat the effects of light scattering in all the spectra recorded at the various temperatures in a consistent manner before any temperature-dependent optical constants could be extracted.

Difficulties due to light scattering were also encountered in the measurements of Grundy and Schmitt. They had to correct each spectrum to compensate for the effects of light scattering, which, in some cases, were quite large. To do this, they divided each spectrum by a “synthetic continuum.”

This synthetic continuum was calculated based on “an examination of the least strongly absorbing wavelength regions of each spectrum, the requirement that spectra of samples of different thicknesses yield mutually consistent absorption coefficients, and the expectation that the spectra at any temperature would be similar to spectra at adjacent temperatures” (Ref. 22, p. 25812).

Our procedure for compensating for the effects due to light scattering is illustrated in Fig. 5. Essentially, we are assuming that the valleys in the 176 K spectra are not affected by scattering losses and that there is minimal temperature dependence at 4449, 5436, and 7000 cm$^{-1}$. As discussed in Section 4, Grundy and Schmitt found little temperature dependence in the imaginary indices of refraction around these three frequencies. Since water ice absorbs more strongly at other frequencies, any errors in the baseline correction would be significantly less at those frequencies. In the analysis of our data it was found that the spectra recorded at 176 K were among the ones that allowed maximum transmission in the valleys around 4449 and 5436 cm$^{-1}$ (and therefore minimum effects due to scattering) for a given thickness, and hence these spectra were used as the basis for our correction for scattering losses. The worst case of light scattering was encountered in our data at 206 K (not included in this study). The baseline of a given spectrum was defined by polynomial (order $\approx 2$) fit through the two points corresponding to minimum absorption in the valleys (4449 and 5436 cm$^{-1}$) and a third point corresponding to the last data point around 7000 cm$^{-1}$ [Fig. 5(a)]. For the frequency region between 4449 and 3700 cm$^{-1}$ the baseline was defined to be the value of the absorbance at 4449 cm$^{-1}$. The absorbance at each of these three frequencies in the case of the 176 K spectra are found to increase linearly with the ice film thickness [Fig. 5(b)]. The results of a linear fit of the absorbance to the film thickness [also shown in Fig. 5(b)] were then used to calculate the correct absorbances at these three frequencies for all the other spectra corresponding to different thicknesses at the other temperatures. These correct absorbances were then used to calculate the correct baselines for these spectra. These correct baselines were then added on to the respective spectra after their original baselines had been subtracted out [Fig. 5(c)]. The resulting baseline-corrected spectra at each temperature were then used as input for the calculation of the optical constants.

A total of at least 13 and as many as 19 films of total thickness varying between $\sim 220$ $\mu$m and $\sim 1$ mm were chosen for the calculation of the optical constants at each temperature. Of these, the thinnest films (approximately 220–460 $\mu$m) with smallest measured transmission of $\sim 3\%$ (maximum absorbance between 1.0 and 1.5) were used to determine the imaginary index of refraction ($k$) in the region of strongest absorption (4763–5214 cm$^{-1}$). The thickest films (approximately 700 $\mu$m–1 mm) were used to determine the imaginary index of refraction.
in the rest of the spectral regions between 3700 and 7000 cm\(^{-1}\). Films of intermediate thickness (approximately 460–700 \(\mu\)m) were used to ensure continuity and also served as a further check of the analysis. Figure 6 shows typical fits between the calculated and the measured absorbance at 166 K that we were able to achieve.

In the calculation of the real index of refraction \(n\) with the Kramers–Kronig relation\(^{28}\) the anchor point was chosen to be the temperature-dependent real in-
The real and the imaginary indices of refraction, \( n_{\text{vis}}(T) \), at the frequency \( v_{\text{vis}} = 15823 \text{ cm}^{-1} \). The temperature-dependent real index of refraction was calculated with the Lorentz–Lorenz equation,

\[
R = \frac{[n_{\text{vis}}(T)^2 - 1]}{\rho(T)[n_{\text{vis}}(T)^2 + 2]}, \tag{1}
\]

where a value of \( R = 0.2072 \text{ cm}^3 \text{ g}^{-1} \) was used for the specific refraction.\(^{31}\) The temperature-dependent density of ice, \( \rho(T) \), was calculated with the relation

\[
\rho(T) = 0.9167 - 1.75 \times 10^{-4}T - 5.0 \times 10^{-7}T^2, \tag{2}
\]

where \( T \) is in celsius and the density is in grams \( \text{cm}^{-3} \).\(^{32}\)

The Kramers–Kronig integration was carried out in the frequency interval of approximately 1.8–185,809 \text{ cm}^{-1}. To extend the values of the imaginary index in the integrand outside the frequency range in which optical constant measurements were made in this study (3700–7000 \text{ cm}^{-1}), the temperature-dependent imaginary indices of Clapp et al.\(^{23}\) were used between \(-3700\) and 800 \text{ cm}^{-1} (these data were chosen since they covered the temperature range of our study). Between 800 and 500 \text{ cm}^{-1} the imaginary indices of Toon et al. at 166 K\(^{28}\) were used. Beyond each end of the frequency range 500–7000 \text{ cm}^{-1} the imaginary index is assumed to be a constant matching the values at 500 and 7000 \text{ cm}^{-1}. These assumptions for the imaginary index outside the 500–7000\text{ cm}^{-1} range have been shown to have an insignificant effect on the real index of refraction between 3700 and 7000 \text{ cm}^{-1}.\(^{28}\)

### 4. Results

The real and the imaginary indices of refraction obtained in this study at 166, 176, 186, and 196 K are presented in Table 2.\(^{34}\) The real indices of refraction at the various temperatures are plotted as a function of frequency in Fig. 7. It can be seen that there is no noticeable temperature-dependence. The Lorentz–Lorenz equation [Eq. (1)] and Eq. (2) predict the real indices of refraction in the temperature range 166–196 K to change only by \(-0.1\%\), consistent with our results. Figure 8(a) shows a comparison of the real indices from this study at 186 K with those of Toon et al.\(^{28}\) at 166 K and Warren\(^{16}\) at 266 K. Figure 8(b) shows the variation of the percentage difference between our results at 186 K and the values in Warren’s compilation adjusted with the Lorentz–Lorenz equation for 186 K.\(^{16}\) From this figure it is seen that the difference is between \(+0.12\%\) and \(-0.22\%\) in the 3700–7000\text{ cm}^{-1} region.

The imaginary indices of refraction, \( k \), obtained in this study at the various temperatures are shown in Fig. 9(a). Figure 9(b) shows the absolute change in the imaginary indices at 196 K relative to the values at 166 K, as a function of frequency. Also shown is the absolute change predicted by the 17-Gaussian model of Grundy and Schmitt.\(^{22}\) It is gratifying to see that our observations in this narrow temperature range of 40 K agree well with the predictions that are based on a study of a much wider temperature range, from 20 to 270 K. The differences in the absolute values between our observation and the prediction based on the research of Grundy and Schmitt\(^{22}\) are most likely due to the different methods used to correct the baselines of the spectra in an attempt to account for the effects of diffuse light scattering at the ice film surfaces. The temperature dependence of the feature around 6070 \text{ cm}^{-1}, observed, for example, by Grundy and Schmitt\(^{22}\) and Ockman,\(^{17}\) is also observed by us. However, smooth trends in the peak maxima or frequency shifts with temperature are hard to make out, since the predicted percentage change for a change in temperature of 10 K varies between 4% and 7% across this frequency region, whereas the uncertainty in our results is expected to be \(-10\%\). The absolute difference between the imaginary indices at 250 K (Gosse et al.\(^{21}\)) and those at 196 K (our data) are compared with that predicted by the model of Grundy and Schmitt,\(^{22}\) in Fig. 9(c).

The model of Grundy and Schmitt\(^{22}\) predicts the variation of \( k \) with temperature to be linear at most frequencies, but at other frequencies a second-order polynomial is required for fitting the predicted variation of \( k \) with temperature. However, we have determined that the Grundy and Schmitt\(^{22}\) variation of \( k \) with temperature along with our 196 K data yields values of \( k \) that differ by a maximum value of 15% compared with the results of using the linear interpo-
lation between 196 and 250 K, this maximum value of the difference occurring at 250 K. In other words, at 250 K the difference between the results of Gosse et al. and those calculated by extrapolation of our data at 196 K with the Grundy and Schmitt variation is at most 11.5%. To avoid any discontinuity in the values around 196 or 250 K, and because the differences between the two methods is smaller than 15% at intermediate temperatures, we have chosen to recommend a linear interpolation between our 196 K data and the 250 K data of Gosse et al. Table 2 thus lists the slope, \(dk_y/dT\), that can be used to interpolate the values of the imaginary indices between our 196 K data and the 250 K data of Gosse et al. according to

\[k(T) = k(196\,K) + \frac{dk_y}{dT}(T - 196)\]  

Table 2.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>166 K</th>
<th>176 K</th>
<th>186 K</th>
<th>196 K</th>
<th>(dk_y/dT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>166 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>176 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>186 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>196 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. (continued)

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>166 K</th>
<th>176 K</th>
<th>186 K</th>
<th>196 K</th>
<th>(dk_y/dT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>166 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>176 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>186 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>196 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 September 2001 / Vol. 40, No. 25 / APPLIED OPTICS 4457
In Fig. 10a our results at 186 K are compared with the results of Grundy and Schmitt\(^\text{22}\) at 250 K; those of Gosse \textit{et al.}\(^\text{21}\) also near 250 K (since the data of Kou \textit{et al.}\(^\text{20}\) and Gosse \textit{et al.}\(^\text{21}\) agree well with each other, only the former was chosen for the comparison for clarity); the new results from the reanalysis of Ockman's spectrum;\(^\text{23}\) and the data from Warren's compilation. Figure 10b shows the variation of the percentage difference calculated as

\[
\% \text{ difference} = \frac{[k(\text{other}) - k(\text{ours})]}{k(\text{ours})} \times 100, (4)
\]

where \(k(\text{other})\) refers to results of Gosse \textit{et al.}\(^\text{21}\), Warren,\(^\text{16}\) the new results from Ockman's spectrum,\(^\text{23}\) and Grundy and Schmitt.\(^\text{22}\) The term "% difference due to \(\Delta T\)" is the percentage difference in the imaginary indices predicted by the 17-Gaussian model of Grundy \textit{et al.}\ for a change in temperature from 270 to 186 K with reference to Warren's compilation and for a change from 250 to 186 K with reference to the other data. Figure 10c shows the frequency regions where the agreement between the various other data and our results are within 10\% and where the agreement is within 20\% overlaid on our \(k\) spectrum at 186 K.

It is seen from Figures 10(b) and 10(c) that after the differences due to temperature are taken into consideration

1. Our imaginary indices are within 10\% of the results of Gosse \textit{et al.}\(^\text{21}\), Kou \textit{et al.}\(^\text{20}\) and the newly derived values from Ockman's spectrum\(^\text{23}\) at almost all the frequencies except in the immediate vicinity of the two valleys around 4400 and 5400 cm\(^{-1}\).
2. Even in these valleys, our results are within 20\% of the results of Gosse \textit{et al.}\(^\text{21}\), Kou \textit{et al.}\(^\text{20}\) and the newly derived values from Ockman's spectrum\(^\text{23}\) whereas those of Grundy and Schmitt\(^\text{22}\) and Warren\(^\text{16}\) differ by much more than 20\%.
3. The imaginary indices of Grundy and Schmitt\(^\text{22}\) are within 5\% of our results in the band maxima but are lower by more than 40\% in the two valleys (approximately 4360–4620 and 5300–6020 cm\(^{-1}\)).
4. With reference to the values in Warren's\(^\text{16}\) compilation, the agreement around the 5000-cm\(^{-1}\) band maximum is between +15\% and −20\%. However, in the approximately 6360–6700-cm\(^{-1}\) region and in the shoulder at frequencies below ~4300 cm\(^{-1}\), the imaginary indices in Warren's compilation\(^\text{16}\) are higher by approximately 20\% and 30\%, respectively. In the two valleys (approximately 4400–4500 and 5360–5780 cm\(^{-1}\)) the values in Warren's compilation\(^\text{16}\) are lower by 30\% and 60\%, respectively.
The spectra of Grundy and Schmitt, like ours, required corrections in order to account for light-scattering effects from the ice samples. In their paper Grundy and Schmitt did not describe the actual calculation of the synthetic continuum to correct the individual spectra for these losses. The much lower values of the imaginary indices of Grundy and Schmitt in the valleys are most likely due to over-correction for scattering losses. Warren chose the lowest values available in the valleys from spectra that had been incompletely analyzed for light losses on the cell walls (values derived from Reding for Fig. 9.

Fig. 9. (a) Imaginary indices of refraction \((k)\) at the temperatures of 166, 176, 186, and 196 K, plotted as a function of frequency. (b) Variation of the absolute change in the imaginary indices \((k)\) at 196 K relative to the values at 166 K, as a function of frequency. The dashed curve represents our experimental observation, and the solid curve shows the absolute change predicted by the 17-Gaussian model of Grundy and Schmitt (c) Variation of the absolute change in the imaginary indices \((k)\) at 250 K relative to the values at 196 K, as a function of frequency. The dashed curve is the difference between the results of Gosse et al. at 250 K and our experimental observation at 196 K. The solid curve is the absolute change predicted by the 17-Gaussian model of Grundy and Schmitt.

Fig. 10. (a) Comparison of the frequency-dependent imaginary indices of refraction \((k)\) obtained in this study with those of Grundy and Schmitt at 250 K, Gosse et al. at 250 K, the new values from the reanalysis of Ockman’s spectrum at 247 K, and Warren’s compilation at 266 K. Data shown here are at their respective temperatures. (b) Temperature-adjusted percentage difference [defined in Eq. (4)] between these sets of data. (c) Frequency regions where the agreement between the various other data and our results are within 10% (black diamonds) and where the agreement is within 20% (gray diamonds), overlaid on our \(k\) spectrum at 186 K (thick black curve).
5. Conclusion

The real and the imaginary indices of water ice have been determined in the 166–196 K temperature region between approximately 3700 and 7000 cm\(^{-1}\). The real indices of refraction have been found to be weakly temperature dependent, consistent with predictions based on the Lorentz–Lorenz equation. The observed temperature dependence in the imaginary indices of refraction as a function of frequency has been compared with predictions based on the 17-Gaussian model of Grundy and Schmitt.

The transmission spectrum of water ice (358-μm sample at 247 K) recorded by Ockman in 1957 was reanalyzed to extract optical constants, taking into account that the transmission was measured through the air–glass–ice–glass–air system. These new results have been found to agree with the results of Gosse et al. and Grundy and Schmitt.

Our imaginary indices have been compared with those of Gosse et al., Kou et al., and Warren’s compilation. Our results agree with those of Gosse et al., Kou et al., and the new results from Ockman’s spectrum to within 10% at almost all the frequencies.

Our imaginary indices have been compared with results from Ockman’s spectrum, Grundy and Schmitt, and Warren’s compilation. Our results agree with those of Gosse et al., Kou et al., and the new results from Ockman’s spectrum to within 10% in the regions around the band maxima and to within 20% in the two valleys between these bands when the differences expected because of temperature effects have been taken into account. The agreement with Grundy and Schmitt is closer in the regions of the band maxima than in the two valleys.

In view of the comparisons of the available data sets, we recommend that, close to 250 K, the imaginary indices of Gosse et al., Kou et al., or the new results from Ockman’s spectrum be used. Between 166 and 196 K our imaginary indices of refraction should be used. For temperatures between 196 and 250 K we propose a linear interpolation scheme, and the slopes at the various frequencies required for this have been provided.

Appendix A: Equations for the Calculation of the Light Energy Transmitted through a Cell

The matrix formalism of Heavens has been used to derive the transmitted energy through the four-layer system described in Fig. 11. The thickness of the ice film, \(d_2\), is assumed to be much smaller than that of the windows. In accordance with Eq. (4) of Heavens the transmitted energy is given by

\[
T = \frac{(t_{12}t_{34}a^2)(t_{12}^{*}t_{34}^{*}a)^{*}}{aa^*}, \tag{A1}
\]

where \(t_{12}\) is the Fresnel coefficient for transmission of light across the \((n-1)n\) interface and \(t_{12}^{*}\) is its complex conjugate. \(n\) is complex and is in general equal to \(1 + r_n\), where \(r_n\) is the Fresnel coefficient for reflection at the \((n-1)n\) interface.

For our system and for normal incidence

\[
r_1 = \frac{1 - n_1}{1 + n_1} \quad \text{(here after referred to as } g_1), \tag{A2}
\]

\[
r_2 = g_2 + ih_2, \tag{A3}
\]

where

\[
g_2 = \frac{n_1^2 - n_2^2 - k_2^2}{(n_1 + n_2)^2 + k_2^2}, \quad h_2 = \frac{2n_1k_2}{(n_1 + n_2)^2 + k_2^2}. \tag{A4}
\]

Therefore

\[
(t_{12}t_{34}a^2)(t_{12}^{*}t_{34}^{*}a)^{*} = l_{14}^2 + m_{14}^2, \tag{A5}
\]

where \(l_{14}\) and \(m_{14}\) are the real and the imaginary parts of the above product and are equal to

\[
l_{14} = (1 - g_1^2)(1 - g_2^2 + h_2^2),
\]

\[
m_{14} = -2g_2h_2(1 - g_1^2). \tag{A6}
\]

The derivation of the denominator in Eq. (A1) is much more complicated and is presented below following the notation of Heavens:

\[
a = p_{14} + iq_{14}, \tag{A7}
\]

where

\[
p_{14} = p_{13} - g_1r_{13}, \quad q_{14} = q_{13} - g_1s_{13}. \tag{A8}
\]

\[
p_{13}, \quad q_{13}, \quad r_{13}, \quad \text{and} \quad s_{13}\]

are given by

\[
p_{13} = p_{12}p_3 - q_{12}q_3 + r_{12}r_3 - s_{12}s_3, \tag{A9}
\]

\[
p_{12}, \quad q_{12}, \quad r_{12}, \quad \text{and} \quad s_{12}\]

are given by

\[
p_{12} = 1 + g_1g_2, \quad q_{12} = g_1h_2, \quad r_{12} = g_1 + g_2, \quad s_{12} = h_2. \tag{A10}
\]
we can now define \( p_3, \ldots, w_3 \) as

\[
\begin{align*}
p_3 &= \exp(\alpha_3) \cos \gamma_3, \\
g_3 &= \exp(\alpha_3) \sin \gamma_3, \\
r_3 &= -g_3 \exp(\alpha_3) \cos \gamma_3 + h_3 \exp(\alpha_3) \sin \gamma_3, \\
s_3 &= -h_3 \exp(\alpha_3) \cos \gamma_3 - g_3 \exp(\alpha_3) \sin \gamma_3, \\
t_3 &= g_3 \exp(-\alpha_3) \cos \gamma_3 - h_3 \exp(-\alpha_3) \sin \gamma_3, \\
u_3 &= g_3 \exp(-\alpha_3) \sin \gamma_3 - h_3 \exp(-\alpha_3) \cos \gamma_3, \\
v_3 &= g_3 \exp(-\alpha_3) \cos \gamma_3, \\
w_3 &= -\exp(-\alpha_3) \sin \gamma_2.
\end{align*}
\]

For the empty cell the following substitutions will have to be made

\[
g_2 = -g_1, \\
h_2 = 0, \\
\alpha_2 = 0, \\
\gamma_2 = 2\pi d_2/\lambda.
\]

Ockman’s 358-\( \mu \)m sample spectrum was recorded with glass windows. The refractive indices of glass that were used were taken from a handbook of optical constants.\(^{25}\) For the real indices of refraction of ice, Warren’s\(^{16}\) values were used. Warren’s\(^{16}\) imaginary indices of refraction of water ice were used as an initial guess in the fitting program. The final values of the imaginary indices of refraction are found by minimizing the squared difference between the measured transmission and that calculated based on the above cell model.

Table 3 gives sample inputs used in the program, along with the final values of the imaginary indices obtained at those frequencies as described above. Also included in the table are the values of the imaginary indices that would be obtained when the transmission through the cell is not taken into account, followed by the percentage error due to the neglect of the correct model. It can be seen that neglecting the reflections at the various interfaces can lead to significant errors in the determination of \( k \). The frequencies shown in Table 3 were chosen to match the local maxima and minima in the absorption spectrum of water ice in this frequency region. It can be seen that the errors range from 2% to 28%, the largest errors occurring at the valleys near the 5000-cm\(^{-1}\) band. These are the same regions were the discrepancies between the previously available values of the imaginary indices were the largest.

We thank W. M. Grundy for his help in accessing his data. We are very thankful to S. G. Warren for sending us the Ockman data and for having saved it for all these years. This research was supported by NASA-EOS grant NAG5–8127 and by NSF-ATM9711969.

References

11. W. H. Knap, M. Hess, P. Stammes, R. B. A. Koelmeijer, and


23. S. G. Warren, Department of Atmospheric Sciences and Geophysics, 524 ATG Bldg., Box 351640, University of Washington, Seattle, Washington 98195-1640, sgw@atmos.washington.edu (personal communication, 1999).


34. These data can be accessed from the following web address: http://cires.colorado.edu/people/tolbert/group/data/data.html.