Overtones of silicate and aluminate minerals and the 5–8 µm ice bands of deeply embedded objects

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ABSTRACT
The distinct patterns, relatively low intensities and peak positions of overtone-combination bands of silicates and oxides suggest that the 5–8 µm spectral region can provide clues for the dust composition when near optically thick conditions exist for the 10-µm silicate feature. We present 1000–2500 cm−1 room-temperature laboratory spectra obtained from powders of silicate, aluminate and nitride minerals and silicate glasses. The spectra exhibit overtone absorption bands with mass absorption coefficients ∼100 times weaker than the fundamentals. These data are compared with the 5–8 µm spectra of deeply embedded young stellar objects observed with the Short Wavelength Spectrometer on the Infrared Space Observatory. Fits of the laboratory data to the observations, after subtraction of the 6.0-µm H2O ice feature and the 6.0-µm feature identified with organic refractory material, indicate that crystalline melilite (a silicate) or metamict hibonite (a radiation-damaged crystalline aluminate) may be responsible for much of the 6.9-µm absorption feature in the observations, with melilite providing the best match. A weaker 6.2-µm absorption in the young stellar object spectra is well matched by the spectra of hydrous crystalline amphibole silicates (actinolite and tremolite). Relative abundances of Si–O in room-temperature amphiboles to low-temperature H2O ice are in the range 0.46–3.9 and in melilite are in the range 2.5–8.6. No astronomical feature was matched by the overtones of amorphous silicates because these bands are too broad and peak at the wrong wavelength. Hence, this analysis is consistent with the 10-µm features of these objects being due to a mixture of crystalline and amorphous silicates, rather than only amorphous silicates.

Key words: astrochemistry – techniques: spectroscopic – circumstellar matter – stars: pre-main-sequence – dust, extinction.

1 INTRODUCTION
The most prominent feature in the spectra of deeply embedded young stellar objects (Fig. 1) is the strong 8–13 µm absorption feature due to the Si–O stretch in silicates. Other strong absorption bands have been attributed to ices and organic refractory material as indicated in the figure, but not all the matches are completely satisfactory, suggesting that comparison with other materials may be worthwhile.

1.1 Identified ice and carbonaceous bands
Absorption of CO2 at 4.27 µm has been studied by Gerakines et al. (1999). The 4.67-µm feature due to CO ice has long been studied from the ground (e.g. Chiar et al. 1995) as well as from space. Analysis of the 5–8 µm absorption features of NGC 7538 IRS 9 was initially carried out by Schutte et al. (1996) and by Keane et al. (2001) for this and other sources (NGC 7538 IRS 9, GL 7009S, W33A, GL 989, GL 2136, Elias 29, S140 IRS 1, W3 IRS 5 and Mon R2 IRS 3). The main part of the 6.0-µm band is assigned to the bending mode of amorphous H2O ice (Tielens & Allamandola 1987), which is supported by the presence of the H2O stretching mode at 3.1 µm (not shown). Keane et al. found that two additional absorptions were present: a 0.05 µm wide band centred at 5.81 µm superimposed on a 0.2 µm wide component at about 5.83 µm. These wavelengths are characteristic of the C=O stretch of carbonyl groups in ketones, aldehydes, carboxylic acids and esters. Recently, Rannier et al. (2004) have tentatively identified this, and part of the 6.9-µm feature, with a combination of formaldehyde (H2CO), formamide (HCONH2) and urea (H2CONH2). A broad 6.2-µm component has been identified with a similar carrier in polycyclic aromatic hydrocarbons (PAHs), hydrogenated aromatic hydrocarbons (HACs) or organic refractory material (ORM; Gibb & Whittet 2002). Both Schutte et al. (1996) and Keane et al. compared the 6.9-µm feature with aliphatic hydrocarbons, methanol and alcohols, carbonyl and...
nitrile groups, \( \text{NH}_4^+ \) and carbonates, but did not obtain a satisfactory match. Keane et al. identified two components in the observed data centred near 6.75 and 6.95 \( \mu \text{m} \) and suggested that the unidentified absorber should be abundant. Schutte et al. (1999) identified a weak narrow absorption feature in the spectrum of W33A at 7.24 \( \mu \text{m} \) with the C–H deformation in HCOOH (formic acid) and found that a similar band at 7.41 \( \mu \text{m} \) could be due either to HCOO\(^-\) (the formate ion) or CH\(_3\)HCO (acetaldehyde). Boogert et al. (1996) identified the band at 7.67 \( \mu \text{m} \) in W33A and NGC 7538 IRS 9 with the deformation mode of solid CH\(_4\) in a polar matrix.

1.2 Overtones and the fundamental Si–O stretch

The overtone-combination bands of silicates and oxides occur in the 5–8 \( \mu \text{m} \) wavelength range. Because these bands are 1/100th the strength of the fundamentals, they are seen only when the Si–O or metal–O stretch are saturated or highly distorted (Fig. 2). Saturation occurs in the 8–12 \( \mu \text{m} \) range where the data are (i) very noisy because the sample is opaque, or (ii) flat-topped like the grossite spectrum where some light has escaped through cracks or thin spots in the film. The 11.5-\( \mu \text{m} \) feature in the melilite film and the 9.2-\( \mu \text{m} \) band in the lizardite spectrum are highly distorted because the samples are nearly opaque at these wavelengths (see Hofmeister, Keppel & Speck 2003, for a full discussion). At room temperature, the overtones are seen in 5–15 \( \mu \text{m} \) thick silicate powder films, whilst the fundamental Si–O stretch is undistorted in films \( \lesssim 1 \mu \text{m} \) (cf. the 0.41-\( \mu \text{m} \) talc spectrum); the individual grains are submicrometre-sized in both cases. The aluminate (hibonite and grossite) films required to see the overtones are 50 \( \mu \text{m} \) thick.

Optically thick or nearly optically thick conditions occur in the environments of deeply embedded objects which have deep 10–\( \mu \text{m} \) absorption features (Fig. 1); sources with the deepest 5–8 \( \mu \text{m} \) features (W33A, AFGL 7009S and W3 IRS 5) have flat-bottomed 8–12 \( \mu \text{m} \) bands and are therefore nearly opaque to light in this wavelength range. Therefore, we hypothesize that there is so much silicate dust towards these sources that overtone absorption features contribute to the 5–8 \( \mu \text{m} \) range. We present room-temperature 1000–2500 cm\(^{-1}\) spectra of the overtone-combination bands of silicates, aluminates and some other meteoritic species, for comparison with the 4–8 \( \mu \text{m} \) region of the astronomical spectra.
2 SOURCES

We model Short Wavelength Spectrometer (de Graauw et al. 1996)
Infrared Space Observatory spectra published by Gibb et al. (2004).
The normalized 4–12 μm spectra and published polynomial contin-
uous are plotted in Fig. 1 and listed in Table 1. GL 989 is a low-
mass B3V star that has formed in a ring-shaped molecular cloud
(Schwartz et al. 1985). Thompson & Tokunaga (1978) obtained
a visual extinction ≳35 mag by dereddening a K-band spectrum
and assuming an early B-type star. ρ-Elias 29 is a deeply embedded
(A_v ∼47 mag) class I low-mass protostar in the ρ-Ophiuchus mole-
cular cloud. Modelling of the 10-μm spectrum of this source suggests
that the silicate dust is similar to that in the diffuse medium and
most of the emission is confined to a region of radius ∼0.36 au
(Bowey, Adamson & Yates 2003). S140 is an H II region located
910 pc away behind ∼23 mag of extinction in a molecular cloud,
which is forming high- and low-mass stars (Evans et al. 1989).
The high-mass young stellar object (YSO) W3 IRS 5 is surrounded by
a molecular cloud containing seven high-mass stars and a clump of
low-mass YSOs (Megeath et al. 1996). In the near-infrared, Mon
R2 IRS 3 is a bright 500-au conical reflection nebula containing two
to three massive early-type stars (IRS 3N, IRS 3S and possibly IRS
3 NE). Infrared speckle imaging suggests that the conical-shaped
nebula is due to collimation of the light of IRS 3 by a 0.500-au disc
(Koresko et al. 1993) and the presence of three further sources within
a KBr beamsplitter. Between 500 and 2000 scans were collected
at a resolution of 1 cm−1 using various methods. For most samples,
films of 10–15 μm thickness were made by compressing a few
grains or coarsely ground powder in a Mao-Bell diamond anvil cell.
A small piece of the film was laid on a 100-μm diameter aperture
and spectra were collected in a Spectrachem infrared microscope.
For the glasses and single crystals, a shard was placed on the aperture.
For the soft hydroxilicates, except for lizardite, powder was com-
pressed between two BaF2 discs, and the thickness was controlled
by an aluminium spacer of either 6 or 12 μm thickness. Spectra were
collected from the discs and samples without condensing the beam.
Because of low band strengths, data for San Carlos olivine and
synthetic (syn) hibonite were collected from sections prepared by
compressing powder in a press normally used to make KBr pellets.
For these samples, air space could not fully be removed, and as a
result band strengths are underestimated, as indicated in the tables.

3.1 Estimated band strengths, κ_pk

Estimated values of the band strength of the largest peaks were
obtained from the following formula

κ_pk = \frac{τ_{pk}}{ρTh}, \tag{1}

where τ is the optical depth at the peak wavelength measured after
baseline subtraction, Th is the thickness of the sample and ρ is the
density of a typical specimen as listed in Roberts et al. (1990). Because
we measure the properties of powders, the actual density is
lower than that of the bulk mineral due to air spaces between grains.
Thus, values of κ_pk could be 15 per cent higher than the tabulated
values. Where two thicknesses are listed, the band strength for the
thinner sample is thought to be more reliable.

3.2 Olivines and pyroxenes

The data for olivines and pyroxenes are presented in Table 2 and
Fig. 3. Peaks are tabulated in micrometres and discussed below in
wavenumbers. Astronomical peaks of interest are centred at 1470
and 1670 cm−1, and are about 100 and 150 cm−1 wide, respectively.
The overtones of crystalline olivines (forsterite and olivine) are
characterized by a series of 50 cm−1 wide peaks between 1430 and
2030 cm−1, which do not appear to shift with changes in Mg to
Fe ratio. The spectrum of Mg2SiO4 (forsterite) glass is charac-
terized by a broad 400-cm−1 peak centred at 1840 cm−1. None of
the olivine features compares well with the astronomical peaks. The
absence of a forsterite from the overtone region is perhaps surprising.

Table 1. Source fluxes and silicate, ice and ORM optical depths given by Gibb et al. (2004). The inferred abundances of H2O ice and
the 6.02-μm optical depths were estimated from the 3.0-μm H2O ice band.

<table>
<thead>
<tr>
<th>Object</th>
<th>F_v(8.0)/Jy</th>
<th>τ_{sil}(9.7)</th>
<th>τ_{3.05}</th>
<th>N_{H_2O} × 10^{18}</th>
<th>τ_{6.02}</th>
<th>τ_{ORM}(6.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GL 989</td>
<td>131</td>
<td>0.72(0.02)</td>
<td>1.43</td>
<td>2.4</td>
<td>0.10</td>
<td>0.07(0.02)</td>
</tr>
<tr>
<td>ρ-Elias 29</td>
<td>37.2</td>
<td>1.32(0.06)</td>
<td>1.85(0.08)</td>
<td>3.4</td>
<td>0.16</td>
<td>0.08(0.02)</td>
</tr>
<tr>
<td>S140</td>
<td>234</td>
<td>1.51(0.02)</td>
<td>1.1</td>
<td>1.9</td>
<td>0.084(0.01)</td>
<td>0.02(0.01)</td>
</tr>
<tr>
<td>W3 IRS 5</td>
<td>338</td>
<td>~5.8</td>
<td>2.78</td>
<td>5.1</td>
<td>0.26</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>GL 2136</td>
<td>213</td>
<td>2.1(0.1)</td>
<td>3.24(0.09)</td>
<td>5.1</td>
<td>0.23(0.04)</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Mon R2 IRS 3</td>
<td>207</td>
<td>2.55(0.09)</td>
<td>1.12</td>
<td>1.9</td>
<td>0.07</td>
<td>0.15</td>
</tr>
<tr>
<td>NGC 7538 IRS 9</td>
<td>66.1</td>
<td>2.23</td>
<td>3.1(0.25)</td>
<td>7.0</td>
<td>0.31(0.02)</td>
<td>0.18(0.02)</td>
</tr>
<tr>
<td>AFGL 7009S</td>
<td>29.3</td>
<td>4.0(0.3)</td>
<td>Sat</td>
<td>–</td>
<td>1.2(0.1)</td>
<td>0.53(0.06)</td>
</tr>
<tr>
<td>W33A</td>
<td>44.1</td>
<td>7.84(0.12)</td>
<td>5.5 ± 1.5</td>
<td>11.0</td>
<td>0.49(0.07)</td>
<td>1.12(0.07)</td>
</tr>
</tbody>
</table>

a‘Sat’ denotes saturated. bW33A estimated from saturated feature (see Gibb et al. 2000).
Table 2. Laboratory spectra of silicate overtones: mineral group, sample, sample thickness (Th), density of bulk mineral, chemistry and origin, estimated band strength of the strongest overtone (κpk), wavelengths of prominent overtones (bold font indicates the strongest peak).

<table>
<thead>
<tr>
<th>Group</th>
<th>Samplea</th>
<th>Th (µm)</th>
<th>ρ (g cm⁻³)</th>
<th>Locationb</th>
<th>κpk (cm⁻² g⁻¹)</th>
<th>Bands (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>Forsterite</td>
<td>12 ± 2</td>
<td>3.3</td>
<td>Mg₂SiO₄; Syn'</td>
<td>73</td>
<td>4.92, 5.21, 5.45, 5.62, 6.00</td>
</tr>
<tr>
<td></td>
<td>Forsterite glass (C)</td>
<td>40</td>
<td>3.3</td>
<td>Mg₂SiO₄; Syn’ (Containerless Research)</td>
<td>27</td>
<td>5.43</td>
</tr>
<tr>
<td></td>
<td>Olive (PP)</td>
<td>60 ± 2</td>
<td>3.3</td>
<td>(Mg₀.006Fe₀.093Mn₀.001)₂SiO₄</td>
<td>&gt;44</td>
<td>4.95, 5.21, 5.45, 5.62, 6.00</td>
</tr>
<tr>
<td></td>
<td>Enstatite</td>
<td>11 ± 1</td>
<td>3.4</td>
<td>(Mg₀.038Fe₀.015Ca₀.004)SiO₃</td>
<td>37</td>
<td>5.13, 6.23, 6.63</td>
</tr>
<tr>
<td>Pyroxene</td>
<td>Diopal0</td>
<td>10 ± 1</td>
<td>3.4</td>
<td>CaMgSi₂O₆; Syn’ (JWU)</td>
<td>32</td>
<td>4.98, 5.07, 6.06, 6.49, 7.14</td>
</tr>
<tr>
<td></td>
<td>Diopal glass (C)</td>
<td>30</td>
<td>3.4</td>
<td>CaMgSi₂O₆; Syn’ (FWU)</td>
<td>18</td>
<td>5.52</td>
</tr>
<tr>
<td></td>
<td>Diopal4/Hd6</td>
<td>10±1</td>
<td>3.4</td>
<td>Ca(Mg₀.92Fe₀.08)Si₂O₆</td>
<td>85</td>
<td>5.07, 5.78, 6.10, 6.49</td>
</tr>
<tr>
<td></td>
<td>Diopal75Hd25</td>
<td>10 ± 1</td>
<td>3.4</td>
<td>Ca(Mg₀.75Fe₀.25)Si₂O₆</td>
<td>65</td>
<td>4.83, 5.07, 6.06, 6.49, 6.99</td>
</tr>
<tr>
<td>Melilite</td>
<td>Åkermanite</td>
<td>10</td>
<td>2.9</td>
<td>Ca₂Mg₂Si₂O₇; Syn’ (UCLA)</td>
<td>130</td>
<td>6.25, 6.76, 6.90</td>
</tr>
<tr>
<td></td>
<td>Melilite</td>
<td>12 ± 2</td>
<td>3.0</td>
<td>Ca₂Mg₂Si₂O₇; Syn' (UCLA)</td>
<td>220</td>
<td>6.05, 6.90</td>
</tr>
<tr>
<td></td>
<td>Gehlenite</td>
<td>10 ± 2</td>
<td>3.0</td>
<td>Ca₂Mg₂Si₂O₇; Syn' (UCLA)</td>
<td>210</td>
<td>5.3, 6.24, 6.74, 7.04</td>
</tr>
<tr>
<td></td>
<td>Gehlenite glass</td>
<td>10</td>
<td>3.0</td>
<td>Ca₂Mg₂Si₂O₇; Syn’ (UCLA)</td>
<td>43</td>
<td>5.41</td>
</tr>
<tr>
<td>Feldspar</td>
<td>Albite (Co)</td>
<td>60 ± 10</td>
<td>2.6</td>
<td>Na₀.98K₀.02AlSi₃O₈</td>
<td>49</td>
<td>5.21, 5.56, 5.71, 6.25, 6.67</td>
</tr>
<tr>
<td></td>
<td>10 ± 1</td>
<td>2.6</td>
<td></td>
<td>Amelia Vu</td>
<td>69</td>
<td>5.56, 5.75, 6.02, 6.21</td>
</tr>
<tr>
<td></td>
<td>Anorthite (Co)</td>
<td>70 ± 10</td>
<td>2.7</td>
<td></td>
<td>94.1 per cent Ca₂Al₂Si₃O₈ + 5.84 per cent Na₀.99K₀.01AlSi₃O₈</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Labradorite</td>
<td>10 ± 1</td>
<td>2.7</td>
<td></td>
<td>66 per cent Ca₂Al₂Si₃O₈ + 33 per cent NaAlSi₃O₈ + 1 per cent KAlSi₃O₈</td>
<td>37</td>
</tr>
<tr>
<td>Amphibole</td>
<td>Tremolite</td>
<td>~12</td>
<td>3.1</td>
<td>K₀.01Na₀.04Ca₀.93(Mg₄.90Fe₂.02)(Al₀.14Si₇.97)O₂(OH)₁₂</td>
<td>130</td>
<td>4.80, 5.12, 5.91, 6.21</td>
</tr>
<tr>
<td></td>
<td>Actinolite</td>
<td>10</td>
<td>3.0</td>
<td>(Ca₁.₄₆Na₀.₄₂)(Mg₄.₄₄Fe₀.₄₆)(Al₀.₃₈Si₇.₉₂)O₂(OH)₂</td>
<td>53</td>
<td>4.81, 5.12, 5.93, 6.21</td>
</tr>
<tr>
<td>Phyllosilicate</td>
<td>Lizardite</td>
<td>5</td>
<td>2.6</td>
<td>Mg₂Fe₂O₅Si₂O₅(OH)₁₂</td>
<td>285</td>
<td>5.86, 6.33, 6.85</td>
</tr>
<tr>
<td></td>
<td>Tale (BaF₂)</td>
<td>6</td>
<td>2.8</td>
<td>Mg₂Si₄O₁₀(OH)₁₂</td>
<td>256</td>
<td>5.21, 5.49, 5.99</td>
</tr>
<tr>
<td></td>
<td>Montmorillonite (BaF₂)</td>
<td>6</td>
<td>2.4</td>
<td>(Na₂Ca₂)₃[AlMg₂Si₄O₁₀–(OH)₁·H₂O]</td>
<td>490</td>
<td>5.42, 6.17</td>
</tr>
<tr>
<td></td>
<td>Saponite (BaF₂)</td>
<td>6</td>
<td>2.3</td>
<td>(Na₂Ca₂)₃[Mg₂Fe₂]Si₄O₁₀–O₁₀(H₂O)₁·4H₂O</td>
<td>850</td>
<td>6.16, 6.41, 6.90</td>
</tr>
</tbody>
</table>

ªPowders in DAC except where indicated: C, chip in microscope, no orientational effects; Co, chip in microscope, orientation may affect measured absorption coefficients; PP, pressed powder (κpk is a lower limit); BaF₂, between BaF₂ discs. ºCaltech = J. Paque, Caltech, FWU = B. Fegley, Washington University; HU = C. A. Francis, Harvard University; JWU = N. Johnson, Washington University; MM = M. R. Ghiara, Museo Mineralogico, Napoli, Italy; WU = Washington University; UCLA = R. C. Newton at University of California, Los Angeles; NHM = Natural History Museum. Syn denotes synthetic. References for preparation techniques: gehlenite and åkermanite (Charlu et al. 1981); forsterite glass (Tangeman et al. 2001); diopside glass (Kubiki, Hemley & Hofmeister 1992). Composition reference: labradorite (Hofmeister & Rossman 1984); tremolite (Johnson & Fegley 2003); lizardite (Cogulu & Laurent 1984).
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Figure 3. Overtone spectra of olivine and pyroxene crystals and glasses. Horizontal dashed lines indicate the vertical offsets and vertical dotted lines show the frequencies of the astronomical features. The spectrum of NGC 7538 IRS 9 is plotted before (grey) and after (black) subtraction of the ice and ORM composites. Bars indicate the tabulated positions of the most prominent peak.

Figure 4. Overtone spectra of melilites and feldspars. Horizontal dashed lines indicate the vertical offsets and vertical dotted lines show the frequencies of the astronomical features. The spectrum of NGC 7538 IRS 9 is plotted before (grey) and after (black) subtraction of the ice and ORM composites. Bars indicate the tabulated positions of the most prominent peak.

given the prominence of the forsterite bands in the spectra of other astronomical objects longwards of 20 µm.

The pyroxene samples include enstatite (an orthopyroxene) and three clinopyroxenes from the diopside (CaMgSi₂O₆; Dp)-hedenbergite (CaFeSi₂O₆; Hd) solid solution series and synthetic diopside (CaMgSi₂O₆) glass. The crystalline pyroxenes each have two or three peaks between 1400 and 1700 cm⁻¹ in the general (but not exact) frequency range of the astronomical absorption features. However, the ~100 cm⁻¹ wide peak near 1970 cm⁻¹ is not seen in the YSO spectra. The glass has a single 600-cm⁻¹ band centred at 1810 cm⁻¹, which is probably too weak to be detected in space.

3.3 Melilites and feldspars

The spectra of melilites and feldspars are listed in Table 2 and Fig. 4. Melilites have double SiO₄ tetrahedra, which share a single apical oxygen atom to give an Si : O ratio of 2 : 7. The overtone region of the melilites is characterized by a main peak near 1500 cm⁻¹. The spectrum of Ca₂Al(AlSi)O₇ (gehlenite) glass has a single weak 500-cm⁻¹ band centred at 1850 cm⁻¹. The spectrum of melilite is most similar to the astronomical 1470 cm⁻¹ peak.

Feldspars have an SiO₂-like structure in which varying numbers of Si⁴⁺ cations are replaced by Al³⁺, leaving sites for the incorporation of metal ions such as Na⁺, K⁺ and Ca²⁺. Feldspars have relatively weak peaks that do not match the astronomical data well. They are centred between 1600 and 1900 cm⁻¹. The anorthite peak at 1640 cm⁻¹ does not provide good fits to the astronomical 1670-cm⁻¹ feature. Differences between the two albite spectra are probably due to changes in crystal orientation.

3.4 Amphiboles and phyllosilicates

The hydrous silicates include two groups, the amphiboles (tremolite and actinolite) and the phyllosilicates (i.e. layer silicates) in Table 2.

Amphiboles are constructed of double chains of SiO$_4$ tetrahedra. Hydroxyl (OH$^{-}$) anions lie in the rings within the double-linked chains at the tetrahedral apices. The overtone spectra of tremolite and actinolite in Fig. 5 consist of a blend of peaks between 1400 and 2100 cm$^{-1}$. The largest peaks are at 1610 cm$^{-1}$. The relatively low intensity of the actinolite band strengths ($\kappa_{pk} = 53$ cm$^2$ g$^{-1}$ compared with 130 cm$^2$ g$^{-1}$ for tremolite) is attributed to this mineral having extensive solid solution on the Mg site and minor solid solution on the Si site. Note that olivine with only 10 per cent substitution of Fe for Mg has considerably weaker overtones than end-member forsterite.

Phyllosilicates (Figs 5 and 6) have the strongest overtones measured with peak $\kappa_{pk}$ values between 256 (talc) and 850 cm$^2$ g$^{-1}$ (saponite). However, none provides a good match to the astronomical spectra. The peak wavelengths of their overtone spectra are between 1620 and 1670 cm$^{-1}$ but the fine structure within the peaks does not match the astronomical data well.

### 3.5 Aluminates, silicon oxides and nitrides

The aluminates, silicon oxides (not silicates) and nitrides studied are listed in Table 3 and Fig. 7. The aluminates, corundum and spinel have very weak $\sim$80 cm$^{-1}$ wide peaks near 1430 cm$^{-1}$. The calcium aluminates, grossite and metamict (radiation-damaged) hibonite have $\sim$150 cm$^{-1}$ wide peaks near the 1470-cm$^{-1}$ astronomical absorption feature. The metamict hibonite also has a weaker overtone near the astronomical 1670-cm$^{-1}$ band. In contrast, the well-ordered synthetic hibonites have much weaker overtones at higher frequencies with the strongest bands near 1380 cm$^{-1}$. The silicon oxide (SiO) powder, sinoite (a meteoritic phase SiN$_2$O) and
the silicon nitrides have a range of overtones that do not match the frequencies of the astronomical bands.

4 FITS TO ASTRONOMICAL SPECTRA

Fits were obtained by $\chi^2$ fitting the laboratory spectra presented in Figs 3–7 to the 5.1–7.4 µm region of the astronomical optical depth spectra obtained by Gibb et al. (2004). Initial attempts to fit the entire region with mineral overtone spectra failed to provide good matches; we were also unable to constrain the optical depths of the ice and organic composites by the addition of overtone components.

Better fits were obtained after subtraction of the Gibb et al. (2004) ice and ORM composites. Satisfactory matches to AFGL 989, AFGL 2136, NGC 7538 IRS 9, AFGL 7009S and W33A were obtained only after exclusion of the 5.6–6.0 µm region, which is characterized by an absorption feature at 5.8 µm; this has been tentatively identified with a combination of formaldehyde (H2CO), formamide (HCONH2) and urea (H2CONH2) by Raunier et al. (2004).

4.1 Single- and two-component fits

Fits to the 6.2- and 6.9-µm features were obtained by fitting the formula

$$\tau_{\text{overt}} = \alpha \tau_{\lambda} + \beta \tau_2 + \gamma$$

where $\alpha$, $\beta$, and $\gamma$ represent the spectra used to fit the 6.2- and 6.9-µm astronomical features, respectively. The laboratory data were normalized to unity at the wavelengths of their overtone peaks near 6.2 and 6.9 µm. Optical depths, $\tau_{\lambda}$, and $\tau_{\lambda}$, and constant $c$ were optimized to provide the best fit to the astronomical spectra by $\chi^2$ fitting. Constant $c$ has no physical meaning because polynomial continua and baselines have been subtracted from the observations and the laboratory data, respectively.

Fits to only the 6.9-µm feature were obtained with the three most promising silicates (âkermanite, melilite, gehlenite) and two aluminates (metamict hibonite and grossite). Poor-quality fits with âkermanite and gehlenite are not shown because of additional strong features that did not match those in the astronomical observations and because the combined 6.24–7.04 µm gehlenite peaks are too broad to match the observations well.

Two-component fits were obtained with hibonite, grossite, melilite and either tremolite or actinolite to fit the 6.2-µm feature. The best results are listed in Table 4 and plotted in Fig. 8. With the exception of Mon R2 IRS 3, which has a negligible 6.2-µm peak, most fits were improved by an amphibole (either actinolite or tremolite) component to fit the 6.2-µm band. Because there is little difference between these laboratory spectra, we give results for only the better matching of the two amphiboles and refer to the 6.2-µm fit as an amphibole fit.

4.2 Best-matching silicate

In all cases, the overtone spectrum of the silicate melilite provided the best match to the previously unidentified 6.9-µm feature. Most (8/9) of the spectra required an additional component of amphibole to fit the 6.2-µm band. Only the fit to Mon R2 IRS 3 was not improved by the addition of an amphibole.

4.3 Best-matching aluminates

Metamict hibonite was the best-fitting aluminate spectrum for five of the nine observations (GL 989, ρ-Elias 29, S140, Mon R2 IRS 3 and W33A) whilst grossite provided a (statistically) better match to W3 IRS 5, GL 2136, NGC 7538 IRS 9 and AFGL 7009S. However, fits with hibonite are preferred because its 6.9-µm profile is narrower and has less structure than that of grossite; for completeness, we have tabulated the results for both aluminates. Because metamict hibonite has a second peak at 6.29 µm, better fits to W3 IRS 5, Mon R2 IRS 3, GL 2136, NGC 7538 IRS 9 and W33A were obtained without the addition of an amphibole. In all cases, fits with aluminates were statistically poorer than those with the best-matching silicates.
4.4 Summary

Melilite provides the best match to the previously unidentified 6.9-µm absorption feature. The aluminate, metamict hibonite provides a poorer match. Amphibole (actinolite or tremolite) overtones also appear to contribute to the 6.2-µm astronomical peak. The combined overtone and ice and organic composites are compared with the Gibb et al. (2004) 5–8 µm astronomical optical depth spectra in Fig. 9.

5 DISCUSSION

5.1 Effect of temperature

We have obtained good matches to the spectra of GL 989, ρ-Elias 29, S140, W3 IRS 5 and AFGL 2136. However, the strong 6.9-µm features of Mon R2 IRS 3, NGC 7538, AFGL7009S and W33A are underestimated by our best fits. The discrepancy probably results from our use of room-temperature spectra. The dust grains responsible for the 6.2- and 6.9-µm YSO absorption features are probably much cooler because 10-K H2O ice spectra were used in most of the composites (see Gibb et al. 2004). At 3.5 K, the absorption bands of crystalline olivines and pyroxenes are observed to split, sharpen and shift to shorter wavelengths (Bowey et al. 2001). The exact response to temperature is specific to each mineral and each absorption band. The increase in band energy at 3.5 K indicates a contraction of the lattice as the temperature is reduced; sharpening and splitting of the bands is due to a reduction in phonon–phonon scattering. Wavelength shifts become less significant at shorter wavelengths (from about 0.0–0.2 µm at 25 µm and 0.9 µm at 80 µm). The observed response parallels the Zallen (1974) rule for high-pressure behaviour. Splitting is unlikely to be significant because the overtones are a combination of many modes which are not resolvable with current astronomical instrumentation. However, band sharpening is probably significant in the 5–8 µm range (at 3.5 K, the widths of 20–80 µm isolated single bands in the olivine, enstatites and diopside are ~90 per cent of their 295-K widths), especially because band enhancements are seen in the 80-K 10-µm spectra of olivines (Day 1976). The sharper bands obtained at lower temperatures would significantly improve the fits to the astronomical spectra and abundances of Si–O and Al–O inferred below.

5.2 Relative abundances

The integrated cross-sections of the overtones per Si–O or Al–O bond (hereafter X–O), σ_{int}, were obtained by multiplying the area of the optical depth spectrum, A, by the ratio of the mean relative molecular mass, \( \bar{m}_r \), to the number of X–O bonds, \( Z \times \tau_{OX} \), for a mole of silicon or aluminium atoms, where Z is the Avagadro number and \( \tau_{OX} \) is the ratio of oxygen to silicon or aluminium in the mineral anion, i.e.

\[
\sigma_{int} = A \frac{\bar{m}_r}{Z \tau_{OX}},
\]

where A is the area of the peak. Because the profiles are not Gaussian, it is inappropriate to use the FWHM and optical depth of the feature to obtain an integrated band strength. Therefore

\[
A = \kappa(\lambda_p) \int_{\lambda_1}^{\lambda_2} \tau(\lambda) \, d\lambda.
\]

The minerals, relative molecular masses, wavelength ranges and integrated cross-sections are listed in Table 5. These cross-sections were used to obtain the estimates of the ratio, R, of the number of X–O bonds to H2O ice in the astronomical environments given in Table 4. Relative abundances of Si–O in room-temperature amphiboles to low-temperature H2O ice are in the range 0.46–3.9 and in melilite are in the range 2.5–8.6.

5.3 Reconciliation with interpretations of the 8–13 µm silicate feature

We have shown that one or two crystalline minerals could be responsible for the 6.9- and 6.2-µm features observed towards deeply embedded objects, but there is little evidence for a substantial contribution to this wavelength range by amorphous silicates. A high abundance of crystalline silicate dust is not consistent with standard interpretations of astronomical 10- and 18-µm features, where a mainly amorphous composition and the presence of only one...
or two crystalline species are assumed (e.g. Kemper, Vriend & Tielens 2004), because these tend to lack the fine structures associated with crystalline silicates. However, a large component of crystalline silicate is consistent with the contrasting approach of Bowey & Adamson (2002), who simulated the effect of a very mixed silicate mineralogy on the 10-μm feature by averaging the spectra of a mixture of crystalline olivines, pyroxenes and phyllosilicates (but not melilites or amphiboles) with varying Mg: Fe ratios and only added an amorphous silicate component if it was required to remove remaining structure. They found that the sharp features due to crystalline minerals could blend to form the bands observed and that the proportion of crystalline minerals contributing to the absorption spectra of young stellar objects in the Taurus Molecular Cloud could be as high as 83 per cent by mass.

The 10-μm features of three of the objects in Table 1 have τ6.2(9.7) ≥ 4 and have a flat-bottomed shape (AFGL 7009S, W33A, W3 IRS 5) similar to the saturated laboratory spectra in Fig. 2, so that it is not possible to determine their degree of crystallinity. The remaining sources (GL 989, ρ-Elias 29, S 140, GL 2136, Mon R2 IRS 3 and NGC 7538 IRS 9) have optical depths between 0.7 and 2.6. The presence of optically thin 10-μm absorption features and 6.2- and 6.9-μm overtones indicates that the light at these two wavelengths has taken different paths through the flared circumstellar disc or torus. Hence, light observed in the overtone region has probably passed through more dust than that observed in the 10-μm silicate feature, and the absorption features observed in the different spectral regions are due to different grain populations of different temperatures, which may have varying chemical and physical properties. A full understanding of the mineralogical and physical properties of circumstellar discs requires spatially resolved observations over a very broad wavelength range, laboratory measurements of grain properties at a variety of temperatures and complete radiative transfer models.

6 SUMMARY

We have presented 1000–2500 cm⁻¹ room-temperature laboratory spectra obtained from powders of silicate, aluminate and nitride minerals and silicate glasses. The spectra exhibit overtone absorption bands with mass absorption coefficients ~100 times weaker than the fundamentals. These data are compared with the 5–8 μm spectra of deeply embedded YSOs observed with the Short Wavelength Spectrometer on the Infrared Space Observatory. Fits of the laboratory data to the observations, after subtraction of the 6.0-μm H₂O ice feature and the 6.0-μm feature identified with ORM, indicate that crystalline mellite or metamict hibonite may be responsible for much of the 6.9-μm absorption feature in the observations, with mellite providing the best match. A weaker 6.2-μm absorption in the YSO spectra is well matched by the spectra of the amphiboles actinolite and tremolite. Relative abundances of Si–O in room-temperature amphiboles to low-temperature H₂O ice are in the range 0.46–3.9 and in mellite are in the range 2.5–8.6. No astronomical feature was matched by the overtones of amorphous silicates, because these bands are too broad and peak at the wrong wavelength. Hence, this analysis is consistent with the 10-μm features of these objects being due to a mixture of crystalline and amorphous silicates, rather than only amorphous silicates. More laboratory data are required at temperatures <80 K to improve the fit to the astronomical spectra, because the overtones would probably sharpen with respect to room-temperature data. Fits with low-temperature spectra would probably also reduce the inferred abundances of Si–O and Al–O.

ACKNOWLEDGMENTS

We thank E. Gibb for providing us with the observations, polynomial continua and ice and ORM composite spectra from Gibb et al. (2004), T. Ziemann and P. Burns (University of Notre Dame) for

Table 4. Two-component fits to the 6.2- and 6.9-μm features in the wavelength range 5.1–7.4 μm. The 5.8-μm band (5.6–6.0 μm range) was excluded during fits to GL 989, GL 2136, NGC 7538 IRS 9, AFGL 7009S and W33A. The letters after the 6.2-μm optical depth fitted indicate the amphibole used for the fit: T, tremolite; A, actinolite. R is the ratio of the number of Si–O or Al–O bonds to H₂O ice (see Section 5.2).

<table>
<thead>
<tr>
<th>N_H₂O</th>
<th>GL 989</th>
<th>ρ-Elias 29</th>
<th>S140</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9-μm candidate</td>
<td>τ6.2</td>
<td>R</td>
<td>τ6.9</td>
</tr>
<tr>
<td>Melilite</td>
<td>0.058A</td>
<td>2.7</td>
<td>0.067</td>
</tr>
<tr>
<td>Metamict hibonite</td>
<td>0.040A</td>
<td>1.9</td>
<td>0.063</td>
</tr>
<tr>
<td>Grossite</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>N_H₂O</th>
<th>NGC 7538 IRS 9</th>
<th>GL 7009S</th>
<th>W33A</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9-μm candidate</td>
<td>τ6.2</td>
<td>R</td>
<td>τ6.9</td>
</tr>
<tr>
<td>Melilite</td>
<td>0.12T</td>
<td>0.50</td>
<td>0.25</td>
</tr>
<tr>
<td>Metamict hibonite</td>
<td>–</td>
<td>–</td>
<td>0.17</td>
</tr>
<tr>
<td>Grossite</td>
<td>0.083T</td>
<td>0.35</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Figure 8. One- and two-component overtone fits (solid black curves) to the 5.1–7.4 \( \mu m \) spectra of deeply embedded objects (grey curves) after subtraction of the ice and organic refractory composites. Two-component fits are indicated by pairs of offset curves, where the dotted curve is the amphibole fit to the 6.2-\( \mu m \) feature (either actinolite or tremolite as stated) and the offset solid curve is the fit to the 6.9-\( \mu m \) feature with either melilite, hibonite or grossite.
Overtones of minerals and 5–8 \(\mu\)m ice bands

Figure 9. Astronomical 5–8 \(\mu\)m optical depth spectra (grey curves) with the combined ice and organic composites and overtone fits (solid curves). Dotted curves peaking near 6.0 are the composites from Gibb et al. (2004).

Table 5. Calculation of integrated cross-sections.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Primary absorber</th>
<th>(r_{O-X}) ((\mu\m)</th>
<th>(\lambda_{pk}) ((\mu\m)</th>
<th>1–(\lambda)2 ((\mu\m)</th>
<th>(\sigma_{int} \times 10^{-20}) (cm(^2) (\mu\m) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melilite</td>
<td>Si–O</td>
<td>3.5</td>
<td>6.89</td>
<td>5.3–7.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Metamict hibonite</td>
<td>Al–O</td>
<td>1.58</td>
<td>6.88</td>
<td>5.6–7.8</td>
<td>3.9</td>
</tr>
<tr>
<td>Grossite</td>
<td>Al–O</td>
<td>1.75</td>
<td>6.86</td>
<td>5.3–9.1</td>
<td>1.3</td>
</tr>
<tr>
<td>Tremolite</td>
<td>Si–O</td>
<td>2.75</td>
<td>6.21</td>
<td>4.5–7.1</td>
<td>8.9</td>
</tr>
<tr>
<td>Actinolite</td>
<td>Si–O</td>
<td>2.75</td>
<td>6.21</td>
<td>4.5–7.1</td>
<td>2.3</td>
</tr>
</tbody>
</table>

providing X-ray diffraction data of the DeKalb diopside, and D. Kremser and G. Benedix (Washington University) for electron microprobe analyses of enstatite, the diopside-hedenburgites, melilite and actinolite. J. Paque (Caltech), C. Francis (Harvard University), M. R. Ghiara (Museo Mineralogico), R. C. Newton (University of California), R. Peterson (Queen’s University, Kingston) and B. Fegley and N. Johnson of Washington University provided us with mineral samples. Minerals have also been obtained from the collections of Washington University and the Natural History Museum. JEB is funded by the UK Particle Physics and Astronomy Research Council (PPARC) and AMH was funded by National Science Foundation grant NSF-AST-9805924. We thank the anonymous referee for a constructive report.

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