#### THE 6 MICRON FEATURE IN PROTOSTARS: EVIDENCE FOR ORGANIC REFRACTORY MATERIAL

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#### **ABSTRACT**

Data from the *Infrared Space Observatory* Short Wavelength Spectrometer have allowed abundances of many species present in interstellar ices to be determined. However, that of  $H_2O$ , the commonest of all ices, has proved controversial because of inconsistencies between results from different vibrational modes: the 6.0  $\mu$ m bending mode predicts column densities systematically higher than the stretching, combination, and libration modes in several lines of sight. We show that this discrepancy can be explained by excess absorption arising in a previously unrecognized blended feature, which we attribute to organic refractory matter (ORM). The strength of the excess absorption at 6.0  $\mu$ m is correlated with that of the 4.62  $\mu$ m "XCN" feature, the carrier of which is thought to form when interstellar ices undergo UV photolysis or ion bombardment. Our results are thus consistent with an origin for the ORM by energetic processing of simple ices.

Subject headings: infrared: ISM — ISM: abundances — ISM: molecules — line: profiles

#### 1. INTRODUCTION

Organic refractory matter (ORM) has long been discussed as a candidate for the carbon-rich component of both interstellar and cometary dust (Greenberg 1982, 1989). ORM is believed to form as a residue, following energetic processing (UV irradiation or ion bombardment) of interstellar ices in the environs of newly formed stars. A number of investigations have demonstrated the viability of such a formation mechanism in the case of laboratory analogs (e.g., Briggs et al. 1992; Strazzulla & Baratta 1992; Jenniskens et al. 1993; Greenberg et al. 1995). Infrared spectra of ORM produced in the laboratory are similar to those of kerogens extracted from carbonaceous meteorites (de Vries et al. 1993; Greenberg et al. 1995). They include features at 3.0 and 3.4  $\mu$ m, attributed to the OH and CH stretches, and overlapping absorptions in the 5–20  $\mu$ m region, attributed to various vibrational modes, such as stretching of C=O, C=C, C-OH, and C-NH, bonds and deformations of CH and NH groups. A model that attributes extinction in the visible to core-mantle grains composed of silicates and ORM is consistent with many of the observed properties of interstellar dust (Li & Greenberg 1997). However, previous evidence for ORM in astrophysical spectra has proved ambiguous or incorrect.

The midinfrared absorption profile of ORM is characterized by a sharp onset of absorption at  $\sim$ 5.5  $\mu$ m, a peak near 6.0  $\mu$ m, and a much more gradual decline toward longer wavelengths (e.g., Fig. 1 of Greenberg et al. 1995). If ORM is present in dust associated with young stellar objects (YSOs) that remain embedded in dense molecular clouds, this profile will be blended with features commonly seen in interstellar ices, notably the 6.0  $\mu$ m absorption attributed to the H<sub>2</sub>O ice bending mode. The 6.0  $\mu$ m feature has proved puzzling: its profile is often not well matched by laboratory spectra for pure H<sub>2</sub>O, suggesting contributions from other species; in some cases, the feature is anomalously strong, leading to column densities inconsistent with those predicted by ice features at other wavelengths (e.g.,

Gibb et al. 2000; Keane et al. 2001). In this Letter we reexamine the profile of the  $6.0\,\mu\mathrm{m}$  feature and show that these discrepancies can be largely resolved if it is assumed that ORM contributes to the absorption in the line of sight (LOS) toward certain luminous YSOs. The spectra obtained with the Short Wavelength Spectrometer (SWS) of the *Infrared Space Observatory (ISO)* provide an ideal resource for this investigation.

#### 2. OBSERVATIONS AND DATA REDUCTION

A detailed description of the SWS, its mode of operation, and the data reduction procedure are given by de Graauw et al. (1996). The data used in this Letter consist primarily of complete grating scans from 2.4 to 45.2  $\mu$ m in AOT mode S01 (speed 3 or 4) at resolving powers of  $\sim$ R/4 and  $\sim$ R/2, respectively (where R, the full-grating resolving power of SWS, ranges from 1000 to 2000). AOT mode S06 scans, which cover limited spectral ranges with the full resolving power of the SWS, were also used as noted in Table 1.

Data reduction was performed at the Space Research Organization of the Netherlands in Groningen, Netherlands, using the standard SWS interactive analysis package and pipeline processing version OLP 10.0. The ISO spacecraft records spectra with a grating that scans from low to high wavelengths and then from high to low wavelengths, resulting in two scans (the "up" and "down" scans). These scans were reduced separately. When flat fielding, we made a reference flat with the downscan, which is less affected by memory effects, and we used this on the up scan. The final up and down spectra were usually found to agree well in shape and flux level, and the final step was to average them. For each source, we then fit a polynomial continuum to the regions from 5 to 5.5  $\mu$ m and longward of 30  $\mu$ m, and we used this to derive an optical depth plot (E. L. Gibb et al. 2002, in preparation). The continuum regions were chosen to avoid the absorption features of  $H_2O$  ice at 6.0  $\mu$ m, an organic feature at 6.8  $\mu$ m, and the 9.7 and 18  $\mu$ m silicate features that extend from about 7.5 to 30  $\mu$ m.

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TABLE 1
SUMMARY OF OBSERVATIONS

|                | Position (J2000.0) <sup>a</sup> |                 |     |             | $t_{ m int}$ |          |
|----------------|---------------------------------|-----------------|-----|-------------|--------------|----------|
| Source         | R.A.                            | Decl.           | AOT | UTC DATE    | (s)          | FILE     |
| W3 IRS 5       | 02 25 40.5                      | 62 05 51.3      | 1.3 | 1997 Jan 17 | 3434         | 42701302 |
|                |                                 |                 | 6   | 1997 Jan 17 | 5668         | 42701224 |
| Mon R2 IRS 3   | 06 07 47.8                      | $-06\ 22\ 56.8$ | 1.3 | 1997 Oct 27 | 3454         | 71101712 |
|                | 06 07 48.2                      | -06 22 54.8     | 6   | 1997 Oct 27 | 4098         | 71101802 |
| W33 A          | 18 14 39.4                      | -175201.4       | 1.4 | 1996 Oct 10 | 6538         | 32900920 |
| AFGL 7009S     | 18 34 20.6                      | -055945.2       | 1.3 | 1996 Apr 17 | 3462         | 15201140 |
| S140           | 22 19 18.2                      | 63 18 47.6      | 1.4 | 1996 Jun 24 | 6538         | 22002135 |
| NGC 7538 IRS 9 | 23 14 01.6                      | 61 27 20.4      | 6   | 1996 Feb 23 | 6894         | 09801533 |

<sup>&</sup>lt;sup>a</sup> Coordinates toward which the *ISO* spacecraft was pointed. Units of right ascension are hours, minutes, and seconds, and units of declination are degrees, arcminutes, and arcseconds.

#### 3. DISCUSSION

#### 3.1. The 6 Micron Excess

It has been noted that there is a discrepancy between the principal  $H_2O$  ice features at 3 and 6  $\mu$ m: the 6  $\mu$ m feature consistently gives larger column densities by factors ranging from just a few percent in sources such as S140 and W3 IRS 5 to nearly 400% in W33 A, as indicated in Table 2. Gibb et al. (2000) examined the 4.5  $\mu$ m combination mode as well as the 3 and 6  $\mu$ m features in W33 A and found that it supports the lower column density implied by the 3  $\mu$ m feature rather than that found by Keane et al. (2001) using the 6  $\mu$ m feature. The 13  $\mu$ m libration mode, although blended with the deep silicate features, is also consistent with a lower column density (E. L. Gibb et al. 2002, in preparation). This appears to be the case in many other sources as well (E. L. Gibb et al. 2002, in preparation). We therefore take the approach of fitting the 6  $\mu$ m feature with laboratory spectra of pure H<sub>2</sub>O ice from Hudgins et al. (1993) using the column density derived from the 3  $\mu$ m feature. Figure 1 shows the 5.5–8  $\mu$ m spectrum of each source with a laboratory spectrum of the H<sub>2</sub>O ice feature superposed. In addition to H<sub>2</sub>O ice absorption, there is also a strong 6.8 µm feature attributed to O-H bending and C-H deformation modes, as well as to the onset at 7.5  $\mu$ m of the broad Si-O stretch feature centered at 9.7  $\mu$ m. The H<sub>2</sub>O ice feature has been scaled to give the column density derived at 3  $\mu$ m in every source except AFGL 7009S, which is saturated in that spectral region. In this case, the column density is from d'Hendecourt, Jourdain de Muizon, & Dartois (1996) and was found using both the 6 and 13.3  $\mu$ m features. As noted by d'Hendecourt et al. (1996), it should be considered an upper limit.

Figure 2 plots the absorption profiles after subtraction of the H<sub>2</sub>O ice component. It can be seen that for the sources with very little discrepancy between 3 and 6  $\mu$ m, S140 and W3 IRS 5, there is no need for an additional absorber. However, the sources with larger excess absorption at 6 µm, W33 A, Mon R2 IRS 3, NGC 7538 IRS 9, and AFGL 7009S, evidently require another absorber. After subtracting the H<sub>2</sub>O ice contribution from each source, we scaled a spectrum of an organic residue from Greenberg et al. (1995) to fit the residual (see Fig. 2). Greenberg et al. (1995) describe three organic residues resulting from processing of initial mixtures of H<sub>2</sub>O, CO, NH<sub>3</sub>, and a CH-bearing molecule (either CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, or CH<sub>3</sub>OH). We find that mixture A ( $H_2O : CO : NH_3 : CH_4$  ratio of 5 : 2 : 2 : 2) best fits the excess absorption in Mon R3 IRS 2, while mixture B  $(H_2O:CO:NH_3:C_2H_2)$  ratio of 5:2:2:1) best fits the absorptions in W33 A and AFGL 7009S. All mixtures fit NGC 7538 IRS 9—the source with the weakest excess absorption—equally well.

There remains a small excess absorption at 5.83  $\mu$ m attributed to the C=O stretch of ice species, such as HCOOH or H<sub>2</sub>CO in some sources, and a Gaussian feature at ~6.8  $\mu$ m, which occurs at the position of C-H deformation modes in saturated hydrocarbons, in all sources (Keane et al. 2001). In addition to this, several sources show another absorption feature at 6.2  $\mu$ m that has not yet been identified. NH<sub>3</sub> is also known to have a feature at 6.2  $\mu$ m. However, even in the sources with the largest NH<sub>3</sub> abundances (W33 A and AFGL 7009S; Gibb, Whittet, & Chiar 2001), the optical depth expected for NH<sub>3</sub> in an H<sub>2</sub>O ice mixture at 6.2  $\mu$ m is only ~0.05, clearly inadequate to explain the excess absorption at 6.2  $\mu$ m (see Fig. 2). The optical depths of these features after subtracting off the organic residue are given in Table 2.

#### 3.2. *XCN*

Laboratory work has shown that the carrier of the 4.62  $\mu$ m XCN feature may be formed when simple ice mixtures are exposed to UV radiation or high-energy protons (Lacy et al. 1984; Bernstein, Sandford, & Allamandola 1995; Elsila, Allamandola, & Sandford 1997; Pendleton et al. 1999; Palumbo et al. 2000), and hence this feature can be considered to be diagnostic of energetic processing. W33 A and AFGL 7009S have deep XCN features, indicating extensive processing of the ice mantle (Whittet et al. 2001 and references therein). The source NGC 7538 IRS 9 has an intermediate XCN feature, while S140 and W3 IRS 5 both have low upper limits on the presence of XCN, indicating that less processing has occurred along the LOS. Mon R2 IRS 3 also has no measurable abundance of XCN. However, most of the CO along this LOS is in the gas phase, and the 3 µm H<sub>2</sub>O ice feature in this source shows evidence of annealing, indicating high temperatures along most of the LOS. XCN is known to be somewhat volatile (Whittet et al. 2001) and may have evaporated along this LOS. With the possible exception of Mon R2 IRS 3, the discrepancy between the 3 and 6 µm H<sub>2</sub>O ice features corresponds loosely to the level of processing in each source as indicated by the presence of XCN.

Considering the strength of the XCN feature and the fact that both XCN and organic residues are formed in the same way in the laboratory, the presence of an organic residue in the spectra of sources like W33 A and AFGL 7009S is not surprising. By this logic, we would expect such a feature to be absent in S140 and W3 IRS 5, as indeed it is. NGC 7538 IRS 9, with its intermediate XCN abundance, also displays excess absorption consistent with an intermediate amount of ORM component. Only Mon R2 IRS 3 exhibits the ORM component with no evidence of XCN. This can be explained if the

q3

| TABLE 2            |
|--------------------|
| SUMMARY OF RESULTS |

|                | $N(H_2O)$<br>( × $10^{17}$ cm <sup>-2</sup> ) |                   |                |                  |              |             |             |       |
|----------------|---|-------------------|----------------|------------------|--------------|-------------|-------------|-------|
| Source         | 6 μm <sup>a</sup>                             | 3 μm <sup>b</sup> | $	au_{4.62}^{$ | $\tau_{\rm ORM}$ | $	au_{5.83}$ | $	au_{6.2}$ | $	au_{6.8}$ | Error |
| W3 IRS 5       | 51  | 63                | < 0.02         |                  | 0.05         | 0.02        | 0.22        | 0.02  |
| Mon R2 IRS 3   | 19  | 59                |                | 0.16             | 0.04         |             | 0.24        | 0.02  |
| W33 A          | 110   | 400               | 1.3            | 1.32             | 0.42         | 0.22        | 1.07        | 0.07  |
| AFGL 7009S     |   | 110               | 0.65           | 0.49             | 0.56         | 0.10        | 0.99        | 0.06  |
| S140           | 20  | 26                | < 0.024        |                  |              | 0.04        | 0.09        | 0.01  |
| NGC 7538 IRS 9 | 70  | 100               | 0.21           | 0.06             | 0.12         | 0.06        | 0.25        | 0.02  |

 $<sup>^{\</sup>rm a}$  Values for W33 A are from Gibb et al. 2000, and values for W3 IRS 5, Mon R2 IRS 3, S140, and NGC 7538 IRS 9 are from Gibb et al. 2001 .

XCN along the LOS has evaporated, an explanation that is consistent with the high ice temperatures indicated by the annealed 3  $\mu$ m feature.

#### 3.3. The OH and CH Stretching Features

The 3.0 and 3.4  $\mu$ m absorptions associated with stretching vibrations of OH and CH bonds, respectively, provide important additional diagnostics of ORM (Greenberg et al. 1995). Indeed, the 3.4  $\mu$ m feature has often been associated with an absorption at this wavelength seen in diffuse phases of the

W33A

AFGL 7009S

AFGL 7009S

MonR2 IRS3 x5

MonR2 IRS5 x3

12

5.5

6.0

6.5

7.0

Wavelength (μm)

Fig. 1.—The 5.5–8  $\mu m$  spectral region for the six sources studied. Overplotted is the laboratory  $H_2O$  ice spectra from Hudgins et al. (1993), scaled to match the optical depth derived at 3  $\mu m$ . Temperature of the laboratory spectra is 10 K for all except Mon R2 IRS 3, for which we used an 80 K spectrum. Several spectra were multiplied by a constant, indicated in the plot, for clarity.

interstellar medium (ISM; Butchart et al. 1986; Adamson, Whittet, & Duley 1990; Sandford 1991; Ehrenfreund et al. 1991; Pendleton et al. 1994). Two questions arise from our proposed identification of the 6  $\mu$ m excess in protostars with ORM: (1) Are the 3.0 and 3.4  $\mu$ m features in ORM visible in the spectra of sources displaying  $\mu$ m excesses? And (2) is the 6  $\mu$ m feature expected to be visible in the diffuse ISM?

The 3.0  $\mu$ m feature in the ORM overlaps the strong OH stretch feature of H<sub>2</sub>O ice. Our spectra of W33 A and AFGL 7009S, in particular, are saturated in this region. In all objects with 6  $\mu$ m excesses, the contribution of ORM to the observed

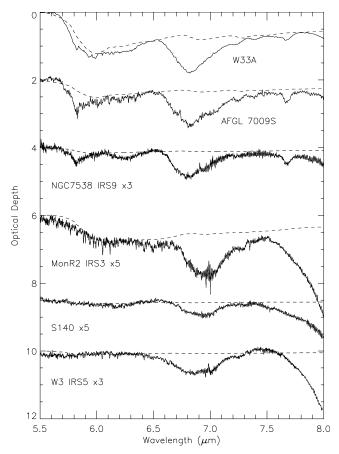


Fig. 2.—The 5.5–8  $\mu$ m spectral region for the six sources studied with the component due to H<sub>2</sub>O ice subtracted off. Overplotted is a spectrum of organic residues made by UV processing of an interstellar ice mixture from Greenberg et al. (1995). Residue A best fits Mon R2 IRS 3. Residue B is plotted over the remaining sources.

<sup>&</sup>lt;sup>b</sup> All values are from Keane et al. 2001, except for S140, which is found in this work.

<sup>&</sup>lt;sup>c</sup> Values for W33 A, NGC 7538 IRS 9, and AFGL 7009S are from Whittet et al. 2001. Upper limits for S140 and W3 IRS 5 are from Gibb et al. 2002.

3.0  $\mu m$  feature is predicted to be small (less than 10%). The 3.4  $\mu m$  feature should contribute to the broad, long-wavelength wing of the  $H_2O$  ice profile. However, the 3.4  $\mu m$  feature is much weaker than those at 3 and 6  $\mu m$  in laboratory ORM spectra, and so the predicted contributions to the observed spectra are again small. In W33 A, the expected optical depth of the 3.4  $\mu m$  feature is less than 0.3, on the order of the noise in this region. W33 A has a very deep long-wavelength wing, and a small feature such as this may easily be hidden (Gibb et al. 2000). The situation is more extreme for AFGL 7009S, with the expected strength of the 3.4  $\mu m$  feature ( $\tau \sim 0.1$ ) being well within the noise limit. The predicted 3.4  $\mu m$  features are even weaker,  $\tau < 0.04$ , in the other sources.

The strong 6.0  $\mu$ m feature present in laboratory ORM spectra (Greenberg et al. 1995) has no counterpart in the diffuse ISM (Whittet et al. 1997, 2001). This does not conflict with our suggestion that the 6  $\mu$ m excess absorption in YSOs is due to an ORM component. The interstellar 3.4  $\mu$ m feature seems securely identified with saturated aliphatic hydrocarbons, and a number of arguments favor an origin in amorphous carbon nanoparticles, such as those forming in the outflows of carbon-rich evolved stars (Schnaiter et al. 1999), rather than in the mantles of micron-sized grains that have been cycled through star formation regions. The evidence includes (1) a strong spectroscopic resemblance between the interstellar 3.4  $\mu$ m feature and that observed in a carbon-rich circumstellar shell (Chiar et al. 1998) and (2) a lack of any detectable polarization excess

in the interstellar feature, supporting an origin in very small grains that fail to align in the ambient magnetic field (Adamson et al. 1999). Hence, ORM appears not to be a widespread component of the diffuse ISM. This could imply that organics formed in protostellar envelopes are not returned efficiently to the ISM or that they undergo subsequent processing that reduces them to amorphous carbon.

#### 4. CONCLUSION

In summary, our results suggest that the discrepancy between  $\rm H_2O$  ice abundances found in many of the LOSs studied to date may result, at least in part, from the presence of additional absorption at 6  $\mu m$  arising in organic residues formed by energetic processing of the icy grain mantles. This processing occurs selectively in the envelopes of certain luminous YSOs. The residues are spectroscopically distinct from major phases of carbonaceous dust present in the diffuse ISM and are not likely to be significant contributors to the 3.4  $\mu m$  interstellar absorption feature.

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