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# The 6.0 and 6.8 $\mu\text{m}$ absorption features in the spectrum of NGC 7538: IRS9\*

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**Abstract.** Short Wavelength Spectrometer observations of the 6.0 and 6.8  $\mu\text{m}$  absorption features towards the obscured young stellar object NGC 7538: IRS9 are presented and compared to the features of a number of species measured in the solid phase. It is found that while solid  $\text{H}_2\text{O}$  provides the bulk of the 6  $\mu\text{m}$  band, additional absorption is required near 5.83  $\mu\text{m}$  and 6.25  $\mu\text{m}$ . It is proposed that formic acid ( $\text{HCOOH}$ ) is a plausible candidate for the blue excess, while the red excess could be related to the C-C stretching mode in aromatic structures. Subsequently, a number of candidates for the 6.8  $\mu\text{m}$  band are reviewed. Unfortunately, none of these appears to satisfy the observational constraints and no plausible identification can at this point be presented.

**Key words:** ISM: dust, extinction – ISM: molecules – infrared: ISM: lines and bands – stars: pre-main-sequence – stars: individual: NGC 7538: IRS9

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## 1. Introduction

Low resolution airborne spectroscopy of luminous young stellar objects (YSO's) shows two broad absorption features at 6.0 and 6.8  $\mu\text{m}$  (Tielens et al. 1984, Tielens & Allamandola 1987). The 6.0  $\mu\text{m}$  feature has generally been assigned to the bending mode of solid  $\text{H}_2\text{O}$  (Tielens & Allamandola 1987), which is supported by the presence of the  $\text{H}_2\text{O}$  stretching mode at 3  $\mu\text{m}$ . Various assignments have been proposed for the 6.8  $\mu\text{m}$  band, but no candidate has gained general acceptance (e.g., Schutte 1996). Presently, the availability of high resolution, high S/N

spectra of ISO's Short Wavelength Spectrometer (SWS) over the full wavelength region warrants a new investigation of these features.

We focus here on one object, the highly embedded massive YSO NGC 7538: IRS9, which shows some of the strongest solid state absorption features (Tielens et al. 1991). SWS data were obtained in the 5.3–8.3  $\mu\text{m}$  region in the full grating mode (AOT06). Being a point source (Willner et al. 1982), the original resolution of the NGC 7538: IRS9 data was equal to the instrumental resolution in this region ( $R \approx 1600$ ). To optimize S/N, the resolution was decreased to 600 by a Gaussian smoothing procedure. In view of the considerable width of the 6.0 and 6.8  $\mu\text{m}$  bands ( $\sim 0.5 \mu\text{m}$ ), this has no effect on the intrinsic shapes. The standard SWS flux calibration, as described by de Graauw et al. (1996) and Schaeidt et al. (1996) was carried out. Treatment of the individual up and down detector scans is described in Boogert et al. 1996.

The spectrum is shown in Fig. 1. It clearly shows the broad 6.0 and 6.8  $\mu\text{m}$  absorption features as well as a sharper dip near 7.7  $\mu\text{m}$ . For comparison the grating spectral response function is also shown. There is no indication of residual structure in the spectrum related to this function. We carefully conclude that the shape of the 6.0 and 6.8  $\mu\text{m}$  absorption bands is robust.

The 7.7  $\mu\text{m}$  band has been identified with solid  $\text{CH}_4$  and is discussed in another paper in this volume (Boogert et al. 1996). In the following we discuss the broad bands on the basis of a comparison with the features of various candidates as measured in laboratory simulation experiments. For details on the experimental procedures, see Gerakines et al. (1995).

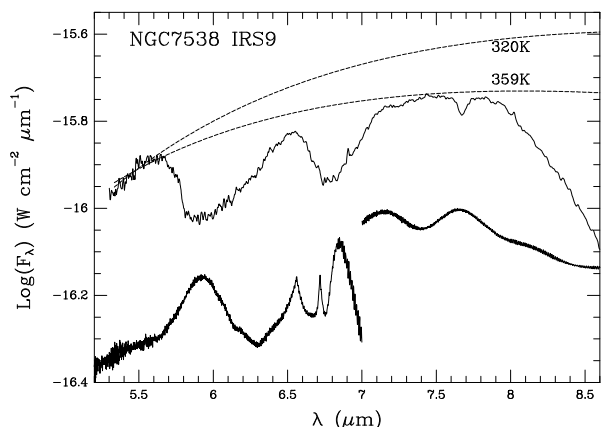
## 2. The continuum

The baseline definition over the 5.25 – 8.0  $\mu\text{m}$  region faces some problems. While ice or organic matrices generally show no appreciable absorption blue of 5.60  $\mu\text{m}$ , the region 7.1–8.0  $\mu\text{m}$  does contain absorption bands. In particular, the  $\text{H}_2\text{O}$

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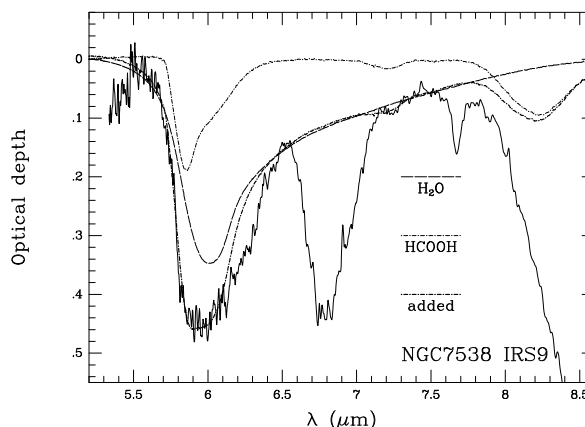
**Fig. 1.** The upper curve shows the SWS AOT06 observations of the 6.0 and 6.8  $\mu\text{m}$  towards NGC 7538: IRS9. Two baseline extremes are shown, corresponding to 320 and 359 K black bodies. The grating spectral response functions are shown below the observations.

bending mode extends out to 7.7  $\mu\text{m}$  (Hudgins et al. 1993), while the 9.7  $\mu\text{m}$  silicate band may extend into the red end of this region as well. In order to assess the resulting uncertainty in the 6.0 and 6.8  $\mu\text{m}$  band shapes we defined baselines under two extreme assumptions (Fig. 1). First we used a 359 K black body. This curve runs through the 5 - 5.6  $\mu\text{m}$  region as well as touches the observed spectrum at 7.50  $\mu\text{m}$ . It thus neglects possible absorption at this position and its slope might therefore be somewhat too shallow. The second extreme is represented by a 320 K black body. This curve follows the steep slope in the 5.25–5.60  $\mu\text{m}$  region, and hence stays considerably above the observed flux level at 7.50  $\mu\text{m}$ . Indeed, a comparison with the overall SWS01 spectrum (Whittet et al. 1996) suggests that this continuum is somewhat too steep. The optical depth plots obtained by subtracting either baseline give very similar results for the 6.8  $\mu\text{m}$  feature. Furthermore no significant variation is observed for the blue wing and the peak position of the 6.0  $\mu\text{m}$  feature. However, a considerable variation is obtained for the red wing of this band. It is considerably deeper for the 320 K baseline, i.e., the 6.0  $\mu\text{m}$  band appears in this case to be more extended towards the red. While keeping the uncertainty in the extension and depth of the red wing in mind, we will use in the remainder the optical depth plot obtained by subtracting the 359 K blackbody for comparison with the laboratory data (Fig. 2).

### 3. Comparison with laboratory data

#### 3.1. The 6.0 $\mu\text{m}$ feature

As discussed in Section 1, the 6.0  $\mu\text{m}$  feature has previously been ascribed to the bending mode of solid  $\text{H}_2\text{O}$ . Fig. 2 compares  $\text{H}_2\text{O}$  ice deposited at 10 K with NGC 7538: IRS9. It can be seen that, while the position of the interstellar feature is well matched by  $\text{H}_2\text{O}$ , the observed band is considerably broader, i.e., shows extra red and blue absorption. This discrepancy cannot be remedied by warm-up of the ice (e.g., Hudgins et al.



**Fig. 2.** Optical depth plot obtained from the observations relative to the 359 K blackbody (Fig. 1). The 6.0  $\mu\text{m}$  feature is compared to solid  $\text{H}_2\text{O}$  at 10K, solid  $\text{HCOOH}$  at 10K, and to the sum of these spectra.

1993). The baseline uncertainty tends to increase the discrepancy (Section 2). Furthermore, calculations show that particle shape effects are negligible for this feature. We conclude that additional components must contribute to the 6.0  $\mu\text{m}$  band.

The blue excess is centered near 5.83  $\mu\text{m}$  and has FWHM  $\approx 0.17 \mu\text{m}$ . This position is characteristic of the C=O stretching mode in organic molecules. For amides ( $\text{R}-\text{CONH}_2$ ) this mode is too blue (5.93  $\mu\text{m}$ ). Furthermore, aldehydes ( $\text{R}-\text{HCO}$ , e.g.,  $\text{H}_2\text{CO}$ ) give a too narrow band (FWHM 0.07 – 0.10  $\mu\text{m}$ ). However, organic acids ( $\text{R}-\text{COOH}$ ) may provide a good fit to the blue excess. This is illustrated in Fig. 2 which shows a fit of the 6.0  $\mu\text{m}$  band with the combined features of  $\text{H}_2\text{O}$  and formic acid ( $\text{HCOOH}$ ) at 10 K. Using a band strength of  $6.7 \times 10^{-17} \text{ cm}$  for the C=O stretching mode (Maréchal 1987), the abundance of  $\text{HCOOH}$  obtained from Fig. 2 equals 3 % ( $\pm 1$  %) of  $\text{H}_2\text{O}$ . While higher organic acids should also be able to match the blue excess, it seems likely that the simplest acid,  $\text{HCOOH}$ , is most readily produced. The column density of the  $\text{H}_2\text{O}$  component of the 6.0  $\mu\text{m}$  band, as shown in Fig. 2, equals  $8.0 \times 10^{18} \text{ cm}^{-2}$ , in close agreement with the value obtained from the 3  $\mu\text{m}$  feature (Allamandola et al. 1992). With a hydrogen column density  $N(\text{H}) = 1.6 \times 10^{23} \text{ cm}^{-2}$  (Tielens et al. 1991), the  $\text{H}_2\text{O}$  abundance then equals  $5 \times 10^{-5}$ . Besides the 5.85  $\mu\text{m}$  band,  $\text{HCOOH}$  has strong features at 3.06 and 8.2  $\mu\text{m}$ , which however blend with the  $\text{H}_2\text{O}$  and silicate features. In addition, it shows two weak bands at peak strength of  $\sim 10$  % of the 5.85  $\mu\text{m}$  feature at 3.87 and 7.23  $\mu\text{m}$ . A hint of the latter feature may perhaps be present in the observations (Fig. 2).

Due to its relatively large peak intensity (close to that of CO), particle shape effects could be of some importance if  $\text{HCOOH}$  would reside in a rather pure form in interstellar ice. However, it appears likely that the  $\text{HCOOH}$  would rather be severely diluted, and in this case such effects should be negligible (Tielens et al. 1991). Of course, in that case the intrinsic profile of the C=O stretching mode may change somewhat. A full investigation of all these aspects of the  $\text{HCOOH}$  assignment of the blue excess

of the 6.0  $\mu\text{m}$  band, as well as a discussion of possible formation mechanisms, is deferred to a later paper.

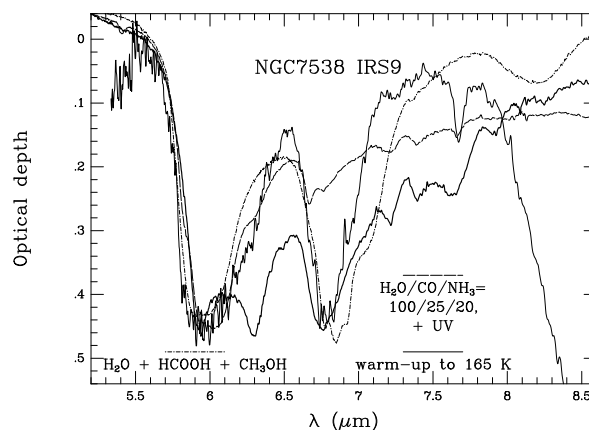
The red excess is centered at  $\sim 6.25 \mu\text{m}$  and has a width of  $\sim 0.2 \mu\text{m}$ . The position and width suggest that C-C stretching modes of aromatic structures in carbonaceous solids might contribute. This would make this feature the absorption counterpart of the well-known 6.2  $\mu\text{m}$  PAH emission feature. The equivalent width of the red excess is  $\sim 8 \text{ cm}^{-1}$ , implying that about 20 % of C along the line-of-sight would be included in aromatic structures (using  $N(\text{C})/N(\text{H}) = 4 \cdot 10^{-4}$ ,  $N(\text{H}) = 1.6 \cdot 10^{23} \text{ cm}^{-2}$  towards NGC 7538: IRS9 (Tielens et al. 1991), and  $\sigma_{\text{int}} = 2 \cdot 10^{-19} \text{ cm}^2/\text{C atom}$  (Schutte et al. 1993)). Such an abundance for carbonaceous solids appears reasonably consistent with models of the refractory component of interstellar grains (Mathis et al. 1983, Greenberg & Chlewicki 1983). It must be noted that the additional very broad aromatic C-C stretch near 7.7  $\mu\text{m}$  would be very hard to distinguish due to the presence of the 6.8  $\mu\text{m}$  band and the onset of the silicate absorption. At a reasonable degree of hydrogenation for such carbonaceous solids ( $\text{H}/\text{C} \approx 0.2$ ) the strength of the 3.3 and 11.3  $\mu\text{m}$  C-H modes would be similar to the 6.2  $\mu\text{m}$  band (Papoular et al. 1991, Guillois et al. 1996) and could perhaps be observed with highly sensitive spectroscopy. Indeed, the detection of a feature near 3.25  $\mu\text{m}$  which possibly corresponds with the aromatic C-H stretching mode was recently reported for a number of YSO's (Brooke et al. 1996, Sellgren et al. 1995). It must be noted that the strength of the red excess depends quite sensitively on the baseline definition; with the 320 K baseline (section 2), its equivalent width increases by approximately a factor of 2.

In summary, we propose that the 6.0  $\mu\text{m}$  absorption feature is contributed by (at least) 3 different components, i.e.,  $\text{H}_2\text{O}$ , an organic acid such as  $\text{HCOOH}$ , and a component responsible for the red excess absorption, possibly a refractory carbonaceous solid. In this view ISO will likely reveal source to source variations of the shape of the 6.0  $\mu\text{m}$  feature.

### 3.2. The 6.8 $\mu\text{m}$ feature

An obvious candidate for the 6.8  $\mu\text{m}$  feature is the C-H deformation mode of organic species. While for  $\text{R-CH}_2\text{-R}$  and  $\text{R-CH}_3$  groups the mode is too narrow, for alcohols ( $\text{R-HCOH-R}$ ) the feature broadens considerably due to the interaction between the CH and OH deformation modes. In particular  $\text{CH}_3\text{OH}$  provided a fairly good match to earlier, low resolution Kuiper Airborne spectra (Tielens & Allamandola 1987, Tielens et al. 1984).

Fig. 3 shows a comparison of the 6.8  $\mu\text{m}$  feature with a composite spectrum produced by adding the composite  $\text{H}_2\text{O}/\text{HCOOH}$  spectrum (Fig. 2) to a spectrum of pure solid  $\text{CH}_3\text{OH}$ , deposited at 10 K (Hudgins et al. 1993). It can be seen that the methanol feature falls somewhat red of the interstellar band. The methanol feature does not shift in ices dominated by  $\text{H}_2\text{O}$ , giving an equally imperfect match (Hudgins et al. 1993). The discrepancy can neither be remedied through warm-up, or by diluting with apolar material, e.g., no shift is seen for  $\text{H}_2\text{O}/\text{CH}_3\text{OH}/\text{CO}_2 = 100/40/60$ . Perhaps the imperfect match of the red wing reflects to some extent the uncertainty in the



**Fig. 3.** A comparison of the 6.8  $\mu\text{m}$  feature with the sum of the spectrum of 10 K solid  $\text{CH}_3\text{OH}$  (from Hudgins et al. 1993) and the  $\text{H}_2\text{O} + \text{HCOOH}$  combination spectrum of Fig. 2. Additionally, a comparison of the 6.8  $\mu\text{m}$  feature with the  $\text{NH}_4^+$  feature obtained by UV photolysis of a  $\text{H}_2\text{O}/\text{CO}/\text{NH}_3 = 100/25/20$  at 10 K, and after warm-up to 165 K.

choice of the continuum. Indeed, the 320 K baseline (Section 2) produces a 6.8  $\mu\text{m}$  band which corresponds slightly better with the methanol feature, and an even steeper baseline would produce further improvement. However, besides the imperfect match, an assignment to methanol faces serious problems with regard to the absence of additional features. The strength of the CH bending mode would require C-H and C-OH stretching modes near 3.54  $\mu\text{m}$  and 9.7  $\mu\text{m}$  of  $\tau = 0.5$  and 1, respectively (d'Hendecourt & Allamandola 1986). Especially the 9.7  $\mu\text{m}$  feature, which is much narrower than the silicate band, should be highly conspicuous but is clearly not observed anywhere near the required strength in the SWS01 scan of NGC 7538: IRS9 (Whittet et al. 1996). While Allamandola et al. (1992) detected the methanol C-H stretch band, the corresponding abundance is  $\sim 4$  times less than necessary to account for the 6.8  $\mu\text{m}$  band. Thus while  $\text{CH}_3\text{OH}$  contributes to the 6.8  $\mu\text{m}$  band at the 25 % level, most of it has to be carried by another species.

An assignment to higher alcohols faces similar problems. Higher alcohols with  $\text{R-CH}_3$  groups, e.g., ethanol, show a strong, sharp, deformation mode at 7.25  $\mu\text{m}$ , and can be excluded. Thus, only species which have an -OH attached to every C atom appear possible. In a mixture of  $\text{H}_2\text{O}/\text{HOCH}_2\text{CH}_2\text{OH} \approx 100/20$ , deposited at 10K, the feature falls at  $\sim 6.90 \mu\text{m}$ , producing a slightly worse fit than methanol. Moreover, like  $\text{CH}_3\text{OH}$ , higher alcohols show strong C-H and C-OH stretching modes near 3.4 and 9.5  $\mu\text{m}$ , which should be highly conspicuous but are not observed. We conclude that an assignment of the bulk of the interstellar 6.8  $\mu\text{m}$  feature to the CH bending modes in alcohols can generally be excluded.

Alternatively, it has been proposed that the 6.8  $\mu\text{m}$  feature may originate in interstellar carbonates (e.g.;  $\text{MgCO}_3$ ; Sandford & Walker 1985). However, carbonates show an additional feature near 11.6  $\mu\text{m}$ , at approximately half the peak strength, but with a considerably smaller width (FWHM  $\approx 0.15 \mu\text{m}$ ; Sandford & Walker 1985). This band should be superimposed on

the silicate 10  $\mu\text{m}$  band, but is not observed in the SWS01 scan of NGC 7538: IRS9 (Whittet et al. 1996). We conclude that an assignment to carbonates is unlikely.

Finally, an assignment to the  $\text{NH}_4^+$  ion has been considered (Grim et al. 1989a). This species was created in the laboratory by irradiation of ices containing  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{NH}_3$ . The reaction path involves the photochemical formation of acids (e.g.,  $\text{HNCO}$ ,  $\text{HCOOH}$ ) followed by proton exchange with the base  $\text{NH}_3$  (Grim et al. 1989b). Fig. 3 shows a comparison with an ice mixture of original composition  $\text{H}_2\text{O}/\text{CO}/\text{NH}_3 = 100/25/20$  following photolysis at 10 K, and after warm-up to 165 K. It can be seen that the  $\text{NH}_4^+$  band is much too weak and furthermore falls somewhat longward of the 6.8  $\mu\text{m}$  feature in the 10 K ice. A rather good match both in position and strength relative to the 6.0  $\mu\text{m}$   $\text{H}_2\text{O}$  band is obtained after partial  $\text{H}_2\text{O}$  sublimation at 165 K. The shift appears to be induced by the  $\text{H}_2\text{O}$  sublimation since it occurs exclusively over the 160 – 180 K interval where the sublimation takes place. However, besides the  $\text{NH}_4^+$  band, a number of other features are apparent in the lab spectra which are not present in the observations (cf., Grim et al. 1989b).

Perhaps the most important objection to the  $\text{NH}_4^+$  identification is the absence of absorptions due to suitable counterions. In the photolyzed residues, the 6.33 and 7.41  $\mu\text{m}$  bands are attributed to a counterion,  $\text{HCOO}^-$ . This is a very general problem. All ions have strong features, e.g.,  $\text{NO}^-$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$  absorb strongly in the 5.5 - 8.5  $\mu\text{m}$  range (Grim et al. 1989b). While an assignment of the XCN band observed near 4.62  $\mu\text{m}$  (Lacy et al. 1984, Whittet et al. 1996) with  $\text{OCN}^-$  has earlier been proposed (Grim & Greenberg 1987), the strength of this feature shows that  $\text{OCN}^-$  can at most account for  $\sim 15\%$  of the necessary counter-charge (Schutte & Greenberg 1996). We therefore conclude at this point that an assignment to  $\text{NH}_4^+$  appears unlikely due to the absence of identifiable counterions towards NGC 7538: IRS9.

In summary, the availability of full ISO spectra allows us to scrutinize a number of proposed assignments for the 6.8  $\mu\text{m}$  band. It is found that no satisfactory candidates are presently available. The observational constraints are nevertheless quite stringent. First, the carrier has no other strong features, since no additional unidentified bands of comparable intensity are observed (Whittet et al. 1996). Second, the feature appears to correlate with the 6.0  $\mu\text{m}$  band rather than with the silicate feature, suggesting an origin in the icy grain mantles (Tielens & Allamandola 1987). If the feature originates in ice, the carrier must be an abundant constituent. For a typical infrared band strength of  $1 \cdot 10^{-17}$  cm, its abundance would be 30 % of  $\text{H}_2\text{O}$ . Clarifying the nature of the 6.8  $\mu\text{m}$  absorption feature remains one of the major challenges in the study of interstellar ices.

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