Detection of solid methanol toward W 33 A

R.J.A. Grim[1], **F. Baas**[1], **T.R. Geballe**[2], **J.M. Greenberg**[1], and **W. Schutte**[3]

[1] Laboratory Astrophysics, Huygens Laboratory, University of Leiden, P.O. Box 9504, NL-2300 RA Leiden, The Netherlands
[2] Joint Astronomy Centre, 665 Komohana Street, Hilo, HI 96720, USA
[3] NASA Ames Research Center, Moffett Field, CA 94035, USA

Abstract. A recently detected absorption feature at 3.53 μm in the spectrum of W 33 A has been assigned to methanol (CH_3OH). Its optical depth implies that methanol is the second most abundant molecule (7% relative to H_2O) in the grain mantles in the line of sight towards W 33 A observed to date. Laboratory experiments have shown that the implied abundance is difficult to explain by UV irradiation of the dust grains alone. Grain surface reactions or condensation directly out of the gas phase must also play roles, but the relative contributions of the various processes are difficult to estimate. The optical depth of the 3.53 μm feature constrains the contribution of methanol to the 6.8 μm feature in W 33 A to be 10% or less, requiring the contribution of at least one other compound to this feature, while the estimated contribution to the 4.9 μm absorption band is even smaller. Only a small contribution of formaldehyde (H_2CO) is consistent with the observed 3.53 μm band profile. In contrast to methanol, formaldehyde can be produced readily by photochemical reactions within the ice mantle.

Key words: interstellar medium: dust – molecules – lines: identifications – spectroscopy

1. Introduction

The presence of ice mantles on interstellar grains is clearly indicated by the characteristic infrared absorption bands of the frozen molecules observed towards many obscured astronomical objects. In the mid-IR, such bands result from the excitation of vibrational modes in the molecules. Many features have first been observed in W 33 A, a deeply embedded young stellar source. Identifications of observed absorption bands with known molecules or molecular groups are not always straightforward because of solid state-induced frequency shifts and line broadening. The molecules or radicals involved are often reactive and can only be studied spectroscopically under circumstances resembling space conditions. This is the reason why the laboratory spectroscopy of photolyzed ice mixtures that are representative of ices on interstellar grains at low temperatures (10 K) has played such an important role in identifying the observed dust features. Not only have molecules such as H_2O, CO, H_2S and OCS (Gillett & Forrest 1973; Merrill et al. 1976; Willner et al. 1982; Lacy et al. 1984;

Geballe et al. 1985; Geballe 1986) been identified in the absorption spectra of IR sources, but information on the physical state and thermal history of identified molecules can sometimes be derived as well. In some cases the situation is less clear. For example, the strong absorption at 4.62 μm in W 33 A, observed simultaneously with the solid CO band, has been assigned to several different species (Lacy et al. 1984; Larson et al. 1985; d'Hendecourt et al. 1986). The latest assignments involve the OCN^- ion (Grim & Greenberg 1987) and Si-H (Nuth & Moore 1988), although for Si-H no match with the spectrum of W 33 A has been given.

Among the many solid state absorption features detected toward W 33 A are two at 6.0 and 6.8 μm. The first of these has been assigned to H_2O (see Willner et al. 1982 and references therein) and the second feature to CH deformation modes within alcohols (Tielens et al. 1984). Since strong absorption features also are expected from methyl(ene) groups in the C–H stretching region (3.3–3.6 μm), we have remeasured this part of the spectrum of W 33 A at moderate spectral resolution, obtaining a considerably higher S/N ratio than has been reported previously at such resolutions (e.g., Larson et al. 1985). Detection of methyl(ene) groups in this wavelength interval is quite difficult, however, due to an overlap with the long wavelength wing of the very deep H_2O ice band in this source.

2. Observations

A spectrum of W 33 A between 2.80 and 3.65 μm was obtained at the United Kingdom 3.8 m Infrared Telescope on 25 May 1987. The facility's 7-channel cooled grating spectrometer was used with an entrance aperture of 5″. The resolution of the instrument in this wavelength band is 0.008 μm. Standard chopping and nodding techniques were employed. Atmospheric absorption features and the overall spectral response of the instrument were removed by ratioing the coadded spectrum to that of a reference star, BS 6378, and the resultant spectrum was flux-calibrated assuming $L = 2.31$ for this star (Glass 1974) and that its spectrum is that of a 9000 K black body. The integration time is 80 s pt^{-1} throughout the spectrum.

Figure 1 shows the resultant spectrum. Between 2.95 and 3.20 μm the spectrum is saturated by H_2O-ice absorption although the bottom of the band is clearly detected. The short wavelength side of the ice band is quite steep; the long wavelength side less steep, typical of (dirty) ice bands in molecular clouds. The noise level in Fig. 1 can best be estimated by the scatter of adjacent points. However, in the interval 3.0–3.4 μm some systematic
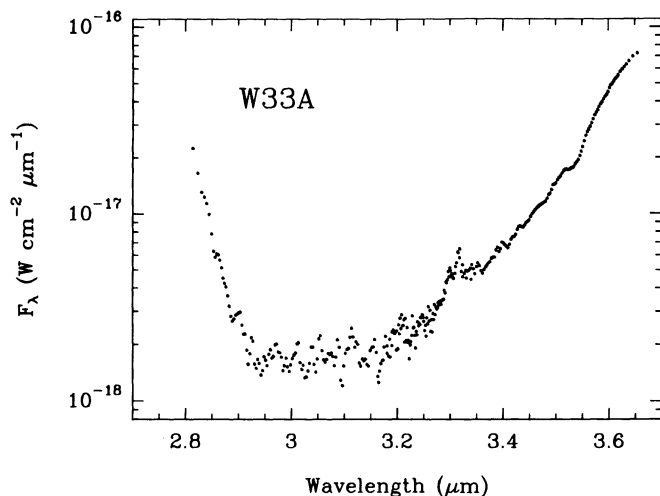
Fig. 1. The observed spectrum of W 33 A in the 2.80–3.65 μm region
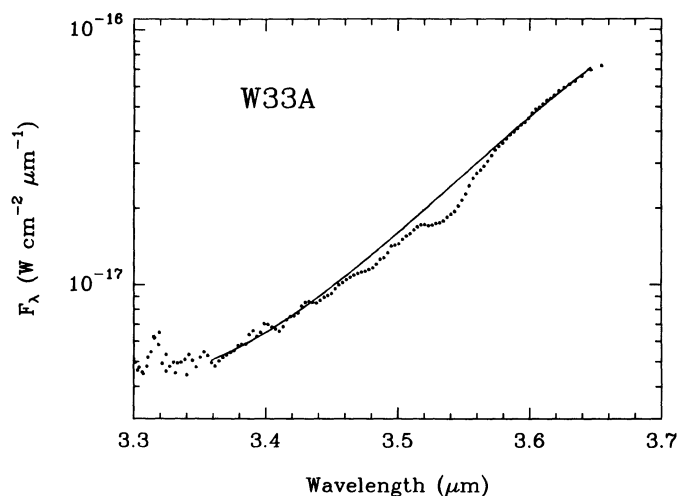

Fig. 2. The 3.30–3.65 μm region of W 33 A showing the baseline curve used to evaluate the 3.53 μm absorption

residual components are also present due to improper correction for strong telluric features (e.g., the CH_4 Q-branch near 3.32 μm). We make no claims regarding the realities of these apparent features near and at the bottom of the ice band. Thus, the only significant feature in the spectrum is a depression in the long wavelength wing at about 3.53 μm.

3. Analysis and identification of the 3.53 μm feature

As the 3.53 μm feature is much narrower than the wing on which it is superimposed, a baseline correction can be made to arrive at the approximate profile of the feature. To achieve this, the wing was fitted with a smooth third order polynomial (Fig. 2) which was subsequently subtracted from the spectrum. Zero absorption was assumed for the 3.36–3.45 and 3.61–3.65 μm intervals. The resulting absorption profile is shown in Fig. 3, where it is compared with laboratory spectra of formaldehyde (H_2CO) and methanol (CH_3OH) diluted in water ice (Fig. 3, solid lines). The laboratory spectra were baseline-corrected using the same method as the observations. The assignment of this feature to CH_3OH is supported by various arguments: (i) the center absorption wavelength is characteristic of simple alcohols, (ii) the spectral shape and width of the observed and laboratory absorption bands are very similar, and (iii) the profile of the only other candidate which is known to be abundant in space and absorbs at the same frequency, H_2CO, does not match the observed profile.

Different baseline correction procedures and higher CH_3OH dilution factors (up to $H_2O/CH_3OH = 20/1$ and $H_2O/NH_3/CH_3OH = 20/2/1$) do not affect the profile of the 3.53 μm feature significantly. The good fit of the CH_3OH laboratory spectrum with that of the interstellar feature therefore does not seem to be accidental and it is concluded that solid phase methanol is present on the grains in the line of sight towards W 33 A.

4. Discussion

4.1. The CH₃OH column density

In addition to the 3.53 μm absorption feature, methanol shows prominent absorptions at 3.08, 3.35, 6.87 and 9.6 μm. It is
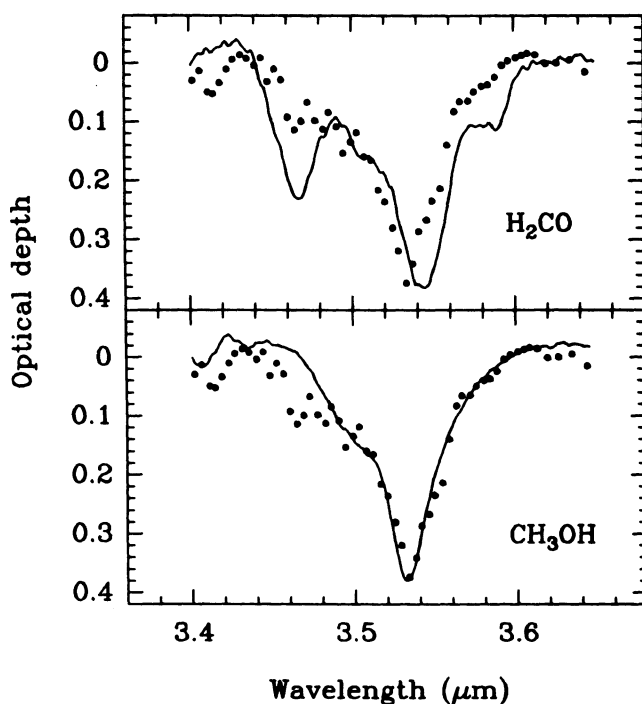

Fig. 3. Comparisons of the 3.40–3.65 μm W 33 A spectrum, after the baseline correction procedure (see text), with laboratory spectra of formaldehyde and methanol in water ice. a) $H_2O/H_2CO = 20/1$ at 12 K and 2 cm^{-1} resolution and b) $H_2O/CH_3OH = 3/1$ under the same conditions (taken from d'Hendecourt & Allamandola 1986)

doubtful, however, that very many of those bands are readily distinguishable from coincident and stronger features. The band at 3.08 μm is blended with the much stronger H_2O ice band. The band at 3.35 μm is not only weaker than the 3.53 μm band, but it is also much broader, extending from 3.2 to 3.6 μm. It may contribute to the long wavelength wing of the ice band, but will probably not be clearly identifiable. Similarly, the 9.6 μm band of CH_3OH is obscured by the 9.7 μm silicate band, as well as being

coincident with telluric ozone absorption. The situation with regard to the 6.87 μm band is less clear. An absorption band roughly centered at 6.8 μm has been observed with the KAO (Soifer et al. 1979; Tielens & Allamandola 1987). According to Tielens et al. (1984) this band is due to the methyl(ene) bending modes in simple alcohols. If the 6.8 μm band is specifically assigned to CH_3OH, a column density relative to H_2O of 55% is implied.

From the observed 3.53 μm profile and the integrated band strength of the 3.53 μm absorption of methanol, the CH_3OH concentration (relative to H_2O) in the interstellar grain mantles towards W 33 A can be calculated. The absorption band strength of the laboratory 3.53 μm band was reevaluated by a careful analysis of existing CH_3OH/H_2O spectra, including those published by d'Hendecourt & Allamandola (1986). This analysis resulted in a somewhat lower value of $5 \ 10^{-18} \ cm \ molecule^{-1}$. The band in W 33 A has a measured equivalent width of $16.4 \ cm^{-1}$, implying a column density of $3.3 \ 10^{18} \ cm^{-2}$. This column density can be compared with the 6.0 μm H_2O column density of $4.7 \ 10^{19} \ cm^{-2}$ (Tielens et al. 1984), resulting in a ratio $[CH_3OH]/[H_2O] = 7\%$ along the line of sight towards W 33 A. Without corrections, the band strength reported by d'Hendecourt & Allamandola (1986) would have given a slightly lower (5%) concentration. It should be noted that this ratio between two volatile molecules is an average along the line of sight that will be different in the warmer and cooler dust surrounding W 33 A. In addition, scattering effects, which are strongly wavelength dependent in this spectral region, can modify this ratio. No correction has been made for this. If scattering plays a role, it would tend to slightly increase the $[CH_3OH]/[H_2O]$ ratio.

4.2. The contribution of CH_3OH to the 6.8 μm absorption

The observed 6.8 μm band implies an optical depth of roughly 50% of that of H_2O when this band is identified with CH_3OH, while the 3.53 μm band only gives 7%. Therefore, a 50% contribution of methanol to the 6.8 μm band is inconsistent with the absorption in the 3.3–4.0 μm region, as the two observed bands cannot simultaneously be fitted to an H_2O/CH_3OH laboratory spectrum. Thus at least one additional carrier must be responsible for the 6.8 μm absorption feature. More specifically, the CH_3OH column density derived in Sect. 4.1 limits the methanol contribution to the 6.8 μm absorption band to ∼10%.

An alternative interpretation of this particular band has been given in terms of the ammonium ion, NH_4^+ (Grim et al. 1989a, b).

4.3. The contribution of CH_3OH to the 4.9 μm absorption

A weak 4.9 μm absorption feature has been detected in W 33 A (Geballe et al. 1985; Larson et al. 1985) and several assignments have been suggested. On the basis of laboratory spectra Geballe et al. proposed an identification with an unspecified sulfur compound, whereas Larson et al. suggested C_3, CN and CH_3OH. The first two candidates of Larson et al. have never been observed in irradiated laboratory astrophysical ices. As in the case of the 6.8 μm band, the detection of the 3.53 μm band allows us to constrain the contribution of CH_3OH to the 4.9 μm band. After conversion of Geballe et al.'s data to optical depth units a band area of $2.9 \ cm^{-1}$ is obtained. Using the 4.9 μm band strength listed in Table 1, roughly 32% of methanol relative to H_2O would be required to explain the 4.9 μm band area of W 33 A. Since the $[CH_3OH]/[H_2O]$ ratio is 4 to 5 times smaller, it might be expected that methanol accounts for at most 20% of the 4.9 μm band. There are two reasons to believe that the methanol contribution to the 4.9 μm band is even lower than that. First, the CH_3OH band profile does not fit the 4.9 μm absorption in W 33 A because the latter is too broad (Fig. 4). Second, the 4.9 μm band was not observed in the IR spectrum of $H_2O/NH_3/CH_3OH = 20/2/1$, which indicates that in a water-rich environment the 4.9 μm band strength is reduced.

4.4. Possible H_2CO contribution

H_2CO is another abundant molecule that is readily formed on and in grain mantles and has absorption features near the 3.53 μm methanol band. However, an assignment of the 3.53 μm absorption to H_2CO is difficult to support, not just because of the shift in the wavelength of its peak absorption (which might be due to a different solid state environment), but largely because of differences in line profiles and the existence, near this wavelength, of other absorption bands of H_2CO which are not seen in the spectrum of W 33 A. H_2CO could account for the weak absorption at 3.46 μm, which is not well matched by methanol. However, as can be seen from Fig. 3, even in that case H_2CO would not be expected to contribute more than 25% to the 3.53 μm band.

Table 1. Integrated band strengths of methanol in pure form and in water ice. The original data from d'Hendecourt & Allamandola (1986) have been re-evaluated using baseline correction procedures similar to that of the 3.53 μm feature as discussed in the text

λ (μm)	Mode	CH_3OH pure		CH_3OH in H_2O	
		dHA 86	This work	dHA 86	This work
3.08	O–H stretch	$1.1 \ 10^{-16}$	$1.2 \ 10^{-16}$		
3.36	C–H stretch	$2.1 \ 10^{-17}$	$1.0 \ 10^{-17}$		
3.53	C–H stretch	$7.6 \ 10^{-18}$	$4.9 \ 10^{-18}$	$5.1 \ 10^{-18}$	$5.0 \ 10^{-18}$
4.90	$2 \nu_2$ overtone		$2.0 \ 10^{-19}$		
6.87	C–H deformation	$1.0 \ 10^{-17}$	$8.7 \ 10^{-18}$	$4.5 \ 10^{-18}$	$5.0 \ 10^{-18}$
8.90	CH_3 rock	$1.3 \ 10^{-18}$	$1.6 \ 10^{-18}$	$1.3 \ 10^{-18}$	$1.3 \ 10^{-18}$
9.61	C–O stretch	$1.8 \ 10^{-17}$	$1.5 \ 10^{-17}$	$1.0 \ 10^{-17}$	$1.0 \ 10^{-17}$

dHA 86: d'Hendecourt & Allamandola (1986)
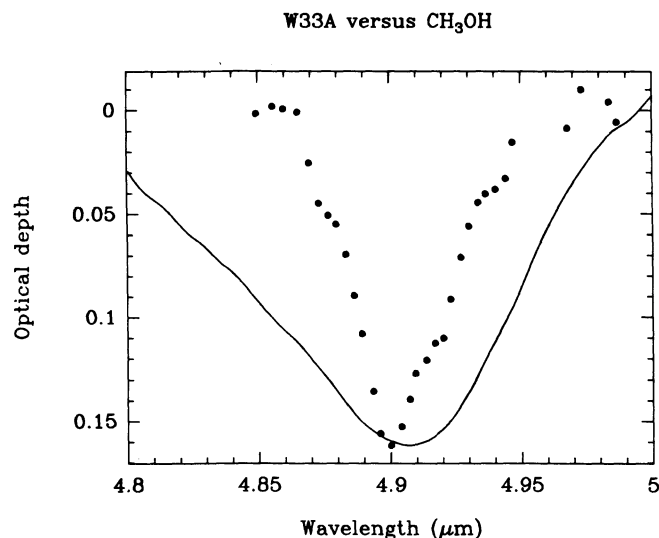
W33A versus CH₃OH

Fig. 4. Comparison of the 4.9 µm band in W 33 A (Geballe et al. 1985) with the $2\nu_2$ mode of solid CH_3OH at 12 K (d'Hendecourt & Allamandola 1986)

Assuming that 25% of the 3.53 µm band is indeed due to H_2CO, we can estimate the abundance of H_2CO relative to H_2O. The value of the integrated strength of the 3.54 µm band of solid phase H_2CO is not well known. Assuming the gas phase absorbance value of $2.1\ 10^{-17}$ cm molecule^{-1} (Pugh & Rao 1976), an H_2CO concentration of 0.5% with respect to H_2O is derived. However, from spectroscopic studies of solid state H_2CO, whether or not diluted in H_2O (van der Zwet 1986), it was found that the intensity of the 3.54 µm band relative to that of its 6.67 µm band is one-tenth that in the gas phase. The assumption that the value of the band strength of the 6.67 µm feature in the solid phase is equal to that in the gas phase thus increases the H_2CO concentration to about 5%. Such concentrations have in fact been measured in UV irradiated, astrophysically relevant ice mixtures (d'Hendecourt et al. 1986; Schutte 1988).

5. CH₃OH formation

Three formation mechanisms may be considered that can account for the presence of CH_3OH. First of all, methanol may be formed by irradiation of the dirty ice mantles by ultraviolet photons. When simulated in the laboratory this process was found to be inefficient. Reported methanol concentrations of less than 2% relative to H_2O were detected, even after prolonged UV irradiation times (Schutte 1988), whereas the H_2CO concentration was found to be much higher. It thus seems rather unlikely that UV photoprocessing *alone* can account for the observed abundance of 7%.

A second process which may account for high methanol abundances is grain surface reactions. Model calculations have shown that concentrations of H_2CO up to 30% of H_2O can be formed by this process (Tielens 1983), but the accuracy of this results suffers from the restricted number of reactions used in the computer simulations (d'Hendecourt et al. 1985). Formation of CH_3OH by surface reactions has not been studied specifically (and experimentally) but seems an obvious extrapolation. It should be noted that in the model calculations methanol dissociation pathways resulting from UV photochemistry have not been

incorporated, whereas this mechanism has clearly been demonstrated to occur (Sandford et al. 1988).

A third process involves the condensation of methanol directly from the gas phase. Generally, the methanol abundance in the gas phase in molecular clouds is at least two orders of magnitude less than that of CO (Irvine et al. 1987). This seems to argue against CH_3OH condensation being significant. On the other hand, one may argue that a low gas phase abundance in turn results from CH_3OH condensation on the cold grains. The estimated CH_3OH desorption rate during explosive heating processes, which roughly equals that of H_2O, results in the preservation of the $[CH_3OH]/[H_2O]$ concentration in the ice mantles (Schutte 1988). The much higher volatility of CO, implying a larger desorption rate, will ultimately lead to an enrichment of the $[CH_3OH]/[CO]$ ratio in the solid phase over that in the gas phase.

The large uncertainties invoked in the above discussed processes do not allow us to make any definite judgement about the formation of methanol, although we emphasize that photochemical methanol formation is probably not sufficiently efficient to account for its observed concentration.

6. Conclusions

Ground-based IR observations of W 33 A at high spectral resolution have revealed a feature at 3.53 µm. The observed spectrum matches laboratory spectra of H_2O/CH_3OH ices. From the observed optical depths and an experimentally derived integrated band strength, a column density of CH_3OH of about 7% relative to H_2O has been derived. This implies that methanol is the second most abundant molecule presently detected in the solid phase of the ice mantles of W 33 A.

The strength of the 3.53 µm band implies that CH_3OH cannot account for more than 10% of the observed band at 6.86 µm in W 33 A, while a significant CH_3OH contribution to the 4.9 µm band in W 33 A is unlikely.

An upper limit to the concentration of H_2CO, which may contribute to the 3.53 µm feature is uncertain, as it depends on the absorption cross-section for solid H_2CO, which is not well known. However, H_2CO is not expected to contribute more than 25% to the 3.53 µm band.

References

d'Hendecourt L.B., Allamandola L.J., 1986, A & AS 64, 453
d'Hendecourt L.B., Allamandola L.J., Greenberg J.M., 1985, A & A 152, 130
d'Hendecourt L.B., Allamandola L.J., Grim R.J.A., Greenberg J.M., 1986, A & A 158, 119
Geballe T.R., Baas F., Greenberg J.M., Schutte W., 1985, A & A 146, L6
Geballe T.R., 1986, A & A 162, 248
Gillett F.C., Forrest W.J., 1973, ApJ 179, 483
Glass I.S., 1974, MNRAS 33, 53
Grim R.J.A., Greenberg J.M., 1987, ApJ 321, L91
Grim R.J.A., Greenberg J.M., Schutte W.A., Schmitt B., 1989a, ApJ 241, L87

Grim R.J.A., Greenberg J.M., Schutte W.A., Baas F., Schmitt B., 1989b, A&A 218, 341

Irvine W.M., Goldsmith P.F., Hjalmarson A., 1987, in: Interstellar Processes, eds. D.J. Hollenbach, H.A. Thronson, Reidel, Dordrecht, p. 561

Lacy J.H., Baas F., Allamandola L.J., Persson S.E., Mcgregor P.J., Lonsdale C.J., Geballe T.R., van de Bult C.E.P.M., 1984, ApJ 276, 533

Larson H.P., Davis D.S., Black J.H., Fink U., 1985, ApJ 299, 873

Merrill K.M., Russell R.W., Soifer B.T., 1976, ApJ 207, 763

Nuth J.A., Moore M.H., 1988, ApJ 329, L119

Pugh L.A., Rao K.N., 1976, in: Molecular Spectroscopy: Modern Research, Volume II, ed. K.N. Rao, Academic Press, New York, p. 165

Sandford S.A., Allamandola L.J., Valero G.J., 1988, Icarus 76, 225

Schutte W.A., 1988, The Evolution of Interstellar Organic Grain Mantles, University of Leiden, Ph.D. Thesis

Soifer B.T., Puetter R.C., Russell R.W., Willner S.P., Harvey P.M., Gillett F.C., 1979, ApJ 232, L53

Tielens A.G.G.M., 1983, Physics and Chemistry of Interstellar Dust, University of Leiden, Ph.D. Thesis

Tielens A.G.G.M., Allamandola L.J., Bregman J., Goebel J., d'Hendecourt L.B., Witteborn F.C., 1984, ApJ 287, 697

Tielens A.G.G.M., Allamandola L.J., 1987, in: Physical Processes in Interstellar Clouds, eds. G.E. Morfill, M. Scoler, Reidel, Dordrecht, p. 333

Willner S.P., Gillett F.C., Herter T.L., Jones B., Krassner J., Merrill K.M., Pipher J.L., Rudy R.J., Russell R.W., Soifer B.T., 1982, ApJ 253, 174

van der Zwet, G.P., 1986, A Spectroscopic Study of Absorption and Emission Features of Interstellar Dust Components, University of Leiden, Ph.D. Thesis