

Letter to the Editor

New infrared absorption features due to solid phase molecules containing sulfur in W33A

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Received December 18, 1984; accepted January 15, 1985

SUMMARY

Two new absorption features are reported in the highly obscured infrared source W33A. The stronger of these occurs at 4.9 μ m; based on laboratory experiments it is due to an as yet unidentified, sulfur-containing molecule on the mantles of dust grains. The weaker feature, at 3.9 μ m, is identified as solid H₂S.

Key Words: Infrared radiation, Interstellar medium: dust, Interstellar medium: molecules, Spectroscopy, Stars: pre-main sequence.

I. Introduction

The infrared object at the position of the compact radio source, W33A, is one of the most heavily obscured sources known, with its extinction estimated to be $A_V \sim 100$ mag (e.g., Capps et al 1978). Because of this and because of its apparent brightness in the mid-infrared spectral region, W33A is perhaps the most suitable candidate for studying the composition of dust grains in molecular clouds. All of the commonly observed mid-infrared solid state absorption features are found in it, and are generally more prominent than in any other source (Capps et al 1978, Soifer et al 1979, Lacy et al 1984, Tielens et al 1984). Indeed, one absorption feature, at 4.62 μ m, is observed in W33A and has not been clearly detected in any other object (Soifer et al 1979, Lacy et al 1984, Geballe 1985).

Except for the observations of Lacy et al (1984) between 4.55 and 4.73 μ m and those at Br α (4.05 μ m) (McGregor et al 1984), only low resolution spectroscopy ($\Delta\lambda/\lambda \lesssim 0.01$) of W33A is available between 3 and 13 μ m. The observations of Lacy et al illustrate how much additional information may be obtained by reobserving this spectral region at higher resolution. With this in mind, we have observed the W33A source from 3 to 5 μ m at the United Kingdom Infrared Telescope (UKIRT) on Mauna Kea at 4 to 8 times higher spectral resolution than that of previously reported spectra. In doing so we have detected two new absorption features, at 3.9 μ m and 4.9 μ m. In the following sections we briefly describe and discuss these observations and related laboratory work.

II. Observations

Spectra of W33A in the 3 - 5 μ m range were first obtained in 1983 July at UKIRT, using its 7-channel grating spectrometer (Wade 1983). A 5" diameter beam

was employed shortward of 4 μ m, a 4" beam longward of 4.5 μ m. In both cases a 30" EW chop was used. The grating was scanned in such a way that individual data points are spaced by one-half of the instrumental resolution. The stars BS6698 and BS7264 were observed shortward and longward, respectively, of 4.5 μ m and at similar hour angles and air masses as W33A. Molecular and atomic absorption features in them were not detected. The W33A spectra were then ratioed by those of the stars, multiplied by blackbody functions appropriate to the stars, and Hanning (triangle) smoothed. Wavelength calibration, obtained from an Argon lamp and from atmospheric features, is accurate to better than 0.005 μ m.

The 1983 spectra showed a prominent and resolved absorption feature at 4.90 μ m and a weak and resolved one centered at 3.93 μ m. New spectra at the wavelengths of these features were obtained at UKIRT in 1984 April and May and were analyzed in a similar fashion to that described above. Both features were confirmed. The 1984 4.9 μ m data, which is an average of four independent spectra and represents a total integration time of 8 minutes, are presented in Fig. 1. Both years' 3.9 μ m data, are combined in Fig. 2, which is an average of 14 independent spectra representing a total integration time of 19 minutes. The spectrum of W33A shortward of 3.8 μ m will be described elsewhere (Greenberg et al 1985).

Figure 1 shows the spectral range 4.55 - 5.02 μ m. In this interval the resolution of the spectrum is approximately 0.008 μ m. Dashed lines at 4.81 and 4.84 μ m indicate the positions of strong telluric H₂O lines. We cannot be certain of the W33A spectrum through these intervals, but we believe it to be flat. An even stronger H₂O absorption at 4.96 μ m makes determination of the W33A spectrum impossible there. Other small wiggles in the spectrum, although above the noise level, could easily be due to incorrect cancellation of other telluric features.

Three prominent absorption features are seen in Figure 1. The one at 4.9 μ m is newly discovered; it is also recently reported by Larson et al (1984). It extends from 4.870 to 4.935 μ m, appearing roughly triangular and slightly asymmetric, with maximum absorption occurring at 4.895 μ m (2043 cm⁻¹). The peak absorption corresponds to $\tau \approx 0.15$ and the equivalent width of the feature is $0.005 \pm 0.001\mu$ m. The other two features, with absorption maxima at 4.62 μ m and 4.675 μ m, are those reported by Lacy et al (1984); their strengths and widths are consistent with the results of those authors.

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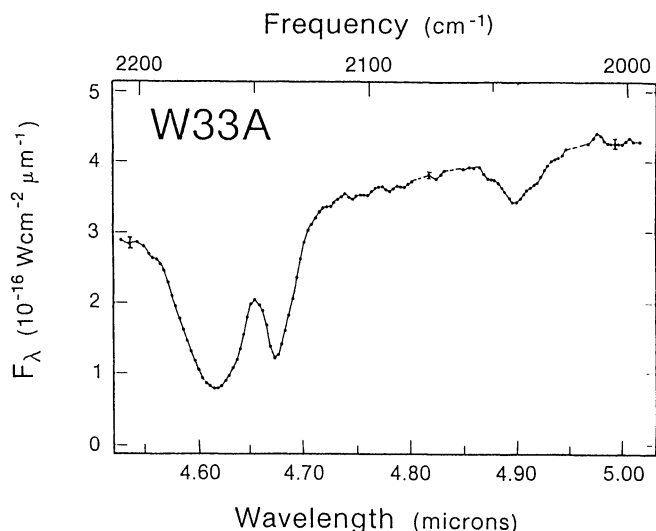


Fig. 1. Spectrum of W33A from 4.55 to 5.02 μm observed at a resolution of 0.008 μm . Dashed lines are drawn at the positions of strong telluric absorptions, where reliable data is lacking. Three average error bars ($\pm 1 \sigma$) are shown. Those near the edges of the spectrum pertain to the intervals $\lambda < 4.56 \mu\text{m}$ and $\lambda > 4.95 \mu\text{m}$; the other pertains to the middle portion of the spectrum. In no case is the statistical uncertainty in a data point more than twice that shown.

Figure 2 shows a spectrum of W33A from 3.78 to 4.03 μm . The resolution is $\sim 0.009 \mu\text{m}$. Telluric absorption is not a problem in this interval. A weak absorption feature is seen to extend from 3.90 to 3.97 μm ; we refer to it hereafter as the 3.9 μm feature and note that it appears to be present in the spectrum of Soifer et al (1979), although not mentioned by them. The greatest depth, in the feature, corresponding to $\tau \sim 0.06$, occurs near the long wavelength edge at 3.96 μm (2525 cm^{-1}). The absorption between 3.90 and 3.94 μm may appear to be of questionable reality; however, in both the 1983 and 1984 spectra absorption over the full 3.90 to 3.97 μm range was observed. It is doubtful that any of the other, smaller deviations from a smooth spectrum in Figure 2 are real. We estimate an equivalent width of $0.0020 \pm 0.0005 \mu\text{m}$ for the 3.9 μm feature.

III. Discussion

The $\sim 0.05 \mu\text{m}$ widths of the two new features suggest either that they are due to vibrational transitions of molecules in the solid state (i.e., in dust grains) or that they are unresolved bands of molecules in the gaseous state. The latter origin, however, probably is ruled out for the 4.9 μm absorption band because of its shape and also is not likely for the 3.9 μm feature, which appears to bear only a marginal resemblance to a vibration-rotation band.

1. The 4.9 μm Feature

The feature seen in W33A at 4.62 μm (2165 cm^{-1}) has been reproduced in laboratory experiments by ultraviolet photolysis and temperature cycling of frozen gas mixtures (Lacy et al 1984). Details of the general experimental conditions and principles

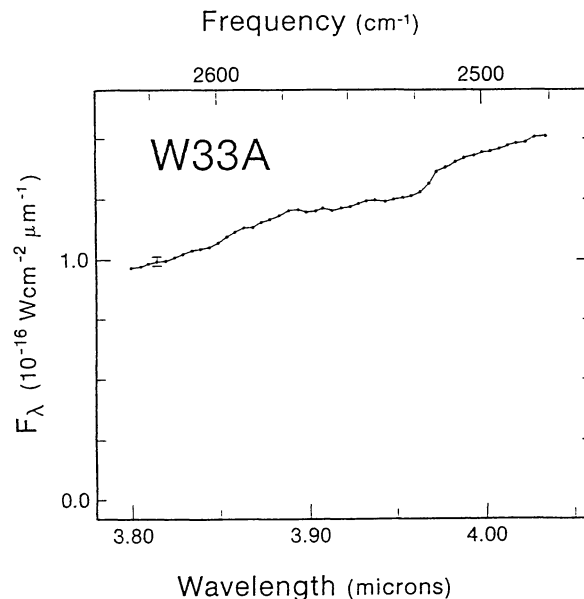


Fig. 2. Spectrum of W33A from 3.78 to 4.03 μm , observed at a resolution of 0.009 μm . The average error bar ($\pm 1 \sigma$) for a data point is shown.

are described by Hagen et al (1979). That feature, attributed to the $-\text{C} \equiv \text{N}$ (cyano) group, remained the most dominant spectral feature after the photolyzed sample had been heated to 150 K. In Figure 3, the observed spectrum of W33A is shown together with the laboratory spectra obtained for a similar experiment, but now with a small amount of sulfur in the form of H_2S added to the initial gas mixture. After photolysis at 10K a new absorption feature appears at $\sim 4.90 \mu\text{m}$ in addition to the previously reported features at 4.62 μm (cyano) and 4.67 μm (solid CO). At 10K the new feature has a FWHM of 25 cm^{-1} and two absorption maxima, at 2045 cm^{-1} and 2038 cm^{-1} , thus appearing to be a blend of two absorption bands. A sequence of infrared spectra taken during sample warm-up clearly shows that the higher frequency component evaporates from the sample at a temperature of about 35K. The other component remains centered at 2038 cm^{-1} (4.907 μm) and with a FWHM of 20 cm^{-1} , giving a very good match with the observed band in W33A. The new band and the cyano band feature remain until about 250K. Figure 3 shows the spectrum taken at 85K, when some solid CO remained in the sample. Apart from the 4.9 μm feature, no other strong features due to the inclusion of sulfur were observed in the photolyzed material at this temperature in the spectral interval 2.5 - 25 μm . The amount of sulfur used in this experiment is a factor of three too large to be consistent with cosmic abundance requirements, and the strength of the 2038 cm^{-1} band has to be scaled down accordingly in Figure 3. From the warm-up experiments, it follows that the molecules responsible for the bands at 2165 and 2038 cm^{-1} are stable and have rather low vapour pressures, two properties that favor their accumulation in grain mantles. Thus, it probably is significant that the ratio of the strengths of these two bands in the laboratory sample, properly scaled for cosmic abundance ratios, is similar to that observed in W33A.

It may be concluded that the 4.9 μm feature in the warmed-up sample is caused by a sulfurcontaining molecule. However, the identity of this molecule is

not known at present. A possible identification might appear to be the carbonyl sulfide (OCS) molecule. In the gaseous state, OCS has a vibrational frequency of 2060 cm^{-1} , close to the frequency of peak absorption of the corresponding feature in the laboratory experiment. It is clear that OCS is present in the laboratory sample after photolysis but before warmup, because in addition to the blend at $4.9\mu\text{m}$ absorption at the wavelengths of its two other fundamental vibrations ($\sim 12\mu\text{m}$ and $\sim 19\mu\text{m}$) are observed then. However, upon warmup these absorptions as well as one component of the blend disappear. Therefore, pure OCS cannot be identified with the laboratory-produced, high temperature residual feature which is shown in Figure 3.

We conclude that the $4.9\mu\text{m}$ feature observed in W33A is identified with at least one of the two laboratory features at $4.9\mu\text{m}$ and, hence, with a sulfur-containing molecule. However, until more sensitive and higher resolution spectroscopy of W33A (especially at longer infrared wavelengths) is available, we cannot rule out either feature. The frequency shift of the W33A feature from either laboratory feature is very small and could be interpreted in terms of different interactions of the absorbing molecule with its neighbors in the two environments. It should be noted that absorption bands at $\sim 2040\text{ cm}^{-1}$ are not unique for a sulfur-containing compound; photolyzed mixtures containing CO and O₂ show a similarly shaped band at 2038 cm^{-1} (d'Hendecourt 1984), which has been identified as a band belonging to the CO₃ radical. This radical is not very stable, however, as the band disappears from the spectrum when the temperature is raised above 20K. The CO₃ band is also very weak compared to the bands seen in the sulfur experiment.

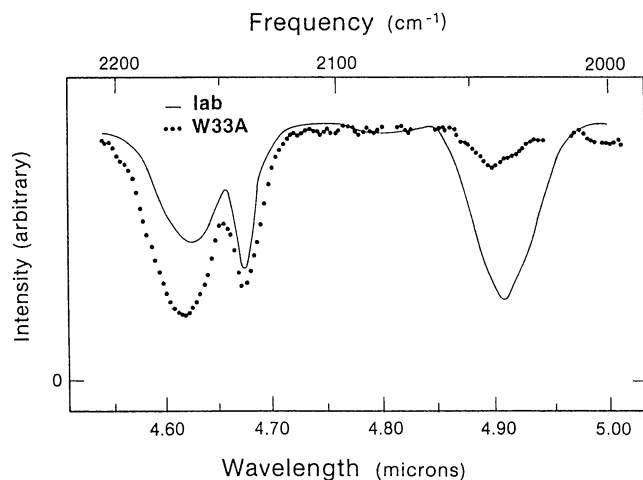


Fig. 3. Laboratory spectrum of a frozen mixture of simple molecules, including H₂S, CO and NH₃, which has been subject to UV-irradiation at 10K and then warmed to 85K. The spectrum of W33A is shown for comparison with its baseline flattened.

The observations and laboratory results described in this letter suggest that the occurrences of the bands at $4.62\mu\text{m}$ and $4.9\mu\text{m}$ should be correlated. In order to further explore this hypothesis one of us (TRG) has obtained a spectrum of the highly obscured source, NGC 2264 IRS, in the $4.8 - 5.0\mu\text{m}$ interval. This object is known to have a strong solid CO feature at $4.67\mu\text{m}$, but no $4.62\mu\text{m}$ feature (Geballe 1985). In the $4.8 - 5.0\mu\text{m}$ spectrum of

NGC 2264 IRS, no evidence was found for the $4.9\mu\text{m}$ band, to optical depth and equivalent width limits which are 4 times lower than that of the same feature in W33A. This suggests that the $4.9\mu\text{m}$ feature may be observable only in sources which show the $4.62\mu\text{m}$ feature, in accord with the laboratory experiments.

2. The $3.9\mu\text{m}$ Feature

A review of the vibrational frequencies of simple and abundant molecular species suggests that an identification of the $3.9\mu\text{m}$ feature lies in the vibrational modes of H₂S. In the gaseous state the fundamentals of two of these modes occur at 2620 and 2633 cm^{-1} ; in the solid form each shifts to lower frequency by $\sim 100\text{ cm}^{-1}$ (see Nakamoto 1978), putting both in close proximity to the observed feature in W33A. In the laboratory experiments a very weak absorption feature, extending roughly from $3.9\mu\text{m}$ to $4.0\mu\text{m}$ was seen in the initial unphotolyzed material which contained H₂S and which later produced the laboratory spectrum in Figure 3. Subsequent laboratory experiments using much larger amounts of H₂S have produced much stronger $3.9\mu\text{m}$ absorptions, whose profiles depend on the relative abundances of other molecular species in the frozen mixtures. While we regard the identification of solid H₂S as the source of the $3.9\mu\text{m}$ feature in W33A to be straightforward, further laboratory studies of the absorption profile and cross section of this feature are in progress and will be reported elsewhere.

Acknowledgements

We wish to thank Anna Lucas for the preparation of the manuscript and the rest of the staff at UKIRT for many types of assistance. We are also grateful to L. J. Allamandola and A. G. G. M. Tielens for some helpful suggestions.

References

- Capps, R. W., Gillett, F. C. and Knacke, R. F., 1978, *Ap.J.* **226**, 863.
- Geballe, T. R., 1985: in preparation.
- Greenberg, J. M., Geballe, T. R., Butchart, I., and Whittet, D. N. B., 1985, in preparation.
- Hagen, W., Allamandola, L. J., and Greenberg, J. M., 1979, *Ap. Space Sci.* **65**, 215.
- d'Hendecourt, L. 1984, Ph.D. Dissertation, Leiden University.
- Lacy, J. H., Baas, F., Allamandola, L. J., Persson, S. E., McGregor, P. J., Lonsdale, C. J., Geballe, T. R. and van de Bult, C. E. P., 1984, *Ap.J.* **276**, 533.
- Larson, H. P., Davis, D. S., Black, J. H., and Fink, U., 1985, *B.A.A.S.* **16**, 959.
- McGregor, P. J., Persson, S. E. and Geballe, T. R., 1984, *P.A.S.P.* **96**, 315.
- Nakamoto, K., 1978, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons, New York.
- Soifer, B. T., Puetter, R. C., Russell, R. W., Willner, S. P., Harvey, P. M. and Gillett, F. C., 1979, *Ap.J. Letters* **232**, L53.
- Tielens, A. G. G. M., Allamandola, L. J., Bregman, J., Goebel, J., d'Hendecourt, L. B., and Witteborn, F. C., 1984, *Ap.J.* **287**, 697.
- Wade, R. 1983, *Proceedings of the S.P.I.E.* **445**, 47.