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# INTERSTELLAR ABSORPTION FEATURES TOWARD THE COMPACT INFRARED SOURCE W33A

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## ABSTRACT

A high-resolution ($\lambda/\Delta\lambda \sim 2000$), broad-bandwidth (3.3–5.0 $\mu$m) spectrum of the compact infrared source W33A is presented. Four absorption features are associated with compositionally distinct components in the interstellar medium: solid-phase $C_3$, CN, or $CH_3OH$ at 4.9 $\mu$m, solid-phase CO and either solid or gaseous $CH_3NC$ near 4.6 $\mu$m, and the well-known "dirty ice" feature near 3 $\mu$m. The analysis of this spectrum supports chemically complex models of grain mantle evolution in cold, quiescent molecular clouds.

*Subject headings:* infrared: sources — interstellar: grains — interstellar: molecules — nebulae: individual

## I. INTRODUCTION

We have recorded a high-resolution ($\lambda/\Delta\lambda \sim 2000$), broad-bandwidth (3.3–5.0 $\mu$m) spectrum of the compact infrared source W33A. This object fortuitously illuminates an intervening column of cold, dense material, thus permitting analyses of quiescent interstellar matter using the techniques of infrared absorption spectroscopy. This opportunity is allowing significant insight into the chemical composition of interstellar grains. A deep absorption at 10 $\mu$m identifies the silicate component of grains in the line of sight to W33A (Capps, Gillett, and Knacke 1978). Another strong absorption at 3.1 $\mu$m is associated with $H_2O$ ice (Capps, Gillett, and Knacke 1978), which presumably coats the silicate grains. Soifer *et al.* (1979) and Tielens *et al.* (1984) observed weaker absorptions in the 4–8 $\mu$m region that they associated with CO, CH, and OH modes. In particular, Soifer *et al.* tentatively assigned a feature at 4.6 $\mu$m to CO, although they noted that, even at their relatively low resolving power ($\lambda/\Delta\lambda \sim 70$), the position of this band was short of that expected for solid or gaseous CO alone. The character of the 4.6 $\mu$m feature was clearly revealed by the higher resolution ($\lambda/\Delta\lambda \sim 840$) W33A observations of Lacy *et al.* (1984). They found two prominent resolved components, one at 4.67 $\mu$m, which they assigned to solid CO, and a second at 4.62 $\mu$m, which they attributed to unspecified cyano group molecules ("XCN") on the basis of laboratory simulations of grain mantle compositions. Their results contributed two significant insights into the nature of interstellar matter: (1) at least in the direction of W33A, much of the interstellar CO may be locked up as ice in grain mantles, and (2) there appears to be a significant amount of photoprocessing of grain mantle material, yielding CN-bearing molecules.

Our new high-resolution observations demonstrate convincingly that only the solid phase of CO can contribute substantially to the 4.67 $\mu$m feature. Also, we suggest that the 4.62 $\mu$m feature could be methyl isocyanide ($CH_3NC$). In addition, we analyze a new feature at 4.9 $\mu$m, observed independently by Larson *et al.* (1984) and Geballe *et al.* (1985), in terms of interstellar $C_3$, CN, or $CH_3OH$. All of our results indicate complex grain surface chemistry, but uniqueness problems remain associated with most molecular assignments.

## II. OBSERVATIONS

The spectra were recorded with a Fourier spectrometer (Larson and Fink 1975) at the NASA 3 m Infrared Telescope Facility (IRTF) on Mauna Kea during 1981 March–April. Each of the dual optical inputs to the spectrometer subtended a field of view of 5.″1, and they were separated by 50″. Differencing of the signals from these two inputs allowed real-time cancellation of most of the infrared thermal background flux without the use of a chopped beam. Residual background levels disappeared during subsequent coaddition of equal numbers of interferograms recorded through each of the spectrometer's entrance apertures. The star α Aurigae was used as a comparison for determining instrumental response and atmospheric transmission.

W33A was observed for relatively brief periods on four different nights (see the log of observations in Table 1). We increased our spectral resolution twice during the run in order to follow up the interesting spectral features that were revealed by preliminary on-site processing of the data. This allowed us to form two nearly independent spectral averages of W33A: one at 4.3 $cm^{-1}$ resolution that includes portions of the data from all observations (total integration time = 2.5 hr), and another at 1.0 $cm^{-1}$ resolution that uses data from just two nights (total integration time = 4.2 hr). These two averages are displayed in the upper part of Figure 1. Each has been divided by the stellar comparison spectrum in order to remove instrumental and telluric features. The stellar spectrum itself appears

TABLE 1

LOG OF OBSERVATIONS

| Object | Date 1981 UT | Integration Time (min) | Air Mass | Spectral Resolution ($cm^{-1}$) |
|---|---|---|---|---|
| W33A ..... | Mar 29 | 37 | 1.39 | 4.3 |
| W33A ..... | Mar 30 | 52 | 1.36 | 2.0 |
| W33A ..... | Mar 31 | 120 | 1.39 | 1.0 |
| α Aur ..... | Apr 1 | 20 | 1.37 | 1.0 |
| W33A ..... | Apr 11 | 130 | 1.34 | 1.0 |

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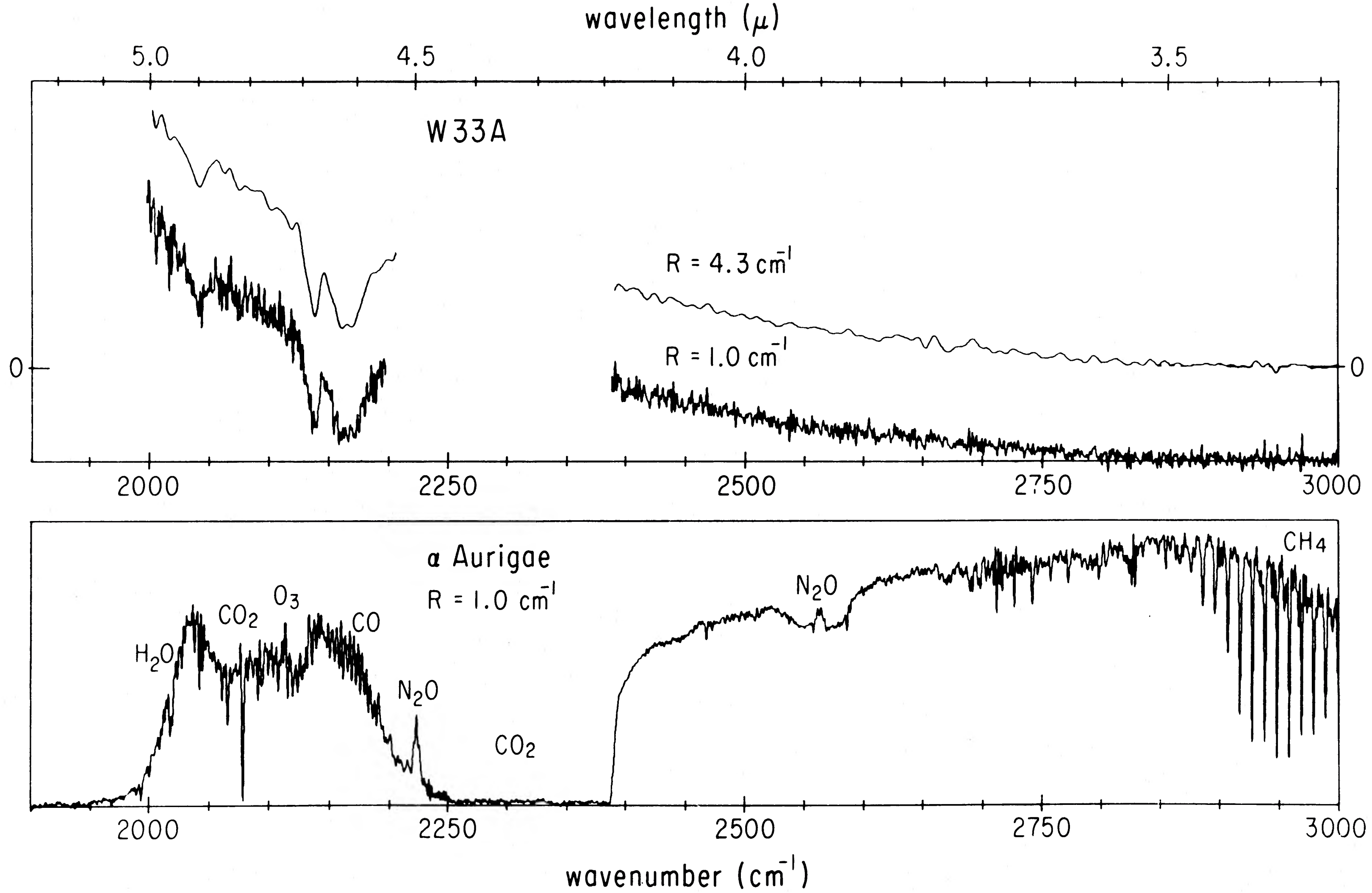

FIG. 1.—*Upper panel*: Two nearly independent spectral averages of W33A have been divided by the spectrum of a comparison star to eliminate telluric absorptions and instrumental response characteristics. The relative intensity scale is linear between zero and the maximum flux near 5 μm. For conversion to absolute flux, the relative intensities may be scaled from $F_\lambda \sim 4 \times 10^{-16}$ W cm$^{-2}$ μm$^{-1}$ at 4.75 μm (Capps, Gillett, and Knacke 1978). *Lower panel*: The stellar comparison spectrum used in the ratio calculations with W33A. The very dry observing conditions at the IRTF are demonstrated by the clean appearance of part of the telluric $CH_4$ band near 3.4 μm.

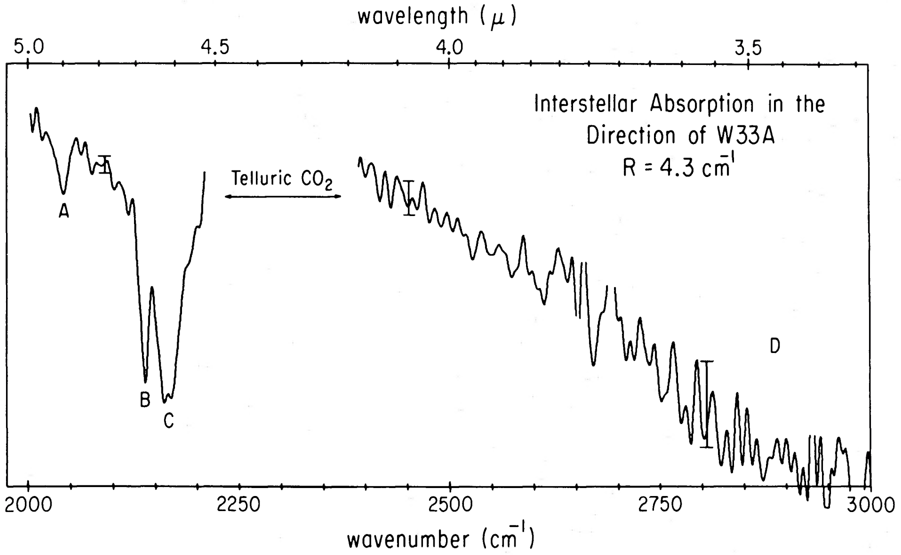

FIG. 2.—The low-resolution ratio spectrum of W33A in Fig. 1 has been processed to remove the color temperatures of α Aur and of the central object in W33A. The resulting spectrum is indicative of the composition of the interstellar medium. This calibration brings out the very deep 3 μm "dirty ice" band (labeled *D*), as well as three additional absorptions labeled *A*, *B*, and *C*. Peak-to-peak noise levels are indicated by error bars. Excess noise from 3.65 to 3.80 μm is due to a known distortion by a harmonic of 60 Hz pickup from an unresolved grounding problem with the spectrometer at the IRTF.

at the bottom of Figure 1; it illustrates the complexity of the terrestrial spectrum even at the relatively modest resolution of 1.0 $cm^{-1}$. Appreciable intensity errors may occur in this wavelength region if telluric $H_2O$, CO, $CO_2$, and $O_3$ are not fully removed from the observational data. All but the strongest of these terrestrial absorptions could be ratioed out of our W33A results as a consequence of the stable, dry conditions at the IRTF and the close air-mass match between the W33A and α Aur averages.

Figure 2 contains a more direct display of the interstellar absorption features in the direction of W33A. It was derived from the low-resolution average of Figure 1 by correcting for the blackbody temperatures of α Aur (~4600 K) and W33A (~450 K; Soifer *et al.* 1979). The error bars in Figure 2 indicate peak-to-peak noise levels at various wavelengths. The noise in the W33A spectrum is white, but as a consequence of multiple ratio calculations the signal-to-noise ratio decreased steadily toward shorter wavelengths in the processed spectrum shown in Figure 2.

From Figure 2 we identify four absorption features that we associate with interstellar material: A, the new feature at 4.9 μm, initially reported by Larson *et al.* (1984) and subsequently confirmed by Geballe *et al.* (1985); B and C, the blended CO–"XCN" feature at 4.6 μm; and D, the long-wavelength wing of the 3 μm ice band. We see no evidence for gaseous interstellar CO or common emission lines from H I (e.g., Brα, Pfβ) or He I that might originate in W33A itself. Our limiting line flux sensitivity in the 4 μm region was about $3 \times 10^{-19}$ W $cm^{-2}$; therefore, the weak Brα emission ($\sim 4 \times 10^{-20}$ W $cm^{-2}$) reported by McGregor, Persson, and Geballe (1984) would have escaped detection in our spectra.

## III. RESULTS

### *a) The Broad Absorption at* 3 μm

This absorption in the spectrum of W33A was assigned at least in part to $H_2O$ ice mantles on silicate grains (Capps, Gillett, and Knacke 1978) in analogy with similar features observed in other sources associated with molecular clouds (Merrill, Russell, and Soifer 1976). This ice feature is so deep in W33A that its long-wavelength wing in Figure 2 extends to about 4 μm (see also Fig. 2 in the broad-band spectral composite in Soifer *et al.* 1979). Laboratory simulations of this feature indicate a "dirty ice" composition, including $H_2O$, $H_2CO$, $NH_3$, etc. (Hagen, Tielens, and Greenberg 1983).

### *b) The Absorptions at* 4.6 μm

The general appearance of the two overlapping absorptions at 4.6 μm in Figure 2 is very similar to that reported by Lacy *et al.* (1984). The narrow component has its maximum optical depth at $2138.3 \pm 0.1$ $cm^{-1}$, and the broad feature is centered at $2165.5 \pm 0.1$ $cm^{-1}$. Lacy *et al.* reproduced all of the observed spectral characteristics of the 4.6 μm features in laboratory experiments involving the ultraviolet irradiation and temperature cycling of "dirty ice" mixtures (see their Fig. 5). They assigned the narrow 2138 $cm^{-1}$ feature to solid CO, and they proposed one or more solids containing C≡N bonds to account for the broad absorption at 2166 $cm^{-1}$. They called this interstellar material "XCN" because they could not identify the specific cyano group molecules responsible for the absorptions in their laboratory simulations. We contribute two additional insights to the interpretation of these features. First, we suggest that a likely candidate for Lacy *et al.*'s "XCN" is methyl isocyanide ($CH_3NC$). Second, at our higher spectral resolution neither of the two prominent 4.6 μm features shows any additional structure beyond that observed at lower resolution. This is illustrated in Figure 1, which compares two nearly independent averages of W33A data at different spectral resolutions. The 4.6 μm features apparently are fully resolved at a spectral resolution of 4.3 $cm^{-1}$ ($\lambda/\Delta\lambda \sim 500$) because, within the noise level, no changes appear in the high-resolution average at 1.0 $cm^{-1}$ resolution ($\lambda/\Delta\lambda \sim 2150$). This fact definitely excludes appreciable absorption by gaseous CO in the spectrum of W33A, and it allows us to estimate the $CO_{gas}/CO_{solid}$ abundance ratio. We elaborate on each of these results below.

### i) *The Feature at* 2138 cm$^{-1}$: *The* $CO_{gas}/CO_{solid}$ *Ratio*

The observations in Figure 1 permit a sensitive search for absorption by gaseous CO along the line of sight to W33A. The importance of spectral resolution for this test is illustrated with the synthetic spectra of CO that are displayed in Figure 3. At 4.3 cm$^{-1}$ resolution the $P$- and $R$-branches form the classic envelope containing the unresolved rotational structure of a diatomic molecule. However, at this low resolution gas-phase CO cannot be uniquely identified if there is the possibility of overlapping solid-state absorptions (e.g., CO ice, "XCN"). In contrast to this situation, at 1.0 cm$^{-1}$ resolution the resolved rotational structure of CO allows immediate spectroscopic discrimination between overlapping gaseous and solid absorptions. In addition, because of very strong saturation in the rotational lines of the $v = 1$–$0$ $^{12}$CO band, transitions in the partially overlapping $v = 1$–$0$ band of $^{13}$CO ($\nu_0 = 2096$ cm$^{-1}$) may produce lines of comparable intensity in spite of the reduced abundance of $^{13}$CO (assuming $^{12}CO/^{13}CO \sim 90$). In the discussion below, all reference to CO therefore implies use of the combined $v = 1$–$0$ bands of $^{12}$CO and $^{13}$CO.

No rotational structure appears above the noise level in visual examination of the 4.6 μm region in our high-resolution observations of W33A. The sensitivity of this search was increased with the use of cross-correlation analysis. We correlated the observed high-resolution ratio spectrum of W33A with a synthetic spectrum of CO that was calculated for typical conditions in a warm molecular cloud [temperature $T \sim 30$ K, column density $N(CO) \sim 10^{18}$ cm$^{-2}$, velocity width $\Delta V \sim 5$ km s$^{-1}$], and it was then convolved with an instrumental line profile to match our spectral resolution. The result of this cross-correlation was negative; that is, the entire pattern of CO lines is not found in our ratio spectrum of W33A. A conservative estimate of the upper limit to the intensity of any of the saturated low-$J$ ($J \leq 7$) lines in CO is established by the peak-to-peak noise level near 2150 cm$^{-1}$, which corresponds to an equivalent width of about 0.14 cm$^{-1}$ per line.

The CO abundance corresponding to this limit can in principle be obtained from a curve-of-growth analysis. The critical parameter is the velocity width to be used for the CO lines. Velocity widths from radio measurements of $^{12}$CO in W33 include 10–14 km s$^{-1}$ in a $1'.5 \times 1'.75$ beam (Goldsmith and Mao 1983) and 11 km s$^{-1}$ in a $2'.3$ beam (Ho, Martin, and Barrett 1981). Corresponding values for $^{13}$CO are 5 and 8 km s$^{-1}$, respectively. These CO line widths are most likely averages of Doppler-shifted emissions in much wider fields of view in the W33 cloud than are appropriate to our near-infrared observations of the infrared source W33A. Thus, we seek additional guidance from other types of measurements. The velocity widths of $NH_3$ transitions at radio wavelengths are usually very narrow compared with those of other molecules in the same source, at least in part because of the spatial restriction of $NH_3$ emission to the denser regions of molecular clouds. For example, in the Taurus dark cloud the velocity widths of $NH_3$ lines were about 0.3 km s$^{-1}$ in a $1'.4$ beam, compared with about 3 km s$^{-1}$ for $^{12}$CO in a slightly smaller beam (Ho *et al.* 1977). In W33 Ho, Martin, and Barrett (1981) found $NH_3$ line widths of about 4.5 km s$^{-1}$ in a $43''$ beam, which are substantially smaller than their CO line widths. We

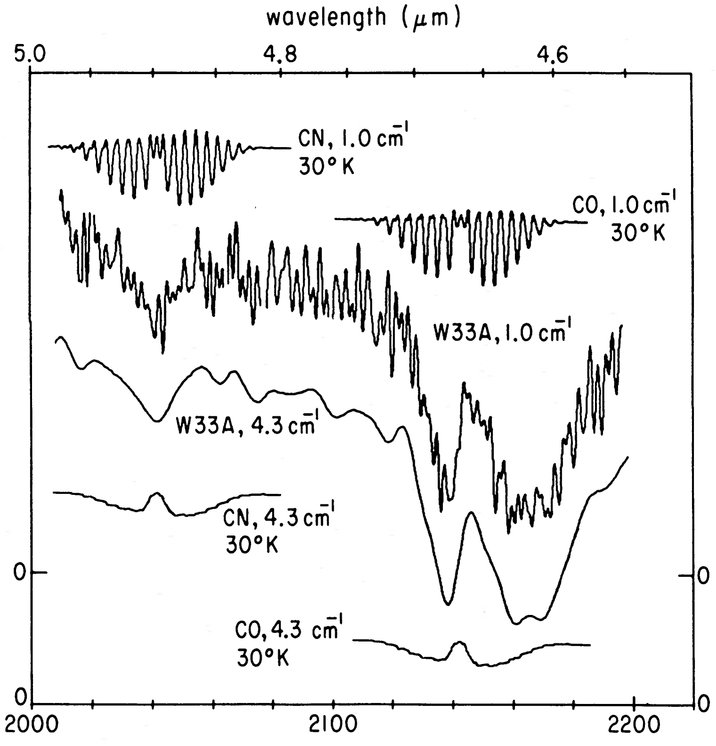

FIG. 3.—The 4.5–5.0 μm region of the spectra of W33A is presented on an expanded scale for comparison with gaseous CO and CN synthetic spectra. Gaseous CN at either 1.0 or 4.3 cm$^{-1}$ resolution is incompatible with the shape of the observed feature at 4.9 μm. In a low-temperature solid, however, an enhanced $Q$-branch and suppressed $P$- and $R$-branches could reproduce the shape and position of the observed feature. Alternatively, solid-phase $C_3$ also could produce the 4.9 μm absorption. Gaseous CO does not contribute significantly to the features near 4.65 μm. However, the predictable modifications to the spectrum of solid CO satisfactorily account for the narrow component at 4.67 μm.

therefore adopt for our CO analysis the smallest line width actually observed in radio emissions from W33, ~5 km $s^{-1}$ in $NH_3$ in a 43″ beam. At short wavelengths there are no other high-resolution spectroscopic observations of W33A that could provide additional guidance. However, in NGC 2024 IRS 2 Black and Willner (1984) measured velocity widths of about 1.5 km $s^{-1}$ in lines of the $v = 2$–0 band of $^{12}CO$ at 2.3 μm. They emphasized that their result had a much smaller velocity dispersion than would have been inferred from observations of radio emission lines of CO in the same source. It is not clear that this behavior should be generalized to include W33A, but in the discussion below we will consider the consequences of CO line widths less than 1.5 km $s^{-1}$.

Our CO abundance was determined with the aid of synthetic spectra calculated for typical values of the temperatures, column densities, and line widths that are expected in cold molecular clouds. Temperature was the least sensitive parameter in our calculations. It was therefore fixed at 30 K, a value intermediate between the values 24 and 33 K inferred from radio data by Ho *et al.* (1977) and Goldsmith and Mao (1983), respectively. For a given velocity width, spectra were calculated for various CO abundances, convolved with the instrumental line profile, and the rotational line intensities were then compared with the observations. The low-$J$ lines in the $v = 1$–0 $^{12}CO$ band were very strongly saturated for all combinations of the adjustable parameters. That is, all test cases fell on the nearly flat portion of the Doppler curve of growth. For our adopted velocity width of 5 km $s^{-1}$, CO spectra with $N(^{12}CO) \leq 10^{18}$ $cm^{-2}$ are consistent with the line intensity criterion that we established above with the use of cross-correlation analysis. For greater velocity dispersion ($\Delta V \geq 10$ km $s^{-1}$), this limit to $N(^{12}CO)$ drops to $10^{17}$ $cm^{-2}$ or less, but $N(^{12}CO)$ could exceed $10^{19}$ $cm^{-2}$ for the very narrow line widths ($\Delta V < 1.5$ km $s^{-1}$) that Black and Willner (1984) suggest may be more appropriate for the narrow beams in near-infrared observations. We therefore adopt $N(^{12}CO) \leq 10^{18\pm1}$ $cm^{-2}$ as our best estimate. This value is consistent with the radio measurement of $3 \times 10^{18}$ $cm^{-2}$ by Goldsmith and Mao (1983). Our large error represents both the considerable uncertainty in choosing an appropriate line width for the near-infrared CO lines and the relative insensitivity to abundance variations caused by the spectra's location on the horizontal portion of the Doppler curve of growth.

Lacy *et al.* (1984) estimated $N(CO_{solid})$ to be about $10^{18}$ $cm^{-2}$, but they did not calculate $N(CO_{gas})$. Rather, they adopted the CO column density from Goldsmith and Mao to conclude that $N(CO_{gas})/N(CO_{solid}) \sim 3$ toward W33A. This ratio becomes less than 1 upon substitution of our upper limit to $N(CO_{gas})$. Therefore, in spite of the large errors, our new data support expectations that, at least in the cold interstellar matter along the line of sight of W33A, a significant fraction of the CO is in the solid phase.

#### ii) *The Feature at* 2165 $cm^{-1}$: *Assignment to* $CH_3NC$

The following spectroscopic and cosmochemical arguments support this assignment. Methyl isocyanide has two strong near-infrared band systems centered at 2166 and 2975 $cm^{-1}$ (Williams 1956). The 2166 $cm^{-1}$ $CH_3NC$ band that we associate with the W33A feature at the same position is the molecule's $\nu_2$ N≡C stretch mode. The second absorption at 2975 $cm^{-1}$ is a complex blend of $\nu_1$ (symmetric C—H stretch), $\nu_5$ (asymmetric C—H stretch), overtone and combination bands. Its presence in the spectrum of W33A would coincide with the 3 μm "dirty ice" feature. Spectra of $CH_3NC$ in low-temperature gas and solid phases are not available. Consequently, on the basis of these limited spectroscopic data, we cannot demonstrate conclusively that the 2166 $cm^{-1}$ feature that we ascribe to $CH_3NC$ results from solid-phase material in grain mantles or from gas-phase absorption in the interstellar medium.

Our tentative identification of $CH_3NC$ can be put to an important test: if this molecule is present in cool molecular clouds, then its isomer methyl cyanide ($CH_3CN$) should also be present. This species is, in fact, observed at radio wavelengths in numerous sources (e.g., Sgr A, Orion KL, comet Kohoutek; see Matthews and Sears 1983 for a summary). This mandates an examination of our W33A spectrum for signatures of $CH_3CN$. Unfortunately, its $\nu_2$ mode occurs at 2267 $cm^{-1}$ (Parker, Nielson, and Fletcher 1957), a spectral region inaccessible from any Earth-based astronomical facility because of saturated telluric $CO_2$ absorption (see the stellar comparison spectrum in Fig. 1). Furthermore, as with $CH_3NC$, the $\nu_1$ and $\nu_5$ modes of $CH_3CN$ coincide with the broad 3 μm ice feature in the W33A spectrum. Thus, our identification of $CH_3NC$ is consistent with the infrared spectrum of $CH_3CN$, but not conclusively constrained by it. This assignment is chemically viable to the extent that $CH_3CN$ is apparently a commonplace component of the interstellar medium, and it should be accompanied by abundant $CH_3NC$. Both $CH_3CN$ and $CH_3NC$ would be produced in isomeric reaction chains involving HCN and HNC with $H_2CN^+$ as an intermediary (Watson 1977; Schiff *et al.* 1980) and in sequences initiated by radiative association reactions involving the methyl ion, $CH_3^+$ (Leung, Herbst, and Huebner 1984). The $N$(HNC)/$N$(HCN) ratio in cool, dark clouds is typically between 3 and 10 (Churchwell, Nash, and Walmsley 1984). This is important to our $CH_3NC$ identification for two reasons. First, the small values of this ratio imply appreciable "chemical shuffling" between HCN and HNC, thereby preventing disproportionate concentrations of either species or, by implication, any of their subsequent products such as $CH_3CN$ and $CH_3NC$. Second, the ratio is greater than unity, favoring the abundance of -NC species over -CN species, everything else being equal. Therefore, we conclude that our identification of $CH_3NC$ in W33A is consistent with the available spectroscopic data and the chemical mechanisms occurring in cool, dark clouds.

### *c) The Absorption at* 4.9 μm

The maximum optical depth of this feature is located at 2041.8 ± 0.3 $cm^{-1}$. Its profile is symmetric within the noise level, and no additional structure appears when the spectral resolution is changed from 4.3 to 1.0 $cm^{-1}$. Its equivalent width is about 2.6 ± 0.4 $cm^{-1}$, similar to that reported by Geballe *et al.* (1985). On the basis of the position and shape of this absorption, we consider three candidate molecules, $C_3$, CN, and $CH_3OH$, all of which are compatible only with absorption by a low-temperature solid.

#### i) $C_3$

The $\nu_3$ asymmetric mode in gaseous $C_3$ is expected to occur at 2040 $cm^{-2}$ (Gausset *et al.* 1965; Treffers and Gilra 1975). For a thermal rotational population at temperatures $T \geq 10$ K, the $P$- and $R$-branches of this band should be distinguishable, even at a spectral resolution of 4.3 $cm^{-1}$ and despite the fact that the spacing of individual lines within the branches is $\lesssim 1$ $cm^{-1}$. However, the observed symmetrical profile at 2042 $\mathrm{cm}^{-1}$ in the W33A spectrum is inconsistent with the expected character of gaseous $C_3$ absorption. The evidence for solid-phase $C_3$ includes laboratory simulations in which this radical may have been produced in $CO/CH_4$ mixtures at 10 K after exposure to ultraviolet radiation (Hagen 1982). A feature appeared at 2027 $\mathrm{cm}^{-1}$ that Hagen tentatively assigned to $C_3$. This is close to the expected position of the $\nu_3$ asymmetric stretching mode in $C_3$, a value that depends upon the type of inert matrix material used in the low-temperature studies (2038 $\mathrm{cm}^{-1}$ in Ar, 2042 $\mathrm{cm}^{-1}$ in Ne; Weltner and McLeod 1964). Unfortunately, no other corroborating transition is available in this region of the infrared spectrum to support the $C_3$ assignment. Alternatively, evidence for longer carbon chain molecules would also strengthen the $C_3$ assignment. Weltner and McLeod (1964) observed strong bands of $C_6$ (2000 $\mathrm{cm}^{-1}$), $C_8$ (1995 $\mathrm{cm}^{-1}$), and $C_9$ (2050 $\mathrm{cm}^{-1}$) in their laboratory experiments. However, Hagen could not find evidence for other carbon chain molecules in spectra of his laboratory simulations of interstellar matter, nor do we observe features at their locations in our astronomical data. It is worth noting that the transition moment for the $\nu_3$ fundamental mode is unusually high, 0.44 debye (Kraemer, Bunker, and Yoshimine 1984). Therefore, a column density $N(C_3)$ of only $1.6 \times 10^{16}$ $\mathrm{cm}^{-2}$ would be required to produce a total equivalent width $w_\nu \sim 2.6$ $\mathrm{cm}^{-1}$ in optically thin absorption.

### ii) CN

Our evidence for CN is summarized in Figure 3. Using molecular constants from Kotlar *et al.* (1980), we synthesized the $v = 1$–0 band of gas-phase CN for the two values of spectral resolution in our W33A averages in Figure 1. At 1.0 $\mathrm{cm}^{-1}$ resolution the rotational structure in this band is resolved, but it does not match the appearance of the 4.9 $\mu$m feature in the high-resolution spectrum of W33A in Figure 1. At 4.3 $\mathrm{cm}^{-1}$ resolution the unresolved *P*- and *R*-branches of gas-phase CN are also incompatible with the appearance of the 4.9 $\mu$m feature at lower resolution in Figure 3. We therefore doubt that gaseous CN contributes appreciably to the observed spectrum, and we do not consider it further. However, if the CN radicals are bound in solids, the 4.9 $\mu$m absorption may be due to solid-phase CN. For this to be credible, the prominent *Q*-branch that is missing in gas-phase excitation of CN must be perturbed into activity in a solid, and the *P*- and *R*-branches must disappear. Such changes do occur in CO. The narrow feature at 2138 $\mathrm{cm}^{-1}$ in the spectrum of W33A that was assigned to solid CO corresponds in position to the missing *Q*-branch in the gas-phase CO spectrum (see Fig. 3), and, conversely, the *P*- and *R*-branches in the synthetic spectrum of gaseous CO do not appear in the observed spectrum of W33A. The small shift ($\sim 6$ $\mathrm{cm}^{-1}$) in the position of the solid CO feature relative to the band center in gaseous CO is probably due to impurities in the solid CO. This interpretation could apply as well to CN. We note in Figure 3 that the missing *Q*-branch at 2042.4 $\mathrm{cm}^{-1}$ in gas-phase CN is nearly coincident with the observed position (2041.8 $\mathrm{cm}^{-1}$) of the 4.9 $\mu$m feature. There is, in addition, significant supporting evidence for our CN interpretation. If CN radicals are photochemically produced in grain mantles, more complex CN-bearing molecules may accumulate as the radicals react with other molecules upon diffusion through the grain mantles. The existence of such secondary products is supported by Lacy *et al.*'s (1984) association of the 2166 $\mathrm{cm}^{-1}$ feature with cyano group molecules and our specific suggestion that $CH_3NC$ is a plausible candidate.

### iii) $CH_3OH$

Methanol is an attractive possibility for two reasons. It is observed in the interstellar medium at radio frequencies, and Hagen, Allamandola, and Greenberg (1980) and Tielens *et al.* (1984) found that, in laboratory simulations of grain mantle compositions, $CH_3OH$ matched several features in the spectrum of W33A. The transition in $CH_3OH$ relevant to our analysis is the $2\nu_2$ C—O stretch mode at 4.9 $\mu$m. Gaseous $CH_3OH$ is not compatible with our spectra of W33A because the *P*- and *R*-branches of the $2\nu_2$ mode are not evident, and the gas-phase transition is centered at 2053 $\mathrm{cm}^{-1}$ (Falk and Whalley 1961), significantly higher than our observed position of 2042 $\mathrm{cm}^{-1}$. In solid-phase $CH_3OH$ the $2\nu_2$ mode shifts to $2040 \pm 4$ $\mathrm{cm}^{-1}$ (Falk and Whalley 1961), and the band becomes much narrower because the rotational structure is suppressed. Its symmetric profile is probably as compatible with our observations at 4.9 $\mu$m as is the spectroscopic evidence presented above for $C_3$ and CN. However, the abundance of $CH_3OH$ that is implied by this assignment presents a problem. The $2\nu_2$ band is weak, and if $CH_3OH$ is indeed responsible for the 4.9 $\mu$m feature in our spectra of W33A, then other, stronger $CH_3OH$ bands should be very evident. Some of the strongest $CH_3OH$ transitions coincide with the deep ice absorption at 3 $\mu$m and the strong silicate feature at 10 $\mu$m, and they would therefore escape detection. Other $CH_3OH$ features occur at 3.82, 3.93, 6.61, 6.80, 6.92, 7.43, 7.96, and 8.76 $\mu$m; see Figure 1 and Table 1 in Falk and Whalley for spectra of solid $CH_3OH$, band positions, and assignments. We see no evidence in our spectra of W33A for any absorptions by solid $CH_3OH$ in the 3.9 $\mu$m region. The expected feature, a superposition of several combination modes, would be rather broad and shallow compared with the $2\nu_2$ band. It is possible that, at the lower signal-to-noise ratio in this region of our spectra, a total equivalent width of about 1 $\mathrm{cm}^{-1}$ could remain undetected. An absorption with these approximate characteristics was recently detected in the spectrum of W33A by Geballe *et al.* (1985), but they did not consider its possible assignment to $CH_3OH$. Several other groups have investigated the role of $CH_3OH$ in the interpretation of the near-infrared spectrum of W33A (Hagen, Allamandola, and Greenberg 1980; Tielens *et al.* 1984). In particular, Hagen, Allamandola, and Greenberg's laboratory simulations at 1 $\mathrm{cm}^{-1}$ resolution are directly comparable with our high-resolution observations of W33A. They did not observe the $2\nu_2$ $CH_3OH$ band in their simulations, probably because of dilution effects in their $CH_3OH$–ice mixtures. It is also interesting to note that they did record a feature near 3.9 $\mu$m, although they did not assign it to a particular molecular group. Thus, these laboratory simulations do not match our spectrum of W33A at 3.9 and 4.9 $\mu$m. We must therefore question whether the coincidence of the $2\nu_2$ mode in solid $CH_3OH$ with the observations at 4.9 $\mu$m is merely fortuitous. On the other hand, the prediction and interpretation of relative intensities in grain mantle spectra are probably the least reliable aspects of spectrochemical analyses. We are therefore reluctant to discount $CH_3OH$ on the basis of intensity arguments alone. The excellent positional agreement with the $2\nu_2$ band and the general compatibility of $CH_3OH$ with other astronomical data and the known chemical properties of the interstellar medium remain compelling reasons to include $CH_3OH$ among potential candidates for the 4.9 $\mu$m feature in the spectrum of W33A.

In summary, we have suggested three interstellar molecules ($C_3$, CN, and $CH_3OH$) as possible assignments to the absorption at 4.9 μm in the spectrum of W33A. Each satisfies spectroscopic requirements concerning band position and band shape, at least to the extent that laboratory spectra are available for comparison. Each candidate is also supported by indirect evidence, such as detections at other wavelengths ($CH_3OH$), laboratory simulations ($C_3$, $CH_3OH$), and expectations based upon probable chemical processes in the interstellar medium (CN). It is possible that all three molecules are present in grain mantles, but it is less likely that all three contribute simultaneously to the 4.9 μm feature in the spectrum of W33A. We believe that it would be premature to choose between them on the basis of available information. This caution is reinforced by other recent interpretations of the infrared spectrum of W33A. For example, Geballe *et al.* (1985) used laboratory simulations to investigate the role of sulfur compounds in grain mantle compositions. They assigned solid $H_2S$ to a weak, broad absorption at 3.9 μm in their spectrum of W33A, and an unknown sulfur-containing compound to the 4.9 μm feature.

These various results clearly illustrate the general uniqueness problem that is associated with spectrochemical analyses of the spectrum of W33A. Specific complications include (1) the typically inadequate state of laboratory data for astrophysical comparisons, (2) the unpredictable influence of impurities in shifting bands formed in the solid state, and (3) the larger list of candidate species as less abundant molecules and weaker bands appear within sensitivity limits. For these reasons, we searched for other molecules that, on the basis of spectroscopic compatibility alone, might also match observed features in our spectrum of W33A. We found, in fact, alternative possibilities for all of the features in the 4 μm region. Some can be dismissed by invoking reasonable abundance arguments. For example, borine carbonyl ($H_3BCO$) has a very strong band at 2164 $cm^{-1}$ assigned to the C—O stretch mode (Cowan 1950). This particular molecule can be discounted because of the very low cosmic abundance of boron, but cosmochemically more acceptable molecules containing the CO group might be as compatible as solid CO itself with the observed feature at 2166 $cm^{-1}$ in the spectrum of W33A. Another example includes the azides, a group of molecules with nitrogen chain bonds. In general, the azides ($XN_3$, $X \neq H$) produce strong bands (the $\nu_2$ asymmetric stretch) near 4.9 μm (Nyquist and Kagel 1971). Also, $HN_3$ showed very strong bands in the 4.6 μm region in matrix isolation experiments at 30 K (Pimentel, Charles, and Rosengren 1966). Nitrogen chain molecules may therefore provide an alternative explanation for all three absorptions in the 4 μm region of the spectrum of W33A. These molecules do not appear in gas-phase chemical models of the interstellar medium, possibly because of their high-temperature instability. In cold grain mantles, on the other hand, nitrogen chain molecules may not be so readily discounted. In fact, Moore *et al.* (1983) observed a narrow feature at 4.9 μm in laboratory spectra of proton-irradiated low-temperature ices which they suggested could be a N—N—N bonded molecule.

In our opinion none of these alternative possibilities is as compelling as those presented above. However, our search was not exhaustive, and current chemical models of grain mantle compositions should not limit the interpretation of observational data. Therefore, the possibility should not be ignored that other molecules may become spectroscopically and cosmochemically compatible with the spectrum of W33A as observations and laboratory simulations improve and as interpretations mature.

## IV. DISCUSSION

The broad-band spectrum of W33A in Figure 2 displays absorptions by three important classes of materials in the interstellar medium.

1. *Easily condensed volatiles.*—Molecules such as $H_2O$, $NH_3$, and $CH_4$ are likely contributors to the 3 μm "dirty ice" band. This feature is observed in many cold molecular clouds; see, for example, the compilation of spectra of Willner *et al.* (1982). Laboratory simulations appear capable of reproducing the various shapes with which this band manifests itself in different astrophysical objects (Hagen, Tielens, and Greenberg 1983).

2. *Solid* CO.—This molecule satisfactorily accounts for the prominent absorption at 4.68 μm. Its presence in the interstellar medium toward W33A was suspected in spectrophotometric data and convincingly demonstrated by higher resolution observations and laboratory simulations (Lacy *et al.* 1984) Our work eliminates any possibility that gaseous CO contributes significantly to the 4.6 μm features in the spectrum of W33A. The conditions under which CO will condense on interstellar grains were recently investigated by Leger (1983).

3. *Photochemical products.*—Molecules other than the primary condensed volatiles listed above are indicated in the spectrum of W33A by absorptions at 4.62 and 4.90 μm. Laboratory simulations suggest that the 4.62 μm feature is due to one or more species containing C and N atoms that result from photochemical processing of primary condensates in grain mantles (Lacy *et al.* 1984). We proposed that $CH_3NC$ is a likely candidate, although low-temperature laboratory simulations are required to discriminate between its gas and solid phases. In addition, we presented evidence for solid-phase absorption by $C_3$ or CN at 4.90 μm. Either radical implies a photochemically active environment within grain mantles. Moreover, either radical is an important intermediary for the synthesis of more complex molecules such as $CH_3NC$. This interpretation competes with that of solid $CH_3OH$, which could simply have condensed onto grain mantles from the gas phase. As an alternative to all of the above possibilities, Geballe *et al.* (1985) suggest an unknown sulfur-containing molecule.

Most, perhaps all, of the molecules implicated above are observed in the solid state. Collectively, these results offer strong observational support for chemically complex models of grain mantle evolution in cold, quiescent molecular clouds. These mantles appear to be likely production zones for complex molecules that can be injected into the gas phase of the interstellar medium following grain-heating episodes. Alternatively, the material may remain locked up in the mantles to provide *in situ* sources of complex molecules in planetesimals and larger-sized bodies. This possibility is especially relevant to questions concerning the bulk composition of cometary nuclei. Infrared spectroscopic observations of heavily obscured objects such as W33A provide compositional links between cometary and interstellar matter that test the hypothesis that comets may have formed from icy grains in the presolar nebula. The compositional results presented above that relate to important topics in cometary science are summarized below; details concerning the cometary studies may be found in reviews by Delsemme (1982) and Wyckoff (1982).

1. *Cometary activity.*—The presence of abundant ices in grain mantles would readily account for the volatile fraction of cometary matter. The major volatile constituent, $H_2O$ ice,

apparently controls the vaporization of the nuclei of most comets, while the much more volatile CO ice could contribute to the enhanced activity of new comets and to the occasional outbursts in older ones.

2. *Sulfur in comets.*—The detection of $S_2$ in comet IRAS-Araki-Alcock (A'Hearn, Feldman, and Schleicher 1983) raised the interesting speculation that $S_2$, as a parent molecule in comets, may require a production mechanism in the interstellar medium before accretion (A'Hearn and Feldman 1984). The possibility that some absorption features in the spectrum of W33A may be due to sulfur-containing molecules (Geballe *et al.* 1985) may eventually lead to experimental tests of A'Hearn and Feldman's hypothesis.

3. CN *in comets.*—CN emission is very pronouced in cometary spectra, but the parent molecules for this radical are not known with certainty. Observations indicate that HCN and $CH_3CN$ are present in cometary nuclei, but the spectrum of W33A suggests that there may be a much more extensive inventory of cyano group molecules as a consequence of grain mantle evolution. An *in situ* source of CN itself is possible if free radicals can remain trapped in an ice matrix over the age of the solar system.

4. *Carbon depletion in comets.*—The C/O abundance ratio is apparently depleted in comets by a factor of about 4. Possible explanations include the early loss of carbon-bearing volatile species from cometary matter, and the presence of unrecognized chemical sinks for carbon. The spectrum of W33A suggests that grain mantle evolution may have transferred substantial amounts of carbon to photolytic products such as cyano group molecules and, possibly, carbon chain molecules. The possible presence of $C_3$ in the spectrum of W33A is especially intriguing in connection with both the missing carbon problem and the origin of $C_3$ in cometary spectra. Emission from this radical peaks near the nucleus, but its parent molecule is unknown. If the feature at 4.9 $\mu$m in our spectrum of W33A could be uniquely assigned to $C_3$, and if $C_3$ can be stored in the cometary $H_2O$ ice matrix over the age of the solar system, then cometary $C_3$ could be classified as a parent molecule itself, and it would indicate a potentially important pathway for storing carbon in carbon chain molecules.

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