DUST PARTICLES AND MOLECULES IN THE EXTENDED ATMOSPHERES OF CARBON STARS

DAYA P. GILRA

Space Astronomy Laboratory, Washburn Observatory, University of Wisconsin, Madison, Wis., U.S.A.

Abstract. It is shown that the absorption due to a circumstellar shell containing solid silicon carbide particles can very nicely explain the observed strong violet opacity in stars in which the carbon to oxygen ratio is > 1. It has been shown by Friedemann and Gilman that solid SiC particles can form in the cooler outer layers of such stars. Thermal re-emission from SiC particles is predicted to be in the 10-13 μ region and recent infrared observations by Hackwell show an emission band in this region, thereby strongly supporting the SiC suggestion. It is also shown that the opacity due to C₃ pseudo-continuum is not adequate to explain the observed violet opacity.

It is suggested that the vibrational bands of C_3 and SiC_2 molecules should be among the major opacity sources in the infrared spectra of the late N-type carbon stars and some of the observed bands may be, at least in part, due to these molecules. The frequencies of their isotopic species have been calculated and attempts should be made to observe these bands.

Thus the atmosphere of a late N-star should be pictured as containing, probably on its outskirts, solid carbon particles. There is some kind of smoke veil around the star causing a reddening by absorption of the ultraviolet.

A veiling effect by smoke has been occasionally envisaged to interpret various astronomical phenomena, even in the case of novae. A late N-star would be a striking example. The smoke veil would vary in variable N-stars.

B. Rosen and P. Swings (1953)

It is well known that in the spectra of late N-type carbon stars the intensity drops very rapidly at about 4400 Å, this rapid drop continuing throughout the ultraviolet. In fact, due to this problem, so far, spectra of very few late N-stars have been photographed shortward of about 4000 Å (Swings *et al.*, 1953, to be precise, spectra of only four stars have been obtained at 4000 Å and of only one star shortward of 3800 Å). More than 40 yr ago Shane (1928) noted that the could photograph the spectrum of Y CVn, a star one can see with the naked eye, in the 4800 Å region with a small quartz slitless spectrograph in *one second*, whereas an exposure of 5 *hours* with the same instrument failed to show any light shortward of 3900 Å.

The late N-type stars also show the 4050 Å bands of C_3 and the blue-green Merrill-Sanford Bands of SiC₂. It was shown by Swings *et al.* (1953) that the intensities of the C_3 and the Merrill-Sanford bands are related to the violet drop in the sense that the stronger the bands, the more pronounced is the violet opacity. They also pointed out that the star U Hya sometimes shows the SiC₂ bands, the C_3 bands and strong violet opacity and sometimes all three are absent. On the basis of these observations Swings *et al.* were led to conclude that the source or sources of the violet opacity are related to the formation of the polyatomic molecules SiC₂ and C₃. (It should be pointed out that

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 SiC_2 as the carrier of the Merrill-Sanford bands was not identified until 1956, Kleman 1956.) Rosen and Swings (1953) and Swings (1953) suggested that circumstellar solid carbon particles may be responsible for the strong violet opacity observed in these stars.

In 1954 McKellar and Richardson (1955) compared their observations of carbon stars Y CVn and U Hya in the blue-violet with the experimental C_3 continuum – it is now believed to be pseudo-continuum (Brewer and Engelke 1962) – and found good agreement. It was shown by Feast (1955) that a similar rapid decrease in intensity at about 4400 Å occurs in some S and C–S stars and suggested that the agent is the same in the two cases. He argued that the source cannot be solid carbon particles as suggested by Rosen and Swings (1953) and Swings (1953) because they are not likely to form in S stars. In a subsequent paper, however, he pointed out (Feast, 1957) that there are apparent differences in the energy distributions in this spectral region in the two cases, the late N-stars on one hand and the S and C-S stars on the other, and the sources of opacity may be different.

Recently Stephenson and Ross (1970) have shown that this phenomenon, the sudden decrease in intensity at about 4400 Å, is a characteristic of quite a few S and C–S stars. They favor Feast's original suggestion (Feast, 1955) that the source of opacity in late N-stars, and S and C-S stars is the same and argue that C_3 cannot be the source for S stars.

Recent observational studies by Catchpole and Feast (1971) and by Greene (quoted by Slettebak, 1972) show that all S-C and C-S stars show strong violet opacity. Greene (quoted by Slettebak (1972), see also Stephenson (1965), and Catchpole and Feast (1971)) has drawn attention to one star, Case 621, in particular. This star has neither ZrO bands which are characteristic of S stars, nor C_2 bands which are characteristic of carbon stars, but has strong violet opacity and shows evidence of SiC₂ bands. It also shows CaCl bands and a very strong Li λ 6707 line. Greene suggests that in the atmosphere of Case 621 the carbon to oxygen ratio is one.

Two points must be noted about this violet opacity effect: its 'sudden' appearance at about 4400 Å and the continued rapid increase throughout the ultraviolet. The main problem to be investigated in this paper is the identification of the source or sources of this dramatic opacity effect in the stars in which the carbon to oxygen ratio is approximately equal to or greater than one. This work has been done in collaboration with Code and the preliminary results, with the predictions, were presented at the Amherst Meeting of the American Astronomical Society (Gilra and Code, 1971), and a detailed paper is in preparation (Gilra and Code, 1972). The other problem to be discussed is the nature of the vibrational bands of C_3 and SiC_2 in the infrared with the possibility that information about the isotopes of carbon and silicon may be obtained from high resolution observations of carbon stars in this spectral region.

1. The Violet Opacity

It has been shown by Friedemann (1969a, b) and Gilman (1969) that solid silicon carbide particles can form in the cooler outer layers of the stars in which the carbon to

oxygen ratio is approximately equal to or greater than one. SiC_2 gas is a major vaporization product of solid SiC such as C_3 is that of graphite (Weltner and McLeod, 1964b). Bands of SiC_2 are seen in the spectra of late N-type carbon stars. A very important point is that depending upon the polytype, temperature, and concentration of impurities, the fundamental absorption edge of SiC lies between about 2.2 eV and 3.3 eV (Choyke, 1969).

Since solid SiC particles can form in the atmospheres of all the stars in which strong violet opacity is observed, let us consider a circumstellar shell containing solid SiC particles. We consider particles of cubic SiC. The imaginary part of the refractive index, k, has been calculated from the absorption coefficient given by Patrick and Choyke (1969) for two cases of cubic SiC: pure, and with nitrogen impurity. Mie calculations have been made for both the cases for a gaussian size distribution with a mean radius of 0.105 μ and a standard deviation of 0.06 μ . (Friedemann (1969b) has calculated the mean radius to be about 0.1 μ .) The resulting albedoes and the extinction cross-sections between 5400 Å and 3600 Å are shown in Figure 1. The curve for albedo 'with nitrogen' is for SiC particles having nitrogen impurity and the albedo curve 'without nitrogen' is for pure SiC. The extinction cross-sections are identical in the two cases. The point to note is the sudden decrease in albedo for both the cases at about 4500 Å and its continued decrease throughout the ultraviolet. The absorption cross-section for 'pure' SiC particles increases by about a factor of 30 between 5200 Å and 3600 Å. (The 'band' in the albedo curve for particles with nitrogen impurity arises because there is an absorption band at about 4000 Å in the bulk crystals with the nitrogen impurity.)

With these cross-sections and albedoes the ratio of the emergent flux to the incident flux, $F(O)/F(\tau)$, was computed using the theory of radiation transfer described by Code (1973). This ratio is plotted against wavelength in Figure 2 for two values of



Fig. 1. The albedoes and extinction cross-sections between 5500 Å and 3500 Å for two cases of SiC particles: pure ('without nitrogen'), and with nitrogen impurity ('with nitrogen'). The extinction cross-sections are identical in the two cases.

the optical depth for each of the two cases: pure SiC particles, and SiC particles with nitrogen impurity. The values for τ given in the figure are $(\sqrt{3})^{-1}$ times the extinction optical depth at λ 5220; for example, the case $\tau = 15$ implies that the extinction optical depth for that case at λ 5220 Å is $15 \times \sqrt{3}$ (= 26). Also plotted in this figure is the observed absorption continuum for Y CVn as given by McKellar and Richardson (1955). The values were measured from their Figure 4 at 50 Å each and a constant vertical shift has been made to match with the theoretical curves.



Fig. 2. The ratio of the emergent flux to the incident flux, $F(O)/F(\tau)$, between 6300 Å and 3500 Å, through a circumstellar shell containing SiC particles using the cross-sections and albedoes given in Figure 1. The values for τ given in the figure are $(\sqrt{3})^{-1}$ times the radial extinction optical depth at λ 5220: for example, the case $\tau = 15$ implies that the radial extinction optical depth for that case at λ 5220 is $15 \times \sqrt{3}$ (= 26). The dots give the absorption continuum of Y CVn as obtained by McKellar and Richardson (1955).

Let us first consider the difficulties with the identification of the C_3 pseudo-continuum (McKellar and Richardson, 1955; Brewer and Engelke, 1962) as the source of the observed absorption continuum. The C_3 identification was based on the apparent similarity between the observed continuum and the experimental C_3 continuum, with the stellar absorption features at 4300–4350 Å and at about 4000 Å significantly aiding the identification. McKellar and Richardson mention in their paper that the observed feature at 4300–4350 Å is not attributable to the λ 4383 2,0 sequence of the Swan bands of C₂ nor to the λ 4315 CH band. They do not mention that the strong red degraded SiC₂ band at λ 4352, which can be seen very clearly in the spectra reproduced by them, can be a significant contributor to this feature. It seems the whole feature is due to these and other (λ 4261 band of SiC₂, etc.) molecular bands in this spectral region. The photoelectric scans by Fay and Honeycutt (1972) of W Ori, a star which shows much stronger SiC_2 bands and much stronger violet opacity than Y CVn (Swings et al., 1953), show this very well. The broad stellar absorption feature at λ 4000 also seems to be due to various discrete molecular absorptions in this region (for a list of absorption features in this region, see Swings et al., 1953). Again, the observations of Fay and Honeycutt support this conclusion. As regards the main absorption continuum, the observations of McKellar and Richardson extended down to only λ 3900. Recent wide band photometry of several carbon stars by Mendoza and Johnson (1965) and the narrow band photometry extending down to λ 3300 of four carbon stars, in particular of Y CVn, by Johnson, Mitchell and Latham (1967) show that the rapid decrease in intensity continues throughout the ultraviolet. For example, the narrow band photometry by Johnson et al. (1967) of Y CVn shows that the stellar flux decreases by a factor of one hundred and fifty between 4020 Å and 3530 Å. On the other hand, the experimental absorption coefficient of C_3 in this spectral region is decreasing (Brewer and Engelke, 1962). We can thus conclude that C_3 is not the major source of opacity in this spectral region in the spectra of late N-type carbon stars. (The nature of the observed stellar SiC_2 and C_3 bands in the optical region and their implications on the opacity problem and the work of Shajn and Struve (1947) will be discussed in detail elsewhere (Gilra and Code, 1972)).

We now compare the observations with our theoretical results for a circumstellar shell of SiC particles as shown in Figure 2. As can be seen, the agreement is very good for both the cases of SiC particles. The extinction optical depth at 5220 Å is about 30. (We are not suggesting that the absorption band at 4000 Å in the theoretical curves for SiC particles with nitrogen impurity is responsible for the observed feature.) The agreement between our theoretical curves and the observations of Feast (1957) of AM Cen, an SC star, is also very good. From their photoelectric observations, Fay and Honeycutt (1972) also find support for our suggestion.

Similar calculations have been performed for circumstellar graphite particles. The absorption coefficient of graphite increases throughout the ultraviolet but there is no 'suddenness' in the increase. Therefore the conclusion is that circumstellar graphite particles do not contribute much to the sudden opacity increase in the blue-violet. It should be possible to calculate an upper limit for the mass in circumstellar graphite particles.

We can obtain the mass in SiC particles in the entire circumstellar shell from the values given in Figures 1 and 2. It comes out to be of the order of 10^{-9} solar masses. The mass thus derived will be an upper limit because the molecular absorptions and the possible contribution from circumstellar graphite particles have not been sub-tracted from the observations. The crystalline structure of circumstellar SiC particles,

the impurities they might have and their temperature also affect the calculations for the mass. But the primary aim here is to identify the major source of this dramatic opacity effect and we can say with reasonable confidence that it is circumstellar SiC particles. Recent infrared observations, as discussed below, by Hackwell (1972) confirm this suggestion.

There is another observational test of the SiC hypothesis. The energy the SiC grains are absorbing in the blue-violet will be re-emitted in the infrared. Based on the calculations of Gilra (1972a), it was predicted by Gilra and Code (1971) that this thermal re-emission should be in the $10-13 \mu$ region, a region in which ground-based observations can be made. The theory is discussed elsewhere (Gilra, 1972a, b) and the main results are given below. For about a tenth of a micron radius particles the *shape* of the particles is the most important parameter, the size is not important and we can use the Rayleigh approximation. Depending upon the shape, the emission band(s) should appear between about 10.2 μ and 12.8 μ . A distribution of *shapes* will make a broad emission feature between about 10.2 and 12.8 μ . The shape is not a significant factor in the absorption in the blue-violet, so the optical depth derived from this region will be, so to speak, redistributed throughout this broad feature in the 10-13 μ region and the optical depth may not be high at any given wavelength in this infrared band. The temperature of the particles depends upon their distance from the star; therefore, the distance may be of some importance.

There is a slight problem, however. The Si–C stretching frequency, v_1'' , of SiC₂ molecules is at 11.75 μ (see the discussion below). In late N-type stars there should be a strong absorption band at 11.75 μ which will somewhat 'fill in' the predicted emission. Observations with high spectroscopic resolution may be required to separate the two effects.

During this symposium Hackwell showed me his scans of two carbon stars, CIT6 and V Hya, in the 10 μ region (Hackwell, 1972). There is a strong emission feature present between about 10 μ and 13 μ almost similar to what the theoretical calculations (Gilra, 1972a, b) show. There is an indication of an absorption feature at 11.75 μ which may be the SiC₂ band. His photometry of carbon stars (Hackwell, 1972) in the infrared also shows emission at 11 μ . An emission feature at 11 μ is also present in the photometry of R CMi, a C-S star.

On the basis of all the theoretical and observational evidence, it seems the existence of circumstellar SiC particles should be considered well-established.

2. C₃ and SiC₂ Bands in the Infrared

Strong vibrational bands of C_3 and SiC₂ should appear in the spectra of late N-type carbon stars in the infrared. A brief discussion of these bands with special emphasis on the possibility of detecting and measuring the isotopic bands is given. To the best of my knowledge there has been no such discussion in the astronomical literature (cf. Spinrad and Wing, 1969; Vardya, 1970), even though most of the information has been available since 1964 (Weltner and McLeod, 1964a, b).

2.1. C_3 bands

For C₃ the asymmetric stretching frequency, v_3'' , is 2040 cm⁻¹ (Weltner and McLeod, 1964a) and the symmetric stretching frequency, v_1'' , is 1224.5 cm⁻¹ (Merer, 1967; Weltner and McLeod 1964a). Since the value 1224.5 cm⁻¹ for v_1'' is somewhat smaller than the value 1240 cm⁻¹ used by Weltner and McLeod, I have recalculated the force constants of C₃ in the ground state from formulas given by Herzberg (1945). The values are:

$$k_{11} = 10.20 \times 10^5 \text{ dyn cm}^{-1},$$

 $k_{12} = +0.397 \times 10^5 \text{ dyn cm}^{-1}.$

(The values calculated by Weltner and McLeod (1964a) are 10.34×10^5 dyn cm⁻¹ and $+0.542 \times 10^5$ dyn cm⁻¹ respectively.) With these force constants one can calculate (Bartunek and Barker, 1935) the corresponding frequencies for the isotopic specicis as was done for v_3 by Weltner and McLeod (1964a) who found very good agreement between the theoretical and experimental values. The values are given in Table I. Also given in Table I are the values of $v_1 + v_3$. The anharmonicity constants x_{13} are not known but should be of the order of 5 to 10 cm⁻¹. Thus the values $v_1 + v_3$ should be within about 5 to 10 cm⁻¹ of the frequencies of the combination band ($v_1 + v_3$). C₃ is a linear symmetric molecule (Gausset *et al.*, 1965) and therefore v_3 and ($v_1 + v_3$) are infrared active whereas v_1 is not (Herzberg, 1945). However, the species C¹²-C¹²-C¹³ and C¹³ C¹³-C¹² are not symmetrical and v_1 for them is infrared active (Herzberg, 1945). Weltner and McLeod (1964a) in their experimental work on the infrared spectrum of C¹³-substituted C₃ observed all the six v_3 bands. Apparently their observations were not extended to the 1200 cm⁻¹ region so the C¹²-C¹²-C¹³ and C¹³-C¹³-C¹² v_1 bands at 1200 cm⁻¹ seem to have remained undetected.

We note from this table that in the spectra of late N-type carbon stars a strong band at 2040 cm⁻¹ (= 4.90 μ) due to C¹²-C¹²-C¹² should be observed. Many of these stars show relatively high abundance of C¹³, but the interpretation is not easy (Fujita, 1970). In these stars all the six bands extending to 1960 cm⁻¹ (= 5.1 μ) may be observed and it should be possible to derive, perhaps less ambiguously, the ratio of C¹²/C¹³. Low resolution infrared spectra of carbon stars CIT 6, CIT 13, and T Cnc

IABLE I Isotopic bands of C ₃				
C-C-C	v_1 (cm ⁻¹)	v_3 (cm ⁻¹)	$v_1 + v_3$ (cm ⁻¹)	
12-12-12	1224.5	2040	3264.5	
12-12-13	1200	2027	3227	
13-12-13	1176	2013	3189	
12-13-12	1224.5	1987	3211.5	
13-13-12	1200	1974	3174	
13-13-13	1176	1960	3136	

obtained by Gaustad *et al.* (1969) show an absorption feature at about 4.9 μ . For T Cnc a 'broad depression' at 5 μ has been observed. They have attributed these absorptions in CIT 6, CIT 13 and T Cnc to the fundamental vibrational band of CN. I would like to suggest that C₃ is a significant contributor to these features.

Some support for this suggestion comes from the broad band photometric observations. Figure 3 shows a color-color plot for 11 carbon stars common in the photometric observations of Mendoza and Johnson (1965) and Gillett et al. (1971). The U-B color is from Mendoza and Johnson and the infrared color [4.9 μ] - [8.4 μ] is from Gillett et al. The horizontal arrows for two stars, the upper point is for T Cnc and the lower point for V CrB, mean that their U magnitudes are fainter than 22 (the V magnitudes are 9.05 and 9.33 respectively). (Incidentally, the values of U-B show very clearly the extreme faintness of the late N-type carbon stars in the ultra-violet.) Figure 3 shows an apparent correlation which can be interpreted to mean that the stronger absorption in the ultraviolet goes with the stronger absorption in the 5 μ region. Since the presence of the 4050 Å C₃ bands is related to the opacity in the ultraviolet (Swings et al., 1953), even though we have shown earlier that C₃ is not a major source of this opacity, it can be inferred that the C₃ bands may be a significant contributor to the opacity in the 5 μ region. However, it is necessary to make observations with high spectroscopic resolution to definitely identify the source(s) of opacity in the 5 μ region.

In the spectra of the three carbon stars, CIT 6, CIT 13 and T Cnc Gaustad et al.



Fig. 3. Infrared color [4.9 μ]-[8.4 μ] (Gillett et al., 1971) against U-B (Mendoza and Johnson, 1965) for 11 carbon stars common in their observational programs. The horizontal arrows for two stars mean that the U magnitudes of these stars are fainter than 22.

(1969) observed, a strong absorption feature is present at 3 μ which they suggested may be due to the v_3 fundamental of either HCN or C_2H_2 . The existence of this feature was confirmed by Low et al. (1970) who remarked that the carbon stars as a group exhibit a broad absorption at about 3250 cm⁻¹, "with the coolest carbon stars having the strongest absorption." They pointed out that the intensity at 3250 cm⁻¹ for T Lyrae is only about 20 percent of the interpolated continuum.

As indicated in Table 1 the $(v_1 + v_3)$ combination band of C₃ occurs at about 3265 cm⁻¹. The photometry of Mendoza and Johnson (1965) for T Lyrae gives V = 8.18 and U > 22, that is, the star shows extremely strong violet opacity. On the basis of a similar argument as made earlier it is suggested that the combination band $(v_1 + v_3)$ of C₃ may be a significant contributor to the observed feature at about 3250 cm⁻¹. Once again, high resolution observations are required to identify the source(s) definitely.

The value of the bending frequency, v_2 is 63.1 cm⁻¹ for C₃ and is quite a low value (Gausset et al. 1965). Several combination bands involving v_2 , $2v_2$, etc. should be observable in the spectra of the late N-type carbon stars. Also, the carbon stars which show relatively high abundance of C¹³ should show the C¹³-C¹³-C¹² and C¹²-C¹²-C¹³ bands at 1200 cm⁻¹.

2.2. SiC₂ bands

Weltner and McLeod (1964b) from their matrix infrared observations obtained the values of v_1 and v_3 fundamentals of SiC₂ as 853 cm⁻¹ and 1742 cm⁻¹ respectively. Verma and Nagaraj (1971) have obtained 134 cm⁻¹ for the v_2 fundamental. SiC₂ is a linear asymmetric molecule (Si-C-C) in the ground state and all the fundamentals are infrared active. The following stretching force constants for SiC₂ in the ground state were calculated by Weltner and McLeod (1964b):

 $k(\text{Si-C}) = 7.43 \times 10^5 \text{ dyn cm}^{-1},$ $k(\text{C-C}) = 7.98 \times 10^5 \text{ dyn cm}^{-1}.$

By assuming that k_{12} is zero, that is how the force constants given above were calculated, I have calculated from the formulas of Bartunek and Barker (1935) the frequencies for the v_1 and v_3 fundamentals for various isotopic species of silicon and carbon (Table II). (In the light of the work of Weltner and McLeod (1964b), and Verma and Nagaraj (1971), the force constants derived by Yamashita (1967) for the ground state are wrong and the 'identification' of the isotopic SiC₂ (Yamashita and Utsumi, 1968) is not correct.)

The v_3 fundamental lies in a spectral region which is not accessible from the ground. It should be possible to observe the absorption due to the v_1 fundamental. A search should be made to detect the isotopic bands; we have as yet no information on the isotopic abundances of silicon. However, the differences are not large and the observations may not be easy to interpret. The observations of V Hya by Hackwell (1972) indicate an absorption feature at 11.75 μ ; it may be the SiC₂ v_1 fundamental band.

Quite a few overtone and combination bands are infrared active and a search for

	TABLE II			
Isotopic bands of SiC ₂				
Si-C-C	$\frac{v_1}{(cm^{-1})}$	(cm^{-1})		
28-12-12	853	1742		
28-12-13	835	1725		
28-13-12	850	1694		
28-13-13	833	1677		
29-12-12	846	1740		
29-12-13	829	1724		
29-13-12	844	1693		
29-13-13	827	1675		
30-12-12	841	1739		
30-12-13	823	1722		
30-13-12	838	1691		
30-13-13	821	1674		

them should be made, especially because, as in the case of C_3 , the bending frequency is low (v_2 is 134 cm⁻¹, Verma and Nagaraj (1971)).

3. Concluding Remarks

(1) The first part of this paper describes the work of Gilra and Code (1971, 1972) on the identification of the source of the violet opacity in the stars in which the carbon to oxygen ratio is approximately equal to or greater than one. The major source was identified as circumstellar solid silicon carbide particles, with circumstellar graphite particles and C_3 molecules being possible minor contributors. There is strong support for this identification from the infrared observations. Thus the 'picture' envisaged by Rosen and Swings (1953), as quoted at the beginning of this paper, is essentially correct, we would just add solid SiC particles with the carbon particles. The behavior of U Hya, as described earlier, is also understood. This identification also confirms the suggestions of Feast (1955) and Stephenson and Ross (1970) that the opacity source should be the same in the late N-type carbon stars and, SC and CS stars.

Detailed observations both in the 10 μ region and in the blue violet are needed for a good understanding of the atmospheric structure of these stars. High resolution observations of some SC and CS stars, in particular, Case 621, which I have identified as IRC 00404, should be made in the 10 μ region.

(2) In the second part a brief discussion of the vibrational bands of C_3 and SiC₂ is given. It is pointed out that C_3 and SiC₂ should be among the major opacity sources in the infrared spectra of late N-type carbon stars. The frequencies of their isotopic species have been calculated and attempts should be made to observe them. From the infrared observations of the C_3 and SiC₂ bands in the spectra of late N-type stars it should be possible

(i) to derive the number densities of the C_3 and SiC_2 molecules,

(ii) to obtain information about the exciting conditions in the regions of the atmosphere in which these molecules exist, and

(iii) to derive the isotopic composition of these molecules. These results will provide us with very valuable information about the atmospheric structure of the late N-type carbon stars.

Acknowledgements

I would like to thank Dr R. D. Verma, Dr S. Nagaraj and Dr John Hackwell for communicating their results in advance of publication. This research has been supported in part by NASA grant NGL 50-002-013.

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