

# PI GRUIS: MOLECULAR IDENTIFICATIONS AND SPECTRAL CLASSIFICATION

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**Abstract.** Identifications of the molecular absorption features in the visible spectrum of the S star Pi Gruis are presented. Moderate dispersion spectrum of  $\pi^1$  Gru covering the region 5800–7300 Å, demonstrates the presence of a multitude of molecular bands. Wavelength measures of well over 150 red-degraded band heads are listed. Nearly 80% of the observed features are identified with the ZrO, LaO, YO, and CeO molecules. Many molecular bands due to ZrO, YO, and CeO are reported identified for the first time. Neither TiO molecular features nor any Ba compounds are detectable.

As a consequence of the presence of bands due to *s*-process oxides and the absence of TiO bands,  $\pi^1$  Gru may be classified as a pure S star. Observed predominance of the ZrO molecule suggests that both the phenomenon of Zr abundance enhancements and chemical equilibrium conditions with a carbon/oxygen ratio between 0.95 and 1.0 may be at play in the atmospheres of cooler pure S stars.

## 1. Introduction

Because of their intermediate position in the sequence M–MS–S–SC–C, coupled with their low atmospheric opacities, the S stars are pivotal in understanding the processes of nucleosynthesis and mixing mechanisms in red giants. The S stars are characterized by an enhancement of the *s*-process elements, as well as by a lower oxygen-to-carbon ratios than those of the M stars (see, e.g., Boesgaard, 1970; Tsuji, 1970; Yamashita, 1973; Scalo and Ross, 1976; Truran and Iben, 1977). The optical spectra of S stars are well-known to be dominated by ZrO, followed by other molecules of *s*-process elements. Overabundances of many of the rare and even unstable elements such as Tc (Merrill, 1952; Peery, 1971, 1979) and Pm (Davis, 1971) is an interesting feature observed in S stars.

Of the nearly 700 S-type stars known (Stephenson, 1976; Wing and Yorke, 1977), probably there could hardly be more than 2% pure S. Among the known very few pure S stars, R Cyg is one which has been comprehensively studied near minimum light at moderate dispersion in the visible region (Wyckhoff and Wehinger, 1976, 1977; Wyckhoff *et al.*, 1978; Wyckhoff and Clegg, 1978). Very recently, Lambert and Clegg (1980) investigated the near-infrared spectrum (8000–11000 Å) at higher resolution (1.8–0.4 Å) to identify any of the Keenan (1950, 1957) and Wing (1972) bands in S stars.

The present paper concerns with the presentation and analysis of the optical spectrum of the S star  $\pi^1$  Gru. The principal goal of this study is to present an atlas of the

spectrum and to interpret the observed spectrum in regard to the chemical equilibrium conditions prevailing in the atmospheres of cool S stars.

We report in Section 2 the observational details and in Section 3, the wavelength measurements of the observed molecular features are described. In Section 4 are presented our identifications of the measured band heads. Spectral classification and the interpretation of the observed spectrum are discussed in Section 5.

## 2. Observations

The very bright S stars  $\pi^1$  Gru (S 5, 7:e) is an irregular, small amplitude variable of from 5.8 to 6.4 visual magnitude and of  $-5.2$  bolometric absolute magnitude (Feast, 1953; Feast *et al.*, 1976). Image tube spectra employed in the present study were obtained (by Mr M. Makkadan for Dr M. K. V. Bappu, during the course of an investigation of atomic lines in cool stars) on 14 November, 1978, using the Kavalur 1-m reflector and the Cassegrain spectrograph. The region traced was 5800–7300 Å and dispersion was 46 Å mm<sup>-1</sup> at H $\alpha$ .

The spectrograms are displayed in plate 1. Some of the strong molecular features identified with ZrO, LaO, YO, and CeO molecules are illustrated in each spectrum. The figure illustrates that the bands of the  $\Delta v = 0$  sequences of the ZrO  $\gamma$  system at 6345 and 6474 Å are the strongest molecular absorption features in the optical region of the spectrum. Note the absence of the TiO features either at 6162 or 7054 Å. Also noteworthy is the absence of ScO orange bands ( $A^2\Pi-X^2\Sigma^+$ ) at 6036 and 6079 Å, which are prominent in S star spectra showing TiO features.

## 3. Wavelength Measurements

Measures of the molecular band heads together with their assignments in the region between 5840 and 7280 Å of the spectrum of  $\pi^1$  Gruis are presented in Table I. All the measured bands are seen to be degraded to longer wavelengths. Wavelength measures in the stellar spectrum are given in column 1. The observed band heads are corrected for a radial velocity of  $-20$  km s<sup>-1</sup> and have mean errors of the order of  $\pm 0.4$  Å with the exception of bands in the region longward of 7200 Å. The band identifications in the region between 7200 and 7300 Å are complicated due to their blending with the atmospheric O<sub>2</sub> and H<sub>2</sub>O features (cf. Moore *et al.*, 1966). The errors in this region are of the order of  $\pm 2$  Å due both to blending with atmospheric absorption features and image-tude distortions near the edge of the spectrograph field. Rough visual estimate of the intensity (on a scale of 0–10) of measured bands is given in column 2. The identified stellar band features are compared with those observed in the laboratory which are set out in column 3. Column 4 presents the identified molecule, followed by the penultimate column 5 which gives the identified band system. The last column 6 contains the vibrational transition of the observed band head.

TABLE I

Molecular band head measurements and identifications in the spectrum (5800–7300 Å) of Pi Gruis

Wavelength (Å) $\pi^1$ Gru	Intensity (visual est.)	Wavelength (Å) lab	Molecule	Transition	Band head assignment $v', v''$
(1)	(2)	(3)	(4)	(5)	(6)
5849.2	5	5849.4	ZrO	B $^1\Pi-X$ $^1\Sigma^+$	2, 0
5859.8	6	5859.8	ZrO	$^1\Sigma^+-X$ $^1\Sigma^+$	0, 0
5867.8	1	5868.0	ZrO	$\gamma(b$ $^3\Phi-a$ $^3\Delta)$	3, 1
5870.2	1	5869.5	LaO	B $^2\Sigma^+-X$ $^2\Sigma^+$	0, 1
5879.1	2				
5893.4	2	5893.4	ZrO + NaD	B-X	3, 1
		5892.9	ZrO	$\Sigma-\Sigma$	1, 1
5917.9	3	5917.7	ZrO	$\beta(c$ $^3\Pi-a$ $^3\Delta)$	2, 3
5924.5	3	5924.0	LaO	B-X	2, 3
5927.4	1	5926.4	ZrO	$\Sigma-\Sigma$	2, 2:
5935.0	3				
5938.1	3	5937.8	ZrO	B-X	4, 2
5940.9	3	5939.1	YO	A $^2\Pi_{3/2}-X$ $^2\Sigma^+$	0, 0
			ZrO	$\beta$	0, 1
5946.7	1	5947.0	ZrO	$\beta;$	3, 4;
			ZrO	$\gamma$	2, 1
5972.6	6	5972.2	YO	A-X	0, 0
5977.1	3	5977.7	ZrO	$\gamma$	3, 2
5981.5	5	5982.7	ZrO	B-X	5, 3:
		5983.3	ZrO	$\gamma$	3, 2
5987.2	4	5987.7	YO	A-X	1,1
5997.8	5				
6003.0	2	6003.6	YO	A-X	2, 2
6008.1	3	6008.5	ZrO	$\gamma$	4, 3
6014.6	2	6014.5	ZrO	$\gamma$	4, 3
6019.2	2	6020.0	YO	A-X	3, 3
6021.9	4	6021.3	ZrO	$\gamma$	1, 0
6027.0	2	6026.0	ZrO	$\gamma$	1, 0
		6028.0	ZrO	B-X	6, 4
6030.0	2				
6036.1	2	6036.7	YO	A-X	4, 4
6038.9	3	6039.1	ZrO	$\beta;$	0, 1;
			ZrO	$\gamma$	5, 4
6046.2	2	6045.8	CeO	B $_1-X_1$	0, 0
6053.9	4	6053.8	ZrO	$\gamma$	2, 1
		6053.9	YO	A-X	5, 5
6058.9	3	6059.3	ZrO	$\gamma$	2, 1
6063.4	3				
6070.4	1	6070.0	ZrO	$\beta$	1, 2
6073.2	3	6072.8	YO	A-X	6, 6
		6073.6	ZrO	B-X	7, 5
6079.5	2	6080.3	CeO	E $_2-X_2$	0, 0
6084.3	2	6083.9	CeO		
6087.0	3	6086.8	ZrO	$\gamma$	3, 2
6090.1	1	6090.2	CeO	E $_2-X_2$	0, 0
6096.0	2	6096.8	YO	A $^2\Pi_{1/2}-X$ $^2\Sigma^+$	0, 0

Table I (continued)

Wavelength (Å) $\pi^1$ Gru	Intensity (visual est.)	Wavelength (Å) lab	Molecule	Transition	Band head assignment $v', v''$
(1)	(2)	(3)	(4)	(5)	(6)
6102.2	3	6102.7	CeO		
6108.0	1	6107.4	CeO		
6110.3	1				
6119.3	4	6119.7	ZrO	B-X	8, 6
		6120.1	ZrO	$\gamma$	4, 3
6124.9	2	6125.4	ZrO	$\gamma$	4, 3
6127.5	5	6127.4	ZrI + ?		
6131.8	8	6132.1	YO	A-X	0, 0
		6131.5	ZrO :	$\beta$	3, 4
6137.0	4	6136.9	ZrO	$\gamma$	1, 0
6142.9	4	6143.2	ZrI + ?		
6147.8	6	6148.4	YO	A-X	1, 1
6153.9	7	6154.3	ZrO	B-X	1, 0
6161.2	2	6161.1	CeO		
6165.0	2	6165.1	YO	A-X	2, 2
6168.1	2	6167.9	CeO		
6170.1	2	6170.2	ZrO	$\gamma$	2, 1
6175.4	3	6175.2	ZrO	$\gamma$	2, 1
6182.8	2	6182.3	YO	A-X	3, 3
6188.8	2	6188.7	ZrO	$\beta$	0, 2
6191.6	1	6192.3	CeO		
6199.5	2	6199.9	YO	A-X	4, 4
6201.5	3	6200.9	ZrO	B-X	2, 1
		6202.0	CeO		
6204.6	2	6204.0	ZrO	$\gamma$	3, 2
6210.4	4	6210.2	ZrO	$\gamma$	3, 2
6213.8	3	6213.0	ZrO	$\Sigma$ - $\Sigma$	0, 1
6217.5	2	6218.0	YO	A-X	5, 5
6222.6	5				
6229.6	5	6229.4	ZrO	$\gamma$	0, 0
6237.2	5	6238.1	ZrO + ?	$\gamma$	4, 3
6242.3	3				
6248.1	3	6247.8	ZrO	B-X	3, 2
		6249.0	ZrO	$\Sigma$ - $\Sigma$	1, 2
6251.5	2				
6257.4	5				
6260.7	2	6261.0	ZrO	$\gamma$	1, 1
6264.2	1				
6267.6	2	6268.3	CeO		
6272.7	1	6273.0	ZrO	$\gamma$	5, 4
6275.9	2	6276.4	CeO		
6280.4	3				
6284.5	1	6285.0	ZrO	$\Sigma$ - $\Sigma$	2, 3
6292.5	3	6292.8	ZrO	$\gamma$	2, 2
6295.3	2	6295.0	ZrO	B-X	4, 3
6301.6	1				
6305.5	3				
6319.8	1	6321.0	ZrO	$\Sigma$ - $\Sigma$	3, 4

Table I (continued)

Wavelength (Å) $\pi^1$ Gru	Intensity (visual est.)	Wavelength (Å) lab	Molecule	Transition	Band head assignment $v', v''$
(1)	(2)	(3)	(4)	(5)	(6)
6324.9	2	6324.6	ZrO	$\gamma$	3, 3
6332.7	1	6333.4	ZrO	$\gamma$	3, 3
6343.1	1	6342.7	ZrO	B-X	5, 4
		6344.0	CeO	$C_2-X_2$	0, 0
6345.0	9	6344.9	ZrO	$\gamma$	0, 0
6351.5	6	6351.2	ZrO	$\gamma$	0, 0
6353.8	3	6354.2	CeO	$C_2-X_2$	0, 0
6356.0	3	6356.3	ZrO	$\gamma$	4, 4
		6357.0	ZrO	$\Sigma-\Sigma$	4, 5
6363.0	2	6362.5	ZrO	$\gamma$	4, 4
		6362.6	CeO	$C_2-X_2?$	1, 1
6378.3	4	6378.4	ZrO	$\gamma$	1, 1
6384.8	3	6384.6	ZrO	$\gamma$	1, 1
6387.7	2	6387.8	ZrO	$\gamma$	5, 5
6390.7	1	6390.8	ZrO	B-X	6, 5
6393.1	1	6393.0	ZrO	$\Sigma-\Sigma$	5, 6
		6394.1	ZrO	$\gamma$	5, 5
6401.9	1				
6412.4	3	6412.3	ZrO	$\gamma$	2, 2
6419.1	2	6419.3	ZrO	$\gamma$	2, 2
6429.0	1	6430.0	ZrO	$\Sigma-\Sigma$	6, 7
		6430.3	CeO		
6435.2	2				
6446.2	1	6446.6	ZrO	$\gamma$	3, 3
6452.4	1	6452.5	ZrO	$\gamma$	3, 3
6462.5	1				
6473.9	10	6473.7	ZrO	$\gamma$	0, 0
6481.3	6	6480.7	ZrO	$\gamma$	0, 0; 4, 4
6495.5	9	6495.3	ZrO	B-X	0, 0
6501.1	2				
6506.1	3				
6508.7	4	6508.0	ZrO	$\gamma$	1, 1
6515.4	2	6515.2	ZrO	$\gamma$	1, 1; 5, 5
6543.4	2	6542.8	ZrO	$\gamma$	2, 2
6545.1	3	6544.7	ZrO	B-X	1, 1
6550.2	1	6549.7	ZrO	$\gamma$	2, 2; 6, 6
6556.8	4				
6572.4	3				
6578.8	3	6578.0	ZrO	$\gamma$	3, 3
6585.5	2	6584.9	ZrO	$\gamma$	3, 3
6594.7	1	6594.4	ZrO	B-X	2, 2
6598.5	2				
6612.5	3	6612.2	ZrO	$\gamma$	4, 4; 0, 1
6620.3	2	6619.6	ZrO	$\gamma$	4, 4; 0, 1
6630.1	2				
6644.6	1	6645.1	ZrO	$\gamma$	1, 2

Table I (continued)

Wavelength (Å) $\pi^1$ Gru	Intensity (visual est.)	Wavelength (Å) lab	Molecule	Transition	Band head assignment $v', v''$
(1)	(2)	(3)	(4)	(5)	(6)
6644.6	1	6646.0	ZrO	$\Sigma-\Sigma$	1, 3:
6650.3	1	6649.5	ZrO	$\gamma$	5, 5
6677.5	1	6678.0	ZrO	$\gamma$	2, 3
6683.0	2	6684.0	ZrO	$\Sigma-\Sigma$	2, 4:
6686.9	2	6686.6	ZrO	$\gamma$	6, 6
6711.1	1	6710.9	ZrO	$\gamma$	3, 4
6718.2	1	6718.0	ZrO	$\gamma$	3, 4
6742.8	2	6743.8	ZrO	$\gamma$	4, 5; 0, 1
6751.9	1	6751.5	ZrO	$\gamma$	0, 1
6762.0	3	6762.4	ZrI + ?		
6775.7	2	6776.7	ZrO	$\gamma$	5, 6
		6777.3	ZrO	$\gamma$	1, 2
6793.2	3				
6812.5	2	6812.5	ZrO	$\gamma$	2, 3
6832.3	3				
6866.5	8	6867.0	CeO + O <sub>2</sub> ⊕		
6885.2	2	6884.6	ZrO	$\gamma$	4, 5
6887.7	3	6887.5	ZrO	$\gamma$	0, 1
6900.8	1	6901.4	CeO + O <sub>2</sub> ⊕		
6903.5	2	6903.4	CeO + O <sub>2</sub> ⊕	B <sub>2</sub> -X <sub>2</sub>	2, 1
6924.1	4	6923.4	ZrO	$\gamma$	1, 2
6931.6	6	6931.7	ZrO	B-X	0, 1
6960.4	2	6959.7	ZrO	$\gamma$	2, 3
6980.8	6	6981.4	CeO + H <sub>2</sub> O⊕		
6984.4	5	6984.5	ZrO + H <sub>2</sub> O⊕	B-X	1, 2
6998.4	5	6998.3	CeO + H <sub>2</sub> O⊕		
7037.1	2	7037.7	ZrO + H <sub>2</sub> O⊕	B-X	2, 3
7039.4	1	7039.5	CeO + H <sub>2</sub> O⊕		
7043.1	1	7043.0	CeO + H <sub>2</sub> O⊕		
		7043.1	ZrO + H <sub>2</sub> O⊕		0, 2
7057.2	2	7057.5	CeO + H <sub>2</sub> O⊕		
7071.8	3	7071.1	ZrO + H <sub>2</sub> O⊕		5, 6
7090.7	1	7091.3	ZrO + H <sub>2</sub> O⊕	B-X	3, 4
7143.0	3	7143.8	ZrO + H <sub>2</sub> O⊕		3, 5
		7143.9	CeO + H <sub>2</sub> O⊕		
7146.1	1	7145.4	ZrO + H <sub>2</sub> O⊕	B-X	4, 5
7152.8	4	7153.5	CeO + H <sub>2</sub> O⊕		
7201.1	3	7199.4	ZrO + H <sub>2</sub> O⊕	B-X	5, 6:
7235	1	7235.7	CeO + H <sub>2</sub> O⊕	B <sub>2</sub> -X <sub>2</sub>	0, 0
7239	5	7234.6	CeO + H <sub>2</sub> O⊕ + ?	<i>n</i>	0, 0
7243	3	7242.4	CeO + H <sub>2</sub> O⊕	B <sub>2</sub> -X <sub>2</sub>	0, 0
7249	4	7249.9	CeO + H <sub>2</sub> O⊕	<i>n</i>	0, 0
7275	4	7275.5	CeO + H <sub>2</sub> O⊕	B <sub>2</sub> -X <sub>2</sub>	1, 1
7278	4	7277.9	CeO + H <sub>2</sub> O⊕		

#### 4. Molecular Identifications

##### 4.1. IDENTIFICATIONS OF ZrO, YO, LaO AND CeO

From Table I, we may infer that most of the strong bands in Figure 1 are identified with ZrO, YO, LaO, and CeO molecules. Of the total of 163 measured features, more than 60% are identified with ZrO, thus indicating the dominance by ZrO of the visible spectrum of Pi Gruis. A brief description on the identification of these individual molecules follows.

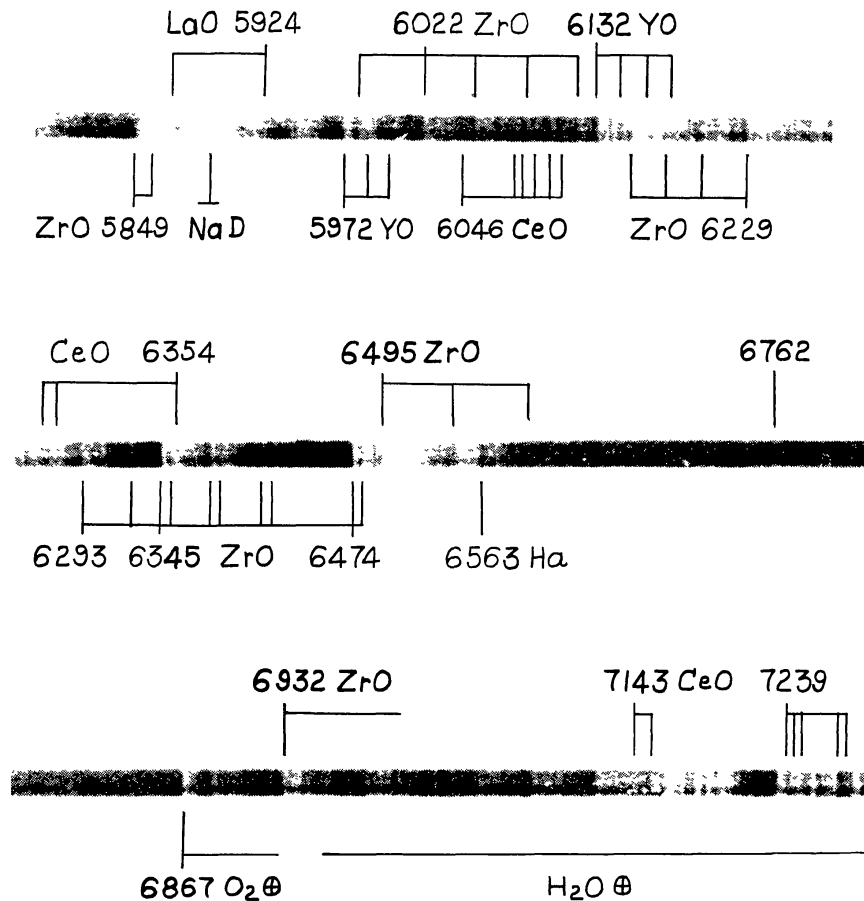


Fig. 1. Image-tube spectrum (original dispersion  $46 \text{ \AA mm}^{-1}$  at  $H\alpha$ ) of  $\pi^1$  Gru, showing some of the intense absorption features identified with ZrO, YO, LaO, and CeO molecules.

(i) *ZrO*. Since the introduction of spectral class S by Merrill (1922), ZrO molecule is notable in the spectra of S stars. Three triplet and four singlet band systems are well-known for the ZrO molecule in the region between 3300 and 8300  $\text{\AA}$  (cf. Huber and Herzberg, 1979). In addition to the prominent  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $A$  and  $B$  systems (Lowater, 1932; Afaf, 1950a, b; Uhler, 1954; Lagerqvist *et al.*, 1954; Uhler and Akerlind, 1956; Akerlind, 1956; Gatterer *et al.*, 1957; Tatum and Balfour, 1973; Lindgren, 1973), two more new band systems are known in the infrared region of the matrix spectrum of ZrO

(Lauchlan *et al.*, 1976). Of the two new systems, the one at 9300 Å ( $b^3\Pi-a^3\Delta$ ) has recently been identified in the gas phase by Phillips *et al.* (1979). Also high resolution analysis of 15 bands of the  $\gamma$  system ( $b^3\Phi-a^3\Delta$ ) has been reported by Phillips and Davis (1979). Of these four known triplet systems, we report herein the identification of  $\gamma$  bands together with few bands of the  $\beta$  system. In the region between 5865 and 7145 Å of the spectrum of Pi Gruis, a total of 72 bands are assigned to the  $\gamma$  system of which 50 are newly identified. As regards the singlet band systems in the visible region (Balfour and Tatum, 1973; Phillips and Davis, 1976a, b), we identify some of the predicted new bands in addition to the known bands of the  $^1\Pi-^1\Sigma$  and  $^1\Sigma-^1\Sigma$  systems (Murty, 1980a, b).

(ii) *YO*. The two prominent band systems, A  $^2\Pi-X^2\Sigma^+$  and B  $^2\Sigma^+-X^2\Sigma^+$ , in the orange and blue-green regions respectively, of the spectrum of YO molecule have recently been investigated by Shin and Nicholls (1977); Bernard *et al.* (1979); and Bernard and Gravina (1980). The bands at 5972 Å (O, OA  $^2\Pi_{3/2}-X^2\Sigma^+$ ) and 6132 Å (O, OA  $^2\Pi_{1/2}-X^2\Sigma^+$ ) are well-known in S star spectra (e.g., Merrill and Greenstein, 1956). Wyckoff and Clegg (1978) observed four bands of the A-X system at 5972, 5988, 6004, and 6132 Å in the spectrum of R Cyg. In addition to these four bands, 11 more bands are identified for the first time in the present study of the spectrum  $\pi^1$  Gru. Of these 11 new bands, only 3 at 5940, 6054, and 6073 are blended with ZrO bands, while the remaining 8 at 6019, 6036, 6096, 6148, 6165, 6183, 6200, and 6218 Å are identified in a relatively uncontaminated region.

(iii) *LaO*. The visible spectrum of LaO (cf. Akerlind, 1962; Rosen, 1970) exhibits two intense band systems in the regions 9730–6850 Å (A  $^2\Pi-X^2\Sigma^+$ ) and 6450–5015 Å (B  $^2\Sigma^+-X^2\Sigma^+$ ). The strongest bands of the red system at 7910.5 Å (0, OA  $^2\Pi_{1/2}-X^2\Sigma^+$ ) and 7379.8 Å (0, OA  $^2\Pi_{3/2}-X^2\Sigma^+$ ) have been used by Nassau and van Albada (1948) to detect faint S stars. Wyckoff and Clegg (1978) identified bands of the red, as well as the green-yellow system in the spectrum of R Cyg. The strongest bands of the B-X system are at 5380.4 (1, 0); 5602.5 (0, 0); 5628.6 (1, 1); 5654.8 (2, 2); 5869.5 (0, 1); 5896.7 (1, 2); 5924.0 (2, 3); and 5951.3 (3, 4). It is possible to identify bands of the  $\Delta v = -1$  sequence only in the present spectrum (5800–7300 Å) of  $\pi^1$  Gru. Of the four intense bands of the  $\Delta v = -1$  sequence, 2 at 5870 and 5924 Å are identified. Of these two bands, the very intense at 5924 Å is conspicuous as seen from plate 1. The other intense band at 5896.7 Å is evidently masked by the NaD lines.

(iv) *CeO*. A detailed laboratory study of the electronic spectrum of CeO has recently been carried out by Barrow *et al.* (1979), who listed more than 300 bands in the region between 3600 and 8600 Å. Owing to the complex nature of the bands structure, even the vibrational analyses are incomplete and thus many of the observed bands remain unassigned. Thanks to the most recent laboratory study of the CeO molecule by Linton *et al.* (1979, 1981), who clearly show the potential value of the laser-induced fluorescence experiments in unravelling the complex structure of the CeO molecular bands. The presence of CeO in stellar spectra has been first proposed by Wyckoff and Wehinger (1977). Subsequently Clegg and Lambert (1978) using higher resolution (0.2 Å) spectra of R Gem and R And have confirmed the existence of CeO in S stars. Recently Lambert



and Clegg (1980) identified two new bands of CeO at 8219.0 and 8234.7 Å ( $A_3-X_3$ ) in the infrared spectrum of R Cyg at minimum light. Moreover, they identified weak red degraded band heads at 8503.3 ( $B_2-X_4$ ), 8560.1 and 8583.7 Å (both unclassified). We identify 32 CeO molecular features in the 6045–7280 Å region of the spectrum of  $\pi^1$  Gru (Murty, 1983); of these, 23 are newly identified. It is, however, unfortunate that only for four bands of these 23, laboratory assignments are available. Quite recently, we reported the identification of 11 CeO features in the visible spectrum of R Cyg (Murty, 1982). These recent identifications of CeO in  $\pi^1$  Gru and R Cyg clearly emphasize the need for additional laboratory study of CeO aimed at classifying the visible and near infrared unidentified bands (cf. Murty, 1980c).

#### 4.2. ABSENCE OF TiO AND Ba COMPOUNDS

Several unidentified features in the S star spectra have been identified by Dubois (1977) as due to TiO, BaO, BaF, and BaCl molecules, using the band head measurements in the low dispersion spectra of R Cyg by Wyckoff and Wehinger (1976). However, an analysis of the higher resolution spectrum of R Cyg by Wyckoff and Clegg (1978) has clearly shown that the identifications proposed by Dubois are incorrect. A very recent study of R Cyg by Lindgren and Olofsson (1980), fully confirms the conclusion of Wyckoff and Clegg (1978) that none of the Ba compounds is present in the S star spectra. In the present study also, neither the intense (O, O) bands of the  $\gamma$  system ( $A^3\Phi-X^3\Delta$ ) at 7054, 7088, and 7126 Å, nor the (O, O) bands of the  $\gamma'$  system ( $B^3\Pi-X^3\Delta$ ) at 6162, 6186, and 6217 Å of the TiO molecule are detectable. Also, a search for BaF and BaO molecules is negative. The prominent bands of the ( $B^2\Sigma^+-X^2\Sigma^+$ ) system of BaF at 7116.0 (0, 0) and 7139 Å and 7139 Å (1, 1) are absent in the spectrum of  $\pi^1$  Gru. Similarly the search for the intense bands of the  $A^1\Sigma-X^1\Sigma$  system of BaO at 5864.5 Å (2, 1) together with other bands in the region 5800–6800 Å is unsuccessful.

### 5. Pure S Star Characteristics

An S star whose spectrum shows up the presence of ZrO, LaO, and YO molecular features and the absence of TiO bands (or weakly present), at moderate dispersion is classified as a pure S star (cf. Keenan, 1966). The present study of the visible spectrum of  $\pi^1$  Gru clearly shows up the unambiguous identification of ZrO, YO, LaO, and CeO molecules. No TiO bands are detectable. Thus the presence of the *s*-process oxides and the absence of TiO suggests that  $\pi^1$  Gru may be classified as a pure S star.

Following on the earlier S star spectral classifications (Keenan, 1954; Keenan and McNeil, 1976), recently Ake (1979) proposed a revised spectral classification system using low dispersion spectra of S stars in the 5450–7000 Å region. Ake (1979) proposed a new abundance index for the S stars based on the observed relative strengths of ZrO, TiO, and NaD. In the light of his abundance index,  $\pi^1$  Gru belongs to the index 5 (see Table IV of Ake) for which  $ZrO \gg 2 \times YO$ ;  $TiO = 0$  with  $0.95 \leq C/O \leq 1.0$ . This classification evidently places  $\pi^1$  Gru in the list of pure S stars. Ake pointed out that

the above index is basically related to the C/O ratio, although it may also be effected by the general enhancement of *s*-process elements. This new C/O index has very recently been modified by Keenan and Boeshaar (1980), based on a revised MK classification applicable to S–SC–C sequence (Boeshaar and Keenan, 1979). Following this revised classification criteria,  $\pi^1$  Gru can be assigned to the spectral type SX/6 (X stands for temperature type and the number 6 is an abundance index which, as suggested by Ake, is a measure of C/O, for which ZrO bands are very strong with no TiO and the estimated C/O = 0.98).

Very recently, Piccirillo (1980) based on the calculations of S star model atmospheres, suggests that although the reduced strength of TiO in S stars is a direct indication of C/O value greater than the solar value of 0.6, the molecular spectra of S stars cannot be interpreted as due to C/O effects alone. His calculations suggest that the observed strength of ZrO in S star spectra attests to Zr enhancements; an enhancement of from 2 to 15 times the solar value of Zr is estimated.

It is thus evident from the recent observational and theoretical studies that the interpretation of the observed molecular spectra in cool S stars is rather complex. At present, one has to consider both the effects of *s*-process enhancements and C/O ratio, for the interpretation of pure S star spectra.

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