UNIDENTIFIED MOLECULAR FEATURES IN THE RED SPECTRUM (5800 TO 7300 Å) OF PI GRUIS*

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Abstract. Moderate dispersion (46 Å mm^{-1} at Hα) image-tube spectrum (5800–7300 Å) of the S star π^1 Gru is found to exhibit several unidentified molecular features, in addition to the well-known bands of the oxides of *s*-process elements. A list is presented of 28 measured unidentified red-degraded bands, of which six, at 5998, 6128, 6143, 6223, 6257, and 6557 Å, are prominent. Of the reported 28 bands, 22 are observed for the first time. A discussion is included on the expected molecular sources of the unidentified features. The possible presence of two new molecules, Pr O and Nd O, in π^1 Gru is suggested.

1. Introduction

Although the S stars are less numerous compared to either the M stars or the C stars, they play a significant role in studies of the processes of nucleosynthesis and mixing in red giants. The spectra of pure S stars, in which TiO bands are either very weak or absent at moderate dispersion, are characterized by the presence of molecular features due to the oxides of *s*-process elements such as, Zr, Y, La and Ce. Despite the numerous band identifications of these oxide molecules, the assignment of many prominent spectral features of the S stars still remains elusive. A great many of unidentified bands have been reported in the visible (Bidelman and Stephenson, 1957; Wyckoff and Wehinger, 1976) and infrared (Keenan, 1950, 1957; Wing, 1972) regions of the spectra of S stars, especially those of the long-period variables near minimum light. Of the many unidentified molecular features reported in the 4400–8000 Å region of the spectra of pure S stars, some have recently been identified with the CeO and ZrO molecules (Wyckoff and Wehinger, 1977; Wyckoff and Clegg, 1978; Murty, 1982). As regards the identification of the infrared bands, it may be noted that only one band at 9900 Å has so far been identified as due to the FeH molecule (Nordh *et al.*, 1977; Wing *et al.*, 1977; Clegg and Lambert, 1978), while the band at 9730 Å has recently been attributed to the ZrO molecule (Murty, 1980a). In spite of these identifications, a large number of molecular features continue to resist identification. Very recently, the 8610 Å Keenan band has been identified (Lindgren and Olofsson, 1980) with the CrH molecule, based on a medium resolution spectrum of R Cyg. However, the higher resolution (0.4 Å) spectrum of R Cyg has clearly shown that the 8610 Å feature is not due to CrH (Lambert and Clegg, 1980). It has been speculated by Lambert and Clegg that sulphides and chlorides spectra of the heavy elements may account for some of the unidentified molecular features.

* This paper is dedicated to the memory of Dr M. K. V. Bappu.

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2. Results

Moderate dispersion spectra (46 Å mm^{-1} at Hα, 5800–7300 Å) of the very bright red giant π^1 Gru (S5,7e), used in the present investigation were obtained (by Mr M. Mekkaden for Dr M. K. V. Bappu, during the course of a study of atomic lines in cool stars) on 14 November 1978, with a Cassegrain image-tube spectrograph attached to the 1 m Kavalur Observatory reflector.

Relevant portions of the spectrograms are illustrated in Figure 1. The strong molecular features due to ZrO, YO and CeO are labelled at the bottom of each spectrum, while the strong unidentified features are labelled with their wavelengths at the top of the spectra.

Band-head measurements of the unidentified features in the spectrum of π^1 Gru, together with those reported by Wyckoff and Clegg in R Cyg are given in Table I. All the unidentified bands observed in both the stars are seen to be red-degraded. The

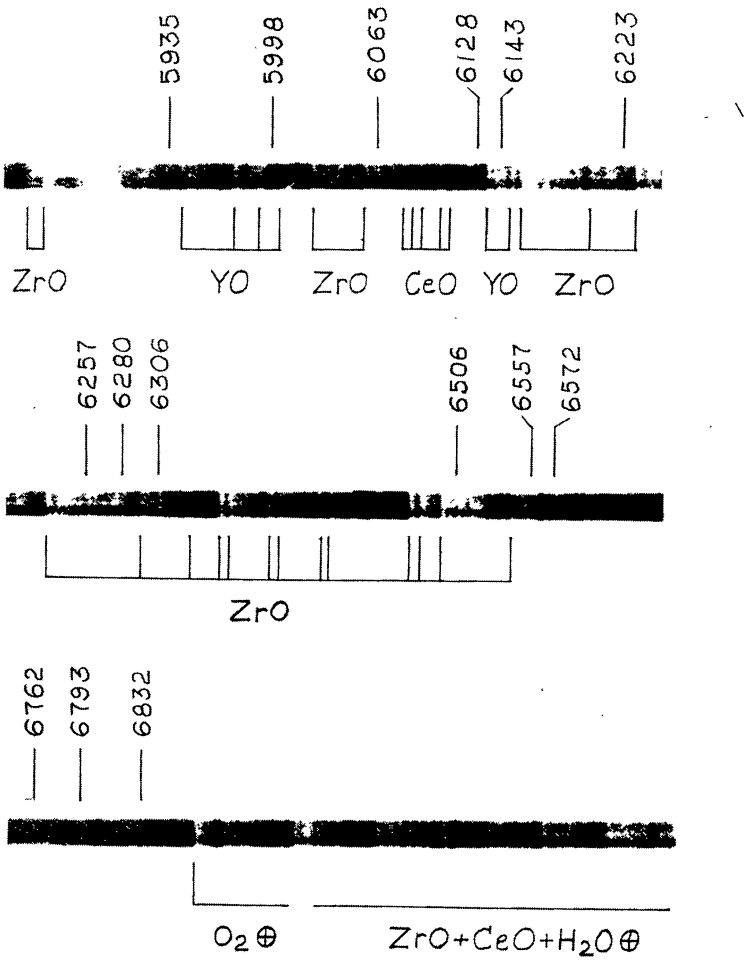

Fig. 1. Image-tube spectrum (original dispersion 46 Å mm^{-1} at Hα) of π^1 Gru. Intense unidentified band features are labelled with their wavelengths at the top of each spectrum.

TABLE I

Unidentified molecular features measured in the spectra of π^1 Gru and R Cyg

π^1 Gru		R Cyg	
λ (Å) (1)	I (Visual est.) (2)	λ (Å) (3)	I (Visual est.) (4)
5879.1	2	–	–
5935.0	3	–	–
5997.8	5	5996.7	1
6030.0	2	6030.8	2
6063.4	3	6062.5	2
6110.3	1	6109.9	1
6127.5	5	–	–
6142.9	4	6142.5	1
–	–	6149.5	1
6222.6	5	–	–
6242.3	3	–	–
6251.5	2	–	–
6257.4	5	–	–
6264.2	1	–	–
6280.4	3	–	–
6301.6	1	–	–
6305.5	3	–	–
6401.9	1	–	–
6435.2	2	–	–
6462.5	1	6462.7	1
6501.1	2	–	–
6506.1	3	–	–
–	–	6545.1	0
6556.8	4	–	–
6572.4	3	–	–
6598.5	2	–	–
6630.1	2	–	–
–	–	6753.7	2
6762.0	3	–	–
–	–	6764.0	2
–	–	6784.8	2
6793.2	3	–	–
6832.3	3	–	–

measured band-heads in the spectrum of π^1 Gru are corrected for a radial velocity of -20 km s^{-1} and have mean errors of the order of ± 0.4 Å. Column (1) gives the unidentified band-head positions in π^1 Gru. In column (2), the approximate visual intensity estimate of the bands is presented. Unidentified bands in the spectrum of R Cyg are listed in column (3), while column (4) contains their rough visual intensity.

3. Discussion

Of the 28 measured features, the bands at 5998, 6128, 6223 and 6257 Å, as seen vividly from Figure 1, are the strongest unidentified features, followed by the bands at 6143 and 6557 Å. It may be noted from Table I that nearly 85% of the total bands are of $I \geq 2$, while 55% are of $I \geq 3$. It is noteworthy that the molecular features observed in π^1 Gru (Murty, 1980b) are more intense and extensive than those observed in the spectrum of R Cyg. In column (3), 11 bands are listed as unidentified in the region between 5800 and 6800 Å of the spectrum of R Cyg (Wyckoff and Clegg, 1978). Of the 11 bands, the band at 6545.1 Å has already been identified (Murty, 1980b) as the (1,1) band of the 6495 Å system of ZrO. It is interesting to note that the unidentified feature at 6149.5 Å matches reasonably well (within the large observational error) with the 6148.4 Å (1,1) band of the $A^2\Pi_{1/2} - X^2\Sigma^+$ transition of YO (Shin and Nicholls, 1977; Bernard *et al.*, 1979). Thus, the 6149.5 Å stellar feature may be identified with the YO molecule (cf. Murty, 1982).

In what follows we describe our attempts at assigning the unidentified features observed in π^1 Gru to any of the known molecular features of the oxides of heavier elements.

ZrO, YO, LaO, and CeO

Since the bands of the *s*-process oxides abound in the optical spectrum of pure S stars, an initial attempt is made to identify the features listed in Table I, with any of the known bands of ZrO, YO, LaO, and CeO. Unfortunately, no convincing band-head coincidences could be found with these molecules. It is however noted that the (9,9) band (6127.4 Å) of the $A^2\Pi_{3/2} - X^2\Sigma^+$ transition of YO, matches well with the 6127.5 Å stellar feature. Nevertheless, mere intensity consideration suggests that the weak (9,9) band of the $A - X$ system may not be the main contributor to the intense 6127.5 Å feature. A very weak unidentified band at 6222.8 Å has been reported in the laboratory spectrum of ZrO by Lowater (1932). Once again, the very intense stellar feature at 6222.6 Å cannot be reconciled with the ZrO molecule. Thus, neither of these molecules could be a major responsible candidate to the 6128 and 6223 Å features. Also we note that the 6128, 6143 and 6762 Å features are blended with intense ZrI lines.

HfO and TaO

The other likely candidates that we have considered for the identification of the bands are the other oxides of *s*-process elements and the rare-earth oxides. It has been suggested by Sauval (1978), that the molecules HfO and TaO may account for some of the unidentified features observed in the spectra of pure S stars. For HfO molecule, most of the intense bands lie in the region between 3200 and 6000 Å. The intense bands at 4102.3, 4252.1 and 5074.7 Å lie outside the available spectral coverage of π^1 Gru. The only intense band at 6021 Å which is suitable for comparison is masked by the (1,0) band of the γ-system of ZrO. For TaO molecule also most of the bands lie in the region 3000–6000 Å, with its most intense band lying at 3747.2 Å. Only two bands at 6291 and

5980 Å are available for comparison and a search for these bands in the spectrum of π^1 Gru is negative. Thus with the presently available spectrum of π^1 Gru, it is not possible to comment on the presence or absence of either HfO or TaO in pure S stars. However, it may be noted that the very recent search by Lambert and Clegg (1980) for the infrared bands of TaO and HfO in the higher resolution (1.8 Å) spectrum of R Cyg at minimum light is negative.

NbO and RuO

Two other molecules of interest which have red-degraded bands in the 4000–8000 Å region are NbO and RuO. A tentative identification of NbO has been reported by Davis and Keenan (1969) in the high dispersion spectrum of R Cyg, based on the identification of 6484 and 6591 Å bands. Three band systems (*A*, *B* and *C*) in the 4200–7100 Å region are known for the NbO molecule (cf. Pearse and Gaydon, 1976). In addition, a recent study of the laboratory spectrum by Lindgren and Olofsson revealed the presence of nine more new bands in the region 7800–8800 Å, with the 7951.7 Å band as the most intense band. The bands of the *A* system are in the 4200–5100 Å region, with the 4689.0 Å band being the most intense band of the system. For the *B* system (5000–6300 Å), two intense bands lie at 6184.9 and 6268.4 Å, in addition to the very strong band at 5200.9 Å, while for the extreme red *C* system the intense bands are at 6737.1 and 6495.6 Å. No coincidences of the above bands are evident with the unidentified features observed in the spectrum of π^1 Gru. Similarly the RuO molecule, whose intense bands lie at 5525.8, 5532.0, 5544.6, 5799.8, 6406.3, 6705.3 and 6744.5 Å, is also not detectable in π^1 Gru. It is surprising to note that although molecular column density estimates predict NbO to be quite abundant at low temperatures in S star spectra, none of the above features is detectable even in the higher dispersion (0.4 Å) spectra (6540–6640 Å) of R Cyg near minimum light (Lambert and Clegg, 1980). It appears likely that a search for the intense bands of the A and C systems at 4689 and 6737 Å respectively, in the higher dispersion spectra of pure S stars might prove worthwhile in establishing the questionable presence of NbO in cooler S stars.

TcO and MoO

As the lines of Tc have been identified in cool star spectra (Merrill, 1952; Peery, 1971 and 1979), it is likely that TcO may be present in pure S stars. A search for the reported laboratory bands of TcO at 6014.5, 6020.1, 6373.1 and 6380.9 Å (cf. Wyckoff and Clegg, 1978), in the spectrum of π^1 Gru is futile mainly because of their blending with the strong ZrO bands. Since Mo is also an *s*-process element necessary for the synthesis of Tc, it is worthwhile to consider the possible presence of MoO in the atmosphere of cooler S stars. Regrettably, no detailed laboratory study of the MoO spectrum is available (cf. Huber and Herzberg, 1979). Of the very slender body of information available, only two red-degraded bands with open structure at 6445.4 and 6509.4 Å are believed to be due to MoO. This region of the stellar spectrum is also dominated by the bands of ZrO, thus rendering difficult any identification of the MoO features.

PrO, NdO, PmO, and GdO

Because of the definitive identification of CeO in pure S stars, one might expect that some of the other oxides of the lanthanide elements could be present in pure S stars. Unfortunately, the band spectra of most of these heavier molecules are either unknown or incompletely analyzed. Recent theoretical studies by Dirscherl *et al.* (1978), based on metal abundances, equilibrium constants and dissociation energies of molecules, suggest the possible presence of rare-earth oxides, such as PrO, NdO, and GdO in the spectra of cooler S stars. We consider here the plausible identification of PrO, NdO, PmO, and GdO in the spectrum of π^1 Gru.

The laboratory spectrum of PrO (praseodymium monoxide) molecule reveals the presence of 22 band systems identified in the region between 5270 and 10830 Å (Shenyavskaya *et al.*, 1973). Of the reported 22 band systems, only two systems (6019 Å band of XVII system and 5597 and 5612 Å bands of XX system) are studied recently under higher resolution by Beaufils *et al.* (1979). In addition to the above band systems, three more unassigned intense bands are known to be present in the spectrum of PrO at 6263.1, 6270.7 and 6278.9 Å (Rosen, 1970). It is interesting to note that two of these bands match reasonably well with the unidentified features in the spectrum of π^1 Gru at 6264 and 6280 Å. The 6270.7 Å band is probably masked by a ZrO γ band. We cannot however, overlook the possibility that the wavelength coincidence for only two bands could be fortuitous as well. Nevertheless, the present identifications, we believe, would provide impetus not only for future laboratory studies of PrO but also to the observational studies of cooler S stars at high resolution. It may be worthwhile to point out that the 8488.8 Å band of PrO has been suggested by Sauval to match well with one Keenan band. We note, however, that there is no Keenan band at or around the 8489 Å region, because those observed in the spectrum of R Cyg lie at 8268, 8464, 8610 and 8820 Å. Thus, none of these bands may be identified with PrO. This conclusion is indeed confirmed following the most recent higher-resolution study of the spectrum of R Cyg by Lambert and Clegg.

The spectrum of NdO (neodymium monoxide) molecule is known to consist of strong red-degraded bands in the region between 4400 to 6630 Å (cf. Pearse and Gaydon, 1976). Unfortunately, no detailed band-head assignments are available for NdO. Nevertheless, we note some encouraging coincidences of the laboratory wavelengths with those observed in the stellar spectrum. There are 17 intense red-degraded bands lying in the region 5970–6630 Å. The laboratory wavelengths at 5999, 6249.9, 6598.3 and 6629.6 Å compare fairly well with the unidentified features at 5998, 6252, 6599 and 6630 Å observed in the spectrum of π^1 Gru. It is likely that additional coincidences may be noted when higher-resolution stellar spectra covering the region 4000–7000 Å, together with detailed laboratory data of the NdO molecule, are available.

The identification of promethium in the spectra of V Cnc and T Sgr by Davis (1971), suggests that overabundances of many rare and even unstable elements is an interesting feature observed in the S star spectra. PmO may thus be an attractive candidate to be considered for its identification in cooler S stars. Unfortunately, the laboratory spectroscopic study of PmO is not yet known.

Seven band systems are known for the GdO (gadolinium monoxide) molecule in the region 4450–6800 Å (cf. Rosen, 1970). Only for two band systems (systems I and II), lying in the region 4600–4900 Å, the band-head assignments are available. Three bands at 6211.8, 6200.9 and 6182.7 are identified with the system VII. None of these bands match with the unidentified stellar features. Further observational studies aimed at identifying the intense bands of the systems I and II at 4615.8 and 4892.0 Å, respectively, might prove valuable to investigate the presence of GdO in S star spectra.

The relatively large dissociation energy of PrO (7.63 eV) and NdO (7.22 eV) (Murad, 1978), may also comment their possible presence in pure S stars. Although the present identifications of PrO and NdO in π^1 Gru are tentative, it appears that oxide molecules of the lanthanide elements hold forth much promise as the most likely candidates to be seen in cooler S stars.

4. Conclusion

In conclusion, it may be pointed out that out of the 28 unidentified features reported in the spectrum of π^1 Gru, only 6 bands are provisionally identified with PrO and NdO molecules. In spite of these identifications, it may be remarked that the intense bands at 6128, 6143, 6223, 6257 and 6557 Å remain unidentified. Evidently, more than one molecule could be responsible for these unidentified features. Moreover, since in the past, many molecular bands have been observed for the first time in the stellar spectra, it appears very likely that many of the unidentified stellar features reported in the past and present studies are yet to be observed in the laboratory. The present study emphasizes that future laboratory studies of the heavy metal oxides, in particular those of the lanthanide elements may usher in further attempts at assigning the unidentified stellar features, although higher-resolution stellar spectra of pure S stars are certainly needed to provide precise comparison with laboratory spectra.

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References

Beaufils, J. Cl., Carette, P., and Blondeau, J. M.: 1979, *J. Molec. Spectrosc.* **77**, 1.
Bernard, A., Bacis, R., and Luc, P.: 1979, *Astrophys. J.* **227**, 338.
Bidelman, W. P. and Stephenson, C. B.: 1957, *Mem. Soc. Roy. Sci. Liège Ser. 4* **18**, 292.
Clegg, R. E. S. and Lambert, D. L.: 1978, *Astrophys. J.* **226**, 931.
Davis, D. N.: 1971, *Astrophys. J.* **167**, 327.
Davis, D. N. and Keenan, P. C.: 1969, *Publ. Astron. Soc. Pacific* **81**, 230.
Dirscherl, R., Michel, K. W., and Cosmovici, C. B.: 1978, *Astron. Astrophys.* **68**, 381.

Huber, K. P. and Herzberg, G.: 1979, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules,* Van Nostrand-Reinhold, New York.
Keenan, P. C.: 1950, *Astron. J.* **55**, 74.
Keenan, P. C.: 1957, *Publ. Astron. Soc. Pacific* **69**, 5.
Lambert, D. L. and Clegg, R. E. S.: 1980, *Monthly Notices Roy. Astron. Soc.* **191**, 367.
Lindgren, B. and Olofsson, G.: 1980, *Astron. Astrophys.* **84**, 300.
Lowater, F.: 1932, *Proc. Phys. Soc.* **44**, 51.
Merrill, P. W.: 1952, *Astrophys. J.* **116**, 21.
Murad, E.: 1978, *Chem. Phys. Letters* **59**, 359.
Murty, P. S.: 1980a, *Astrophys. Space Sci.* **68**, 513.
Murty, P. S.: 1980b, *Astrophys. J.* **240**, 585.
Murty, P. S.: 1982, *Astrophys. Letters*, in press.
Nordh, H. L., Lindgren, B., and Wing, R. F.: 1977, *Astron. Astrophys.* **56**, 1.
Pearse, R. W. B. and Gaydon, A. G.: 1976, *The Identification of Molecular Spectra*, 4th ed., Chapman and Hall, London.
Peery, B. F., Jr.: 1971, *Astrophys. J.* **163**, L1.
Peery, B. F., Jr.: 1979, *Publ. Astron. Soc. Japan* **31**, 461.
Rosen, B.: 1970, *Selected Constants – Spectroscopic Data Relative to Diatomic Molecules*, Pergamon, London.
Sauval, A. J.: 1978, *Astron. Astrophys.* **62**, 295.
Shenyavskaya, E. A., Egorova, I. V., and Lupanov, V. N.: 1973, *J. Molec. Spectrosc.* **47**, 355.
Shin, J. B. and Nicholls, R. W.: 1977, *Spectrosc. Letters* **10**, 923.
Wing, R. F.: 1972, *Mem. Soc. Roy. Sci. Liège, Ser. 6* **3**, 123.
Wing, R. F., Cohen, J., and Brault, J. W.: 1977, *Astrophys. J.* **216**, 659.
Wyckoff, S. and Clegg, R. E. S.: 1978, *Monthly Notices Roy. Astron. Soc.* **184**, 127.
Wyckoff, S. and Wehinger, P. A.: 1976, *Mem. Soc. Roy. Sci. Liège, Ser. (6)* **9**, 445.
Wyckoff, S. and Wehinger, P. A.: 1977, *Astrophys. J.* **212**, L139.