

Zirconium sulphide in S stars

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Accepted 1988 October 25. Received 1988 October 14; in original form 1988 June 2

Summary. Spectra in the *J*-band from 7400 to 9700 cm⁻¹ (1.05–1.35 μm) are presented for three Mira variables types M and S observed near minimum light. The three programme stars exhibit a range in C/O and a progression of spectral features as a function of C/O. Two striking sets of triple-headed bands have been discovered in the *J*-band spectrum of the S-type Mira R And. The bandheads, which are degraded to longer wavelengths are at 7877, 7957, 8030 cm⁻¹ and 8379, 8459, 8530 cm⁻¹. The former triplet, which is the stronger of the two, is also present in the mild S star χ Cyg, but not in the M star R Cas. Additional heads are found in R And at 7477 cm⁻¹, near the short-wavelength edge of the atmospheric window, and at 8968, 9031, 9063 cm⁻¹. The bands are identified as the Δ*v* = -1, 0, 1 and 2 sequences of a predicted (³Π–³Δ) transition of ZrS. Additional conspicuous features in the spectra of χ Cyg and R Cas are identified with VO, TiO and H₂O bands. An earlier proposal that ZrS may be responsible for the majority of the Keenan–Wing bands in the near-infrared (0.7–1.1 μm) is favourably supported by recent laboratory and theoretical work, and the most prominent of these bands can now be identified with singlet and triplet transitions of ZrS. The bands provide a rare opportunity to measure sulphur abundances in the photospheres of late-type stars.

1 Introduction

Few spectra of the coolest late-type stars have been taken in the 1.1–1.4-μm atmospheric window (the ‘*J*-band’ of wideband photometry). This is probably due to the required change of detector between observations at wavelengths longward and shortward of 1.1 μm. The ‘optical’ detectors such as CCDs, Reticons, photomultipliers or photographic plates which are used shortward of 1.1 μm do not reach the *J*-band, while the ‘infrared’ detectors (such as InSb,

*Operated by the Association of Universities for Research in Astronomy Inc., under contract with the National Science Foundation.

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PbS or HgCdTe photovoltaic cells) which give access to the *J*-band are also capable of reaching much farther into the infrared. Considerable work has been done on spectra of cool stars at wavelengths shorter than $1.1\ \mu\text{m}$ and longer than $2.0\ \mu\text{m}$, while the *J*-band has been ignored. Observations in the *J*-band have also been discouraged by the fact that most late-type stars show only bands of well-known molecules such as CN and TiO in that region. There is, however, ample evidence to indicate that the *J*-band may be a rich hunting ground for new molecular bands in stars of sufficiently low effective temperature.

Of the cool stars, the stars of type S have the most interesting spectra in the previously studied $0.7\text{--}1.1\text{-}\mu\text{m}$ region just to the blue of the *J*-band. Spectra of S stars show a large number of molecular absorption bands which are either not seen, or only weakly seen, in cool stars of other spectral types. Most prominent among the bands enhanced in the S stars are the oxides of heavy metals such as ZrO, CeO and LaO. Bands of metallic hydrides (e.g. CaH, FeH) also are strengthened in spectra of S stars. Many bands in the near-infrared ($0.7\text{--}1.1\ \mu\text{m}$) spectra of S stars have resisted identification and are commonly referred to as the Keenan–Wing (K–W) bands after Keenan (1950) who discovered the red-degraded bands at 8464, 8610 and 8820 Å, and Wing (1972) who found additional unidentified bands at 9235, 9730, 9900, 10300 and 10520 Å. The 9900 Å band was later attributed to FeH (Nordh, Lindgren & Wing 1977). Most of the K–W bands have been observed only near minimum light in cool Mira-type variables, and only in stars showing strong S characteristics.

In this paper we report on medium- to high-resolution spectroscopy of three cool Mira variables in the $1.0\text{--}1.4\text{-}\mu\text{m}$ region. The stars selected for observation – the M star R Cas, the mild S star χ Cyg, and the strong S star R And – are all relatively cool Miras with periods near 410 d. All were observed near minimum light, and all three spectra show obvious molecular absorption bands, a number of which are both very strong and previously unreported. While the dependence of band strength on the C/O ratio is clear, it is important to note that R And is not a ‘pure’ S star; that is, the TiO and VO bands that are seen in normal M stars are present in R And in addition to, but weaker than the ZrO and LaO bands that characterize type S.

Potential carriers of the K–W bands were reviewed by Lambert & Clegg (1980, hereafter LC) who suggested that sulphides of the heavy metals – and, in particular, ZrS – were viable candidates. In the absence of laboratory spectra of ZrS, LC’s suggestion could not be confirmed directly. Supporting evidence included a detection of YS in a spectrum of R And. Recent laboratory work by Winkel (1987), however, provides strong evidence that several of the K–W bands are due to ZrS. Here we review the case for ZrS in light of the strong bands discovered in the *J*-band spectra as well as the laboratory work of Winkel and recent *ab initio* studies of ZrS by Langhoff & Bauschlicher (1988). The identification of ZrS bands in the spectra of S stars provides an opportunity to determine sulphur abundances (and possibly isotopic abundance ratios) in these stars and may give an additional clue to the nuclear processes responsible for their abnormal compositions.

2 Observations

2.1 FTS SPECTRA

The three programme stars were observed with the Fourier transform spectrometer (Hall *et al.* 1978) on the Kitt Peak 4-m reflector. Details of the observations are given in Table 1. All three stars are large-amplitude Miras with wide reported ranges in spectral type and asymmetric light curves with the time of visual minimum light occurring near phase 0.60. The spectra were taken within about 0.1 period of the light minima, when the spectral types were presumably at or near their latest. The R And spectrum and the associated reference spectrum were observed

Table 1. Spectroscopic observations.

Star	Spectral Type Range	Date	Phase	Peak S/N ^a	Resolution (cm ⁻¹)
R And	S3,5e-S7,5e	1986 Nov 14	0.71	153	1.85
χ Cyg	S7,1e-S10,1e	1986 Feb 17	0.54	127 184	0.14 1.85
R Cas	M6e-M10e	1986 Mar 20	0.73	86 145	0.14 1.85

^aApodized, function I2 of Norton & Beer (1976).

at an apodized (function I2, Norton & Beer 1976) resolution of 1.9 cm^{-1} . The other two stars and their reference stars were observed at high resolution as part of a monitoring project for a separate programme. These two spectra were apodized to the resolution of the R And spectrum as well as being used at high resolution.

Spectra were obtained of the *J*-band ($1.1\text{--}1.4 \mu\text{m}$) and then of the combined *K*- and *H*-bands ($1.5\text{--}2.5 \mu\text{m}$) in separate integrations. The *K*- and *H*-band spectra show no obvious surprises; the CO $\Delta\nu = 2$ and $\Delta\nu = 3$ bandheads in all three stars and the H₂O bands in the M10 star R Cas are the dominant features. The *K*- and *H*-band spectra will not be discussed further

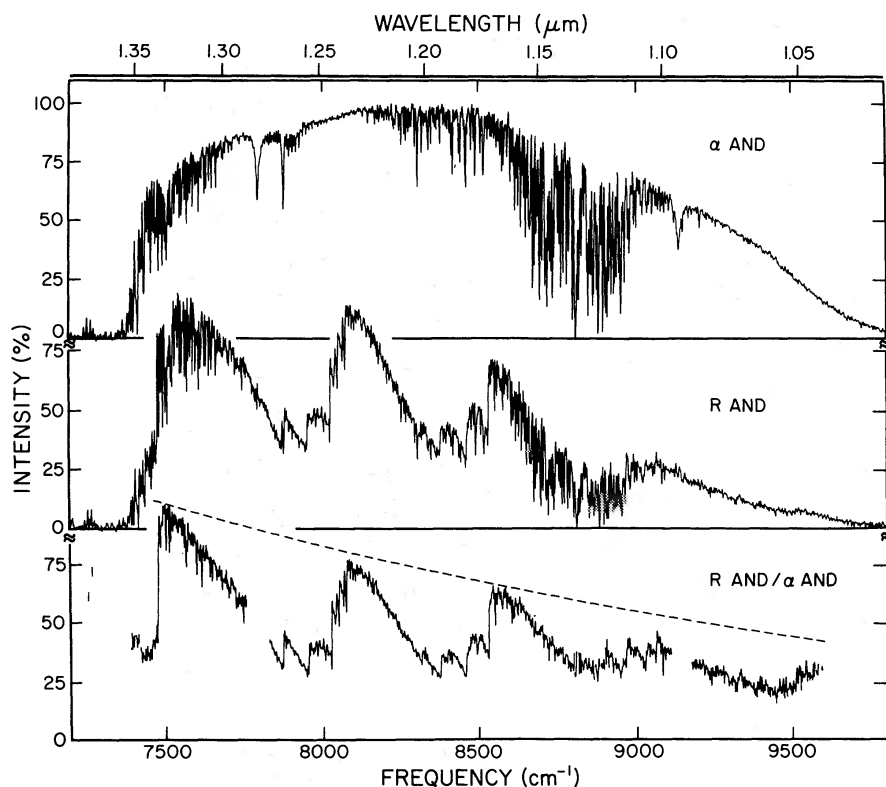


Figure 1. *J*-band spectrum of R And. The top panel shows the observed spectrum of α And (B8Ivp), the main feature of which is telluric lines. The middle panel is the spectrum of R And, observed at the same airmass. The bottom panel shows the R And spectrum divided by the spectrum of α And. A correction has been made to remove the 10 000 K effective temperature of α And. Gaps occur in the ratioed R And spectrum where the signal in the reference spectrum becomes weak or where strong hydrogen lines occur in α And. Note that the stellar hands are more clearly defined in the ratioed spectrum (bottom panel). The 'continuum' shown in the bottom panel is a 1850 K blackbody.

in this paper. By contrast, the *J*-band spectra of all three stars contain several sets of strong absorption bands, all degraded to longer wavelengths, and most having well-defined bandheads.

The *J*-band spectrum of R And on the instrumental system of the spectrograph and filter is shown in the central panel of Fig. 1. Above it is the spectrum of the early-type star α And, observed on the same night at the same air mass. Except for two broad hydrogen lines ($P\beta$ and $P\gamma$), all lines in the spectrum of α And are telluric, most of them due to water vapour. By dividing the spectrum of R And by that of α And, the telluric lines are effectively removed and the spectral features of R And are seen more clearly (lower panel). In addition to the two strong sets of bands near 8000 and 8500 cm^{-1} that are easily seen in the raw spectrum, a strong bandhead near 7500 cm^{-1} appears in the corrected spectrum as well as two broad regions of absorption toward higher frequencies. None of these bands had previously been reported in any stellar spectrum, and as we pointed out in a preliminary announcement (Wing & Hinkle 1987), they do not appear in S stars at warmer phases.

In Fig. 2 the corrected spectrum of R And (top) is compared to similarly corrected spectra of χ Cyg (centre) and R Cas (bottom). In each case the slope of the ratioed spectrum has been removed by dividing by an appropriate blackbody function. It is immediately evident that some of the new bands in R And are also present, but weaker, in χ Cyg, and also that χ Cyg and especially R Cas have strong bands that are not present in R And.

Table 2 summarizes the molecular bandheads found in the spectra of the three programme stars. The majority of the bands longward of roughly 9000 cm^{-1} (1.1 μm) are reported here for the first time. Of the programme stars, the S-type variable R And has the most striking spectrum. Two very strong bands, each consisting of triple bandheads, are obvious near 7950

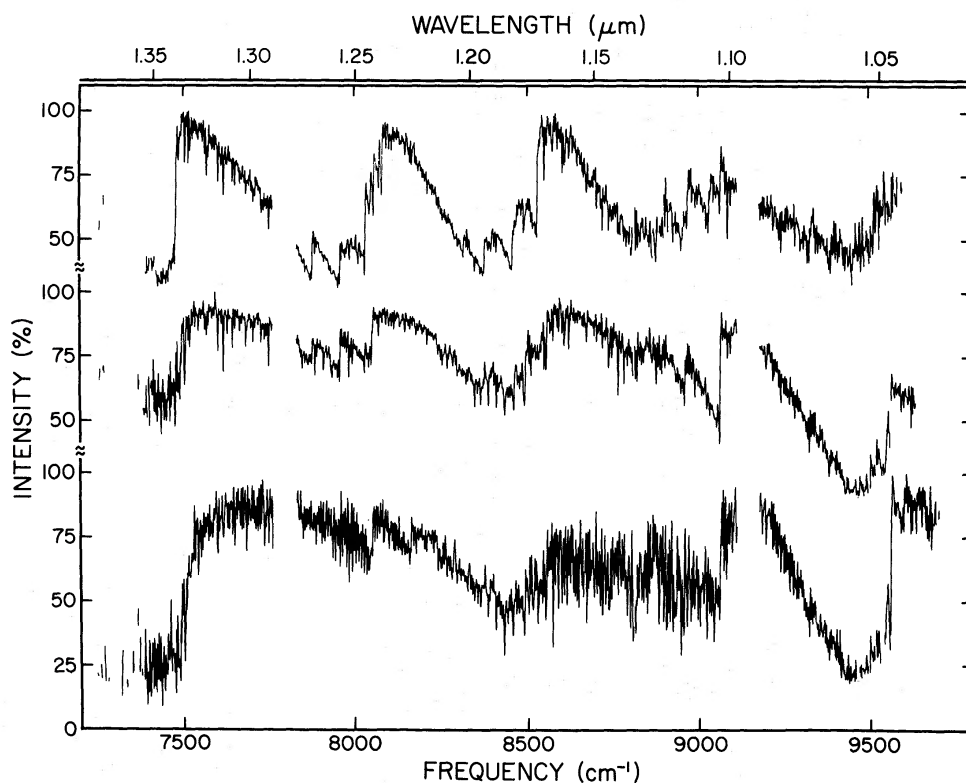


Figure 2. *J*-band spectra of R And (top), χ Cyg (middle) and R Cas (bottom). Each spectrum has had the telluric lines removed by ratioing to a hot star and has been normalized to a best fitting blackbody. The blackbody temperatures are 1850, 2000 and 2100 K, respectively.

Table 2. *J*-band molecular features.

Band Head ^a (cm ⁻¹)	Star	Comment ^b	Identification
7400*	χ Cyg, R Cas	Very strong in R Cas	H ₂ O
7478	R And		ZrS
7877	R And, χ Cyg	Weak in χ Cyg	ZrS
7957	R And, χ Cyg		ZrS
8030	R And, χ Cyg		ZrS
8050	χ Cyg, R Cas		TiO ϕ (0-1)
8081	R And	A series of four relatively sharp features at 8044, 8056, 8069, 8081 cm ⁻¹	ZrS
8163	R Cas		?
8320	R And	Weak	ZrS
8379	R And		ZrS
8400*	χ Cyg, R Cas	About 300 cm ⁻¹ full width	VO A-X $\Delta v=-1$
8459	R And		ZrS
8530	R And		ZrS
8850*	R And	About 400 cm ⁻¹ full width, possible weak heads at 8968, 9031, 9063 cm ⁻¹	ZrS + ?
8962	χ Cyg		TiO ϕ (1-1)
9062	χ Cyg, R Cas		TiO ϕ (0-0)
9450*	R And, χ Cyg, R Cas	Strengthens with decreasing C/O; in χ Cyg and R Cas a bandhead appears at 9556 but band continues to deepen to 9450 cm ⁻¹ .	VO A-X $\Delta v=0$ ZrS and/or ZrO in R And?

^aFeatures marked with * do not have conspicuous bandheads. The wavenumber applies to the approximate central frequency.

^bAll features with sharp bandheads degrade to longer wavelengths.

and 8400 cm⁻¹ (1.26 and 1.19 μ m). A strong bandhead exists near the long-wavelength limit of the *J*-filter bandpass at 7477 cm⁻¹ and may be a third member of this system. Careful examination reveals what may be a fourth triple bandhead near 9000 cm⁻¹. The strongest triplet near 7950 cm⁻¹ is present weakly in χ Cyg. In R Cas, and to a lesser extent χ Cyg, many stellar H₂O lines cross the *J*-band window and provide some of the many sharp features. R Cas has been previously noted to have strong stellar H₂O features in the 1.5–2.5- μ m region (Hinkle, Scharlach & Hall 1984). In both χ Cyg and R Cas, a strong band is present at 9450 cm⁻¹ with a head at about 9556 cm⁻¹ (1.05 μ m); this is the well-known VO band often used for spectral classification. Other sharp bandheads are obvious at 8050 and 9062 cm⁻¹ and, in χ Cyg only, at 8962 cm⁻¹. The spectra of χ Cyg and R Cas show a roughly 400 cm⁻¹ depression at 8400 cm⁻¹ which does not have an obvious bandhead. R Cas has one bandhead at 8163 cm⁻¹ not shared by χ Cyg.

2.2 LOW-RESOLUTION SCANS

Nine days after the discovery of the strong bands in R And, the region of the 1.25- μ m band was scanned in R And and a variety of other stars with a cooled grating spectrometer on the

Kitt Peak 1.3-m telescope on 1986 November 23. The interval 1.220–1.282 μm (7800–8200 cm^{-1}) was scanned at a resolution $\lambda/\Delta\lambda = 470$. The 1.245-, 1.257- and 1.270- μm (8030, 7957 and 7877 cm^{-1}) bandheads were clearly present in R And, but not in the three other S stars observed at warmer phases (χ Cyg, R Cyg and T Cam). A weak band was seen in χ Cyg near 1.244 μm , but the accompanying heads at 1.257, and 1.270 μm are apparently absent whereas in R And the absorption is stronger at these heads. The 1.244- μm band, which also is present in the late-M Mira variable R Cas, is identified below as due to the 0–1 band of the TiO ϕ system. V Cyg, a cool carbon star observed near minimum light, has a featureless spectrum at the resolution of this spectrometer.

2.3 RETICON SPECTRA

Selected intervals across the near-infrared spectrum of R And were recorded at the McDonald Observatory with the 2.7-m reflector and its Reticon-equipped coude spectrometer. An individual exposure covers 400 Å at a resolution of 0.6 Å. The hot star α And was observed either just before or after R And. In the ratio R And/ α And, the telluric lines are removed. Spectra centred at wavelengths 8300 and 8700 Å were obtained on 1987 February 2, at 9300 Å on 1986 December 13, and at 9720 and 10140 Å on December 15. Since minimum brightness occurred early in 1986 October followed by a maximum in 1987 March, the bandheads recorded on the McDonald spectra are not necessarily representative of those present at minimum brightness. In the 8300 Å region, a pair of strong double-headed bandheads is the most striking feature. The shorter wavelength heads may be identified with the Keenan bands at 8274 and 8283 Å (see fig. 1 of LC who show the spectrum of the pure S star R Cyg). The other strong doublet at 8433 and 8442 Å was *not* seen in R Cyg. On the other hand, the strong bands in R Cyg at 8476 and 8481 Å and the weaker LaO head at 8454 Å are present in R And as unremarkable undulations of the spectrum that is dominated by the 8433–8442 Å bands. LC had earlier noted that the 8476–8481 Å heads were not detectable in R And. Keenan bands seen by LC in R Cyg at 8610, 8821 and 8843 Å are not prominent in R And, although broad and shallow bandheads are present at 8610 and 8628 Å. The second head had been suspected in R And and two other stars by LC. Since the band profiles are very smooth with no hint of rotational structure, we suspect that the carrier of these bands is a heavy molecule. In stars less C-rich than R And (e.g. R Cas), the VO B–X 0–1 and 1–2 bands may contribute to the absorption near 8600 Å. The 8821 Å band is present weakly in R And, but the companion at 8843 Å is barely discernible. The ZrO b' -a 0–0 bandheads at 9299 and 9316 Å dominate the 9300 Å exposure. One can also identify the corresponding 1–1, 2–2 and 3–3 heads. The Wing 9246 Å band is clearly present in R And, and an apparently weaker head occurs at 9214.5 Å. Between 9200 and 9290 Å, there are several weak features that may be blended atomic lines or distorted molecular bandheads. This confusing appearance extends across the 9720 Å exposure. The Wing 9736 Å band is present as a weak depression. Two or three other possible heads may be present. The character of the spectrum changes longward of 9896 Å where FeH contributes lines that are about 20 per cent deep at our resolution. In R And, the Wing band at 10135 Å appears as one of a triplet or quartet of similar bands at 10069, 10135, 10207 and (possibly) 10280 Å. Evidence for TiO is readily found, e.g. the heads at 8205 (γ system 0–1), 8433, 8442 and 8452 Å (ϵ system 0–0), and 8859 and 8868 Å (δ system 0–0). Emission lines of Ca II, Ti I and Zr I are scattered across the 8300 and 8700 Å exposures. The weaker Zr I lines appear with inverse P Cyg profiles with the emission at about -30 km s^{-1} relative to the absorption lines.

3 Discussion

The newly discovered triple-headed bands in the region of the *J*-filter are discussed in the context of the K-W bands and recent developments in the laboratory and theoretical spectroscopy of FeH, TiO, VO, ZrO and ZrS. Table 2 lists the new bands and other features in the bandpass of the *J*-filter. The following discussion covers the new bands as well as those listed by LC in the wavelength region spanned by the Keenan and Wing bands.

3.1 BANDS OF PREVIOUSLY IDENTIFIED MOLECULES

3.1.1 CO

The $\Delta v = 4$ vibration-rotation bands of CO occur in the *J*-filter bandpass. In R And and χ Cyg the CO $\Delta v = 3$ bands, which occur in the *H*-filter bandpass, are strong (Hinkle *et al.* 1984). However, a search of the spectra of the three S stars for the 4-0, 5-1, 6-2 and 7-3 band heads, at 8464.9, 8358.4, 8252.3 and 8146.4 cm^{-1} respectively, and for individual CO lines in these bands was unsuccessful. The 7-3 band head is in a clean region of the spectra and is definitely not present. Higher-order band heads which fall at smaller wavenumbers were not searched for because of strong stellar TiO and ZrS bands. The most favourable phase for detecting CO in Mira variables is about 0.20 (see, for example, fig. 7 of Hinkle *et al.* 1984) because the CO column density has reached maximum and the photosphere remains hot enough to minimize blending from other molecular lines. With this in mind, a high-resolution spectrum of χ Cyg taken at phase 0.21 was examined for CO $\Delta v = 4$ lines, and again the lines were not found.

3.1.2 FeH

Iron hydride was identified in stellar spectra by Nordh *et al.* (1977) and Wing, Cohen & Brault (1977). Individual rotational lines of a band near 9896 Å were identified by Clegg & Lambert (1978) with absorption lines in the spectra of K and M dwarfs, M giants, and the S star R Cyg. However, it was only recently that the laboratory spectrum was subjected to a rotational and vibrational analysis. Phillips *et al.* (1987, see also Balfour, Lindgren & O'Connor 1983a,b) give a rotational analysis for seven bands of a $4^4\Delta-4^4\Delta$ system with its 0-0 head at 9896 Å. The lower $4^4\Delta$ state appears to be the ground state of the molecule (Stevens, Feigerle & Lineberger 1983; Stevens Miller, Feigerle & Lineberger 1987; Bauschlicher & Langhoff 1988).

The bandhead of the 1-0 band at 8692 Å is an indistinct feature in both LC's spectrum of R Cyg and ours of R And. The 2-1 band with a head at 9020 Å may well contribute to the weak observed head near 9014 Å (see LC) and continuing absorption to longer wavelengths. Davis & Hammer (1981) note that a strong Zr I line falls near 9014 Å. This atomic line may displace the stellar bandhead to the blue. The 1-1 bandhead at 10253 Å falls in a broad depression to which several transitions may contribute (see remarks on ZrO *b'-a*). Although the 0-1 head at 11939 Å or 8374 cm^{-1} is nearly coincident with one of the new stellar bands, FeH is unlikely to be the major contributor. Similarly, the 1-2 head at 12389 Å or 8069 cm^{-1} is unlikely to be more than a minor contributor to the *J*-band spectra of these three cool stars.

FeH is expected to have several low-lying states, and hence, other transitions are quite likely to be present in infrared spectra of S stars. However, any FeH bands would be expected to have an open rotational structure and to appear as broad, weak features that are resolvable into lines at high resolution. It is most improbable that FeH is the carrier of the strong new bands in the *J*-band.

3.1.3 TiO

R Cyg, the star whose near-infrared spectrum was discussed by LC, is known as pure S star; i.e. bands of TiO do not appear in its spectrum at any phase. Spectra of the S stars R And and χ Cyg, on the other hand, are known to contain TiO bands. Indeed, our McDonald spectra of R And show the TiO δ -system 0-0 heads at 8859 and 8868 Å as well as evidence of the γ -system 0-1 head at 8205 Å and the ϵ -system (Linton & Broida 1977) heads at 8433, 8442 and 8452 Å. However, since the 8433 and 8442 Å heads were observed to be much stronger than the 8452 Å head, TiO is probably not the dominant contributor to the former two bandheads in R And at the observed phase. LC did not find this pair in the pure S star R Cyg.

In the *J*-band spectrum of χ Cyg, there is a band with a prominent sharp head at 9062 cm⁻¹. The band is present in the spectrum of R Cas. In the high-resolution spectrum of χ Cyg, the band's rotational structure is well resolved. This is the TiO ϕ -system's 0-0 band observed in the laboratory by Pettersson & Lindgren (1962) and Galehouse, Brault & Davis (1980). Early observations of this band in stellar spectra are cited by Spinrad & Wing (1969). The 1-1 bandhead at 8962 cm⁻¹, to our knowledge not previously reported in stellar spectra, is clearly visible in the spectrum of χ Cyg. The 0-0 head may be weakly present in the spectrum of R And.

The strength of the $\phi(0-0)$ band in χ Cyg encouraged us to search for the 0-1 band; the 1-0 band falls outside the interval covered by the *J*-band filter. A stellar bandhead at 8049 cm⁻¹ and its accompanying resolved lines seen at high resolution is readily identified as the 0-1 band previously seen in laboratory spectra (Galehouse *et al.* 1980). On the high-resolution spectrum the 1-2 head near 7957 cm⁻¹ is also visible. This feature is probably also present in the low-resolution spectrum of R Cas (Fig. 2), although the low-resolution spectrum of χ Cyg shows that the region is crossed by other bands which we suppose are the ZrS bands so prominent in the spectrum of R And.

3.1.4 VO

The prominent absorption in R Cas and χ Cyg centred at about 9450 cm⁻¹ or 10580 Å is primarily due to the VO $A^4\Pi-X^4\Sigma^-$ 0-0 band. This feature is extremely sensitive to temperature in late M stars and, on the photometric classification systems of Wing (1971) and Lockwood (1972), serves as the principal temperature criterion in the interval M6-110 (Wing & Lockwood 1973). Photographic spectra showing the vibrational structure of the band in a sequence of M stars were published by Spinrad & Wing (1969), who also gave bandhead wavelengths. According to the rotational analyses reported by Cheung, Taylor & Merer (1982), the shortest wavelength head of the 0-0 band is the satellite $^5R_{43}$ head at 9558 cm⁻¹ (or 10460 Å) which is described as 'intense' in the laboratory emission spectrum. This head we identify with the sharp head seen in R Cas at 9556 cm⁻¹. The R_4 , R_3 , R_2 and R_1 heads run from about 9525 to 9481 cm⁻¹ so that this VO $\Delta v = 0$ sequence accounts in a qualitative sense for the broad absorption around 9450 cm⁻¹ in R Cas and χ Cyg. In the spectrum of R And, VO A-X is probably the leading contributor to the absorption in this region, although the heads are less distinct and appear to be interfered with by another absorber.

Since the A-X 0-0 band is so strong in R Cas and χ Cyg, we would expect the 0-1 band to be present. Cheung *et al.* (1982) report its $^5R_{43}$ head to be at 8558 cm⁻¹ with the R_4 to R_1 heads from about 8525 to 8481 cm⁻¹. These VO transitions are surely the dominant contributor to the broad absorption assigned to 8400 cm⁻¹ in Table 2. In the high-resolution spectrum of χ Cyg, several individual VO bandheads are visible. The VO bands appear more clearly in χ Cyg because the stronger VO bands in R Cas are merged with the H₂O bands on the shorter wavelength side. The 0-2 bands starting at the $^5R_{43}$ head near 7550 cm⁻¹ may

contribute to the deep absorption seen in the spectrum of R Cas and less strongly in χ Cyg. However, inspection of the relative depths of the 7400, 8400 and 9450 cm^{-1} depressions clearly shows that VO is not the leading contributor at 7400 cm^{-1} . In R Cas and χ Cyg, H_2O is probably the primary molecule.

In laboratory spectra, Merer *et al.* (1987) have identified additional quartet and doublet transitions within the *J*-filter bandpass. These include the 0–0 band of the $D^4\Delta$ – $A^4\Pi$ system near 9600 cm^{-1} , a $^2\Delta$ – $^2\Phi$ band also near 9600 cm^{-1} , and a complex group of $^2\Pi$ – $^2\Delta$ transitions between 7000 and 8000 cm^{-1} . With lower state excitation energies of a least 1 eV, these transitions seem unlikely to contribute significantly to the stellar spectra; the excitation energy of the $^2\Phi$ state has not been determined experimentally.

3.1.5 CN

The CN molecule's red ($A^2\Pi$ – $X^2\Sigma^+$) system has its 0–0 band in the tail of the strong VO bands. In our spectra taken near minimum light, the CN bands are weak or absent. In particular, the R_2 and R_1 heads at 9150 and 9119 cm^{-1} , respectively (Davis & Phillips 1963) are not seen. Bands of the red system are, however, seen in S stars near maximum light (e.g. Spinrad & Wing 1969, fig. 4). Wing (1972) has presented evidence that the 0–0 band is still present at minimum light in the pure S stars R Cyg and W Aql, but that it disappears at advanced phases in R And.

3.1.6 ZrO

When LC considered possible identifications for the K–W bands, they noted that laboratory exploration of the near-infrared spectrum of ZrO was far from complete, and hence, that this abundant molecule might yet account for some of the bands.

Thanks to the analysis of a laboratory spectrum by Phillips, Davis & Galehouse (1979), strong stellar bandheads at 9299.3 Å and 9316.2 Å may be identified with the 0–0 band of the ZrO molecule's $b'^3\Pi$ – $a^3\Delta$ system. The 0–0 heads dominate the 9300 Å McDonald exposure of R And. Although present only as minor ripples superimposed on the deep absorption from the 0–0 band, one can identify the 1–1, 2–2 and 3–3 heads. (In the laboratory spectra, another system appears to be intermingled with this 0–0 band; Phillips *et al.* remark that heads at 9318, 9342 and 9356 Å probably belong to a second system.) With estimated Franck–Condon factors $q_{01}/q_{00}=0.03$ (LC), the 0–1 bandheads may be expected in spectra of S stars. Predicted wavelengths (see LC) based on the known vibrational constants for the $a^3\Delta$ state put the heads between 10168 (R_3 head) and 10183 Å (R_1 head) with the origins of the Q branches about 40 Å to the red. Although the heads are not prominent, LC's spectrum of R Cyg shows a broad depression that is attributable to this $\Delta v = -1$ sequence. The 1–0 band was estimated by LC to be near 8600–8620 Å; vibrational constants for the $b'^3\Pi$ state have not yet been determined spectroscopically. Davis & Hammer (1981) propose a *tentative* identification with heads at 8599 ($R_3?$) and 8601 Å ($R_1?$) seen in laboratory spectra. As LC noted, the $\Delta v = +1$ sequence can be accommodated in this vicinity and yet not be the major contributor to the Keenan band near 8610 Å.

A singlet system ($B^1\Pi$ – $A^1\Delta$) from the first excited singlet state appears to contribute to LC's spectrum of the pure S star R Cyg. Hammer & Davis (1981) provide an analysis of the $B^1\Pi$ – $A^1\Delta$ system with the R branch head of its strongest band ($v' - v'' \equiv 0-0$) at 10515 Å. This band contributes to the Wing band at 10520 Å in R Cyg; LC's high-resolution spectrum shows it to consist of two heads at 10515 Å (the R branch head) and 10529 Å (the developing Q branch from a band origin at 10528 Å). A broad and weakening depression extends to

longer wavelengths from the 10 515 Å head. This is the $\Delta v = 0$ sequence and the 1–1 R head at 10 607 Å is identifiable in the spectrum of R Cyg. These positive identifications provided first by Davis & Hammer (1981) confirm LC's more probable choice for this ZrO 0–0 band. In all three stars considered here, bands of the oxides such as TiO and VO are stronger than in the pure (i.e. TiO bands are undetectable at all phases) S star R Cyg observed by LC. The ZrO $B-A$ $\Delta v = 0$ sequence extending to longer wavelengths from the 10 515 Å 0–0 head may be a contributor to the broad absorption feature in the spectrum of R And near 10 700 Å (Fig. 2) but, in the spectrum of χ Cyg and certainly of R Cas, the VO $A-X$ $\Delta v = 0$ bands (see above) provide the principal absorption in this region. In the S stars, ZrS and not ZrO may be the leading contributor to this broad absorption. In particular, the $\Delta v = 3$ $b^3\Pi - a^3\Delta$ ZrS bands (see below) have predicted bandheads near 10 500, 10 580 and 10 670 Å. A significant contribution from a molecule other than ZrO is suggested by Wing's (1972) report that the behaviour of the 10 520 Å band across a sample of S stars is like that of the 8820 Å and 9235 Å bands (both now attributed to ZrS – see below) but unlike that of the ZrO bands.

Davis & Hammer (1981) attributed the stellar bands at 8274.0 and 8282.8 Å to the R and Q heads of a new ZrO system. A preliminary analysis yielded a rotational constant within the expected range for ZrO. The table summarizing the laboratory work refers to 'isotopic branches' for this double-headed band. Identification of such branches is not discussed further by Davis & Hammer, but we presume that these branches are further evidence for the identification of ZrO as the carrier.

Finally, Davis & Hammer (1981) presented observations of several additional near-infrared bands which coincide with the stellar K–W bands and which they attributed to unclassified bands of ZrO. These bands have been shown by Stringat (1980, personal communication) and Winkel (1987) to be due to ZrS and are discussed in the following section.

3.1.7 H_2O

Previous low-resolution spectroscopy of M giants in the 1.2–2.5- μ m region demonstrated that water is a significant contributor to the spectrum (Johnson *et al.* 1968). The 1.05–1.35- μ m region contains a number of water bands, 14 having been identified in laboratory spectra (Flaud *et al.* 1979; Mandin *et al.* 1986). Four bands are the most intense: $2\nu_2 + \nu_3$, $2\nu_1$ and $\nu_1 + \nu_3$ with band origins spanning 6800–7200 cm^{-1} and $\nu_1 + \nu_2 + \nu_3$ with band origin at 8810 cm^{-1} [Mandin *et al.* 1986; Benedict 1948, 1955 (see Mohler 1955)]. Of these four bands, $\nu_1 + \nu_3$ has an integrated band strength many times that of the others. This can be noted in Fig. 2 where the stellar 7200 cm^{-1} H_2O band in R Cas is nearly opaque while the 8800 cm^{-1} band is considerably weaker.

High-resolution spectroscopy of an oxygen rich Mira (Hinkle & Barnes 1979) has shown that the water excitation temperature is in the 1000–2000 K range. Assuming that the current spectra have similar excitation temperatures, much higher rotational levels are excited than in the telluric spectrum or in laboratory spectra taken at ambient temperature. Hinkle & Barnes observed strong lines in the 1.8 μ m $\nu_2 + \nu_3$ band with $J'' > 20$, this implies that $\nu_1 + \nu_3$ contributes to the current spectra at wavenumbers larger than 8000 cm^{-1} and that high excitation lines from the four strongest bands mentioned above could be expected scattered throughout the 1.1–1.35- μ m region. Since water is an asymmetric top molecule, the spectrum is both rich and complex with an apparent lack of structure; the identification of water lines away from the band origins is difficult and requires high-resolution spectra. In addition to the high rotational levels, hot bands (transitions between vibrationally excited levels) should also be present. Laboratory studies utilizing flame rather than the ambient-temperature sources currently employed will be needed for future high-resolution work in the 1.1–1.4- μ m region on oxygen rich stars so that high J -lines and hot bands may be utilized.

3.2 IDENTIFICATION OF ZrS

LC's proposal that ZrS may account for some of the K-W bands was, for lack of direct laboratory identifications of ZrS electron transitions, based on several pieces of indirect evidence: (i) ZrS and other heavy element sulphides are predicted to be abundant in the atmosphere of an S star; (ii) several of the potential sulphides are known or expected to have strong electronic transitions in the near-infrared; (iii) a detection of YS was provided for R And near minimum light; and (iv) the gross structure of the K-W bands is compatible with the sulphide proposal (differences between bands lead to vibrational energy differences $\Delta G_v \sim 400\text{--}500\text{ cm}^{-1}$, and the lack of rotational structure supports the small rotational constants, $B_v \sim 0.2\text{ cm}^{-1}$, expected of a sulphide).

Although laboratory spectroscopy of ZrS has not yet resulted in the classification of a single band, evidence in support of LC's proposal now exists. Stringat (1980, private communication) obtained photographic spectra using a hollow cathode containing ZrS₂. Most of the K-W bands not due to ZrO from 6400 to 9500 Å (or FeH) were recorded with an intensity uncorrelated with the intensities of known ZrO bands in the same region; a trace of oxygen in the hollow cathode lamp led to strong ZrO bands. Winkel (1987) recorded the emission spectrum of ZrS in the range 5300–10 000 Å using the National Solar Observatory's Fourier transform spectrometer. The source was a carbon tube furnace containing ZrS₂ and solid zirconium. These spectra confirm that ZrS is the carrier of K-W bands. Preliminary rotational analysis of one band was reported by Winkel.

Table 3. Spectroscopic constants of low-lying states of ZrS and ZrO.

State	ZrO				ZrS			
	$T_e(\text{cm}^{-1})$		$\omega_e(\text{cm}^{-1})$		$T_e(\text{cm}^{-1})$		$\omega_e(\text{cm}^{-1})$	
	Pred.	Obs. ^a	Pred.	Obs.	Pred.	Obs. ^a	Pred.	Obs.
d ³ Φ	16685	17170	780	856.7	11710	A+11730 ^b	436	---
B ¹ Π	17297	15443	845	859.4	11076	10866 ^b	491	489 ^b
c ³ Σ ⁻	13183	---	888	---	---	---	---	---
b ³ Π	11052	12072	910	---	7890	A+8008 ^c	517	506 ^c
A ¹ Δ	5360	5904	943	942.3	5520	---	516	---
a ³ Δ	1157	1387	929	938.1	209	A	522	557 ^c
X ¹ Σ	0	0	970	976.5	0	0	560	548.4 ^d

^aFor the triplet states, T_e is given for the state with $\Omega = \Lambda$ (i.e. ³Π₁, ³Δ₂ or ³Φ₃) which is not displaced by a normal spin-orbit interaction. Langhoff & Bauschlicher (1988) compare their predicted T_e 's with a weighted average of the observed T_e 's of the three fine structure levels where the weights were $2\Omega + 1$. Such a weighting scheme is appropriate for LS-coupled atomic terms, but not for simple molecular terms where the spin-orbit interaction results in equidistant fine-structure levels. These two different ways of defining T_e for a triplet state give values differing by less than 150 cm^{-1} . The observed values of T_e and ω_e for ZrO are taken from Davis & Hammer (1988) and references cited by them.

^bThe observed values are based on the *tentative* identifications of stellar K-W bands – see text.

^cFrom identifications of the new bands in the R And spectrum as the $\Delta v = -1, 0, +1$ and $+2$ sequences of the b - a system (see text).

^dFrom laboratory spectroscopy of the $E^1\Sigma - X^1\Sigma$ system (Simard, Mitchell & Hackett 1988).

Additional and important evidence on the electronic transitions of ZrS is provided by *ab initio* predictions of the low-lying electronic states of ZrS (Langhoff & Bauschlicher 1988). Results of these calculations are shown in Table 3 together with a comparison between the observations and the *ab initio* predictions for ZrO. It is a fair assumption that ZrO is a realistic test case of the predictions for ZrS. For ZrO, the differences $T_e(\text{pred}) - T_e(\text{obs})$ range from 1854 cm^{-1} ($B^1\Pi$) to -1020 cm^{-1} ($b^3\Pi$) for a mean $|T_e(\text{pred}) - T_e(\text{obs})| = 827 \text{ cm}^{-1}$, and the predicted ω_e are, with the sole exception of the $d^3\Phi$ state, remarkably close to the observed values.

In light of these comparisons for ZrO, we may suppose that the strong new bands in the J-band spectrum of R And belong to the $b^3\Pi - a^3\Delta$ system of ZrS. Our preferred assignment of the bandheads is as follows:

$v-v'$	$\sigma_{v'v''} (\text{cm}^{-1})$		
0-1	—	—	7477
0-0	7877	7957	8030
1-0	8379	8459	8530

These assignments correspond to $T_{00} \approx 7957 \text{ cm}^{-1}$, $T_e(^3\Pi) - T_e(^3\Delta) \approx 8008 \text{ cm}^{-1}$ (see footnote a to Table 3), $\Delta G''_{1/2} = 553 \text{ cm}^{-1}$, $\Delta G'_{1/2} = 502 \text{ cm}^{-1}$, $\omega'_e = 506 \text{ cm}^{-1}$ and $\omega''_e = 557 \text{ cm}^{-1}$ on the assumption that $\omega_e x'_e \approx \omega_e x''_e \approx 2 \text{ cm}^{-1}$ — see LC who suggested an empirical relation $\omega_e x_e(\text{ZrS})/\omega_e x_e(\text{ZrO}) \approx 0.6$. Small changes in a bandhead's profile introduced by isotopic wavelength shifts between the several varieties of ZrS have been ignored in the computation of the ω'_e s. The ω'_e s derived from the R And spectrum are very close to values expected from LC's empirical recipe: $\omega_e(\text{ZrS})/\omega_e(\text{ZrO}) = 0.58 \pm 0.03$ for excited states or $\omega'_e = 498 \text{ cm}^{-1}$ and $\omega''_e = 543 \text{ cm}^{-1}$. For the $^3\Pi$ state, the derived ω_e is in good agreement with the *ab initio* prediction. The agreement is less satisfactory for the $^3\Delta$ state. The derived excitation energy $T_e(^3\Pi) - T_e(^3\Delta)$ of 8008 cm^{-1} is consistent with the *ab initio* prediction of 7681 cm^{-1} .

Each Δv sequence is expected and observed to be compact: e.g. if the higher order terms are neglected, $\sigma_{v+1,v+1} - \sigma_{v,v} = \omega'_e - \omega''_e = -47 \text{ cm}^{-1}$. With this preferred assignment, the separation of the sub-bands [e.g. $\sigma(R_3) - \sigma(R_2)$ and $\sigma(R_2) - \sigma(R_1)$] is small ($\sim 75 \text{ cm}^{-1}$) and much less than separations between the different Δv sequences. One reason for preferring the above vibrational assignments is that the sub-band separations are similarly small for the corresponding transitions in ZrO (the 9300 Å bands).

It is possible to identify two of the heads of the 2-0 band in the broad 8850 cm^{-1} absorption; i.e. $\Delta G'_{3/2} = 9031 - 8530 = 501 \text{ cm}^{-1}$ and $8968 - 8459 = 509 \text{ cm}^{-1}$ (see Table 2), a value equal within the uncertainties to the expected value $\Delta G'_{3/2} = \Delta G'_{1/2} - 2\omega_e x'_e \approx \Delta G'_{1/2} - 4 \approx 498 \text{ cm}^{-1}$. The third head near 8880 cm^{-1} is badly blended. The predicted 0-2 heads fall in an opaque terrestrial band, and the 0-3 heads, which should be weak or absent, fall near 6360 cm^{-1} among strong CO $\Delta v = 3$ bands. The weak heads shortward of the 0-0 band at $8044, 8056, 8069$ and 8081 cm^{-1} may belong to satellite branches.

Two alternative assignments were briefly considered. Is the 0-0 band at 7477 cm^{-1} instead of $7877-8030 \text{ cm}^{-1}$? Although we exclude this assignment on the grounds that it leads to large (45 cm^{-1}) inequality in the separations 1-0 to 0-0 and 2-0 to 1-0, one must recognize that intruding bands may distort such separations. As a second alternative, we might wish to suppose that the three strong absorptions ($7400, 8000, 8500 \text{ cm}^{-1}$) each represent a sub-band of the 0-0 band. However, this requires that, relative to ZrO, the ZrS $^3\Delta$ and/or $^3\Pi$ levels show very different spin-orbit splittings.

Inspection of Table 3 suggests that strong K-W bands now firmly attributed to ZrS through

the laboratory spectroscopy of Stringat (1980, private communication) and Winkel (1987) are likely to belong to the $B^1\Pi-X^1\Sigma$ and $d^3\Phi-a^3\Delta$ transitions. Before discussing our attempts to assign the most prominent K-W bands to these ZrS transitions, one piece of recent laboratory evidence should be described. Simard, Mitchell & Hackett (1988) observed ZrS by laser-induced fluorescence in a supersonic beam of ZrS molecules. Two band systems were detected in the 4130–7000 Å interval. The R-heads of the 0–0 bands are at $20\,219\text{ cm}^{-1}$ (4944 Å) and $20\,208\text{ cm}^{-1}$ (4947 Å). The former is tentatively identified as the $E^1\Sigma^+-X^1\Sigma^+$ transition. The identification of the latter has yet to be determined. If, as seems probable, the lower state of these band systems is indeed the molecule's ground state, these new observations provide vibrational constants that K-W bands originating from this state must satisfy: $\omega_e = 548.4\text{ cm}^{-1}$, $\omega_e x_e = 1.67\text{ cm}^{-1}$ or $\Delta G_{1/2}(X^1\Sigma^+) = 545.2\text{ cm}^{-1}$. Furthermore, we assume that the separations due to the fine structure splittings of the $^3\Phi$ and $^3\Delta$ terms are likely to be comparable to those seen in the corresponding (γ -system) transitions of ZrO (about 300 cm^{-1}). Langhoff & Bauschlicher (1988) estimate that the Franck-Condon factors are $q_{00} \approx 0.7$ and $q_{01} \approx 0.3$ and, hence, both the 0–1 and 1–0 bands are likely to be detectable in spectra in which the ZrS K-W bands are strong. The fact that the separations between the $\Delta v = 0$ and ± 1 sequences of the triplet and singlet bands may be comparable to the fine structure triplet splittings complicates attempts to classify the K-W bands. [Langhoff & Bauschlicher (1988) did not include the $E^1\Sigma^+$ state among their predictions and, hence, Simard *et al.*'s estimated excitation energy cannot be used as a test of the *ab initio* predictions.]

The five most prominent K-W bands are at 8476/81, 8610, 8821/43, 9246 and 9736 Å. Our *tentative* assignment of these K-W bands to the two ZrS transitions is based on the fact that, if the strong 9246 Å band is a 0–0 band and the weaker 9736 Å band is a 0–1 band, one finds $\Delta G_{1/2}'' = 546\text{ cm}^{-1}$, a value equal to that (545.2 cm^{-1}) obtained for the ZrS ground ($X^1\Sigma$) state by Simard *et al.* (1988). This correspondence suggests that the 9246 and 9736 Å heads may be the 0–0 and 1–0 bands of the $B^1\Pi-X^1\Sigma^+$ transition. The 1–0 $B-X$ band could be a contributor to the double-headed 8821/8843 Å band. Then, one finds $\omega_e(B^1\Pi) \approx 489\text{ cm}^{-1}$ (8843 Å) or 518 cm^{-1} (8821 Å). The former value is in excellent agreement with the *ab initio* predictions (Table 3) for ω_e and T_e for which we find $10\,866\text{ cm}^{-1}$ as compared to $11\,076\text{ cm}^{-1}$ in Table 3. If $\omega_e(B^1\Pi) \approx 489\text{ cm}^{-1}$, the 2–0 $B-X$ band is predicted close to 8476 Å where a strong Keenan band is found. Our *tentative* assignments for the $d^3\Phi-a^3\Delta$ 0–0 heads are 8481, 8610 and 8821 Å. The predicted 0–1 heads (8898, 9040 and 9274 Å) do not correspond to pronounced bandheads in LC's spectrum of R Cyg, but could, perhaps, be accommodated. The predicted locations of the 1–0 heads are 8180, 8260 and 8490 Å when the *ab initio* ω_e for $d^3\Phi$ is adopted. These predictions do not match wavelengths of unidentified stellar bands, but weak bands could be masked by neighbouring absorption bands. The tentative identifications for the 0–0 bands lead to unequal splitting of the sub-bands (177 and 278 cm^{-1}); the equivalent splittings for the ZrO γ -system are 292 and 315 cm^{-1} (Phillips & Davis 1979). The latter anomalous (i.e. unequal) splittings are a result of spin-orbit and spin-spin interactions. If our identifications are correct, these interactions are more severe for the ZrS states. Our identifications give $T_e(d^3\Phi) - T_e(a^3\Delta) \approx 11\,730\text{ cm}^{-1}$, a value consistent with the *ab initio* predictions.

These tentative identifications of K-W bands with specific ZrS transitions were developed from the realization that the pairing of the 9246 and 9736 Å bands provides a separation $\Delta G_{1/2}''$ equal to the laboratory measurement of the (presumed) ground state. The qualification 'tentative' is retained because the separation $\Delta G_{1/2}''$ inferred from the pairing of the 9246 and 9736 Å K-W bands is also equal within the measurement errors to the value 553 cm^{-1} inferred for the $^3\Delta$ state using the new bands in the J -filter bandpass. This equality means that one might wish to identify the 9246 and 9736 Å bands as a 0–0 and its 0–1 band of the

$d^3\Phi$ – $a^3\Delta$ transition. Then, the other 0–0 bands may be the K–W bands at 8476/81 and 8821 (and/or 8843) Å with their 0–1 bands at about 8893 and 9270, respectively, but both fall within deep absorption from 0–0 bands. With the predicted ω_e of the $^3\Phi$ state, the 1–0 bands are expected at 8180, 8490 and 8890 Å. Although the spectrum of R Cyg does not show distinct bandheads at these wavelengths, LC's spectrum could accommodate these heads. With this identification of the 0–0 bands, their separations are larger than in ZrO: $F_3 - F_2 = 455$ cm^{-1} and $F_2 - F_1 = 520$ cm^{-1} for ZrS, but 292 and 315 for ZrO. In this alternative scheme, the 8610 Å Keenan band is taken to be the 0–0 B – X band. At the 0–1 bandhead's predicted wavelength of 9034 Å, there is no distinct head in LC's spectrum of R Cyg, but a weak band could be accommodated. The 1–0 B – X band is predicted to fall near 8264 Å and a weak band may be accommodated between the 8236 Å CeO and 8274 Å (ZrO?) heads.

4 Conclusions

Thanks to recent laboratory and theoretical work on the spectrum of ZrS, strong absorption bands seen in the spectra of S stars near minimum light may be identified with triplet and singlet transitions between low-lying states of ZrS. In particular, strong triple-headed bands discovered here in a J -band spectrum of the S star R And may be attributed to the $\Delta v = -1, 0, +1$ and $+2$ sequences of the $b^3\Pi$ – $a^3\Delta$ transition of ZrS. This transition has not yet been detected in the laboratory. Identification of the stellar bands with the ZrS transition is made on the basis of *ab initio* predictions (Langhoff & Bauschlicher 1988). Several other bands known as the Keenan–Wing bands are attributable to ZrS. These bands are seen in laboratory spectra of ZrS (Stringat 1980; Winkel 1987) and appear to be due to the $B^1\Pi$ – $X^1\Sigma$ and $d^3\Phi$ – $a^3\Delta$ transitions.

The J -band spectrum of R And is dominated by the ZrS $^3\Pi$ – $^3\Delta$ sequences. The spectrum of the less extreme S star χ Cyg is marked by strong bands of VO A – X $\Delta v = 0$ and -1 and TiO ϕ -system $\Delta v = 0$ and -1 (weak). The ZrS $^3\Pi$ – $^3\Delta$ bands are unremarkable in χ Cyg; the $\Delta v = 0$ sequence contributes near 8000 cm^{-1} . Absorption due to stellar H_2O is present near 7400 cm^{-1} and 8700 cm^{-1} . In the spectrum of R Cas, an M-type long period variable, the dominant transitions are due to VO A – X , TiO ϕ -system, and H_2O ; a weak head at 8163 cm^{-1} remains unidentified.

In addition to the completion of the laboratory work on ZrS from the visible to the infrared, astronomical studies are needed to search stellar spectra for other abundant sulphides such as CeS, YS and LaS; LC found two bandheads of YS in a spectrum of R And. Additional information on the presence of sulphides in S stars may still be gleaned from stellar spectra. A survey of the near-infrared and infrared spectra of variable stars of differing C/O ratio from minimum to maximum brightness should reveal the interrelationships between the principal bands. A programme of laboratory spectroscopy must be developed before other sulphides can be found in spectra as rich as that of R And. A puzzle alluded to by LC remains: studies of molecular dissociation equilibrium for cool stars predict that the sulphides should be nearly as abundant in carbon stars as in S stars, but the K–W bands appear only in the S stars. Our suspicion is that either the predicted sulphide abundances have been overestimated for carbon stars because the association of sulphur into CS and/or SiS has been underestimated, or the Zr in carbon stars is associated with carbon rather than sulphur.

Acknowledgments

We thank Professor R. Stringat for undertaking the initial laboratory experiments that resulted in a spectrum of ZrS, Dr R. Winkel for sending us a copy of his presentation to the Ohio State

University Molecular Spectroscopy Symposium, Drs S. Langhoff and C. Bauschlicher, Jr, for a preprint describing their *ab initio* calculations of ZrS, and Dr B. Simard for useful discussions. We appreciate the efforts of Dr V. V. Smith to obtain spectra of R And at the McDonald Observatory. This research has been supported in part at the University of Texas by the National Science Foundation (grant AST 86-14423) and the Robert A. Welch Foundation (grant F-634).

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