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# THE PREDICTED INFRARED SPECTRUM OF ZrO AND ITS POSSIBLE PRESENCE IN S STARS

(Letter to the Editor)

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**Abstract.** The unidentified absorption feature at  $9730 \pm 5 \text{ \AA}$  observed in the spectra of pure S stars is provisionally identified with the predicted  $9732 \text{ \AA}$  (0, 0) band of the  $e^1\Pi-c^1\Delta$  transition of ZrO molecule. Relative band strengths and band head positions of *this* transition in the 8300–12 500  $\text{\AA}$  region are presented to assist both laboratory and stellar spectral studies. The insistent need for the laboratory study of gas phase infrared spectrum of ZrO is accentuated.

## 1. Introduction

The spectra of pure S stars are known to exhibit many unidentified absorption features in the visible and infrared regions. Keenan (1950) discovered four red degraded bands in the near-infrared region of the spectrum of R Cyg. In addition to the Keenan bands, Wing (1972) reported five more unidentified bands in the  $1 \mu\text{m}$  region of the spectra of pure S stars, R Cyg and W Aql. Wyckoff and Wehinger (1975) observed many unidentified band features in the region between 4400 and 7300  $\text{\AA}$  of the spectra of S stars. Recently, Dubois (1977) proposed the identification of twelve bands in the 8200–9800  $\text{\AA}$  region, as due to the bands of the  $A-X$  system of BaF molecule. Unfortunately, all his identifications are proved to be incorrect following the high-resolution studies, by Wyckoff and Clegg (1978), of the spectra of R Cyg near minimum light. Thus, at present the problem of identification of the near-infrared and  $1 \mu\text{m}$  region bands remains unsolved, with the exception of a single band at 9900  $\text{\AA}$  which has been recently identified with the FeH molecule (Nordh *et al.*, 1977; Wing *et al.*, 1977; Clegg and Lambert, 1978).

Recent identifications of molecular bands in the spectra of R Cyg (Wyckoff and Clegg, 1978) demonstrate that the spectra of pure S stars are dominated by the oxides of the *s*-process elements: Zr, Y, La and Ce. It is therefore worthwhile to consider some of the spectra of ZrO involving low-lying electronic states in order to aid in any further search of ZrO in the spectra of S stars.

## 2. Low-Lying States of ZrO

Three low-lying electronic states,  $X^1\Sigma^+$ ,  $X'^3\Delta_r$  and  $c^1\Delta$ , are known for the ZrO molecule (Rosen, 1970). Absorption from the  $X^1\Sigma^+$  and the  $X'^3\Delta_r$  states have appeared in the spectra of S stars (Herbig, 1949; Davis and Keenan, 1969) and,

consequently, the true ground state of the molecule is uncertain. However, the presence of the singlet  $A$  system ( $b^1\Sigma^+ - X^1\Sigma^+$ ), and the absence of the triplet systems in the spectra of ZrO trapped at very low temperatures in solidified rare gas matrices, established that the  $^1\Sigma^+$  state is the true ground state of ZrO (Weltner and McLeod, 1965).

Recent studies of the laser induced photoluminescence spectra of ZrO isolated in Ne at 4 K (Lauchlin *et al.*, 1976) resulted in identifying infrared emissions at 9675 and 9100 Å, tentatively assigned as due to the (0, 0) bands of the  $e^1\Pi - c^1\Delta$  and  $E^3\Pi - X'^3\Delta$  transitions. These assignments placed the energies of the  $c^1\Delta$  and  $X'^3\Delta$  states at about 5200 and 1650  $\text{cm}^{-1}$  above the  $X^1\Sigma^+$  ground state. Thus, bands due to the  $e^1\Pi - c^1\Delta$  and  $E^3\Pi - X'^3\Delta$ , transitions are expected to appear in the infrared region, and are yet to be observed in the laboratory gas phase spectrum. These bands may be of some significance for the infrared spectral studies of S stars. However, if these bands are to be used in any stellar studies, laboratory measurements of their position and transition probabilities are needed. Nevertheless, it is possible, since the molecular constants are known for the  $e^1\Pi$  and  $c^1\Delta$  states, to predict the expected spectrum of the  $e^1\Pi - c^1\Delta$  transition based on the calculated Franck–Condon intensity factors.

### 3. Calculations and Results

Molecular constants used in the present study for the  $e^1\Pi$  and  $c^1\Delta$  states are given in Table I. The position of the  $c^1\Delta$  state with respect to the  $X^1\Sigma^+$  ground state is not known in the gas phase and, as a consequence, the accurate term value for the  $c^1\Delta$  state is not available except for an estimated value of 5000  $\text{cm}^{-1}$  by Brewer and Green (1969). In the present study, an approximate value of 5130  $\text{cm}^{-1}$  is estimated based on the known Ne matrix value of 5200  $\text{cm}^{-1}$ . It has been shown in the previous studies

TABLE I  
Molecular constants for the  $e^1\Pi - c^1\Delta$  transition of  
ZrO\*

Quantity	$e^1\Pi$ state	$c^1\Delta$ state
$T_e, \text{cm}^{-1}$	1 5441.78	5130.00
$\omega_e, \text{cm}^{-1}$	859.44	938.1
$\omega_e x_e, \text{cm}^{-1}$	2.918	1.80
$\omega_e y_e, \text{cm}^{-1}$	-0.0081 2	—
$B_e, \text{cm}^{-1}$	0.402 501	0.4173
$\alpha_e, \text{cm}^{-1}$	0.001 920	0.0012
$r_e, \text{Å}$	1.755 84	1.725

\* Molecular constants for the  $e^1\Pi$  state are from Phillips and Davis (1976); and for  $c^1\Delta$  state are from Afaf (1950a), Akerlind (1956) and the present study. The symbols are conventional (Herzberg, 1950).

TABLE II

Franck–Condon factors ( $q_{v'v''}$ ) and  $r$ -centroids ( $\bar{r}_{v'v''}$ , Å) for the  $e^1\Pi-c^1\Delta$  transition of ZrO\*

$v'$	$v''$					
	0	1	2	3	4	5
0	0.840	0.146	0.013	0.001	—	—
	1.743	1.828	1.897	1.958	—	—
1	0.146	0.570	0.245	0.036	0.003	—
	1.658	1.752	1.834	1.903	1.962	—
2	0.013	0.246	0.365	0.305	0.064	0.007
	1.580	1.656	1.760	1.840	1.908	1.965
3	0.001	0.035	0.306	0.215	0.333	0.096
	1.519	1.588	1.675	1.767	1.847	1.913
4	—	0.003	0.064	0.335	0.112	0.335
	—	1.525	1.595	1.685	1.775	1.853
5	—	—	0.007	0.095	0.335	0.036
	—	—	1.532	1.604	1.694	1.784

\* The upper member of each entry is the FC-factor ( $q_{v'v''}$ ) and the lower member is the  $r$ -centroid ( $\bar{r}_{v'v''}$ , Å).

involving Ne matrices (Weltner and McLeod, 1965; Brom and Broida, 1975) that matrix shifts in electronic term values and in vibrational constants are generally less than 1% of the gas-phase value and the Ne matrix thus provides a pseudo-gas-phase environment for diatomic molecules (Lauchlan *et al.*, 1976). The ZrO photoluminescence spectra demonstrated the pseudo-gas-phase character of neon matrices. For the  $e^1\Pi-X^1\Sigma^+$  and  $b^1\Sigma^+-X^1\Sigma^+$  systems, the matrix shifts of  $\nu_{00}$  are 0.8% and 0.6%, respectively (Lauchlan *et al.*, 1976). The matrix shift for the  $\nu_{00}$  value in Ne matrix ( $10\,333\text{ cm}^{-1}$ ) for the present  $e^1\Pi-c^1\Delta$  system also differs by 0.6% from the predicted gas-phase value ( $10\,272\text{ cm}^{-1}$ ), thus justifying the adopted electronic term value of  $5130\text{ cm}^{-1}$  for the  $c^1\Delta$  state in the gas phase.

Values of Franck–Condon (FC) intensity factors are calculated by the method (Fraser and Jarman, 1953) which involves the use of the Morse potential function for the states involved in the transition. In view of the small maximum values of vibrational quantum numbers involved in the band systems of ZrO, the Morse model is probably fairly realistic. The calculated  $q_{v'v''}$  values are given in Table II. In addition, the  $r$ -centroids ( $\bar{r}_{v'v''}$ ), which are useful for a study of the variation of electronic transition moment with internuclear separation, are also evaluated by the method described by Nicholls and Jarman (1956). These values are also included in Table II. If it is assumed that the electronic transition moment is constant, the band strengths are represented by the Franck–Condon factors ( $q_{v'v''}$ ).

#### 4. Discussion

The change of  $\Delta r_e$  of internuclear separation in the  $e^1\Pi-c^1\Delta$  transition is relatively very small (0.031 Å). Consequently, the primary Condon locus is quite narrow and  $q_{00}$  is the largest factor for this band system. Thus, it is seen from Table II that the bands of the  $\Delta v = 0$  sequence are most intense, followed by bands of the  $\Delta v = \pm 1$  and  $\pm 2$  sequences. The (0, 0), (1, 1) and (2, 2) are the most intense bands of the system. The magnitude of the  $q_{v'v''}$  values indicates that it is very unlikely that the

TABLE III  
Predicted spectrum of the  $e^1\Pi-c^1\Delta$  transition of ZrO

Sequence	Band		Wavelength ( $\lambda$ , Å)
	$v'$	$v''$	
$\Delta v = +2$	2	0	8 350
	3	1	8 415
	4	2	8 482
	5	3	8 553
	6	4	8 626
	7	5	8 702
	$\Delta v = +1$	1	0
2		1	9 056
3		2	9 130
4		3	9 207
5		4	9 287
6		5	9 370
7		6	9 457
8		7	9 547
$\Delta v = 0$	0	0	9 732
	1	1	9 810
	2	2	9 890
	3	3	9 975
	4	4	10 063
	5	5	10 154
$\Delta v = -1$	0	1	10 706
	1	2	10 796
	2	3	10 889
	3	4	10 987
	4	5	11 090
	5	6	11 197
	6	7	11 309
	7	8	11 426
$\Delta v = -2$	0	2	11 892
	1	3	11 997
	2	4	12 108
	3	5	12 223
	4	6	12 344
	5	7	12 472

bands (3, 0) and beyond – and, similarly, bands (0, 3) and beyond in the  $v'$  ( $v'' = 0$ ) and  $v''$  ( $v' = 0$ ) progressions, respectively – would be observed experimentally.

The expected intense band head positions of the  $e^1\Pi-c^1\Delta$  transition are calculated using the molecular constants given in Table I, in order to aid the laboratory study of the gas-phase spectrum and the stellar spectra of cool S stars. In Table III the predicted spectrum of the  $e^1\Pi-c^1\Delta$  transition, consisting of bands of the  $\Delta v = 0, \pm 1$  and  $\pm 2$  sequences, is presented. The bands of this transition, as seen from Table III, are expected to lie in the 8300–12 500 Å region, with the (0, 0) band at 9732 Å. Most of the intense bands are expected to be present in the 8900–11 500 Å wavelength region.

### 5. Assignment of the Unidentified 9730 Å Band

It is interesting to notice that the most intense 9732 Å (0, 0) band of the  $e^1\Pi-c^1\Delta$  system coincides with the  $9730 \pm 5$  Å unidentified feature reported by Wing (1972). Thus, it is enticing to identify the  $9730 \pm 5$  Å band with the ZrO molecule – this identification being supported by the predicted band head coincidence as well as its band strength. It is probable that the intense (1, 1) band at 9810 Å may be present together with the (0, 0) band in pure S stars. These propositions must, however, be considered tentative in view of the uncertainty involved in the electronic energy value of the  $c^1\Delta$  state. It is thus obvious that the laboratory study of the infrared spectrum of ZrO in the gas phase needs exigent attention. Also, high-resolution infrared spectra of pure S stars near minimum light are certainly desirable to permit a more detailed comparison with laboratory spectra.

None of the remaining unidentified features is found to coincide with the other bands of the  $e^1\Pi-c^1\Delta$  system. It is very likely, as has already been suggested by Keenan (1957), that the unidentified bands may arise from a number of different sources. CeO, a prominent *s*-process oxide (Wyckoff and Wehinger, 1977; Wyckoff and Clegg, 1978), may be a possible candidate to be considered for any of the unidentified features. The laboratory study of the CeO spectrum covers in the red up to 8800 Å (Barrow *et al.*, 1979). An extension of this study into the 1 μm region would appear to be very valuable in view of its astrophysical significance.

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