THE ASTROPHYSICAL JOURNAL, 240:363–367, 1980 August 15

ON THE $e\,^1\Pi$–$X\,^1\Sigma^+$ AND $^1\Sigma^+$–$X\,^1\Sigma^+$ TRANSITIONS OF ZrO RELATED TO S STAR SPECTRA

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Received 1979 November 26; accepted 1980 March 3

ABSTRACT

In view of the prevalent interest in the singlet band systems of ZrO, which are present in the spectra of pure S stars, values of band intensity factors (FCFs) and *r*-centroids are evaluated and displayed for the $e\,^1\Pi$–$X\,^1\Sigma^+$ and $^1\Sigma^+$–$X\,^1\Sigma^+$ transitions. The results suggest the possible presence of new bands in both the systems and warrant a reinvestigation of the spectrum of ZrO in the 5500–6600 Å region. Predicted band head positions of the new bands are presented to aid both laboratory and stellar spectral studies.

Subject headings: line identifications — molecular processes — stars: S-type — transition probabilities

I. INTRODUCTION

The spectrum of the ZrO molecule is of considerable astrophysical interest since it is one of the main absorption features in the spectra of S-type stars. Experimental and theoretical investigations on the electronic states of the molecule and transitions between them are therefore important in the interpretation of stellar absorption studies. The gas phase electronic spectrum of ZrO is well known to exhibit three triplet and four singlet band systems in the 3300–8300 Å region. Recently two more new systems have been tentatively identified in the infrared region by Lauchlan, Brom, and Broida (1976), during their laser-induced photoluminescence spectral studies of ZrO trapped in neon at 4 K. All the experimentally observed states and transitions below 3.5 eV are shown in the energy level diagram of Figure 1.

Values of the Franck-Condon factors (FCFs) and *r*-centroids for band systems are required for the astrophysical determination of stellar abundances and excitation temperatures. Schoonveld and Sundaram (1974) reported Morse FCFs and *r*-centroids for the triplet band systems of ZrO. Recently, the $e\,^1\Pi$–$X\,^1\Sigma^+$ (6495 Å) and $^1\Sigma^+$–$X\,^1\Sigma^+$ (5860 Å) band systems have been identified by Wyckoff and Clegg (1978) in the spectra of the pure S star R Cyg. In view of the current interest in the singlet band systems of ZrO, it was felt to be desirable to evaluate the values of FCFs ($q_{v'v''}$) and *r*-centroids ($\bar{r}_{v'v''}$) for the 6495 Å and 5860 Å band systems. The evaluated values of $q_{v'v''}$ are used to explain the intensity distribution of bands in the systems. Furthermore, based on the values of $q_{v'v''}$, expected band head positions of unobserved bands are presented to benefit any further laboratory and stellar spectral identifications of ZrO.

II. CALCULATIONS AND RESULTS

Molecular constants for the $X\,^1\Sigma^+$, $e\,^1\Pi$, and $^1\Sigma^+$ states of ZrO used in the present study are given in Table 1. For the $X\,^1\Sigma^+$ and $e\,^1\Pi$ states, accurate molecular constants are available following the recent high-resolution studies of the $e\,^1\Pi$–$X\,^1\Sigma^+$ system by Phillips and Davis (1976*b*). For the upper $^1\Sigma^+$ state of the $^1\Sigma^+$–$X\,^1\Sigma^+$ system, only approximate molecular constants are available, from a rotational structure study of the (0, 0) and (1, 1) bands by Phillips and Davis (1976*a*). An approximate value of 870 cm^{-1} is known for ω_e–$2\omega_e x_e$. If one uses this value together with the known α_e value in the Pekeris (1934) relation

$$\alpha_e = 6(\omega_e x_e B_e^{\,3})^{\frac{1}{2}}/\omega_e - 6B_e^{\,2}/\omega_e\,,$$

an approximate $\omega_e' x_e'$ value of 3 cm^{-1} is obtained.

Franck-Condon factors are calculated by the method described by Fraser and Jarmain (1953), which involves the use of a Morse potential function. To verify the applicability of the Morse function, the values of α_e are calculated using the Pekeris relation. The calculated values of α_e (0.001914 and 0.002049 cm^{-1} for the $X\,^1\Sigma^+$ and $e\,^1\Pi$ states, respectively) are found to be in good agreement with the experimental values (0.001954 and 0.00192 cm^{-1}), thus suggesting that the Morse function is a good approximation for these states. The values of *r*-centroids ($\bar{r}_{v'v''}$), which are required for a study of the variation of electronic transition moment with internuclear separation, are calculated by the method of Nicholls and Jarmain (1956). If it is assumed that the electronic transition moment is constant, then the band strengths are represented by the values of $q_{v'v''}$. In Tables 2 and 3 are presented the values of $q_{v'v''}$, $\bar{r}_{v'v''}$, and $\lambda_{v'v''}$ for the 6495 Å and 5860 Å systems, respectively.

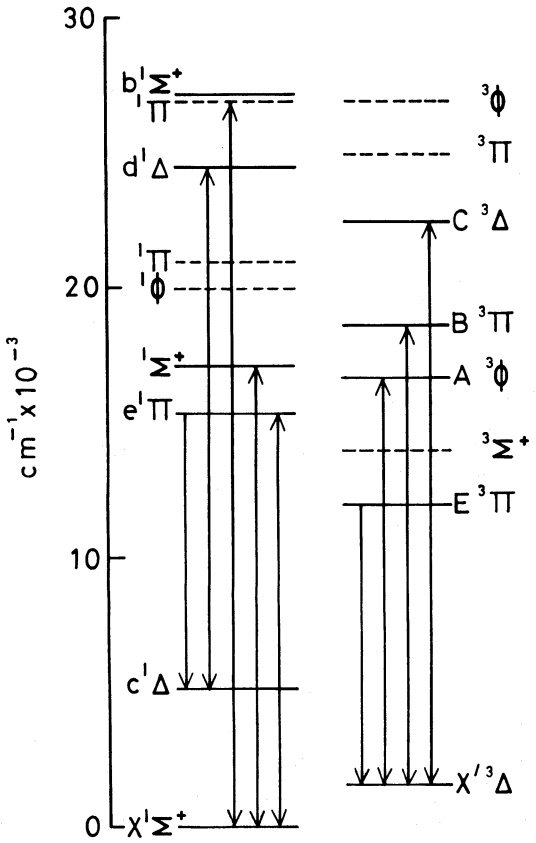

FIG. 1.—Energy levels and observed transitions (below 3.5 eV) of the ZrO molecule. States shown by dashed lines were predicted by Brewer and Green (1969) but yet to be observed. Arrow heads indicate whether transitions were observed in absorption or emission or both.

III. DISCUSSION

a) $e\ ^1\Pi$–$X\ ^1\Sigma^+$ *Transition* (*6495 Å system*)

The magnitude of the $q_{v'v''}$ values, as seen from Table 2, indicates that the (0, 0) is the most intense band of the system, followed by the bands of the $\Delta v = \pm 1$, ± 2, and ± 3 sequences. It is very unlikely that in the v' progression ($v'' = 0$), bands with $v' \geq 4$ would be observed, or that in the v'' progression ($v' = 0$), bands with $v'' \geq 4$ would be observed. This conclusion is entirely in accord with the experimental study of the band system. However, it is worthwhile to notice that the intensities of unobserved (1, 1) and (2, 2) bands of the $\Delta v = 0$ sequence and (3, 2), (4, 3) and (5, 4) bands of the $\Delta v = +1$ sequence are comparable (in some cases, more intense) with the observed bands of the system. Thus, additional bands of the $\Delta v = 0$ and $+1$ sequences are expected, suggesting the need for a reinvestigation of the spectrum of ZrO.

In order to aid the search for new bands, both in laboratory and in stellar spectra, the expected band head positions are calculated using the molecular constants given in Table 1. The expected band positions for some of the bands have already been given by Phillips and Davis (1976*b*). Additionally, some more expected band head positions of the $\Delta v = \pm 1$, ± 2, and ± 3 sequences are calculated and the results are presented in Table 4. It may be seen from Table 4 that the region 6245–6490 Å is of particular interest, wherein bands of the $\Delta v = +1$ sequence are expected to be present. It should, however, be noted that this region is dominated by the intense bands of the triplet γ-band system and consequently high-dispersion spectrograms are required to discern new bands of this system.

b) $^1\Sigma^+$–$X\ ^1\Sigma^+$ *Transition* (*5860 Å system*)

The change of Δr_e of the internuclear separation for this transition is very small (0.038 Å). The primary Condon locus is therefore very narrow, and q_{00} is the largest factor. It is seen from Table 3 that the (0, 0) and (1, 1) bands of the $\Delta v = 0$ sequence are most intense, followed by the bands of the $\Delta v = \pm 1$ and ± 2 sequences. Since only four bands of the $\Delta v = 0$ sequence are experimentally observed [out of which only the (0, 0) and (1, 1) band head positions are accurately known], a thorough investigation of the spectrum of ZrO for the $\Delta v = \pm 1$ and ± 2 bands is desirable, as indicated by the magnitude of the FCFs.

Expected positions of the intense bands are calculated, and the results are presented in Table 5. The band head positions (uncertain by at least ± 1 Å) given in Table 5 are certainly not of suitable accuracy for use in high-resolution spectral studies, in view of the uncertainty involved in the vibrational constants of the upper state of this system; nevertheless, the results indicate the regions, wherein the new bands are expected to occur. Thus the regions 5570–5800 Å and 6200–6500 Å are of considerable interest during a

TABLE 1

MOLECULAR CONSTANTS FOR THE $X\ ^1\Sigma^+$, $e\ ^1\Pi$ AND $^1\Sigma^+$ STATES OF THE ZrO MOLECULE

State	T_e[a] (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	$\omega_e y_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	r_e[b] (Å)
$X\ ^1\Sigma^+$	0.0	976.51	3.462	0.00052	0.423608	0.001954	1.711911
$e\ ^1\Pi$	15441.78	859.44	2.918	−0.00812	0.402501	0.00192	1.75584
$^1\Sigma^+$	17110.8	876	3	...	0.405615	0.00165	1.74946

[a] T_e values are calculated from $T_e = \nu_{00} - G'(0) + G''(0)$, where $G(0) = \omega_e/2 - \omega_e x_e/4 + \omega_e y_e/8$.

[b] r_e values are calculated with $\mu(^{90}Zr^{16}O) = 13.57904$ amu and $r^2 = 16.8575/\mu B(Å^2)$.

TABLE 2

FRANCK-CONDON FACTORS ($q_{v'v''}$), r-CENTROIDS ($\bar{r}_{v'v''}$, Å), AND OBSERVED BAND HEADS ($\lambda_{v'v''}$, Å) FOR THE $e\,^1\Pi$–$X\,^1\Sigma^+$ TRANSITION OF THE ZrO MOLECULE

	v''					
v'	0	1	2	3	4	5
0	0.697	0.253	0.045	0.005	...	...
	1.737	1.800	1.861	1.921	...	...
	6495.3	6931.7	7426.9			
1	0.249	0.281	0.343	0.107	0.018	0.002
	1.678	1.745	1.807	1.867	1.928	1.989
	6154.3		6984.5	7483.7		
2	0.047	0.332	0.075	0.334	0.169	0.038
	1.614	1.687	1.752	1.814	1.874	1.934
	5849.4	6200.9		7037.7	7540.9	
3	0.006	0.110	0.315	0.004	0.272	0.216
	1.531	1.624	1.696	1.760	1.821	1.881
		5893.4			7091.3	7598.4
4	0.001	0.021	0.169	0.248	0.010	0.191
	1.470	1.547	1.635	1.704	1.768	1.828
			5937.8			7145.4
5	...	0.003	0.044	0.209	0.166	0.050
	...	1.482	1.562	1.645	1.713	1.775
				5982.7		

NOTE.—First entry: Franck-Condon factor, $q_{v'v''}$. Second entry: r-centroid, $\bar{r}_{v'v''}$ (Å). Third entry: Observed band head, $\lambda_{v'v''}$ (Å).

TABLE 3

FRANK-CONDON FACTORS ($q_{v'v''}$), r-CENTROIDS ($\bar{r}_{v'v''}$, Å), AND OBSERVED BAND HEADS ($\lambda_{v'v''}$, Å) FOR THE $^1\Sigma^+$–$X\,^1\Sigma^+$ TRANSITION OF THE ZrO MOLECULE

	v''					
v'	0	1	2	3	4	5
0	0.765	0.205	0.027	0.002	...	...
	1.734	1.807	1.877	1.948	...	...
	5859.8					
1	0.203	0.407	0.312	0.069	0.008	0.001
	1.664	1.742	1.814	1.884	1.954	2.026
		5859.8				
2	0.029	0.303	1.183	0.348	0.117	0.018
	1.584	1.673	1.749	1.820	1.890	1.960
			5926.4			
3	0.003	0.073	0.331	0.060	0.334	0.163
	...	1.596	1.682	1.757	1.827	1.897
				5960.6		
4	...	0.010	0.120	0.310	0.007	0.290
	...	1.479	1.607	1.691	1.764	1.834
5	...	0.001	0.023	0.164	0.260	0.002
	...	...	1.504	1.618	1.699	1.772

NOTE.—Entries are as in Table 2.

TABLE 4

PREDICTED INTENSE BANDS (*R*-HEADS) FOR THE $e\,^1\Pi$–$X\,^1\Sigma^+$ TRANSITION OF THE ZrO MOLECULE

SEQUENCE	BAND v'	BAND v''	WAVELENGTH λ (Å)
$\Delta v = +3$	3	0	5574.9[a]
	4	1	5616.9[a]
	5	2	5659.2[a]
	6	3	5701.9
	7	4	5745.0
$\Delta v = +2$	2	0	5849.4
	3	1	5893.4
	4	2	5937.8
	5	3	5982.7
	6	4	6028.0
	7	5	6073.6
	8	6	6119.7
	9	7	6166.2
$\Delta v = +1$	1	0	6154.3
	2	1	6200.9
	3	2	6247.8[a]
	4	3	6295.0[a]
	5	4	6342.7[a]
	6	5	6390.8
	7	6	6439.2
	8	7	6488.1
$\Delta v = 0$	0	0	6495.3
	1	1	6544.7[a]
	2	2	6594.4[a]
	3	3	6644.4[a]
	4	4	6694.8[a]
	5	5	6745.5[a]
$\Delta v = -1$	0	1	6931.7
	1	2	6984.5
	2	3	7037.7
	3	4	7091.3
	4	5	7145.4
	5	6	7199.4[a]
	6	7	7254.1
	7	8	7309.2
$\Delta v = -2$	0	2	7426.9
	1	3	7483.7
	2	4	7540.9
	3	5	7598.4
	4	6	7656.2
	5	7	7714.5
	6	8	7773.2
	7	9	7832.3
$\Delta v = -3$	0	3	7993.8[a]
	1	4	8055.2[a]
	2	5	8116.9[a]
	3	6	8178.9
	4	7	8241.3[a]

[a] Predicted band head positions reported by Phillips and Davis 1976*b*.

TABLE 5

PREDICTED INTENSE BANDS (*R*-HEADS) FOR THE $^1\Sigma^+$–$X\,^1\Sigma^+$ TRANSITION OF THE ZrO MOLECULE

SEQUENCE	BAND v'	BAND v''	WAVELENGTH λ (Å)
$\Delta v = +2$	2	0	5319
	3	1	5351
	4	2	5383
	5	3	5415
	6	4	5447
	7	5	5479
$\Delta v = +1$	1	0	5576
	2	1	5609
	3	2	5642
	4	3	5675
	5	4	5708
	6	5	5742
	7	6	5775
	8	7	5809
$\Delta v = 0$	0	0	5860
	1	1	5894
	2	2	5929
	3	3	5963
	4	4	5998
	5	5	6033
$\Delta v = -1$	0	1	6213
	1	2	6249
	2	3	6285
	3	4	6321
	4	5	6357
	5	6	6393
	6	7	6430
	7	8	6466
$\Delta v = -2$	0	2	6608
	1	3	6646
	2	4	6684
	3	5	6721
	4	6	6759
	5	7	6797

search for new bands of this system. For a study of this band system also, high-dispersion spectrograms are necessary since the above regions are dominated by the intense bands of the triplet β and γ systems of ZrO. A successful identification of new bands would provide accurate vibrational constants for this system, which in turn would enable one to improve the data of transition probabilities.

The author is thankful to Dr. M. K. V. Bappu for his interest in this study and to Mr. S. Duraikannu for typing the manuscript.

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