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### Original Publication Citation

Bittner, D. M., & Bernath, P. F. (2018). Spectroscopic constants and line positions for TiO singlet states. *Astrophysical Journal Supplement Series*, 236(2), 46 doi:10.3847/1538-4365/aabfe8

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# Spectroscopic Constants and Line Positions for TiO Singlet States

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Received 2018 March 26; revised 2018 April 17; accepted 2018 April 17; published 2018 June 14

## Abstract

A consistent set of spectroscopic constants for the  $a^1\Delta$ ,  $d^1\Sigma^+$ ,  $b^1\Pi$ ,  $c^1\Phi$ , and  $f^1\Delta$  states of  $^{48}\text{Ti}^{16}\text{O}$  has been determined from analysis of the  $b^1\Pi$ - $a^1\Delta$ ,  $b^1\Pi$ - $d^1\Sigma^+$ ,  $c^1\Phi$ - $a^1\Delta$ , and  $f^1\Delta$ - $a^1\Delta$  systems. Three Fourier transform emission spectra have been used for the analysis. New bands of the  $b^1\Pi$ - $a^1\Delta$  and  $c^1\Phi$ - $a^1\Delta$  systems have been fitted. The first analysis of the  $c^1\Phi$ - $a^1\Delta$  system using Fourier transform spectra is also provided. Extensive and improved line positions are measured. TiO is prominent in the spectra of oxygen-rich cool stellar objects and may be present in hot-Jupiter exoplanet atmospheres.

*Key words:* methods: laboratory: molecular – molecular data – techniques: spectroscopic

*Supporting material:* machine-readable table

## 1. Introduction

The diatomic TiO molecule is of considerable astronomical importance. TiO is present in the atmospheres of oxygen-rich low-mass stellar objects. M dwarfs have strong absorption features from TiO bands and the relative intensities of TiO band heads are used for classification of the M subtypes (Kirkpatrick et al. 1993). In later spectral types, L and T, TiO features are weaker or absent. TiO features have been used to discriminate between magnetically active and inactive stars (Bochanski et al. 2007). Model atmosphere calculations have been performed for M dwarfs and require the inclusion of TiO opacities (Kirkpatrick et al. 1993; Allard & Hauschildt 1995; Allard et al. 2000).

Absorption features from the atmosphere of hot-Jupiter HD 209458b have been tentatively assigned to be due to TiO (Désert et al. 2008). TiO was suggested to be both in the upper and lower parts of the atmosphere. For the hot-Jupiter WASP-12b, conflicting evidence for TiO was found (Sing et al. 2013; Stevenson et al. 2014). Detection of TiO on WASP-19b (Sedaghati et al. 2017), WASP-76b, and perhaps on WASP-121b (Tsiaras et al. 2018) has recently been reported. Fortney et al. (2008) proposed two classes of hot Jupiters, the pM class, which is warm enough to have appreciable opacities due to TiO and VO, and the pL class, which is cooler. Due to the opacity in the upper atmosphere, TiO has been proposed to contribute to thermal inversions in the atmospheres of highly irradiated planets. Radiative-convective radiative-transfer models and a model of particle settling in the presence of turbulent and molecular diffusion have shown this to be problematic but not impossible (Spiegel et al. 2009).

TiO was detected at (sub)millimeter wavelengths in the red supergiant VY Canis Majoris and its circumstellar environment (Kamiński et al. 2013). The TiO emission is so far inconsistent with models of the photosphere and of dust formation.

Schwenke (1998) has calculated line lists for singlet–singlet, triplet–triplet, as well as forbidden transitions. Potential energy curves were determined using the RKR (Rydberg–Klein–Rees) procedure, with spectroscopic constants determined by fitting transitions to a Hamiltonian model. Transition dipole moment functions and dipole moment functions calculated by Schwenke and Langhoff (1997) have been used. The coupling between states has been estimated using ab initio calculated

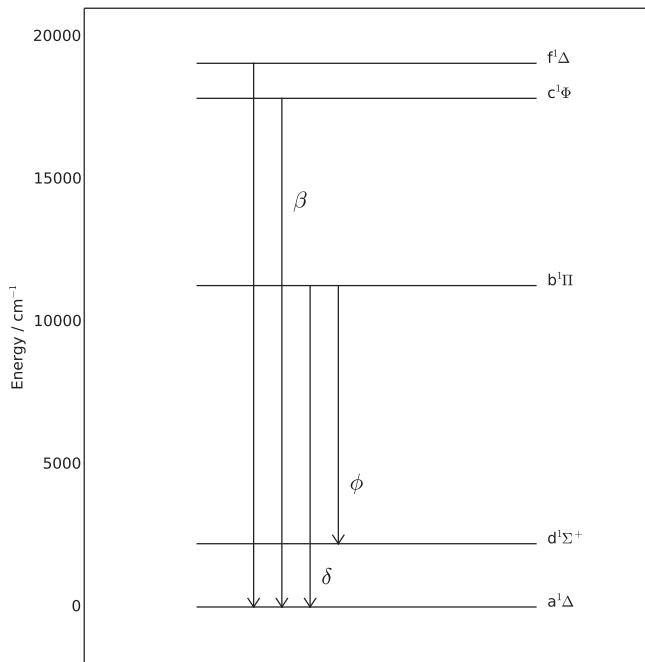
spin–orbit and rotational–orbit matrix elements. For better agreement with experiments, the coupling was adjusted in a fitting procedure.

Plez (1998) also provided a line list for singlet–singlet and triplet–triplet allowed transitions. The line list was calculated using molecular constants determined from experimental data. The mixing between states was not estimated for the line strength calculations that used transition moment functions from Langhoff (1997).

A comparison of energy levels obtained by the Measured Active Rotational–Vibrational Energy Levels (MARVEL) analysis (McKemmish et al. 2017) with Schwenke’s line list was reasonable, in general, but deviations in energy increased with increasing  $J$ . Agreement with the experimentally derived levels for some states was poor. The vibrational spacing in the line list by Plez (1998) was found to be incorrect for the singlet states when compared to the MARVEL energy levels.

Cross-correlation of the high-resolution transmission spectrum of HD 209458b with synthetic spectra of model atmospheres containing TiO transitions tentatively ruled out detection of TiO in the exoplanet atmosphere (Hoeijmakers et al. 2015). The model atmospheres used TiO line lists by Schwenke and Plez, and these line lists were found to be unsatisfactory. Improvement in the line positions should facilitate TiO detection by such cross-correlation retrieval methods.

The  $\Delta v = 0$  bands of the  $c^1\Phi$ - $a^1\Delta$  system were the first TiO singlet bands to be analyzed (Lowater 1929). The rotational analysis of the 0–0 band was first done by Phillips (1950) together with a rotational analysis of  $\Delta v = 0$  bands of the  $b^1\Pi$ - $a^1\Delta$  system. Rotational analyses for bands of the  $e^1\Sigma^+$ - $d^1\Sigma^+$ ,  $f^1\Delta$ - $a^1\Delta$  and  $b^1\Pi$ - $d^1\Sigma^+$  systems were first provided by Phillips & Davis (1971), Linton (1972), and Galehouse et al. (1980), respectively. Further measurements of these systems were carried out by Lindgren (1972), Linton & Singhal (1974), and others. Pure rotational transitions are available for the  $X^3\Delta$  state from (sub)millimeter-wave (Namiki et al. 1998; Lincowski et al. 2016) and microwave-optical double resonance (Steimle et al. 1990) spectroscopic studies. Pure rotational transitions were not measured in any singlet states.



**Figure 1.** Term energies ( $T_0$ ) of the fitted electronic states and fitted band systems (arrows).

In this article we provide a complete reanalysis of the  $b^1\Pi$ - $a^1\Delta$ ,  $b^1\Pi$ - $d^1\Sigma^+$ ,  $c^1\Phi$ - $a^1\Delta$ , and  $f^1\Delta$ - $a^1\Delta$  systems (Figure 1). Known and new bands were fitted using three Fourier transform emission spectra.

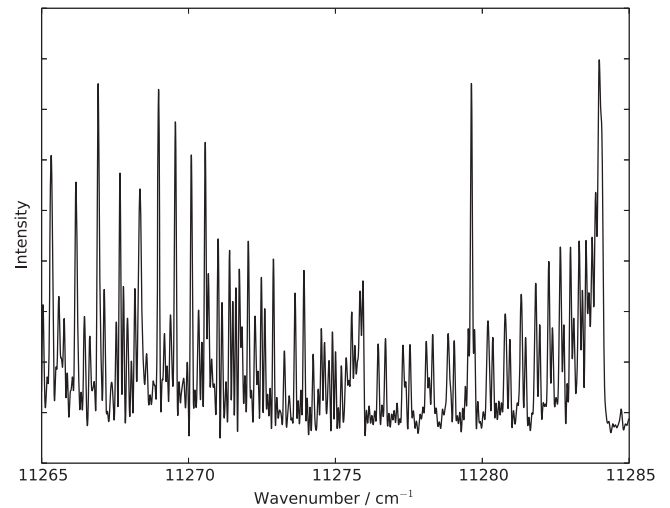
## 2. Experimental

Three emission spectra have been used for the analysis of TiO reported in this paper. The spectra were measured with the 1 m Fourier transform interferometer associated with the McMath–Pierce Solar Telescope of the National Solar Observatory at Kitt Peak.

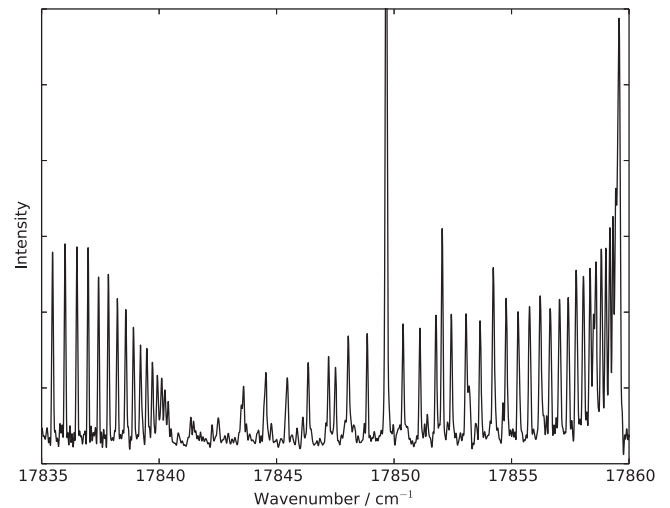
The first spectrum was measured on 1977 June 29 (770629R0.001). The spectrum was obtained by averaging 34 scans over about 4 hr of integration and covered a spectral range of  $9000$ – $22,000$   $\text{cm}^{-1}$ , with a spectral resolution of  $0.044$   $\text{cm}^{-1}$ . The interferograms were recorded at a sampling rate of 2500 Hz. The visible beam splitter, a CG475 filter and a silicon photodiode detector were used for data acquisition. A 15 cm quartz tube with a window on one end was used as a sample cell with a continuous flow of gas. TiO was formed in a microwave discharge of an  $\text{O}_2$  and  $\text{TiCl}_4$  mixture diluted in 20 Torr He. A more detailed description is provided by Brandes & Galehouse (1985). For our analysis, a zero-filling factor of four was used for all spectra.

The second spectrum was also measured on 1977 June 29 (770629R0.005). Twelve scans were averaged in  $\sim 1.5$  hours of integration and covered a spectral range of  $3800$ – $12,000$   $\text{cm}^{-1}$ , with a spectral resolution of  $0.015$   $\text{cm}^{-1}$ . An InSb detector was used and the  $5000$ – $11,000$   $\text{cm}^{-1}$  bandpass was set by the visible beam splitter and a GaAs filter. The microwave discharge source was the same as that used for the first spectrum, with a total pressure of 22 Torr. A more detailed description is provided by Galehouse et al. (1980).

The third spectrum was measured on 1985 January 19 (850116R0.002). The spectrum was obtained by averaging



**Figure 2.** Part of the  $b^1\Pi$ - $a^1\Delta$  system spectrum showing the 0–0 band R branch band head and low-J transitions from the Q and P branches.



**Figure 3.** Part of the  $c^1\Phi$ - $a^1\Delta$  system spectrum showing the 0–0 band R branch band head and low-J transitions from the Q branch.

thirteen scans in  $\sim 1.5$  hours of integration. The spectrum covered  $9000$ – $21,000$   $\text{cm}^{-1}$ , with a spectral resolution of  $0.044$   $\text{cm}^{-1}$ . The UV beam splitter was used with blue-enhanced photodiode detectors and a CG495 colored glass filter. TiO was generated in a carbon tube furnace at 1950 K at a pressure of 50 Torr from outgassing.

$A^3\Phi$ - $X^3\Delta$  lines (Ram et al. 1999) have been used to calibrate the third spectrum with a calibration factor of 1.00000020. This calibration was transferred from the third to the second spectrum, with strong lines measured in both, giving a calibration factor of 0.99999924. Ti atomic lines (Kramida et al. 2018) have been used to calibrate the first spectrum. In addition to the calibration factor, a spectral shift was necessary to properly calibrate the first spectrum described above, due to a missing point or points in the spectrum. A linear calibration of  $0.9999935x + 0.0763102$  was used. The absolute accuracy of the calibration was estimated as  $0.004$   $\text{cm}^{-1}$  or better.

A precision of about  $0.003$ – $0.007$   $\text{cm}^{-1}$  was calculated for strong transitions in the 0–0 bands of the fitted systems.

**Table 1**  
Spectroscopic Constants of TiO Singlet States in Units of  $\text{cm}^{-1}$

	$T_v$	$B_v$	$D_v \times 10^7$	$q_v \times 10^4$	$qD_v \times 10^9$
$a^1\Delta v = 0$	0	0.53624855(795)	6.0293(115)	...	...
$a^1\Delta v = 1$	1009.2251(17) <sup>a</sup>	0.53326822(803)	6.0620(117)	...	...
$a^1\Delta v = 2$	2009.4713(23)	0.53027079(832)	6.0958(126)	...	...
$a^1\Delta v = 3$	3000.7380(63)	0.5272249(110)	6.0620(230)	...	...
$d^1\Sigma^+ v = 0$	2218.7148(17)	0.54767029(796)	6.3765(114)	...	...
$d^1\Sigma^+ v = 1$	3231.9999(19)	0.54431122(818)	6.4011(127)	...	...
$d^1\Sigma^+ v = 2$	4235.5196(25)	0.54094485(860)	6.4280(150)	...	...
$d^1\Sigma^+ v = 3$	5229.2965(47)	0.5375690(130)	6.4570(480)	...	...
$d^1\Sigma^+ v = 4$	6213.342(20)	0.5342159(874)	6.799(825)	...	...
$d^1\Sigma^+ v = 5$	7187.687(12)	0.5308122(248)	6.620(100)	...	...
$b^1\Pi v = 0$	11272.7586(12)	0.51204209(793)	6.4113(115)	-1.6325(73)	2.26(12)
$b^1\Pi v = 1$	12183.9225(14)	0.50916700(794)	6.4644(115)	-1.5562(85)	1.71(18)
$b^1\Pi v = 2$	13086.4304(23)	0.50624702(832)	6.5076(130)	-1.506(21)	1.95(54)
$b^1\Pi v = 3$	13980.2088(45)	0.50329705(973)	6.5770(180)	-1.437(20)	[2.26] <sup>b</sup>
$c^1\Phi v = 0$	17840.4826(16)	0.52159845(833)	5.1540(130)	...	...
$c^1\Phi v = 1$	18750.0717(26)	0.51863964(854)	6.3810(140)	...	...
$c^1\Phi v = 2$	19649.6283(36)	0.51537391(945)	6.9890(170)	...	...
$c^1\Phi v = 3$	20539.8720(71)	0.5118329(145)	7.1110(540)	...	...
$f^1\Delta v = 0$	19068.9639(18)	0.50232706(825)	6.5016(131)	...	...
$f^1\Delta v = 1$	19938.0688(32)	0.4993020(110)	6.6400(290)	...	...

#### Notes.

<sup>a</sup> The value in parenthesis is the error estimate (one standard deviation) for the parameter.

<sup>b</sup> Value held fixed in the fit.

### 3. Spectral Analysis and Discussion

The three spectra discussed in Section 2 have been used to fit the bands of four systems, with all bands being connected. A consistent set of constants is determined from a simultaneous fit of all lines. The rotational temperature of TiO generated in the microwave discharge is lower than that obtained using the furnace. The lines from the furnace spectrum extend to higher  $J$  values.

The 0–0, 1–1, 0–1, 1–0, 1–2, and 2–3 bands of  $b^1\Pi$ – $a^1\Delta$  ( $\delta$  system) were fit. Transitions of  $\Delta v = -1$  and  $\Delta v = 1$  band sequences of the  $\delta$  system are fitted for the first time; only transitions from the  $\Delta v = 0$  sequence have been assigned before, most recently by Ram et al. (1996).

The 0–0, 1–1, 0–1, 1–0, 2–0, 0–2, 1–2, 2–1, 2–3, 3–2, 1–3, 2–4, and 3–5 bands of  $b^1\Pi$ – $d^1\Sigma^+$  ( $\phi$  system) were fit. An extensive analysis of the system was done by Galehouse et al. (1980). Using the same spectrum used by Galehouse et al., we could not confidently assign transitions for the previously reported 3–1, 4–2, and 3–4 bands.

The 0–0, 1–1, 2–2, 3–3, 1–0, 2–1, and 3–2 bands of  $c^1\Phi$ – $a^1\Delta$  ( $\beta$  system) were fit. The first analysis of the  $\Delta v = 1$  band sequence of the  $\beta$  system is presented; only the  $\Delta v = 0$  sequence has been assigned before. The 0–0 band has been most recently reported by Amiot et al. (1996). An extensive analysis of the  $\Delta v = 0$  sequence up to the 3–3 band was provided by Linton (1974) using data from a grating spectrograph.

The 0–0, 1–1, 0–1, 1–0, and 1–2 bands of  $f^1\Delta$ – $a^1\Delta$  system were fit. An extensive analysis of the system was done by Brandes & Galehouse (1985). Using the same spectrum used by Brandes and Galehouse, we could not confidently assign transitions for the previously reported 2–1 band. As described in Section 2, a spectral shift was needed for the calibration. We found our lines to be shifted to lower wavenumbers by about

$0.025 \text{ cm}^{-1}$ , compared with the Brandes & Galehouse line positions.

Parts of the 0–0 band spectrum of the  $b^1\Pi$ – $a^1\Delta$  and  $c^1\Phi$ – $a^1\Delta$  systems are shown in Figures 2 and 3, respectively. Figures showing the bands of the  $b^1\Pi$ – $d^1\Sigma^+$  and  $f^1\Delta$ – $a^1\Delta$  systems can be found in Galehouse et al. (1980) and Brandes & Galehouse (1985), respectively.

Spectroscopic constants from all previously known TiO singlet systems have been fitted, excluding the  $e^1\Sigma^+$ – $d^1\Sigma^+$  system (Phillips & Davis 1971; Lindgren 1972), as transitions of the system were not observed in our spectra. The fitting was done using PGOPHER by Western (2017) and the determined spectroscopic constants are provided in Table 1. The line positions and the spectrum used for each line position are provided in Table 2.

Effective constants were determined for the  $c^1\Phi$  state. Inclusion of spin–orbit interaction for this state with the  $C^3\Delta$  state (Namiki et al. 2003) was not required in the fitting. However, the perturbation was noticeable in the residuals.

In the fitting, the term energies were set relative to the non-existent  $v = 0 J = 0$  level of the  $a^1\Delta$  state. The term energy of  $a^1\Delta v = 0 J = 0$  was determined by Kaledin et al. (1995) to be  $3444.367(1) \text{ cm}^{-1}$ . A term energy of  $3446.481(8) \text{ cm}^{-1}$  for  $a^1\Delta v = 0 J = 2$  was determined by MARVEL analysis relative to  $v = 0 J = 1$  of  $X^3\Delta_1$ .

### 4. Conclusions

Using high-quality Fourier transform spectrometer spectra, a consistent set of spectroscopic constants for most of the known singlet states of TiO has been determined with improved accuracy and precision over the previous data. The spectroscopic constants and line positions can be used for cross-correlation retrieval methods and for the calculation of line lists.

**Table 2**  
Line Positions of TiO in PGOPHER Line List Style

Molecule	$M'$	$J'$	$S'$	$\#'$	$M''$	$J''$	$S''$	$\#''$	Position	Branch	Name
LinearMolecule	b1Pi	45	0	4	d1Sigma+	45	1	6	6735.7276	Q(45)	: b1Pi $v = 3$ 45 f—d1Sigma+ $v = 5$ 45 e : 770629005_Apo_Cal.dpt—Overlays
LinearMolecule	b1Pi	43	0	4	d1Sigma+	43	1	6	6740.6132	Q(43)	: b1Pi $v = 3$ 43 f—d1Sigma+ $v = 5$ 43 e : 770629005_Apo_Cal.dpt—Overlays
LinearMolecule	b1Pi	42	1	4	d1Sigma+	42	0	6	6742.9677	Q(42)	: b1Pi $v = 3$ 42 f—d1Sigma+ $v = 5$ 42 e : 770629005_Apo_Cal.dpt—Overlays

(This table is available in its entirety in machine-readable form.)

We thank J. N. Hodges for calibrating and zero-filling the spectra and M. Dulick for help with the Kitt Peak spectral data archive. Financial support was provided by the NASA Exoplanet Program (grant NNX16AB51G). We also thank T. Masseron for discussions on TiO singlet states. The National Observatory, is operated by the Association of Universities for Research in Astronomy, under co-operative agreement with the National Science Foundation.

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