

## NEAR-INFRARED SPECTROSCOPY OF TiO: LABORATORY MEASUREMENTS AND IDENTIFICATION IN SUNSPOTS

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## ABSTRACT

The high-resolution spectrum of the  $\delta$ -system ( $b^1\Pi-a^1\Delta$ ) of TiO, excited in a hollow cathode lamp, has been observed using a Fourier transform spectrometer. The 0–0 and 1–1 bands of this transition have also been identified in the spectrum of a sunspot umbra. The combined laboratory and solar measurements have been used to obtain improved molecular constants for the  $b^1\Pi$  and  $a^1\Delta$  states of TiO.

*Subject headings:* methods: laboratory — molecular data — sunspots

## 1. INTRODUCTION

The TiO molecule is the best-characterized transition metal oxide (Huber & Herzberg 1979; Merer 1989). The visible and near-infrared spectra of M stars are dominated by TiO and VO absorption (Merrill, Deutsch, & Keenan 1962). The detailed classification of M stars by photometry or spectroscopy (Kirkpatrick, Henry, & McCarthy 1991) depends on the relative intensities of the near-infrared TiO and VO bands (Sharpless 1956; Lockwood 1969, 1972).

Partly as a result of TiO's astrophysical importance, the laboratory spectroscopy and the theoretical calculation of molecular properties are particularly extensive. Since the most recent review of the TiO literature by Merer in 1989, there have already been many additional papers. Two new ab initio calculations are available (Bauschlicher, Langhoff, & Komornicki 1990; Schamps, Senessal, & Carette 1992). The Steimle group at Arizona State University has measured the dipole moment (2.96 D) and the hyperfine structure (Steimle & Shirley 1989; Steimle et al. 1990; Fletcher et al. 1993). The  $C^3\Delta$ ,  $B^3\Pi$ , and  $X^3\Pi$  molecular constants have been improved by laser and Fourier transform spectroscopy (Gustavsson, Amiot, & Verges 1991; Amiot et al. 1995). The radiative lifetimes of the  $A^3\Phi$ ,  $B^3\Pi$ , and  $C^3\Delta$  states have been measured (Doverstal & Weijnitz 1992; Carette & Schamps 1992). Kaledin, McCord, & Heaven (1995) have determined a new value for the  $a^1\Delta-X^3\Delta$  separation by laser excitation spectroscopy of the forbidden  $C^3\Delta_a-a^1\Delta$  transition. Simard & Hackett (1991) have also improved the spectroscopic constants of the low-lying  $E^3\Pi$  state. Finally, new measurements of the chemical reaction rates of Ti atoms to form TiO molecules are available (Campbell & McClean 1993) as well as a TiO matrix isolation absorption spectrum (Williamson, Roser, & Vala 1994).

The spectroscopy of TiO dates back to the early part of this century, when Fowler (1904) matched laboratory spectra of TiO with astronomical spectra of M-type stars in the visible region. Hale, Adams, & Gale (1906) identified the green  $\alpha$  bands ( $C^3\Delta-X^3\Delta$ ) of TiO in sunspots, and the following year Hale & Adams (1907) found the red  $\gamma$  bands ( $A^3\Phi-X^3\Delta$ ) in the same source. More recently, the yellow-red  $\gamma'$  bands ( $B^3\Delta-X^3\Delta$ ) (Wöhl 1971) and the  $\beta$  bands

( $c^1\Phi-a^1\Delta$ ) (Sotirovski 1972) have also been identified in sunspots, and additional work has been performed on the  $\alpha$  and  $\gamma$  systems (Makita 1968; Weber 1971; Sotirovski 1971, 1972; Lambert & Mallia 1972; Engvold 1973). These data were used to determine temperatures and Ti isotope abundances (Lambert & Mallia 1972) in sunspots and M stars (Phillips & Davis 1987; Clegg, Lambert, & Bell 1979).

The rich TiO spectra contain several additional band systems that have been identified in the laboratory and in M-type stars. For example, Lockwood (1969, 1972, 1973) found bands of the  $\delta$  system ( $b^1\Pi-a^1\Delta$ ) and  $\phi$  system ( $b^1\Pi-d^1\Sigma^+$ ) near 1  $\mu\text{m}$  for Mira variables.

Although readily found in M stars, the near-infrared TiO bands have not been reported previously in sunspots. In this paper we have measured the 0–0 and 1–1 bands of the  $\delta$  system ( $b^1\Pi-a^1\Delta$ ) in a sunspot umbra and combined these data with new laboratory measurements to obtain improved molecular constants. In addition, a few lines of the 0–0 band of the  $\phi$  system ( $b^1\Pi-d^1\Sigma^+$ ) have been identified near 9000  $\text{cm}^{-1}$  (1.1  $\mu\text{m}$ ) in the same sunspot spectrum.

## 2. EXPERIMENTAL

## 2.1. Laboratory Observations

The emission spectrum of TiO was observed in a titanium hollow cathode lamp. The cathode was prepared by pressing a Ti rod in a hole in a copper block. The central part of the rod was then bored through to provide a 1 mm layer of Ti metal on the inside of the hollow cathode. The initial aim of this experiment was a search for the spectra of TiH and TiD in the red and near-infrared region. The lamp was operated with about 2.0 Torr of Ne and 80 mTorr of  $\text{H}_2$  or  $\text{D}_2$  at a current of 400 mA at 430 V. In these experiments, we observed complex spectra of TiH and TiD in the near-infrared near 1  $\mu\text{m}$  as well as several impurity TiO bands in the 10000–15000  $\text{cm}^{-1}$  region. The TiO bands observed in the TiD experiments were much stronger than those in the TiH experiments. Even though  $\text{O}_2$  gas was not added to the lamp, we obtained strong TiO spectra from the small amount of metal oxide found on the surface of the cathode and from oxygen-containing impurities in the system.

The spectra of TiH, TiD, and TiO were recorded using the 1 m Fourier transform spectrometer associated with the McMath-Pierce Solar Telescope of the National Solar Observatory. The spectra in the 10000–16000  $\text{cm}^{-1}$  region were recorded using Si-diode detectors, a quartz beam splitter, and OG570 filters. The spectra were recorded at a resolution of 0.02  $\text{cm}^{-1}$ , with 10 scans co-added in about 1 hr of integration.

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The spectral line positions were extracted from the observed spectra using a data reduction program called PC-DECOMP developed by J. Brault. The peak positions were determined by fitting a Voigt line shape function to each spectral feature.

In addition to the TiD bands, the final spectrum also contained Ti and Ne atomic lines. The Ne atomic lines were used for absolute wavenumber calibration using the measurements of Palmer & Engleman (1983). The TiO lines have widths of about  $0.03 \text{ cm}^{-1}$  and appear with a maximum signal-to-noise ratio of about 10:1 in the 0–0 band, so the absolute accuracy and precision of the measurements is expected to be of the order of  $\pm 0.002 \text{ cm}^{-1}$ .

## 2.2. Solar Observations

The spectrum of the ( $b^1\Pi-a^1\Delta$ ) transition of TiO has also been observed in the spectrum of a sunspot umbra. A large sunspot was observed in 1981 March with the Fourier transform spectrometer of the McMath-Pierce Solar telescope. The spectrum extended from about 9000 to 17000  $\text{cm}^{-1}$  and had an unapodized resolution of  $0.055 \text{ cm}^{-1}$ . The strongest of the TiO  $\delta$  lines are about 15% deep, about the same depth as the accompanying FeH lines (Wing, Cohen, & Brault 1977). The region of the TiO  $\delta$  lines, about 10960 to  $11250 \text{ cm}^{-1}$ , also has numerous Zeeman split atomic lines, miscellaneous weak unidentified solar lines, and many telluric lines, making it difficult to pick out more than fragments of the 0–0 and 1–1 bands. The near-infrared spectrum as a whole shows a vast number of lines, presumably mostly due to TiO, and this section containing the TiO  $\delta$  bands is the only one to our knowledge that has been measured.

## 3. DATA ANALYSIS AND DISCUSSION

The TiO bands observed in the  $10000-15000 \text{ cm}^{-1}$  spectral region with the hollow cathode source are classified into two electronic transitions customarily called the  $\gamma$  and  $\delta$  systems. The bands near  $11275 \text{ cm}^{-1}$  are due to the  $b^1\Pi-a^1\Delta$  transition ( $\delta$  system), while those in the  $12500-15000 \text{ cm}^{-1}$  belong to the  $A^3\Phi-X^3\Delta$  transition ( $\gamma$  system). The ( $b^1\Pi-a^1\Delta$ ) bands are weaker in intensity than the  $A^3\Phi-X^3\Delta$  bands, and only the 0–0 and 1–1 bands of the  $b^1\Pi-a^1\Delta$  transition were identified in our hollow cathode and sunspot spectra. In the hollow cathode spectrum, the  $A^3\Phi-X^3\Delta$  transition consists of  $\Delta v = 0$  and  $\pm 1$  sequence bands involving vibrational levels up to about  $v = 3$  in the ground and excited state.

In the present paper, we report on the analysis of the  $b^1\Pi-a^1\Delta$  transition of TiO using both laboratory and solar measurements. The TiO lines were identified easily in the solar spectrum by the characteristic doublet pattern caused by the  $\Lambda$ -doubling in the  $b^1\Pi$  state. A part of the laboratory spectrum of the 0–0 band is presented in Figure 1, along with the corresponding sunspot spectrum. There is a very good correspondence between the molecular features of the two spectra, confirming the presence of the  $\delta$  transition in the sunspot data. A number of high- $J$  rotational lines were identified in the solar spectrum using predictions based on the fitted constants obtained using the laboratory data. Since the excitation temperature of the sunspot spectrum is high, rotational lines with  $J$  up to 108 could be identified. The two sets of measurements were combined in order to obtain improved molecular constants for the ground and excited states. Since we have observed only the 0–0 and 1–1

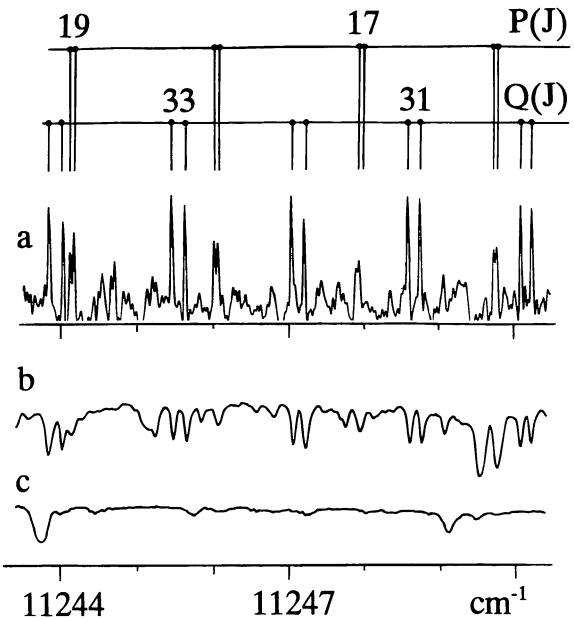


FIG. 1.—A part of the spectrum of the 0–0 band of the  $\delta$  system ( $b^1\Pi-a^1\Delta$ ) of TiO. (a) Laboratory spectrum; (b) sunspot spectrum; (c) photospheric spectrum.

vibrational bands, we have fixed the lower state  $\Delta G(1/2)$  vibrational interval to  $1009.231 \text{ cm}^{-1}$  from the work of Brandes & Galehouse (1985) on the  $f^1\Delta-a^1\Delta$  transition.

In order to determine the rotational constants, the observed line positions were fitted with the following customary energy level expression for  $^1\Pi$  and  $^1\Delta$  states:

$$F(J) = T_v + B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3 \pm 1/2\{q_v J(J+1) + q_{Dv} [J(J+1)]^2\}.$$

The spectrum of the 1–1 band is much weaker in intensity than the 0–0 band. The wavenumbers of the observed transitions are provided in Table 1. For those lines that are common to both laboratory and sunspot spectra, only the laboratory measurements are provided in this table. The constants obtained from this fit are provided in Table 2. The combination of low-temperature hollow cathode data and high-temperature solar data has resulted in improved molecular constants.

There have been three previous measurements of the 0–0 band of the  $\delta$  system of TiO (Phillips 1950; Linton & Singhal 1974; Davis, Littleton, & Phillips), but our data set is in general more precise and more extensive. The 1–1 band of the  $b^1\Pi-a^1\Delta$  transition has not been reported previously, although other transitions connecting to  $v = 1$  of the  $b^1\Pi$  state (Galehouse, Brault, & Davis 1980) and  $v = 1$  of the  $a^1\Delta$  state (Brandes & Galehouse 1985) are known. Table 2 provides a comparison of our constants with some of the previous spectroscopic constants.

Further into the infrared, the sunspot spectrum shows a few lines of the  $Q$ -branch of the 0–0 band of the  $\phi$  system ( $b^1\Pi-d^1\Sigma^+$ ) of TiO (Brandes & Galehouse 1985). Although these lines are very weak with maximum absorptions of about 2%, they are definitely present.

The TiO and FeH (Wing et al. 1977) lines dominate the near-infrared spectra of the umbra of both sunspots and M-type stars. The VO molecule is also prominent in M-type stars, but we could not find clear evidence for it in the spectra of sunspot umbrae.







TABLE 2  
SPECTROSCOPIC CONSTANTS (in cm<sup>-1</sup>) OF THE  $a^1\Delta$  AND  $b^1\Pi$  STATES OF TiO

CONSTANT	$a^1\Delta$		$b^1\Pi$		Previous Values <sup>b</sup>	
	Present Values		Present Values			
	$v = 0$	$v = 1$	$v = 0$	$v = 1$		
$T_v$	0.0 <sup>c</sup>	1009.231 <sup>d</sup>	0.0	1009.231(1)	11272.75499(39)	
$B_v$	0.5362275(47) <sup>e</sup>	0.5339238(12)	0.536168(20)	0.533227(13)	12183.92710(47)	
$10^7 \times D_v$	5.9978(51)	5.946(31)	5.93(76)	5.971(46)	0.5120246(47)	
$10^{14} \times H_v$	-7.70(67)	...	...	...	6.353(31)	
$10^4 \times q_v$	...	...	...	...	6.3903(51)	
$10^9 \times q_{Dv}$	...	...	...	...	...	

<sup>a</sup> Constants of Brandes & Galehouse 1985.

<sup>b</sup> Constants of Davis et al. 1986.

<sup>c</sup> Fixed value.

<sup>d</sup> Fixed to the value of Brandes & Galehouse 1985.

<sup>e</sup> One standard deviation in the last digits.

Titanium has a relatively high cosmic abundance, and Ti atomic lines are prominent in solar and stellar spectra. Titanium ( $\text{Ti}^+$ ) atomic lines (but not Ti or TiO) can also be found in absorption in diffuse molecular clouds (Black 1987). Titanium is heavily depleted in interstellar clouds, and TiO has not been found in dark clouds (Millar et al. 1987; Churchwell et al. 1980). Titanium, however, has a vapor pressure of 1 Torr at  $2132^\circ\text{C}$ , and TiO has a very strong bond with a dissociation energy  $D_0 = 6.4 \text{ eV}$  (Huber & Herzberg 1979), so that TiO forms readily in stellar atmospheres and sunspots. In addition to these favorable thermodynamic considerations, titanium atoms react rapidly

with any oxygen-containing species to form TiO (Campbell & McLean 1993).

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