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THE ROTATIONAL SPECTRUM OF TiO_2

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ABSTRACT

The rotational spectrum of titanium dioxide (TiO_2) has been detected by laser-ablation molecular beam Fourier transform microwave spectroscopy. Thirteen *b*-type rotational transitions up to $J = 9$ and $K_a = 4$ were measured for the most abundant isotopic species $^{48}TiO_2$ in the frequency range 7–42 GHz with accuracies of 1–10 kHz, allowing for the precise determination of rotational and centrifugal distortion parameters. In addition, eight and six rotational transitions of the rare isotopic species $^{46}TiO_2$ and $^{50}TiO_2$, respectively, have been recorded in the same frequency range. From the derived spectroscopic parameters, rest frequencies of TiO_2 can now be calculated to better than 1 km s^{-1} in equivalent radial velocity up to fairly high J and K_a at millimeter wavelengths, enabling radioastronomical searches for this stable, highly polar transition metal dioxide in space. Preliminary results of two searches for TiO_2 in space are presented.

Subject headings: ISM: molecules — line: identification — molecular data — radio lines: general — stars: AGB and post-AGB

1. INTRODUCTION

Titanium is one of the more abundant transition metals in space, with an abundance relative to hydrogen of $\sim 9 \times 10^{-8}$ in the solar system (Anders & Grevesse 1989). It has been detected in molecular form in the gas phase as TiO and TiH in stellar atmospheres of cool M-type stars, (e.g., Clegg et al. 1979; Yerle 1979). Electronic transitions of TiO are so prominent in M and S stars, that they dominate large parts of their optical spectra and are even used for stellar classification of cool stars. Moreover, the large variations in optical luminosity of Mira stars are most likely caused by to molecular absorption of TiO and changes in its formation in the stellar atmosphere (Reid & Goldston 2002).

Model calculations indicate that titanium dioxide, TiO_2, is readily formed in stellar atmospheres where TiO is found, but at an abundance that is only around an order of magnitude lower abundance than that of TiO (Sharp & Huebner 1990). Both species, as well as atomic Ti, are expected to become depleted into grains starting at temperatures as high as 1640 K because of their highly refractive nature and the formation of $CaTiO_3$. The very stable TiO_2 is considered as one of the primary condensates for grain growth in O-rich AGB stars (Jeong et al. 2003). However, the temperature dependence of TiO and TiO_2 depletion is poorly known. Observations of the electronic spectrum of TiO toward the M-type peculiar red supergiant VY Canis Majoris indicate rotational temperatures as low as 600 K, and possibly even lower (Phillips & Davis 1987). With sufficient amounts of TiO, and presumably TiO_2, still in the gas phase at these low temperatures, these species may be detectable by radioastronomical observations in cooler regions of stellar atmospheres or farther out in circumstellar shells.

The interstellar medium (ISM) is enriched with heavy elements in the form of atoms, molecules, and dust via outflows of AGB stars, and to a lesser degree through supernovae and outflows from early-type stars. It has been suggested that the composition of interstellar dust grains resembles that of O-rich stellar envelopes (Turner 1991). If so, it is not surprising that refractory elements in general, and titanium in particular, are found to be highly depleted in the ISM (Jenkins 2004). Jenkins (1987) states depletion factors of 10–500 for atomic titanium relative to its solar abundance in the warm and cold diffuse medium, respectively. A large amount of titanium might already enter the ISM in a condensed form, i.e., depleted onto dust grains formed in circumstellar shells, and further accretion of atomic titanium onto grains might occur in the colder interstellar gas. There exist, however, no observational evidence yet if atomic titanium is indeed completely locked up in grains, or if the depletion is caused in part by the formation of Ti-containing molecules, like TiO or TiO_2. To date there is no definitive radioastronomical evidence of TiO toward stellar atmospheres or in molecular clouds (Churchwell et al. 1980; Millar et al. 1987; Menten 2003). Although the failure to find TiO in the millimeter band may indicate that Ti has indeed been depleted into grains, it is possible that this element is present in the gas phase, but in a molecular form other than TiO—e.g., as TiO_2. Furthermore, a detectable amount of Ti in the form of the highly stable TiO_2 may be released from grains in shocked regions of molecular clouds.

While titanium monoxide has been extensively studied in the optical (e.g., Kobayashi et al. 2002) and at high-resolution in the millimeter band (Steimle et al. 1990; Namiki et al. 1998), and the chemically and structurally related dioxides ZrO_2 and HfO_2 have been investigated at high-resolution in the gas phase (Brugh et al. 1999; Lesarri et al. 2002), spectroscopic work on TiO_2 is scarce, and that performed to date has only been at low resolution. In those studies, TiO_2 was generated either by vaporization (Weltner & McLeod 1965; McIntyre et al. 1971) or laser ablation (Chertihin & Andrews 1995), and then isolated in solid rare gas matrices, where it was studied by visible and infrared (IR) spectroscopy (Weltner & McLeod 1965; McIntyre et al. 1971) or by IR spectroscopy only (Chertihin & Andrews 1995). These studies confirmed a closed-shell $^1A_1$ electronic ground state for TiO_2 with a bent C_{2v} geometry, as predicted by ab initio calculations (Ramana & Phillips 1988); a bond angle of $113^\circ \pm 5^\circ$ was derived from the $^{16}O/^{18}O$ isotopic shift of the ν_3 asymmetric stretching

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mode. The only gas phase investigation of TiO_2 is an IR spectrum at high temperatures (DeVore & Gallaher 1983) and photoelectron spectroscopy of TiO_2^- (Wu & Wang 1997). None have been done at high enough spectral resolution to determine the rotational constants of TiO_2 and the precise geometrical structure of this molecule.

Here we report high-resolution rotational spectroscopy of TiO_2 produced by laser ablation. In addition to the normal isotopic species $^{48}TiO_2$, several rotational lines of $^{46}TiO_2$ and $^{50}TiO_2$ have also been observed in natural abundance, which provides definitive evidence for the composition and structure of the new molecule. With the precise radio frequencies provided here, astronomical searches for this highly polar (6.7 D, from our ab initio calculations) transition metal oxide have been started, and first, preliminary, results will be described. A more detailed account of our laboratory investigations, including detection of several other rare isotopic species of Ti with hyperfine structure ($^{47}TiO_2$, $^{49}TiO_2$), and of $Ti\,^{18}O_2$ and $^{16}OTi\,^{18}O$, and a more detailed discussion of the structural properties of TiO_2 will be given elsewhere.

2. EXPERIMENTAL SETUP

Rotational transitions of TiO_2 were measured in the frequency range 7–42 GHz with a molecular beam Fourier transform microwave (FTM) spectrometer described in detail by McCarthy et al. (2000). TiO_2 was produced by laser ablation, using a newly constructed source (Brünken et al. 2006) for producing refractory molecules in the gas phase. In our source, as in similar ones (Smalley 1983; Suenram et al. 1990; Hensel et al. 1993) the fundamental (1064 nm) or second harmonic (532 nm) output of a Q-switched Nd:Yag laser (Minilite, Continuum) is focused on a rotating and translating target rod. The ablated material is seeded in an inert buffer gas (Ne) via a commercial solenoid valve (General Valve), and is then cooled rotationally to a few Kelvin as the plasma expands adiabatically into a large vacuum chamber; gas flow rates of 15–25 cm^3 $minute^{-1}$ at standard temperature and pressure were typical at a pressure of 250 kPa behind the nozzle. The ablation laser is synchronized with the gas pulse (duration 300–400 μs) and the excitation microwave pulse at a repetition rate of 6 Hz; the strength of the TiO_2 lines was found to be quite sensitive to the delays between these three pulses.

Measurements on TiO_2 were done with two different target rods. The first consisted of microcrystalline TiO_2 powder (99.9+%; Sigma Aldrich), which was pressed into a stable rod (Banser et al. 2006) by using a small amount of commercial binder (methyl cellulose, <4%). The strongest lines were observed with the ablation laser operated on the fundamental at maximum output power ($\sim$28 mJ $pulse^{-1}$) and a laser spot size on the rod of $\sim$400 μm. The addition of molecular oxygen (4%) to the carrier gas was found to increase the strength of the lines by a factor of 2–3. Rotational lines of comparable strength were also obtained by ablating a pure Ti rod (99.7% metals basis; Alfa Aesar) in the presence of 2% O_2 in Ne.

The search for rotational lines of TiO_2 was facilitated by ab initio calculations at the B3LYP/cc-pVTZ level of theory done with Gaussian 98 (Frisch et al. 1998). The basis set is included in the basis set library of the program for O; the Ti basis set was taken from Bauschlicher (1999). The calculated equilibrium bond length, bond angle and dipole moment of TiO_2 are 1.641 Å, 112.0°, and 6.7 D, respectively; $A_e = 31242$, $B_e = 8540$, and $C_e = 6707$ MHz were obtained as equilibrium rotational constants for $^{48}TiO_2$. The obtained structure agrees well with previous DFT calculations (Walsh et al. 1999; Grein 2007).

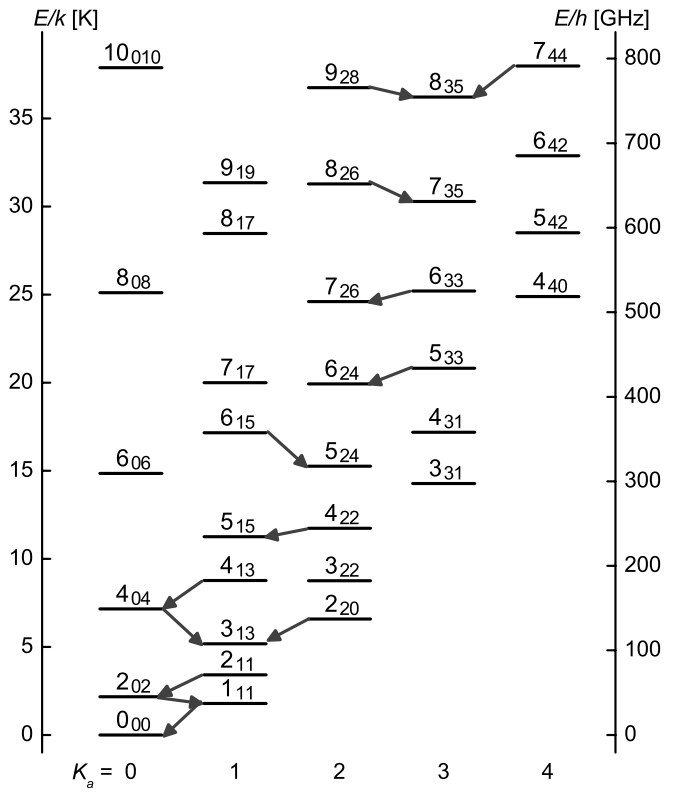

FIG. 1.—Portion of the rotational energy level diagram of TiO_2, showing transitions measured for the main isotopic species, $^{48}TiO_2$.

3. MEASUREMENTS AND ANALYSIS

TiO_2 is a closed-shell asymmetric rotor fairly close to the prolate limit ($\kappa = -0.84$) with a large permanent dipole moment along the b-inertial axis. The two equivalent oxygen atoms are bosons, so that half of the rotational levels—those with $K_a + K_c$ odd, are missing. Nevertheless, many b-type rotational transitions were accessible in the centimeter-wave band with our FTM spectrometer. A portion of the rotational energy level diagram of $^{48}TiO_2$, indicating transitions that have been measured, is shown in Figure 1.

Initial searches for the $J_{K_a,K_c} = 1_{1,1}$–$0_{0,0}$ and $2_{1,1}$–$2_{0,2}$ transitions were undertaken near 37.5 and 26 GHz, respectively, on the basis of theoretical predictions. The experimental conditions used were those that optimize microwave transitions of ZrO_2 (Brugh et al. [1999], using a commercially available ZrO_2 target rod [MgO stabilized; Ortech Inc.]), because the lowest frequency transitions of TiO ($\sim$63.3 GHz) lie well above of the frequency ceiling of our microwave spectrometer. In both searches, a single, isolated line quite close in frequency (<2%) to the theoretical prediction, was found. Subsequent searches for the corresponding lines of the less abundant $^{46}TiO_2$ and $^{50}TiO_2$ isotopic species yielded lines at the expected isotopic shifts, with intensities in good agreement with those expected from the natural abundance of the Ti isotopes (8.3% for ^{46}Ti, 73.7% for ^{48}Ti, 5.2% for ^{50}Ti). A third transition, $2_{0,2}$–$1_{1,1}$, was found rather quickly for each of these three isotopic species (see Fig. 2) by assuming that the inertial defect $\Delta = I_c - I_b - I_a$ of TiO_2 was slightly smaller than those of the related ZrO_2 (0.23 amu Å^2; Brugh et al. 1999) and HfO_2 (0.24 amu Å^2; Lesarri et al. 2002) molecules.

In all, 13 transitions of the normal species $^{48}TiO_2$ with rotational quantum numbers up to $J = 9$, $K_a = 4$ (arrows in Fig. 1) and $E = 26$ cm^{-1} have been measured to an accuracy of 2–10 kHz.

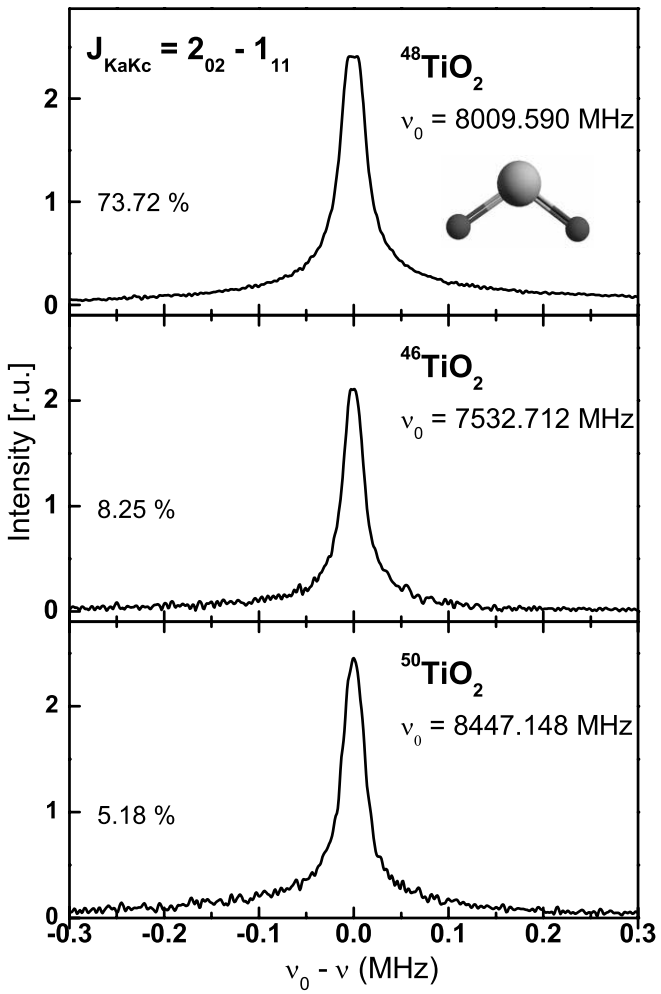

FIG. 2.—$J_{K_aK_c} = 2_{02}$–1_{11} rotational transition for three ($^{48}TiO_2$ $^{46}TiO_2$, and $^{50}TiO_2$) isotopic species of TiO_2 recorded in natural abundance. The intensity has been scaled according to the isotopic abundance. The integration time is 30 s for the main isotopomer (*top*) and ~8 minutes for the two rarer isotopomers (bottom).

For the rarer isotopic species $^{46}TiO_2$ and $^{50}TiO_2$, eight and six transitions, respectively, have been measured in natural abundance. A complete list of the measured lines is given in Table 1. The rotational and leading centrifugal distortion constants from a standard *A*-reduced Hamiltonian have been fitted to the data using Pickett's SPFIT/ SPCAT program suite (Pickett 1991). The ratios of the quartic distortion constants were constrained to those obtained by empirical force field calculations, while the ratios of the sextic parameters Φ_K were taken from ab initio calculations. The best-fit spectroscopic parameters are summarized in Table 2.

There can be no doubt that the observed lines arise from TiO_2. The fact that the species is generated by laser ablation of TiO_2 or of Ti and subsequent reaction with O_2 indicates that we are observing a titanium oxide. The derived spectroscopic parameters are in good agreement with those calculated ab initio for TiO_2 as do the ground state effective bond length and bond angle of 1.651 Å, 111.57°, derived from the rotational constants in Table 2 with the theoretical equilibrium values. No Zeeman splitting was observed in the presence of a magnetic field, confirming a closed-shell molecule. The small positive inertial defect of 0.202 amu Å^2 is consistent with a fairly rigid planar molecule, the spin statistics imply a C_2 symmetry axis and two identical bosons in the molecule. Furthermore, we were able to observe the less abundant isotopic species at the expected isotopic shifts with intensities expected from the abundances of naturally occurring ^{46}Ti, ^{47}Ti, ^{48}Ti, ^{49}Ti, and ^{50}Ti, and with resolved hyperfine structure for the ^{47}Ti and ^{49}Ti species.

4. DISCUSSION AND CONCLUSION

With the present data the rotational spectrum of TiO_2 can be predicted to about 1 km s^{-1} in equivalent radial velocity over the entire radio band (<300 GHz), for energy levels with $J'' \leq 20$, $K_a \leq 6$ and lower state energies as high as 100 cm^{-1}, allowing for sensitive astronomical searches in circumstellar shells and molecular clouds. Such predictions will be available in the catalog section of the Cologne Database for Molecular Spectroscopy[4] (CDMS; Müller et al. 2001, 2005).

Oxygen-rich circumstellar shells, where strong optical absorption of TiO, as well as mm-wavelength emission lines of molecular species like SiO, SO_2, CO, and HCN, are found, may be the best places to find TiO_2. In 2006 December we undertook a

[4] See http://www.astro.uni-koeln.de/vorhersagen.

TABLE 1
MEASURED ROTATIONAL TRANSITIONS OF $^{48}TiO_2$, $^{46}TiO_2$, AND $^{50}TiO_2$

	$^{48}TiO_2$			$^{46}TiO_2$			$^{50}TiO_2$		
$J_{K_aK_c}$ =	Frequency (MHz)	Uncertainty (kHz)	$O-C$[a] (kHz)	Frequency (MHz)	Uncertainty (kHz)	$O-C$[a] (kHz)	Frequency (MHz)	Uncertainty (kHz)	$O-C$[a] (kHz)
1_{11}–0_{00}	37133.5950	3.0	−2.3	37689.1324	3.0	2.5	36621.4683	3.0	−1.4
2_{11}–2_{02}	25877.3012	2.0	1.7	26353.4084	3.0	0.7	25440.4435	4.0	−2.2
4_{13}–4_{04}	33618.4945	3.0	1.5	33950.7147	3.0	−2.8	33319.4690	3.0	0.6
2_{02}–1_{11}	8009.5912	2.0	1.0	7532.7114	1.0	−0.2	8447.1487	1.0	0.2
4_{04}–3_{13}	41342.1296	5.0	7.9						
2_{20}–3_{13}	29423.3712	2.0	−2.3	30822.9231	5.0	−2.1	28139.7474	2.0	0.9
4_{22}–5_{15}	9741.6774	3.0	1.1	10882.5502	5.0	6.3	8705.8141	4.0	−1.7
6_{15}–5_{24}	39545.6944	2.0	−1.5	37955.5276	3.0	0.3			
5_{33}–6_{24}	18473.8258	3.0	0.5						
6_{33}–7_{26}	12465.6519	3.0	2.1	14728.1420	5.0	−3.5			
8_{26}–7_{35}	20687.2500	3.0	1.3						
9_{28}–8_{35}	11253.1454	3.0	0.7						
7_{44}–8_{35}	36774.5253	10.0	1.1						

[a] Observed frequency minus frequency calculated from the best-fit set of spectroscopic parameters in Table 2.

TABLE 2
SPECTROSCOPIC PARAMETERS OF TiO_2 (IN MHz)

Parameter	$^{48}TiO_2$	$^{46}TiO_2$	$^{50}TiO_2$
A	30520.541 48 (165)	31051.480 24 (193)	30031.664 25 (175)
B	8471.758 38 (54)	8471.564 74 (54)	8471.935 46 (52)
C	6613.587 31 (47)	6638.200 85 (53)	6590.319 09 (49)
$\Delta_J \times 10^3$	8.363 2 (123)	8.394 6 (124)	8.334 2 (123)
$\Delta_{JK} \times 10^3$	−94.397 (110)	−96.101 (112)	−92.464 (107)
$\Delta_K \times 10^3$	732.445 (151)	757.180 (156)	710.028 (147)
$\delta_J \times 10^3$	2.981 5 (40)	2.965 7 (40)	2.995 9 (40)
$\delta_K \times 10^3$	16.819 (141)	17.304 (144)	16.365 (137)
$\Phi_K \times 10^6$	39.3 (85)	41.3 (89)	37.5 (81)

NOTE.—Numbers in parentheses are one standard deviation in units of the least significant figures.

search for TiO_2 with the IRAM 30 m radio telescope[5] toward the red supergiant VY CMa, the high mass-loss Mira variable IK Tau (both of M spectral type) and the S-star χ Cyg. Note that the former two objects are oxygen-rich in which the O abundance, [O], is larger than the carbon abundance, [C]. In contrast, in S-type stars [O] $\approx$ [C]. Apart from the ubiquitous CO, χ Cyg shows prominent mm-wavelength SiO emission. In addition, these sources have high mass loss rates and prominent absorption features of TiO in the visible. The search was based on a number of transitions in the frequency range 100–260 GHz that probe different excitation energies, since it is difficult to estimate the excitation conditions for this molecule in these sources. No lines of TiO_2 where detected toward IK Tau and χ Cyg, but two emission features at transition frequencies of TiO_2 were detected toward VY CMa. Whereas the $16_{0,16}$–$15_{1,15}$ transition at 218.1 GHz is barely detected above the noise, there is a clear 3 σ detection of a feature at the frequency (255.9 GHz) of the $18_{1,17}$–$17_{2,16}$ transition. Overlap of this possible TiO_2 line with that of an unknown species or a high velocity component of SO_2, however, cannot be ruled out entirely at this point. Both tentatively detected transitions have high upper state energies (63.4 and 86.6 cm^{-1}, respectively), and no lines with lower energies were detected, indicating, if correct, an excitation temperature for TiO_2 above 300 K. Further measurements of similarly high energetic lines are required.

Very recently, we also searched for TiO_2 toward the high-mass star-forming region Sgr B2 (M). Several other species containing refractory elements have been observed toward this source, many in absorption in their lowest energy transitions against the strong continuum of Sgr B2 (M) (e.g., SiO, SiS Peng et al. 1995; Dickinson & Kuiper 1981). It is the only interstellar source where SiN has been detected (Schilke et al. 2003), or where a transition metal (FeO) has tentatively been detected by its radio spectrum to date (Walmsley et al. 2002; Furuya et al. 2003). We used the Australian Telescope Compact Array[6] in its compact (H75) configuration to search for the ground state $1_{1,1}$–$0_{0,0}$ transition of TiO_2 at 37.133 GHz. A weak absorption feature ($\tau = 0.0008$) was detected at this frequency during observations in 2007 October. However, an unambiguous detection toward this moderately line-rich source requires the observation of additional transitions at similar energies. Further radioastronomical observations are planned, and detailed accounts of the astronomical searches for TiO_2 and TiO will be given.

Other molecules containing transition metals may be detectable with the present laboratory techniques. Obvious candidates are the isoelectronic and structurally similar titanium disulfide TiS_2 and the mixed oxide sulfide of titanium, OTiS. Quantum chemical calculations predict dipole moments comparable to that of TiO_2 for these closed-shell species (H. S. P. Müller 2007, private communication). Both are heavier than TiO_2, so that a larger number of rotational transitions are accessible with our microwave spectrometer; they might be produced by either ablating a pure sample of TiS_2 or of Ti in the presence of CS_2, H_2S or OCS.

With an efficient production mechanism for TiO_2 now established, it is feasible to measure its gas-phase electronic spectrum for the first time. The transition energy of 2.4 eV of the $1\ ^1B_2 \leftarrow X\ ^1A_1$ transition of TiO_2 is fairly well constrained by matrix spectroscopy (Weltner & McLeod 1965; McIntyre et al. 1971) and by theoretical calculations, which also yield vibrational frequencies for the ground and excited electronic states (Grein 2007). With a calculated oscillator strength of 0.014 (McIntyre et al. 1971) this transition should be readily detectable with present sensitive laser techniques such as REMPI or CRD. Such investigations might yield the optical detection of TiO_2 in O-rich stellar atmospheres, and clarify its role in dust formation in circumstellar envelopes. It should be noted that Wallerstein & Gonzalez (2001) find an unidentified emission feature toward the M supergiant VY Canis Majoris at 530.538 nm, very close to that expected for the above transition of TiO_2.

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