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Elvire De Beck[1], Wouter Vlemmings[1], Sébastien Muller[1], John H. Black[1], Eamon O'Gorman[1], Anita M. S. Richards[2], Alain Baudry[3,4], Matthias Maercker[1], Leen Decin[5,6] and Elizabeth M. Humphreys[7]

[1] Department of Earth and Space Sciences, Chalmers University of Technology, Onsala Space Observatory, 43992 Onsala, Sweden

[2] Jodrell Bank Centre for Astrophysics, School of Physics and Astronomy, University of Manchester, Manchester M13 9PL, UK

[3] Université de Bordeaux, LAB, UMR 5804, 33270 Floirac, France

[4] CNRS, LAB, UMR 5804, 33270 Floirac, France

[5] Instituut voor Sterrenkunde, Katholieke Universiteit Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium

[6] Sterrenkundig Instituut Anton Pannekoek, University of Amsterdam, Science Park 904, 1098 Amsterdam, The Netherlands

[7] European Southern Observatory, Karl-Schwarzschild-Strae 2, 85748 Garching, Germany

E-mail: [1] elvire.debeck@chalmers.se

Abstract. Titanium dioxide, TiO$_2$, is a refractory species that could play a crucial role in the dust-condensation sequence around oxygen-rich evolved stars. We present and discuss the detections of 15 emission lines of TiO$_2$ with ALMA in the complex environment of the red supergiant VY CMa. The observations reveal a highly clumpy, anisotropic outflow in which the TiO$_2$ emission likely traces gas exposed to the stellar radiation field. We find evidence for a roughly east-west oriented, accelerating bipolar-like structure, of which the blue component runs into and breaks up around a solid continuum component. We see a distinct tail to the south-west for some transitions, consistent with features seen in the optical and near-infrared. We find that a significant fraction of TiO$_2$ remains in the gas phase outside the dust-formation zone and suggest that this species might play only a minor role in the dust-condensation process around extreme oxygen-rich evolved stars like VY CMa.

1. Introduction

The driving mechanism of the winds of oxygen-rich evolved stars is not well understood. Radiation pressure on dust through absorption and scattering of stellar light is thought to play a crucial role. The size and chemical composition of dust grains are critical to the efficiency of these processes. It is hence essential to address which gas-phase species provide the primary seeds for the dust-formation sequence in oxygen-rich outflows. TiO$_2$ is considered an important seed refractory species with possibly higher nucleation rates than SiO [1, 2]. Detections of presolar TiO$_2$ grains [3] support the importance of this species in the dust-condensation sequence.

Emission from gas phase TiO$_2$ has to date only been detected towards VY CMa [4, 5, 6], an extreme red supergiant at 1.2 kpc distance [7]. VY CMa's circumstellar environment exhibits a high degree of morphological complexity, from optical to radio wavelengths and on spatial scales from a few to several thousands of AU [6, 8, 9, 10, 11, 12, 13]. ALMA observations spatially resolved the H$_2$O maser emission and the submillimeter continuum emission, leading to a most

accurate determination of the stellar position [14] and the discovery of a bright continuum component south-east of the star [15].

2. Observations

We retrieved ALMA science verification data on VY CMa from the ALMA archives. The observations, data calibration and reduction are described by [14]. An overview of the spectral coverage and representative rms noise values for the six spectral windows in ALMA's band 7 ($\sim 0.9\,\mathrm{mm}$; $\sim 320\,\mathrm{GHz}$) and one in band 9 ($\sim 0.45\,\mathrm{mm}$; $\sim 660\,\mathrm{GHz}$) is given by [4]. With projected baselines of $14\,\mathrm{m}$ up to $2.7\,\mathrm{km}$, the spatial resolution at $\sim 320\,\mathrm{GHz}$ and $658\,\mathrm{GHz}$ is $\sim 0.2''$ and $\sim 0.1''$, respectively, and the maximum recoverable scales are $8.3''$ and $4.0''$.

3. Results

We analysed spectra extracted for a $1''$ diameter region around the stellar position, since no TiO_2 emission is detected beyond this aperture. We detect 15 lines with upper-level energies E_{up}/k in the range $48-676\,\mathrm{K}$ and signal-to-noise ratios $S/N \approx 5-17$ at velocity resolutions $0.9-7.6\,\mathrm{km\,s^{-1}}$ (table 1, figure 1). Of the 15 lines of TiO_2 detected with ALMA, only 2 were detected with SMA, owing to a ~ 10 times lower noise level in the ALMA data.

The TiO_2 emission is for the first time spatially resolved in the ALMA observations and shows a high level of morphological complexity, described in detail by [4]. The TiO_2 emission traces multiple wind components, as seen in figure 2. We find a red-shifted outflow to the west and a blue-shifted outflow to the east. At increasingly blue-shifted velocities the emission moves towards the bright clump C south-east of the star and then appears to curve and break up around it with the northern peak brighter than the southern one. With the clear exception of this interaction of the TiO_2 gas with C, the west and east outflows seem roughly symmetric around the star and aligned with the axis connecting the star and C. We rule out an equatorially enhanced environment such as a disk or ring, based on the spatial distribution of the TiO_2 emission at different velocities. We rather suggest an accelerating bipolar-like outflow at lower densities. We also find a predominantly blue-shifted south-west outflow, approximately perpendicular to the axis connecting the star and C, connecting the star and the south-west clump, a feature detected in the mid-infrared [11].

Whereas the H_2O maser emission in the "valley" between the star and C implies that C is

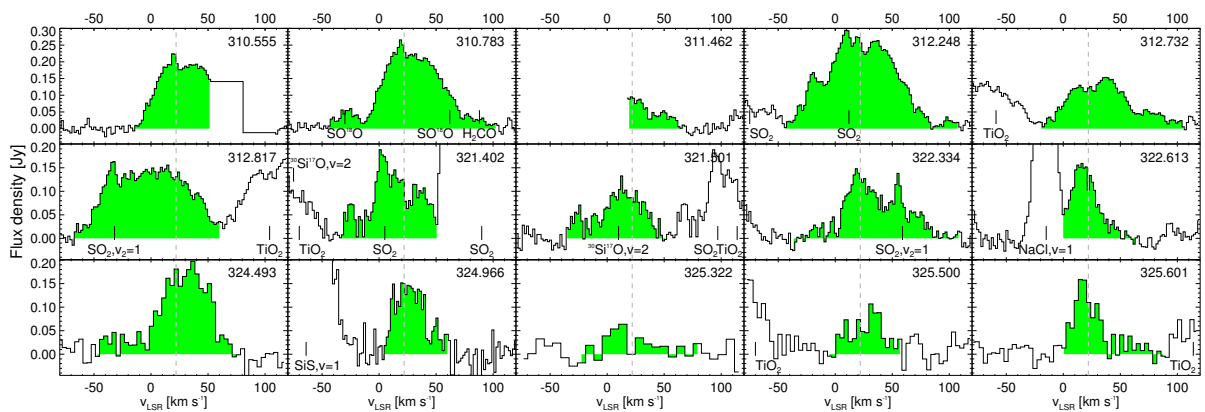**Figure 1.** TiO_2 spectra extracted for a $1''$ diameter aperture around the stellar position. The vertical dashed lines indicate the stellar v_{LSR} of $22\,\mathrm{km\,s^{-1}}$, the shaded areas the v_{LSR}-ranges from table 1. We indicated (tentative) identifications of species other than TiO_2 in the panels.

Table 1. Overview of detected TiO_2 lines as detected in the spectrum extracted in a $1''$ diameter aperture centred on the star. Columns list transition, rest frequency, upper-level energy, minimum and maximum v_{LSR} reached, velocity resolution and rms noise at which the identification was made, and peak and integrated flux.

| Transition $J'_{K'_a,K'_c} - J_{K_a,K_c}$	ν_{lab} (MHz)	E_{up}/k (K)	v_{min} (km s^{-1})	v_{max} (km s^{-1})	Δv (km s^{-1})	Rms (mJy)	Peak (Jy)	I (Jy km s^{-1})
$22(1,21) - 21(2,20)$	310554.735	180.5	-15.2	51.3	1.0	16	0.22	9.57
$23(1,23) - 22(0,22)$	310782.713	182.4	-43.9	102.3	1.0	16	0.27	15.28
$40(8,32) - 39(9,31)$	311462.082	675.9	19.4	66.7	1.9	10	0.10	2.31
$7(5,3) - 6(4,2)$	312248.341	47.9	-43.7	80.96	1.9	16	0.29	20.32
$10(4,6) - 9(3,7)$	312732.066	57.7	-19.4	105.1	1.9	16	0.15	9.43
$30(3,27) - 30(2,28)$	312816.809	354.4	-68.2	60.0	1.9	16	0.16	12.98
$11(4,8) - 10(3,7)$	321401.936	65.7	-33.9	50.5	0.9	24	0.19	7.24
$28(2,26) - 28(1,27)$	321501.043	298.8	-35.0	51.2	0.9	24	0.13	4.76
$35(8,28) - 35(7,29)$	322333.594	532.4	-36.4	108.1	1.0	19	0.15	7.03
$33(8,26) - 33(7,27)$	322612.696	481.4	-0.1	63.9	1.0	18	0.16	4.18
$23(2,22) - 22(1,21)$	324492.930	196.1	-47.9	79.4	1.9	29	0.21	9.64
$37(8,30) - 37(7,31)$	324965.693	586.5	3.6	59.8	1.9	30	0.15	4.92
$26(1,25) - 26(0,26)$	325322.035	246.5	-25.2	81.8	7.6	21	0.11	1.85
$26(4,22) - 25(5,21)$	325500.415	281.5	-7.7	55.7	3.8	28	0.13	2.75
$28(8,20) - 28(7,21)$	325600.792	367.0	-0.4	90.2	3.8	28	0.18	3.89
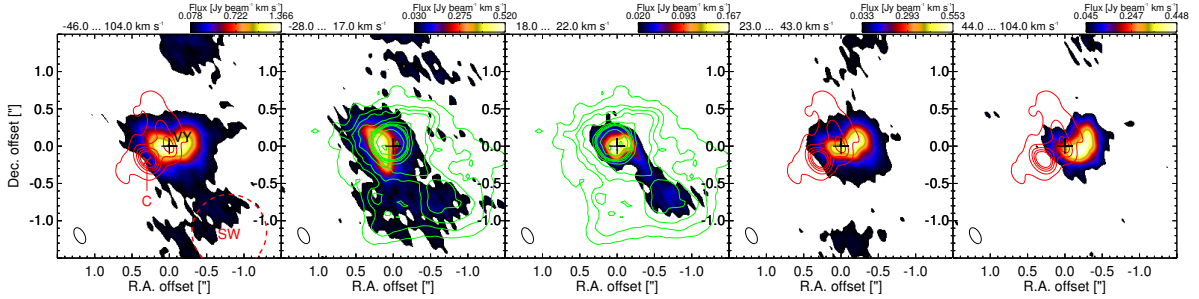
Figure 2. TiO_2 morphology. Colour maps of emission at $310.78\,GHz$ integrated over the v_{LSR}-ranges indicated at the top left of each panel, cut off at 3σ. Red contours (1st, 4th, and 5th panel) show the $321\,GHz$ continuum at $[3, 20, 40, 60, 80]\sigma$; green contours (2nd and 3rd panel) show HST emission at $[3, 5, 7, 10, 20, 30, 40, 50, 100, 200]\sigma$ [12]. In the 1st panel we marked the position of the star ($+$, VY; black) and of the continuum component (x, C; red) to the southeast [14, 15], and the position and approximate extent of the south-west clump (SW, dashed $1''$ diameter circle; red) [11]. The apparent north-south emission is thought to arise from dynamic-range limitations in the peak channels.

close to or in the plane of the sky [14], the observations suggest that the TiO_2 gas breaks up around C while moving towards the observer, placing C "at least partially" in front of the plane of the sky. It is therefore likely that the H_2O masers and the TiO_2 emission probe parts of the outflow east of the star with different physical properties. Whereas the masers are probably excited through shocks at high densities [14], TiO_2 is more likely excited through radiation, at lower outflow densities (see below). In the denser regions, TiO_2 might not be excited and/or it might be efficiently depleted from the gas phase. The latter is, however, less likely (see below). We therefore suggest that TiO_2 traces the blue-shifted wind to the east with lower densities

which runs into and curves around C.

From a rotational-diagram analysis we derive a column density $N_{\rm col} = 5.65 \pm 1.33 \times 10^{15}\,{\rm cm}^{-2}$ and a rotational temperature $T_{\rm rot} = 198.0 \pm 28.5\,{\rm K}$, in agreement with [5], although the kinetic temperature in the excitation region of TiO_2 varies from more than $1000\,{\rm K}$ down to $\sim 100\,{\rm K}$ [16]. Assuming an average mass-loss rate of $2 \times 10^{-4}\,M_\odot\,{\rm yr}^{-1}$, an average velocity of $20\,{\rm km\,s}^{-1}$, and an $0.9''$ diametric extent, at $1.2\,{\rm kpc}$, we find an abundance $TiO_2/H_2 \approx 3.8 \pm 0.9 \times 10^{-8}$. We however urge careful interpretation of these numbers, since the high dipole moment of TiO_2 supports efficient radiative excitation and possibly electron–TiO_2 collision rates large enough to exceed H_2–TiO_2 collision rates in case of a sufficient ionisation degree close to the star [4]. These effects could invalidate the LTE approach used in this simple analysis.

Taking into consideration the high dipole moment of TiO_2, the ratio between the collisional and radiative transition rates of TiO_2, and the strong resemblance between the TiO_2 emission measured with ALMA and the earlier scattered-light observations at $1\,\mu{\rm m}$ we put forth that the TiO_2 gas is radiatively excited. As such, the measured emission traces parts of the outflow where the stellar radiation field is least attenuated. From the comparison to the continuum at $\sim 321\,{\rm GHz}$, we derive that TiO_2 is excited in the directions with lower dust densities. The absence of detected TiO_2 emission north of the star could then point at efficient obscuration of this part of the outflow, in line with the observations of e.g. [12]. Attenuation of the stellar radiation field to the east and west of the star is limited. From this, we do not expect an equatorial enhancement of the mass-loss rate, since this would likely have induced more efficient dust formation, which is not seen in the continuum.

Since the TiO_2 emission is seen at radial distances from the star far beyond the dust-condensation region, and along directions where dust continuum is observed, we claim that TiO_2 is not a tracer for overall low grain-formation efficiency, but that much of it remains in the gas phase. The strong correspondence between the TiO_2 emission and the south-west tail of dust-scattered stellar light supports this. We also consider the high derived column density and suggest that TiO_2 might play only a minor role as a primary dust seed around VY CMa.

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