ALMA observations of TiO$_2$ around VY Canis Majoris

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ABSTRACT

Context. Titanium dioxide, TiO$_2$, is a refractory species that could play a crucial role in the dust-condensation sequence around oxygen-rich evolved stars. To date, gas phase TiO$_2$ has been detected only in the complex environment of the red supergiant VY CMa. It is essential to address which gas-phase species provide the primary seeds. TiO$_2$ is considered an important seed refractory species with possibly higher nucleation rates than SiO (e.g. Jeong et al. 2003; Lee et al. 2015). Moreover, presolar TiO$_2$ grains were tentatively identified by Nittler & Alexander (1999). Since SiO nucleation was found to be more relevant than previously thought under the relevant pressure and temperature conditions (Nuth & Ferguson 2006; Gail et al. 2013), it is crucial to characterise the role of TiO$_2$. The effect of non-stationarity on the nucleation is unknown. Shocks are, however, known to be present in the upper atmospheres of these evolved stars (e.g. Chiavassa et al. 2011). Here we aim to constrain the distribution and excitation of TiO$_2$ around VY CMa in order to clarify its role in dust formation.

Methods. We analyse spectra and channel maps for TiO$_2$ extracted from ALMA science verification data.

Results. We detect 15 transitions of TiO$_2$, and spatially resolve the emission for the first time. The maps demonstrate a highly clumpy, anisotropic outflow in which the TiO$_2$ emission likely traces gas exposed to the stellar radiation field. An accelerating bipolar-like structure is found, oriented roughly east-west, of which the blue component runs into and breaks up around a solid continuum component. A distinct tail to the south-west is seen for some transitions, consistent with features seen in the optical and near-infrared.

Conclusions. 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.

Key words. supergiants – stars: individual: VY Canis Majoris – stars: mass-loss – circumstellar matter – submillimeter: stars

1. Introduction

The dust-formation sequence in the outflows of oxygen-rich evolved stars is not well understood. It is essential to address which gas-phase species provide the primary seeds. TiO$_2$ is considered an important seed refractory species with possibly higher nucleation rates than SiO (e.g. Jeong et al. 2003; Lee et al. 2015). Moreover, presolar TiO$_2$ grains were tentatively identified by Nittler & Alexander (1999). Since SiO nucleation was recently indicated to be more relevant than previously thought under the relevant pressure and temperature conditions (Nuth & Ferguson 2006; Gail et al. 2013), it is crucial to characterise the role of TiO$_2$. The effect of non-stationarity on the nucleation is unknown. Shocks are, however, known to be present in the upper atmospheres of these evolved stars (e.g. Chiavassa et al. 2011). Here we aim to constrain the distribution and excitation of TiO$_2$ around VY CMa in order to clarify its role in dust formation.

O’Gorman et al. (2015, hereafter O’Gorman et al. 2015) describe the submillimeter continuum emission and report on a bright component south-east of the star, indicative of anisotropic mass loss.

TiO$_2$ is expected to be consumed by the nucleation process, but the detection of TiO$_2$ emission by K+13a already suggested that a significant amount could possibly survive the dust formation. K+13a did not spatially resolve TiO$_2$ emission at angular resolutions $\geq 1''$. The ALMA observations now allow us to characterise the emission and the role of TiO$_2$ in the dust-formation process in more detail.

2. Observations

We retrieved ALMA science verification data on VY CMa from the ALMA archives. The observations and data calibration and reduction are described by R+14. Table 1 shows the spectral coverage and representative rms noise values for the six spectral windows in ALMA’s band 7 (~0.9 mm; ~320 GHz) and one in band 9 (~0.45 mm; ~660 GHz). With projected baselines of 14 m up to 2.7 km, the spatial resolution at ~320 GHz and 658 GHz is ~0.2 and ~0.1, respectively, and the maximum recoverable scales are 8′′3 and 4′′0. The synthesised beam sizes are obtained using natural weighting.

The data reduction and quality of the continuum emission images at 321 GHz and 658 GHz are discussed in detail by R+14 and O+15. No imaging artefacts are expected to arise from the
Table 1. Spectral coverage of the ALMA observations.

| Setting | Frequency range (GHz) | Resolution (MHz) | rms noise (mJy beam\(^{-1}\)) | Beam ("x", PA) |
|---------|-----------------------|------------------|-------------------------------|---------------|
| 321     | 309.501–310.437       | 0.98             | 3                             | 0.23 × 0.13, 28.27° |
| 321     | 310.501–311.437       | 0.98             | 2                             | 0.23 × 0.13, 28.48° |
| 325     | 312.035–313.908       | 1.9              | 3                             | 0.24 × 0.13, 29.48° |
| 321     | 320.725–321.662       | 0.98             | 3                             | 0.22 × 0.13, 27.31° |
| 321     | 321.986–322.923       | 0.98             | 3                             | 0.22 × 0.13, 27.55° |
| 325     | 324.181–326.054       | 1.9              | 6                             | 0.22 × 0.12, 29.27° |
| 658     | 657.002–658.873       | 3.9              | 15                            | 0.11 × 0.06, 29.89° |

Notes. Setting names refer to those used for the released ALMA CSV data, focusing on the H2O masers at 321 GHz, 325 GHz, and 658 GHz.

Fig. 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 km s\(^{-1}\), the shaded areas the \(v_{LSR}\)-ranges from Table 2. We indicate identifications of species other than TiO\(_2\) in the panels.

We note that the spectral window 312–314 GHz suffered from poor continuum subtraction owing to line crowding and a consequent lack of line-free spectral range. This causes a fraction of the continuum emission to leak into the channel maps of the TiO\(_2\) lines at ~312 GHz (Figs. A.4–A.6). The emission seen at the position of clump C can be entirely attributed to the continuum itself, i.e., we can rule out molecular contribution at this position. The lines presented in Fig. 1 and Table 2, and consequently also the reported peak and integrated intensities, were corrected for this effect on a line-to-line basis.

The imaged TiO\(_2\) lines in the 312–314 GHz spectral window also show a contribution north-north-east and south-south-west of the star. These features are artefacts of the cleaning procedure likely caused by imperfect phase corrections on a number of intermediate baselines. The phase corrections were transferred from the self-calibrated 325 GHz maser line located in the atmospheric absorption region.

3. Results

We analysed spectra extracted for a 1" diameter region around the stellar position. We show below that no TiO\(_2\) emission is detected beyond this aperture. TiO\(_2\) identifications are based on the Cologne Database for Molecular Spectroscopy (CDMS; Müller et al. 2001, 2005; Brünken et al. 2008). We detect 15 lines with upper-level energies \(E_{\text{up}}/k\) in the range 48–676 K and signal-to-noise ratios \(S/N\) ≈ 5–17 at velocity resolutions 0.9–7.6 km s\(^{-1}\) (Table 2, Fig. 1). Of the TiO\(_2\) lines detected by K+13a; K+13b only those at 310.55 GHz and 310.78 GHz are observed with ALMA. The peak fluxes of the ALMA and SMA detections are consistent within the uncertainties. Moreover, of the other 13 lines of TiO\(_2\) detected by K+13c, none were detected in the SMA survey, owing to a noise level in the ALMA data that was approximately 10 times lower. We detect no TiO\(_2\) emission at ~660 GHz owing to the higher rms noise (Table 1). We detect no isotopic variants of Ti, consistent with the solar isotopic abundance ratios.

We expect no large flux losses in the ALMA observations of TiO\(_2\) given the ~8" recoverable scale at ~320 GHz. The presence of large-scale emission with low surface brightness cannot be entirely excluded, but is unlikely and will not change our main conclusions.

Blending, proximity to strong lines, line crowding, and intrinsic line-shape irregularities complicate the identification of TiO\(_2\) emission. The lines at 310.55 GHz and 311.46 GHz are only partially covered in the observations; we believe the former to be a firm detection and the latter to be tentative. In both cases, no other candidate could be identified. Uncertainties on the relevant TiO\(_2\) frequencies are <2 MHz, except for the transition at 311.462 GHz, where it is 5.555 MHz (Brünken et al. 2008).

The TiO\(_2\) lines detected with ALMA exhibit broad line profiles, as do those detected by K+13a. Assuming\(^1\) a stellar \(v_{LSR}\) of 22 km s\(^{-1}\), we find that the emission is very asymmetric in velocity space, ranging typically from ~15 km s\(^{-1}\) to ~60 km s\(^{-1}\) (Fig. 1). The apparent extension of the blue wing of some lines to ~45 km s\(^{-1}\) is likely coincidental and due to line blending, but

\(^1\) See K+13b for a discussion of \(v_{LSR}\).
Table 2. Overview of detected TiO$_2$ lines.

| Transition $J_{K_a,K_c}$→$J_{K_a,K_c}$ | $\nu_{db}$ (MHz) | $E_{ag}/k$ (K) | $\nu_{min}$ (km s$^{-1}$) | $\nu_{max}$ (km s$^{-1}$) | $\Delta \nu$ (mJy) | Peak (Jy) | $I$ (Jy km s$^{-1}$) | Size SW tail |
|--------------------------------------|-----------------|-----------------|-----------------|-----------------|-------------------|---------|-----------------|-------------|
| 22(1, 21)→21(2, 20)                 | 310 554.735     | 180.5            | −15.2           | 51.3            | 1.0               | 16      | 0.22            | Y           |
| 23(1, 22)→22(0, 22)                 | 310 782.713     | 182.4            | −43.9           | 102.3           | 1.0               | 16      | 0.27            | Y           |
| 40(8, 32)→39(9, 31)                 | 311 462.082     | 675.9            | 19.4            | 66.7            | 1.9               | 10      | 0.10            | 2.31        |
| 7(5, 3)→6(4, 2)                     | 312 248.341     | 47.9             | −43.7           | 80.96           | 1.9               | 16      | 0.29            | 20.32       |
| 10(4, 0)→9(3, 7)                    | 312 732.066     | 57.7             | −19.4           | 105.1           | 1.9               | 16      | 0.15            | 9.43        |
| 30(3, 27)→30(2, 28)                 | 312 816.809     | 354.4            | −68.2           | 60.0            | 1.9               | 16      | 0.16            | 12.98       |
| 11(4, 10)→9(3, 7)                   | 321 401.936     | 65.7             | −33.9           | 50.5            | 0.9               | 24      | 0.19            | 7.24        |
| 28(2, 26)→28(1, 27)                 | 321 501.043     | 298.8            | −35.0           | 51.2            | 0.9               | 24      | 0.13            | 4.76        |
| 35(8, 28)→35(7, 29)                 | 322 333.594     | 532.4            | −36.4           | 108.1           | 1.0               | 19      | 0.15            | 7.03        |
| 33(8, 26)→33(7, 27)                 | 322 612.696     | 481.4            | −0.1            | 63.9            | 1.0               | 18      | 0.16            | 4.18        |
| 23(2, 22)→22(1, 21)                 | 324 492.930     | 196.1            | −47.9           | 79.4            | 1.9               | 29      | 0.21            | 9.64 (≤0.5 |
| 37(8, 30)→37(7, 31)                 | 324 965.693     | 586.5            | 3.6             | 59.8            | 1.9               | 30      | 0.15            | 4.92        |
| 26(1, 25)→26(0, 26)                 | 325 322.035     | 246.5            | −25.2           | 81.8            | 7.6               | 21      | 0.11            | 1.85        |
| 26(4, 22)→25(5, 21)                 | 325 500.415     | 281.5            | −7.7            | 55.7            | 3.8               | 28      | 0.13            | 2.75        |
| 28(8, 20)→28(7, 21)                 | 325 600.792     | 367.0            | −0.4            | 90.2            | 3.8               | 28      | 0.18            | 3.89        |

Notes. Parameters listed for spectrum extracted in a 1″ diameter aperture centred on the star. See also Fig. 1. Columns are transition, rest frequency, upper-level energy, minimum and maximum $v_{LSR}$ reached, velocity resolution and rms noise at which the identification was made, peak and integrated flux, maximum diameter size of the integrated emission at 3σ level, and a marker for emission in the south-west tail (Y, N, ?, and – for yes, no, maybe, and unknown). Species other than TiO$_2$ detected inside the plotted spectral windows are marked in Fig. 1.

we cannot exclude an actual TiO$_2$ contribution. Blend candidates are indicated in Fig. 1 and Table 2. The lines with $E_{ag}/k = 48$ K$^2$, 58 K, 182 K, 532 K exhibit features in their red wings that extend to $v_{LSR} ≈ 105$ km s$^{-1}$. A similar high-velocity outflow is also visible for some lines presented by K$^{v+13}a$.

3.1. Spatial distribution

The detected TiO$_2$ emission is, for the most part, spatially resolved by the ALMA observations with a 0″23×0′′13 beam (see Figs. A.1–A.16), but several transitions show spatially unresolved emission at a 2 km s$^{-1}$ velocity resolution. We note a very complex behaviour of the emission peaks, with some only appearing in one channel and not in the neighbouring channels. The often spatially unresolved (≤145 AU) peaks in the different velocity channels of all lines imply a clumpy and/or anisotropic wind. The maps for 310.55 GHz ($E_{ag}/k = 181$ K) and 310.78 GHz ($E_{ag}/k = 182$ K) reveal that these two lines behave almost identically. Corresponding velocity channels (Figs. A.1, A.2) trace roughly the same regions of the circumstellar environment and exhibit similar intensities, implying that these two lines are very tightly coupled in their excitation. Figure 2 shows the morphology of the TiO$_2$ emission at 310.78 GHz and the positions of the star (VY), the continuum component C (O+15: R+14), and the south-west clump detected at $\lambda ≈ 1–5$ μm at ~1″ from the star (Smith et al. 2001; Humphreys et al. 2007; Shenoy et al. 2013).

Given the similar energy levels, quantum numbers, and Einstein-A coefficients of the transitions at 310.55 GHz, 310.78 GHz, and 324.49 GHz, one expects similar line intensities and spatial distributions. However, although the channel-to-channel peaks of the 324.49 GHz emission (Fig. A.11) correspond quite well to those of the other two, which strengthens its identification as TiO$_2$, its intensity is clearly lower. It is hard to explain this discrepancy, but we note that as a consequence of the sensitivity of the atmospheric transmission at ~325 GHz to the atmospheric water-vapour content the rms noise is ~4 times higher and the flux calibration could be compromised.

The emission at 322.61 GHz, 322.33 GHz, and 324.96 GHz behaves similarly but with weaker and spatially somewhat more confined red-wing emission. Unfortunately, many of the TiO$_2$ lines are blended (both in frequency and spatially) with emission from other species.

The discussion below is focussed on the morphology at 310.78 GHz with Fig. 2 as a visual guide. Overall, the detected TiO$_2$ emission moves from west to east, across the stellar position, with velocities evolving from reddest to bluest. All lines show emission close to the star at the stellar $v_{LSR}$. In particular, all lines with $E_{ag}/k ≥ 360$ K are centred on VY and emit mainly across $v_{LSR} ≈ 0–40$ km s$^{-1}$ (Fig. 1), implying that these trace a central part of the outflow that may be accelerating.

At $v_{LSR} ≥ 44$ km s$^{-1}$ the emission is mainly situated west of VY with a marginal contribution close to it. The emission is highly variable with $v_{LSR}$, doubly peaked in most velocity channels, and shows a hook-like feature at its western edge. The latter could relate to the north-west knot defined by Humphreys et al. (2007) based on HST observations, though more analysis is needed to investigate the nature of this feature.

At $22 < v_{LSR} < 44$ km s$^{-1}$ we find multiple emission peaks in most velocity channels, with those closest to VY slightly brighter than the west offset peaks. The integrated emission is elongated along a direction roughly parallel to the axis connecting the peak position of C and VY, at a PA ≈ 125°.

At $18 ≤ v_{LSR} ≤ 22$ km s$^{-1}$ the transients at ~310 GHz show a bright tail extending south-west of VY at a PA ≈ 220°, i.e. almost perpendicular to the axis connecting VY and C. This tail reaches ~1″ away from VY, out to the south-west clump of Shenoy et al. (2013) and agrees very well with the features detected by e.g. Smith et al. (2001) at wavelengths $\lambda ≈ 1–2.14$ μm. The emission at 310.78 GHz extends slightly further south-west than that at 310.55 GHz. Since the most extended emission

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2 Continuum subtraction is hampered by the high line density. The red wing of the line is affected, but still shows the feature they have in common.
exceeds $5\sigma$, we suggest that the difference is real and that clumpiness in the outflow strongly influences the excitation of individual lines.

At 312.73 GHz and 312.82 GHz we find signs of emission in the south-west tail, but these are likely artefacts from the cleaning procedure (see Sect. 2). At 311.46 GHz we see emission within the spatial region where the south-west tail is located, although at higher $v_{LSR}$ than the transitions at $\sim$310 GHz. This could be due to the south-west tail covering a wider velocity range than reported above, by a line blend, or a misidentification of the line as TiO$_2$. We unfortunately do not have information for $v_{LSR} < 22$ km s$^{-1}$ for this line. No other transition shows detectable emission within the south-west tail, but most show a slight bulge of emission at $\sim0.2'$ south-west of the star, at the base of the south-west tail. Figure A.17 shows a comparison for all lines to the south-west tail observed at 310.78 GHz.

At $v_{LSR} < 18$ km s$^{-1}$ the high-intensity emission is situated entirely east of VY, elongated, and oriented at $\sim15'−25'$ east from north. With bluer velocities the emission moves towards C and then appears to break up with a northern peak brighter than the southern one (e.g. Fig. A.2). Remarkable is that the low-intensity component of the 310.78 GHz transition closely resembles the scattered light at 1.2 kpc, which we mark in the figure. We find this strong correspondence at these blue velocities for no other TiO$_2$ transition. If the high- and low-intensity components have different intrinsic wind velocities, they could be spatially separated and trace different parts of the outflow.

3.2. Excitation conditions

We investigate the excitation of TiO$_2$ lines via a rotational diagram analysis (Fig. 3). Intensities, source sizes, and rms noise values are taken from Table 2. Severely blended or only partially covered lines are excluded from the analysis. We derive a source-averaged column density $N_{\text{col}} = 5.65 \pm 1.33 \times 10^{15}$ cm$^{-2}$ and a rotational temperature $T_{\text{rot}} = 198.0 \pm 28.5$ K, in agreement with K+13a. We note that the kinetic temperature in the excitation region of TiO$_2$ varies from more than 1000 K down to $\sim$100 K (Decin et al. 2006). Assuming an average mass-loss rate of $2 \times 10^{-4} M_\odot$ yr$^{-1}$ (e.g. De Beck et al. 2010), an average velocity of 20 km s$^{-1}$, and an 0.9 diametric extent, at 1.2 kpc, we find an abundance TiO$_2$/H$_2$ $\approx 3.8 \pm 0.9 \times 10^{-8}$.

The high dipole moment of TiO$_2$ (3.63 Debye; Wang et al. 2009) supports efficient radiative excitation and $T_{\text{rot}}$ could hence reflect an average continuum brightness temperature as opposed to a gas kinetic temperature in the case of collisional excitation. Additionally, the large dipole moment induces electron-TiO$_2$ collision rates large enough to exceed H$_2$–TiO$_2$ collision rates if the fractional ionisation exceeds a few 10$^{-6}$. We could not find a value for VY CMa, but based on the result $n_e/m_\text{i} = 3.8 \times 10^{-4}$ for the red supergiant α Ori (Harper et al. 2001) this type of excitation could be relevant. We discuss the competition between collisional excitation and radiative excitation in more detail below, in Sect. 4.1.

4. Discussion

4.1. Excitation of titanium dioxide

Many effects need to be taken into account in a full treatment of the excitation and radiative transfer of rotational transitions of TiO$_2$. Important molecular data are lacking: although the rotational energy levels and radiative data are well determined for TiO$_2$ in CDMS (Müller et al. 2001, 2005; Brünken et al. 2008), no rates exist for excitation of TiO$_2$ by hydrogen-impact nor have the vibration-rotation spectra been fully analysed.

For illustration of the transition rates for TiO$_2$, consider two of the observed rotational transitions at 312.248 and 324.965 GHz with properties summarised in Table 3. Collisional excitation at the kinetic temperature of the gas can dominate only when the downward rate of collision-induced transitions exceeds $5\sigma$.

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Fig. 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 $3\sigma$. Red contours show the 321 GHz continuum at [3, 20, 40, 60, 80]$\sigma$, green contours show HST emission at [3, 5, 10, 20, 30, 40, 50, 100, 200]$\sigma$ (Smith et al. 2001). In the first panel we mark the position of the star (+, VY; black) and of the continuum component (x, C; red) to the south-east (O+15; R+14), and the position and approximate extent of the south-west clump (SW, dashed 1" diameter circle; red Shenoy et al. 2013). The apparent north-south emission is thought to arise from dynamic-range limitations in the peak channels.

Fig. 3. Rotational diagram. Lines indicated in red are blended or only partially covered in the observations and are excluded from the fitting procedure. All intensities, source sizes, and rms noise values are taken from Table 2. The fit results and uncertainties are shown with the blue and grey dashed lines and are indicated at the top right.
Table 3. Summary of properties of selected transitions of TiO$_2$.

| $J'(K'_1,K'_2)$–$J''(K''_1,K''_2)$ or vibrational band | $\nu$ (GHz) | $A_{\nu,\ell}$ (s$^{-1}$) | $\sum_{\nu} A_{\nu,\ell}$ (s$^{-1}$) | $n_0$ (cm$^{-3}$) | $T_{\text{rad}}$ (K) | $\rho_{\text{rad}}$ (s$^{-1}$) |
|----------------------------------------------------------|-------------|--------------------------|--------------------------|-----------------|-----------------|-----------------|
| 7(5,3)–6(4,2)                                            | 312.24      | 4.34 × 10$^{-3}$         | 5.04 × 10$^{-3}$         | 5 × 10$^7$      | 26.2            | 5.7 × 10$^{-3}$  |
| 7(5,3)–7(4,4)                                            | 206.094     | 6.95 × 10$^{-4}$         | ...                      | ...             | 15.3            | 7.6 × 10$^{-4}$  |
| 7(5,3)–8(4,4)                                            | 84.567      | 7.31 × 10$^{-6}$         | ...                      | ...             | 7.15            | 9.6 × 10$^{-6}$  |
| 37(8,30)–37(7,31)                                       | 324.966     | 4.76 × 10$^{-3}$         | 4.63 × 10$^{-2}$         | 5 × 10$^8$      | 27.7            | 6.3 × 10$^{-3}$  |
| 37(8,30)–36(9,27)                                       | 205.259     | 2.62 × 10$^{-4}$         | ...                      | ...             | 15.2            | 2.9 × 10$^{-4}$  |
| 37(8,30)–36(7,29)                                       | 821.811     | 2.96 × 10$^{-2}$         | ...                      | ...             | 94.3            | 5.7 × 10$^{-2}$  |
| 37(8,30)–36(5,31)                                       | 1235.577    | 1.17 × 10$^{-2}$         | ...                      | ...             | 132.4           | 2.0 × 10$^{-2}$  |
| $v_1 = 1$–$0$                                            | 28.840      | 3.6                       | 3.6                       | $^a$             | 350             | 7.2 × 10$^{-2}$  |
| $v_2 = 1$–$0$                                            | 9863        | 7.2 × 10$^{-2}$           | 7.2 × 10$^{-2}$           | $^a$             | 300             | 2.0 × 10$^{-2}$  |
| $v_3 = 1$–$0$                                            | 28.030      | 42                        | 42                        | $^a$             | 350             | 9.0 × 10$^{-1}$  |

Notes. Columns list the transitions (rotational and vibrational), the frequency $\nu$ at which these transitions occur, their transition probability $A_{\nu,\ell}$, inverse lifetime $\sum_{\nu} A_{\nu,\ell}$, critical density $n_0$, radiative temperature $T_{\text{rad}}$, and the calculated pumping rate $\rho_{\text{rad}}$. $^a$ Appropriate collision rates are unknown; therefore, no critical density is tabulated for the vibrational transitions.

greatly exceeds the downward rates of radiative transitions for each upper state. This condition can be translated to a critical density $n_0 = \sum_{\nu} A_{\nu,\ell}/q_0$, where $A_{\nu,\ell}$ is the spontaneous transition probability of each transition from upper state $u$ to lower state $\ell$. To estimate this density, we assume a characteristic quenching rate coefficient $q_0 = 10^{-10}$ cm$^3$ s$^{-1}$ for rotational transitions induced by collisions with neutral species H or H$_2$. Values for $n_0$ are listed in Table 3. Assuming a mass-loss rate of 10$^{-4}$ $M_\odot$ yr$^{-1}$, such densities are however reached only at distances from the star lower than $\sim$0.065, whereas TiO$_2$ is excited over a much larger region, where the density quickly decreases to a few 10$^5$ cm$^{-3}$.

In addition, collision rates for electron impact have been computed in the Born approximation. Because the electric dipole moment of TiO$_2$ is so large, electron-impact rates are expected to show a strong propensity for radiatively allowed transitions. Computed rates are likely to be accurate within 50%. Under an assumed very low fractional electron density of 10$^{-7}$, the collision-induced downward transition rate for the 312 GHz transition is for 5% due to electron collisions. Assuming the fractional ionisation reported for α Ori (3.8 × 10$^{-8}$) electron collisions would completely dominate over neutral (hydrogen) collisions by a factor of the order of 100 or more and might compete well with infrared pumping.

We note that the upper state of the 312 GHz transition decays mainly by the observed transition itself, while the upper state of the high-excitation 324 GHz transition is depopulated more rapidly by submm-wave transitions at 821 and 1235 GHz. As a consequence, a much higher density would be required to excite the 324 GHz line by collisions than the 312 GHz line.

The continuum intensity of VY CMa is so large at infrared and submm wavelengths that radiative excitation (pumping) must be taken into account. If the observed continuum flux of VY CMa is assumed to arise within a 0′3 diameter region (O+15) and to be diluted by a geometrical factor 1/9 over the 0′9 extent of the observed TiO$_2$ emission, then the average Planckian radiation brightness temperatures are estimated to be $T_{\text{rad}} \geq 25$ K at 312 to 324 GHz. The corresponding pumping rates (absorption and stimulated emission) in this radiation field can be expressed as

$$\rho_{\text{rad}} = \frac{A_{\nu,\ell}}{\exp(h\nu/kT_{\text{rad}})-1}$$

for each radiative transition that connects states of interest. The basic radiative data for TiO$_2$ are collected in Table 3. Although the fundamental bands of the three vibrational modes have not been fully analysed rotationally, the band frequencies and band strengths are approximately known (Grein 2007). In the adopted continuum model, the infrared intensity is high enough to drive absorption in vibration-rotation lines at rates of the order of 0.01 to 1.0 s$^{-1}$. In order for collisional excitation in a pure rotational transition $\mu \rightarrow \ell$ to compete with infrared pumping in VY CMa, a density much greater than $n_0 \approx (\rho(v_1) + \rho(v_2) + \rho(v_3) + \sum_{\ell} A_{\nu,\ell})/q_0 \approx 10^{10}$ cm$^{-3}$ would be required. The radiative rates in Table 3 suggest that radiative excitation is likely to be very important for TiO$_2$ in VY CMa. Therefore, the rotational temperature derived in Sect. 3.2 might have no direct relationship to the kinetic temperature. Because the observed transitions in the present study span a wide range of excitation energies, the simple rotation-diagram analysis still provides a useful first estimate of the molecular column density and abundance.

4.2. Outflow components

From the comparison to the continuum at $\sim$321 GHz, we derive that TiO$_2$ is excited in the directions with lower dust densities. The absence of detected TiO$_2$ emission north of the star could then point to efficient obscuration of this part of the outflow, in line with the observations of e.g. Smith et al. (2001). 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.

The TiO$_2$ emission traces multiple wind components. We find a red outflow to the west and a blue outflow to the east. With the clear exception of the interaction of the TiO$_2$ gas with clump C in the east, the two seem roughly symmetric around the...
star and aligned with the axis connecting VY and C. We rule out an equatorially enhanced environment such as an expanding disk or ring, based on the spatial distribution of the TiO\textsubscript{2} emission at different $\theta_{\text{LSR}}$. We rather suggest an accelerating bipolar-like outflow at lower densities. We also find a predominantly blue south-west outflow, connecting the star and the south-west clump, approximately perpendicular to the VY – C connecting axis. We find no north-east counterpart in TiO\textsubscript{2} emission, likely implying that the south-west tail is indeed caused by an event in one preferred direction, as opposed to a bipolar event.

4.3. Interaction of blue outflow with clump C

Whereas the H\textsubscript{2}O maser emission in the “valley” between VY and C implies that C is close to or in the plane of the sky ($R_{\text{v1}}$), the observations suggest that the TiO\textsubscript{2} gas breaks up around C while moving towards the observer, placing C – at least partially – in front of the plane of the sky. We therefore deem it likely that the H\textsubscript{2}O masers and the TiO\textsubscript{2} emission probe parts of the outflow east of VY with different physical properties. Whereas the masers are probably excited through shocks at high densities, TiO\textsubscript{2} is more likely excited through radiation, at lower outflow densities. In the denser regions, TiO\textsubscript{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\textsubscript{2} traces the blue-shifted wind to the east of VY with lower densities which runs into and curves around C.

4.4. Titanium dioxide and scattered light

K+13b reported emission offset by $\sim$1” south-west from the central molecular emission for multiple species. However, owing to lower sensitivity they did not find indications for this in the TiO\textsubscript{2} emission, whereas we clearly detect the south-west tail at $\sim$310 GHz (see Sect. 3.1).

The likelihood of radiative excitation of TiO\textsubscript{2} and the agreement between the south-west tail in the TiO\textsubscript{2} emission and the scattered stellar light at 1\,\textmu m from Smith et al. (2001) suggest the presence of a tail of gas and dust lit up by a stellar radiation field less attenuated than at other position angles. The bulge south-west of the star seen for most TiO\textsubscript{2} transitions is consistent with this. We infer a lower degree of attenuation and from that a lower (dust) density south-west of the star. We speculate that the suggested localised ejection leading to the formation of the south-west clump (Shenoy et al. 2013) could have created a cavity in the dense material close to the star.

Given the agreement with the blueshifted TiO\textsubscript{2} emission, the outflow traced by the scattered light is likely oriented out of the plane of the sky. The lack of consistent $\theta_{\text{LSR}}$ coverage over the different TiO\textsubscript{2} transitions, however, further complicates the three-dimensional and kinematic constraints. In-depth analysis of all other emission lines detected with ALMA is needed to constrain the basic properties of the south-west tail.

4.5. Titanium dioxide and dust formation

If the nucleation of TiO\textsubscript{2} can occur at $\leq$2000 K (e.g. Lee et al. 2015), one expects TiO\textsubscript{2} depletion from the gas phase initiated close to the star, i.e. within a few stellar radii. From the ALMA observations O+15 put an upper limit to the dust-condensation radius of $\sim$0.06 ± 0.02 $\approx$ 10 stellar radii. The TiO\textsubscript{2} emission is present close to the star and out to $\lesssim$0.45 in directions without extended continuum emission. Where TiO\textsubscript{2} and the bulk dust coexist, the emission extends to $\sim$0.20, well beyond the dust-condensation radius. Since the TiO\textsubscript{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\textsubscript{2} is not a tracer for low grain-formation efficiency. The strong correspondence between the TiO\textsubscript{2} emission and the south-west tail of dust-scattered stellar light (see Sect. 3.1 and Fig. 2) supports this. We also considered the high derived column density and suggest that TiO\textsubscript{2} plays only a minor role as a primary dust seed around VY CMa.

Since the ALMA observations covered no transitions of TiO, we cannot expand the discussion of K+13a on the relation between TiO, TiO\textsubscript{2}, and the dust.

5. Conclusion

We detect 15 transitions of TiO\textsubscript{2} in high-resolution ALMA observations of the red supergiant VY CMa. The main emission region spans $\sim$0.9 ($\sim$1080 AU) in a roughly east-west oriented direction, centred on the star. The behaviour of the gas is complex throughout $\theta_{\text{LSR}}$-space with bright peaks appearing only in very confined $\theta_{\text{LSR}}$-ranges, implying that the outflow is very clumpy, on spatial scales not resolved by the current observations with a 0.23 $\times$ 0.13 beam. We observe a tail of TiO\textsubscript{2} emission extending out to $\sim$1” south-west of the star, consistent with structures seen in the optical and near-infrared. It is oriented out of the plane of the sky and mainly covers projected velocities of a few km s\textsuperscript{-1}, but reaches up to $\sim$40 km s\textsuperscript{-1} in some cases. We suggest that the TiO\textsubscript{2} in this tail is illuminated by stellar radiation penetrating through a low-density cavity in the south-west part of the circumstellar environment of the star, potentially created by the ejection that led to the south-west clump. Within a bipolar-like TiO\textsubscript{2} outflow, the blue-shifted emission exhibits a strongly different orientation and behaviour than the red-shifted emission, suggesting that the stellar wind runs into the large body of dust situated $\sim$0.335 ($\sim$400 AU) south-east of the star.

We suggest that TiO\textsubscript{2} might play only a minor role in the dust-condensation process in the complex outflow around VY CMa, and potentially also around other oxygen-rich evolved stars with extreme mass outflows. High-resolution imaging is however still needed to correlate the emission of TiO\textsubscript{2} with that of TiO, and to further investigate the relative importance of silicon, titanium, and other metals in the dust condensation.

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Appendix A: Maps of titanium dioxide emission

Figures A.1 to A.15 show channel maps of the detected TiO$_2$ emission lines (Table 2, Fig. 1) at a velocity resolution of 2 km s$^{-1}$, covering the range −14 ≤ $v_{LSR}$ ≤ 78 km s$^{-1}$. This $v_{LSR}$-range covers the bulk of all TiO$_2$ emission; emission at more extreme velocities is no longer visible in the channel maps. Figure A.16 shows integrated-intensity maps for all listed lines, covering the $v_{LSR}$-ranges indicated in Table 2. Figure A.17 shows a comparison of the TiO$_2$ line emission to the south-west tail detected at 310.78 GHz, which is discussed in Sects. 3.1 and 4.4.

![Channel maps of the TiO$_2$ emission at 310.55 GHz, at a 2 km s$^{-1}$ velocity resolution. Black contours show the continuum measured with ALMA at 321 GHz (O+15; R+14). The stellar position is indicated with a white cross. Spatial scales are indicated in the top left panel and are the same for all panels. The colour scale starts at the 3σ level and is plotted as the square root of the flux for increased contrast.](image-url)
Fig. A.2. Same as Fig. A.1, but for TiO$_2$ emission at 310.78 GHz.
Fig. A.3. Same as Fig. A.1, but for TiO$_2$ emission at 311.46 GHz.
Fig. A.4. Same as Fig. A.1, but for TiO$_2$ emission at 312.25 GHz.
Fig. A.5. Same as Fig. A.1, but for TiO$_2$ emission at 312.73 GHz.
Fig. A.6. Same as Fig. A.1, but for TiO₂ emission at 312.82 GHz.
Fig. A.7. Same as Fig. A.1, but for TiO\textsubscript{2} emission at 321.40 GHz. Artefacts in channels with $v_{\text{LSR}} \geq 55$ km s\textsuperscript{-1} are due to the presence of strong SO\textsubscript{2} emission. See also Fig. 1.
Fig. A.8. Same as Fig. A.1, but for TiO$_2$ emission at 321.50 GHz.
Fig. A.9. Same as Fig. A.1, but for TiO$_2$ emission at 322.33 GHz.
Fig. A.10. Same as Fig. A.1, but for TiO$_2$ emission at 322.61 GHz.
Fig. A.11. Same as Fig. A.1, but for TiO$_2$ emission at 324.49 GHz.
Fig. A.12. Same as Fig. A.1, but for TiO$_2$ emission at 324.96 GHz.
Fig. A.13. Same as Fig. A.1, but for TiO$_2$ emission at 325.32 GHz.
Fig. A.14. Same as Fig. A.1, but for TiO$_2$ emission at 325.50 GHz.
Same as Fig. A.1, but for TiO$_2$ emission at 325.60 GHz.
Fig. A.16. Integrated-intensity maps of TiO$_2$ emission. Colour maps show the intensity integrated over the $n_{\text{J}}$ range indicated in Table 2 and Fig. 1 and cut off at 3$\sigma$. Contours show the ALMA 321 GHz continuum. Labels indicate the positions of the star (+, VY) and the continuum component (x, C) to the south-east (O+15; R+14), and the position and approximate extent of the south-west clump of Shenoy et al. (2013, SW and a dashed 1″ diameter circle). The presence of cleaning artefacts, mainly at ~312 GHz, is addressed in Sect. 2.
Fig. A.17. Comparison of TiO$_2$ emission lines listed in Table 2 to south-west tail at 310.78 GHz (red contours) and HST image (black contours). Emission integrated over $19 \leq v_{LSR} \leq 22$ km s$^{-1}$ plotted at $>3\sigma$ (colour scale). Emission of 311.46 GHz was omitted since the relevant $v_{LSR}$-range is not covered by the observations.