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LETTERS

Chemical complexity in the winds of the oxygen-rich supergiant star VY Canis Majoris

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The interstellar medium is enriched primarily by matter ejected from old, evolved stars[1,2]. The outflows from these stars create spherical envelopes, which foster gas-phase chemistry[3–5]. The chemical complexity in circumstellar shells was originally thought to be dominated by the elemental carbon to oxygen ratio[6]. Observations have suggested that envelopes with more carbon than oxygen have a significantly greater abundance of molecules than their oxygen-rich analogues[7]. Here we report observations of molecules in the oxygen-rich shell of the red supergiant star VY Canis Majoris (VY CMa). A variety of unexpected chemical compounds have been identified, including NaCl, PN, HNC and HCO^+. From the spectral line profiles, the molecules can be distinguished as arising from three distinct kinematic regions: a spherical outflow, a tightly collimated, blue-shifted expansion, and a directed, red-shifted flow. Certain species (SiO, PN and NaCl) exclusively trace the spherical flow, whereas HNC and sulphur-bearing molecules (amongst others) are selectively created in the two expansions, perhaps arising from shock waves. CO, HCN, CS and HCO^+ exist in all three components. Despite the oxygen-rich environment, HCN seems to be as abundant as CO. These results suggest that oxygen-rich shells may be as chemically diverse as their carbon counterparts.

Circumstellar envelopes are unique chemical laboratories. Molecules are thought to form near the hot, dense stellar photosphere by a combination of equilibrium and non-equilibrium (that is, shocks and stellar photodissociation) processes[8]. As the gas flows from the star, molecular abundances 'freeze-out' until the outer edge, where the chemistry is further modified by interstellar ultraviolet radiation[3,4]. Chemical compounds in these shells apparently survive thousands of years as the star evolves to its final stage[5].

Oxygen is typically more abundant than carbon on the surface of main sequence stars, with a roughly solar ratio of C/O = 0.5 (refs 6, 9). Stars in a certain mass range, however, pass through the asymptotic giant branch (AGB), where they undergo substantial convection. 'Dredge-up' events mix carbon from the interior helium-burning shell to the surface such that the C/O ratio becomes >1 (ref. 6), resulting in 'carbon-rich' as opposed to 'oxygen-rich' envelopes, which vary in chemical complexity. The C-rich envelope of the AGB star IRC+10216, for example, contains over 60 different chemical compounds, including unusual carbon chain radicals[5]. In contrast, only 10–12 compounds have been identified in the most chemically interesting oxygen-rich evolved stars, such as IK Tau[10].

VY Canis Majoris (VY CMa) is an oxygen-rich[11] supergiant (~25 solar masses, $25M_\odot$) star with a luminosity of 500,000 times that of the Sun and an effective temperature near 3,000 K (ref. 12). The mass loss rate of VY CMa is substantial ($\sim 2\times10^{-4} M_\odot\ \mathrm{yr}^{-1}$), resulting in a clumpy envelope consisting of arcs, knots and jets on the scale of 10″ (~15,000 AU), evident in Hubble Space Telescope images[12] (Fig. 1). Molecular line observations trace a shell expanding at a velocity of $\sim 40\ \mathrm{km\,s^{-1}}$ (ref. 13). Aperture synthesis maps of CO and maser

Table 1 | Molecular abundances in VY Canis Majoris

Molecule*	Source radius (arcsec)		Abundance relative to H_2		
	Spherical wind	Red/blue flow	Spherical wind	Red-shifted flow	Blue-shifted flow
CN	6	8.5	2×10^{-8}	3×10^{-8}	1×10^{-8}
CO	6	8.5	5×10^{-5}	6×10^{-5}	8×10^{-5}
CS	0.5	0.7	1×10^{-7}	4×10^{-8}	1×10^{-7}
H_2O	0.1		4×10^{-4} †		
H_2S	6	8.5	7×10^{-8}	2×10^{-7}	1×10^{-7}
HCN	3	3.5	8×10^{-5}	4×10^{-5}	4×10^{-5}
HCO^+	6	8.5	2×10^{-8}	2×10^{-8}	2×10^{-8}
HNC		0.7		2×10^{-8}	2×10^{-8}
NaCl	0.25		8×10^{-9}		
NH_3				4×10^{-6} ‡	4×10^{-6} ‡
NS		8.5		1×10^{-8}	6×10^{-9}
OH				maser	maser
PN	0.5		4×10^{-8}		
SiO	6		$\sim1\times10^{-5}$		
SiS	0.5	0.7	7×10^{-6}	2×10^{-6}	7×10^{-7}
SO		8.5		5×10^{-8}	4×10^{-8}
SO_2		8.5		4×10^{-7}	3×10^{-7}

Abundances are relative to H_2. Abundances and source sizes were derived by modelling the line profiles, assuming an appropriate geometry and mass loss rate. In almost all cases, at least two transitions were simultaneously fitted to establish abundances. Collisional excitation was assumed. See Supplementary Information for details.
* Bold denotes first time observed towards VY CMa.
† Ref. 28.
‡ Ref. 29.

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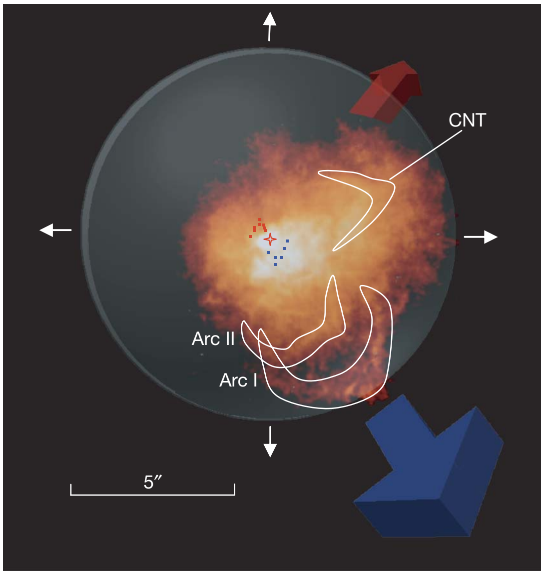

Figure 1 | Model of the molecular outflows in VY CMa, superimposed on the HST infrared image. The spherical wind is represented by the white arrows and the semi-transparent circle, whereas the two directed expansions are indicated by the (large) blue and red arrows. Positions of the red- and blue-shifted OH masers are shown (small rectangles) relative to the central star (red diamond), as well as the locations of the infrared features Arc 1 and Arc 2, located to the southwest, and the Curved Nebulous Tail (CNT), which appears northwest of the star[12]. The blue-shifted flow is slightly inclined relative to the line of sight, following the orientation of the masers. The arcs seem to follow the blue-shifted expansion. The red-shifted flow is oriented at a larger angle relative to the line of sight, roughly in the direction of the CNT. These infrared features probably trace shocks associated with the two expansions.

emission from OH, H_2O and SiO indicate structure of the order of an arcsecond, suggesting the presence of a tilted, expanding disk or a bipolar outflow[14,15].

Oxygen-rich circumstellar shells have never been studied in equivalent detail to the carbon-rich counterparts. Therefore, we began a spectral survey of VY CMa at wavelengths of 1, 2 and 3 mm (75–270 GHz) using the 12-m telescope and the Sub-Millimeter Telescope (SMT) of the Arizona Radio Observatory. In the course of our observations, seven molecules new to this source were discovered (NaCl, HCO^+, PN, CS, NS, HNC and SiS), bringing to 17 the total number of chemical compounds found in the envelope of VY CMa (Table 1).

The spectral-line profiles varied between species. SiO and PN were found to have roughly triangular line shapes (Fig. 2), tracing a spherical wind concentrated in the plane of the sky, with line widths $\Delta v_{1/2}$ (full-width at half-maximum) near 40 km s^{-1}. NaCl exhibited a much narrower line profile ($\Delta v_{1/2} \approx 14$ km s^{-1}), and arises from the interior region where the maximum outflow velocity has not yet been attained. SO_2 and SO display asymmetric horn-shaped profiles, with distinct blue- and red-shifted components near -7 km s^{-1} and 42 km s^{-1}, respectively. The horned profile in SO_2 is strikingly similar to that found in the OH 1,612 MHz maser transition[14], as shown in Fig. 2. SO_2, however, exhibits the same line shape in multiple transitions over a wide range of energies, consistent with a Boltzmann distribution with temperature $T \approx 50$ K. Furthermore, the blue-shifted feature in both molecules is almost identical in shape, suggesting a collimated flow close to the line of sight. In

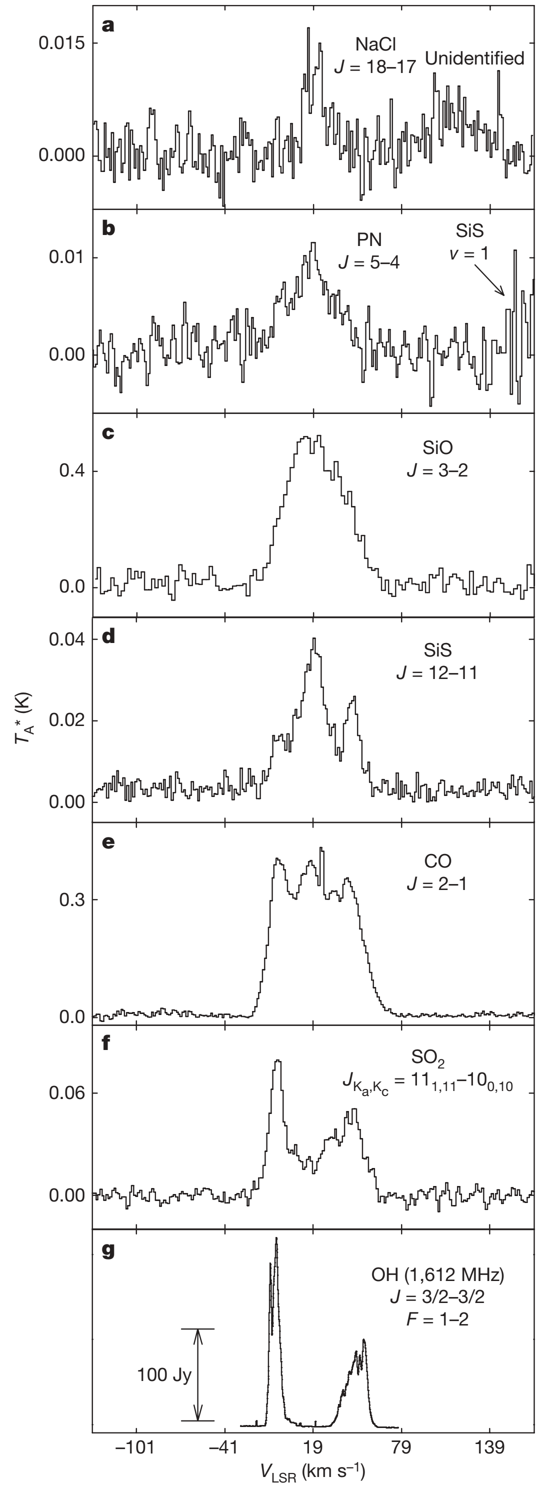

Figure 2 | Sample molecular spectra from VY CMa, measured with the Arizona Radio Observatory's Sub-millimeter Telescope (SMT), showing the variation in line profiles. The receiver used for these observations was an ALMA Band 6 prototype system[30], which produced exceptional total system temperatures (single sideband) of $T_{sys} \approx 120$–140 K on the sky. Various rotational transitions of molecules measured in the 1–2-mm wavelength region are shown (**a**–**f**), as well as the OH 1,612 MHz maser emission from ref. 14 (**g**). The spectrum in **c** was obtained with the 12-m telescope. The spectra are plotted in terms of intensity (T_A*, in K) versus velocity with respect to the local standard of rest (V_{LSR}, in km s^{-1}). The intensity scale for the OH data are in Janskys (Jy). The quantum numbers of the particular rotational transition displayed are given to the right of each spectrum. As these data illustrate, NaCl (**a**), PN (**b**) and SiO (**c**) exclusively trace the spherical wind, whereas the two directed outflows are prominent in SO_2 (**f**). SiS (**d**) and CO (**e**) are found in all three regions. The NaCl line is particularly narrow because this molecule disappears before the terminal outflow velocity is achieved. SO_2 and the OH maser profiles (**f** and **g**) are remarkably similar, suggesting that these species are linked chemically and dynamically. The narrow spike that appears in the CO spectrum near 25 km s^{-1} in LSR velocity arises from background gas. Spectral resolution for all data except the OH line is 1 MHz.

contrast, the red-shifted emission in SO_2 lies at lower projected expansion velocities than the terminal value indicated by this species itself and the maser emission. This difference indicates that the bulk of the red-shifted material is moving at a substantial angle relative to the line of sight. Many species, including SiS, HCN, H_2S, CO and CS, are present in all three flows. Comparison with previous CO and HCN data suggests that these regions extend to radii 6″–8″ from the central star[16,17].

The similarity of the OH and SO_2 line profiles indicate that the blue-shifted outflow is oriented to the southwest, like the masers, and encompasses the infrared dust features Arc 1 and Arc 2 (see Fig. 1). Potassium emission lines from Arc 1 also show a strong, blue-shifted feature with a velocity almost identical to that of the molecular spectra[18,19], suggesting that the arcs trace shocks created in the flow. Atomic absorption lines from the 'Curved Nebulous Tail' (CNT) have the same peak velocities as the red-shifted molecular lines. The red-shifted outflow therefore probably lies to the northwest, with the masers on the eastern edge. These two expansions seem to be unrelated; they exhibit different line shapes and molecular rotational temperatures. Large convective cells[20], as observed in the supergiant Betelgeuse[21], could be their origin.

The chemistry in the envelope of VY CMa differs with physical location. NaCl is present only in the spherical flow close to the photosphere, and probably condenses into grains at a radius near 0.25″. NaCl has previously been observed in the carbon-rich shells of two AGB stars[5,22], but is more abundant in VY CMa. SiO, in contrast, survives well into the spherical flow, reaching the terminal velocity. The abundance of this species is estimated to be $\sim 10^{-5}$, relative to H_2, in a 12″ region. (Abundances quoted here are relative to H_2, unless stated otherwise: see Supplementary Information.) A large fraction of the elemental silicon is therefore in gas-phase SiO, as opposed to silicate particles. SiS has a narrower line width than its oxide counterpart ($\sim 25\ \mathrm{km\,s^{-1}}$ versus $\sim 42\ \mathrm{km\,s^{-1}}$), suggesting that it condenses out or reacts to form other species, well before SiO. Modelling of the observed SiS transitions indicates a source size of 1″, consistent with an early disappearance, and an abundance of 7×10^{-6} (Supplementary Information). Unlike SiO, however, SiS also appears in the red- and blue-shifted expansions. PN exists exclusively in the inner part of the spherical flow with a 1″ source size and an abundance of $\sim 4 \times 10^{-8}$. These observations are the first conclusive identification of PN in circumstellar gas[23].

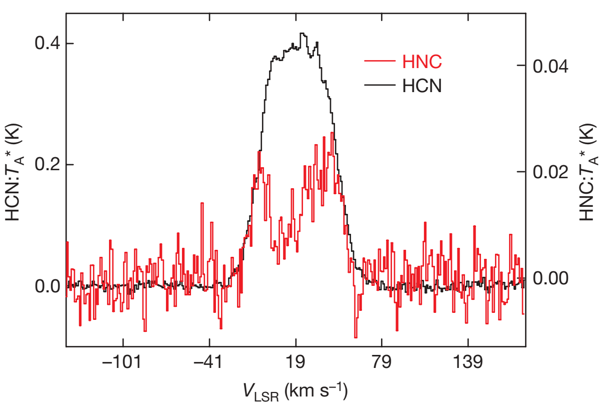

Figure 3 | Comparison of spectra for the metastable isomers HCN and HNC in VY CMa. The $J = 3 \rightarrow 2$ rotational transitions of both species are shown in the figure. The HNC spectrum is displayed in red, whereas that for HCN is plotted in black. HNC shows only the red- and blue-shifted flows, whereas HCN has a contribution from the spherical wind as well. The HNC/HCN ratio is roughly 0.001 for the directed flows, indicating high temperature formation[26], perhaps due to shocks. The spectra were measured in the 1-mm wavelength band using the SMT. The scale on the left-hand side of the spectra applies to the HCN data, whereas that on the right is for HNC. Spectral resolution for both lines is 1 MHz.

Six carbon-bearing species are present in VY CMa: CO, HCN, HNC, CN, CS and HCO^+. Shock and 'mixed' chemistry models have predicted the synthesis of HCN and CS in O-rich environments[8,17,24], and these species indeed are observed in several O-rich shells[17,25]. The models compute an HCN abundance at least a factor of ten less than CO, whereas observations have found HCN/CO < 1/100. In contrast, CO and HCN in VY CMa seem to have comparable abundances in all three flows, roughly 5×10^{-5} (Table 1). The appearance of HCO^+ is completely unexpected; this molecular ion had not been identified previously in circumstellar gas, and its existence in such material is not predicted by 'mixed' chemistry models[8,17]. HNC, the metastable isomer of HCN (ref. 26), is also an unusual species for O-rich shells[25]. This molecule is present exclusively in the directed flows, probably generated by the shock dissociation of HCN as the expansions drive into the spherical wind (Fig. 3).

SO_2, NS and SO predominantly exist in the red- and blue-shifted outflows. The similarity of their line profiles to OH suggests these species are related dynamically. Models have predicted that the creation of OH quickly leads to SO and SO_2, provided there is available sulphur[13,27]. Sulphur may arise from the dissociation of CS and SiS, and OH is a shock product of H_2O. Nitrogen for NS is probably produced from dissociated HCN. For both SiS and HNC, the red-shifted component seems to have stronger emission, whereas the blue-shifted wing is dominant in SO_2, SO and NS, showing chemical variation and suggesting shock differences in the two expansions.

Molecular production in VY CMa and its associated morphology cannot be explained by the usual spherical models of circumstellar synthesis, even when modified by non-equilibrium or 'mixed' chemistries. Shock waves and grain sputtering are likely to be influencing abundances. The diverse chemistry of VY CMa may be characteristic of red supergiant stars, induced by their complex process of mass loss.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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