COMPARATIVE SPECTRA OF OXYGEN-RICH VERSUS CARBON-RICH CIRCUMSTELLAR SHELLS: VY CANIS MAJORIS AND IRC +10216 AT 215–285 GHz

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Received 2010 April 23; accepted 2010 July 21; published 2010 August 13

ABSTRACT

A sensitive (1σ rms at 1 MHz resolution ~3 mK) 1 mm spectral line survey (214.5–285.5 GHz) of VY Canis Majoris (VY CMa) and IRC +10216 has been conducted to compare the chemistries of oxygen- and carbon-rich circumstellar envelopes. This study was carried using the Submillimeter Telescope of the Arizona Radio Observatory with a new Atacama Large Millimeter Array type receiver. This survey is the first to chemically characterize an O-rich circumstellar shell at millimeter wavelengths. In VY CMa, 128 emission features were detected arising from 18 different molecules; and in IRC +10216, 720 lines were observed, assigned to 32 different species. The 1 mm spectrum of VY CMa is dominated by SO2 and SiS. In IRC +10216, C2H and SiC2 are the most recurrent species. Ten molecules were common to both sources: CO, SiS, SiO, CS, CN, HCN, HNC, NaCl, PN, and HCO+. Sulfur plays an important role in both VY CMa, but saturated/unsaturated carbon dominates the molecular content of IRC +10216, producing CH2NH, for example. Although the molecular complexity of IRC +10216 is greater, VY CMa supports a unique “inorganic” chemistry leading to the oxides PO, AIO, and AOH. Only diatomic and triatomic compounds were observed in VY CMa, while species with four or more atoms are common in IRC +10216, reflecting carbon’s ability to form multiple strong bonds, unlike oxygen. In VY CMa, a new water maser (ν2 = 2) has been found, as well as vibrationally excited NaCl. Toward IRC +10216, vibrationally excited CCH was detected for the first time.

Key words: astrochemistry – circumstellar matter – stars: AGB and post-AGB – stars: individual (IRC +10216, VY CMa) – supergiants

1. INTRODUCTION

The chemistry of carbon-rich circumstellar shells of evolved stars has been the subject of investigation since the early days of millimeter astronomy (e.g., Wilson et al. 1971). One approach to elucidating the chemical properties of such objects is to continuously measure their spectra across a wide frequency range, namely, a spectral line survey. A number of such surveys have been carried out for C-rich envelopes, in particular that of IRC +10216, the best-studied asymptotic giant branch (AGB) star of this type, which lies at a distance of 150 pc and has a mass-loss rate of ~3 × 10−5 M⊙ yr−1 (Agúndez & Cernicharo 2006). In total, seven band scans of IRC +10216 have been performed (e.g., Avery et al. 1992; Kawaguchi et al. 1995; Cernicharo et al. 2000), including the very latest 1 and 2 mm survey by He et al. (2008). More recently, an 80–276 GHz spectral survey has also been conducted of the post-AGB star CRL 618 (Pardo et al. 2007). These studies, along with ISO and others, have helped to demonstrate the presence of 71 different chemical compounds in IRC +10216, and about 20 in CRL 618. Carbon-rich circumstellar shells thus remain some of the most chemically complex objects in the Galaxy. It is estimated that perhaps 50% of evolved stars have oxygen-rich, as opposed to carbon-rich, circumstellar envelopes (Kwok 2004). Observations have shown that on the red giant/supergiant branches, stars are oxygen-rich (O > C), as well as many on the AGB (e.g., Milam et al. 2009). It is thought that the “third dredge-up” on the thermal pulsing AGB branch converts an oxygen-rich star to a carbon-rich one, hence the appearance of objects such as IRC +10216 (Herwig 2005). Nonetheless, the regular occurrence of O-rich circumstellar shells would suggest that they are chemically relevant and theorists have considered them in their modeling (Willacy & Millar 1997). Yet, few observational studies have been carried out for these objects. Furthermore, only a limited number of molecular species have been identified in O-rich stars (Mont et al. 1993; Olofsson et al. 1991); consequently, it has been speculated that such objects lack chemical complexity (Olofsson 2005). In order to systematically evaluate the chemistry of oxygen-rich circumstellar shells and directly compare them to their C-rich analogs, we have conducted a 1 mm (215–285 GHz) spectral line survey of both VY Canis Majoris (VY CMa) and IRC +10216, using the Submillimeter Telescope (SMT) of the Arizona Radio Observatory (ARO). VY CMa is an oxygen-rich supergiant star with a massive envelope, at a distance of 1.1 kpc and a mass-loss rate of ~3 × 10−4 M⊙ yr−1 (Smith et al. 2001). This study was motivated in part by the advances in receiver technology resulting from the Atacama Large Millimeter Array (ALMA). The survey was conducted over a three year period using an ALMA-type sideband-separating (SBS) receiver with exceptional noise temperatures, baseline stability, and image rejection. It is the most sensitive survey to date, with typical rms noise levels of 3 mK (1 MHz resolution), and sometimes better, across the entire 70 GHz band. The complete data set is being published in another paper (Tenenbaum et al. 2010, Paper II), and an in-depth chemical abundance analysis is underway (J. L. Dodd et al. 2010, in preparation). Here, we present an overview of the relative chemical compositions of VY CMa and IRC +10216, and additional discoveries from the survey.
2. OBSERVATIONS

The measurements were conducted from 2007 February through 2009 December using the ARO 10 m SMT on Mt. Graham, AZ. The 1 mm receiver used was dual-polarization and employed ALMA Band 6 SBS mixers. Image rejection was typically $\geq 15$ dB, and LO shifts were done at all frequencies to establish any image contamination. The temperature scale at the SMT is measured as $T_A^*$, derived by the chopper wheel method, where the radiation temperature is defined as $T_R = T_A^*/\eta_b$, and $\eta_b$ is the main-beam efficiency. Over the 1 mm band, the beam size ranged from $\theta_b = 35''$ to $26''$ and the average beam efficiency was $\eta_b = 0.74$. Typical system temperatures were 200–450 K, with receiver temperatures of 60–80 K. Pointing accuracy is estimated to be $\sim \pm 2''$.

Observations were conducted in beam-switching mode with a $\pm 2''$ subreflector throw. The spectra were measured in 1 GHz intervals across the range 214.5–285.5 GHz, using 1 MHz resolution filter banks as back ends, typically configured in parallel mode (2 $\times$ 1024 channels). The data were then smoothed to 2 MHz resolution. The average integration time per 1 GHz interval is 8.6 hr, and the total integration time vested in the survey is $\sim 1700$ hr. Linear baselines were removed from the data and line parameters were established from the SHELL or GAUSS fitting routines in CLASS. For more detail, see Tenenbaum et al. (2010, Paper II).

3. RESULTS

The survey is summarized in Figure 1 and Table 1. Figure 1 displays the entire data sets for both VY CMa and IRC +10216, showing the relative spectral line density. A 1 GHz section of the survey at 267 GHz is shown in more detail. It is obvious from this figure that IRC +10216 contains far more spectral features at the lower intensity levels ($T_R < 0.1$ K). In fact, 720 individual lines were detected in IRC +10216, as opposed to 130 for VY CMa, a difference of about a factor of 6. Moreover, there are more unidentified lines in the C-rich shell, as the spectrum at 267 GHz illustrates. (Identification were made on the basis of public catalogs and the spectroscopic literature and checked for internal consistency.) The most abundant molecules in both sources, from preliminary analysis, are CO and HCN, followed by CS and SiS in IRC +10216 and SiO and SiS in VY CMa. A total of 123 U-lines were found in this survey for IRC +10216, but only 14 for VY CMa. Unidentified lines therefore compose about 17% of the total spectral features in IRC +10216 at this wavelength, and 10% in VY CMa. A nearly identical percentage of U-lines was found in the 2 mm survey of IRC +10216 by Cernicharo et al. (2000), using the IRAM 30 m. However, VY CMa is almost a factor of 10 more distant ($T_A = 2–11$ mK). The remainder of the features are primarily due to short-carbon-chain species and simple refractory molecules with Si, P, Al, and K. Furthermore, a new molecule, PH$_3$, was discovered in this survey (Tenenbaum et al. 2008), and CH$_2$NH has been identified for the first time in a circumstellar shell (see Section 4.2).

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In Table 1, the chemical compounds identified in each source and the number of detected transitions per species are listed. The molecules which are common to both objects appear at the top of each column (in bold font). They include six carbon-bearing molecules (CO, HCN, CN, HCO$^+$, HNC, CS), two with silicon (SiO, SiS), and the exotic refractories PN and NaCl. The abundances of these molecules in IRC +10216 are typically an order of magnitude higher than in VY CMa.

In the 1 mm spectrum, 32 different species have been identified in IRC +10216. SiC$_2$ and C$_2$H in their various isotopologues ($^{30}$SiC$_2$, $^{29}$SiC$_2$, and $^{13}$CCCH, $^{13}$C$^{13}$CCCH, $^{13}$CC$^{13}$CH, and $^{13}$CC$^{13}$CH) and excited vibrational states (SiC$_2$: $v_3 = 1$ and 2, C$_4$H: $v$ = 1, 20, and 2$^3$) are responsible for 36% of the observed lines. Another major contributor, with 47 lines, is SiS in the $v = 0–4$ states and isotopic variants ($^{30}$SiS, $^{30}$SiS, $^{30}$SiS, $^{30}$SiS, $^{30}$SiS, and $^{30}$SiS). SiC$_2$, C$_2$H, and SiS account for the majority of lines in IRC +10216 at 2 mm, as well (Cernicharo et al. 2000). NaCN gives rise to 38 total lines, all with weak intensities ($T_A = 2–11$ mK). The remainder of the features are primarily due to short-carbon-chain species and simple refractory molecules with Si, P, Al, and K. Furthermore, a new molecule, PH$_3$, was discovered in this survey (Tenenbaum & Ziurys 2008), and CH$_2$NH has been identified for the first time in a circumstellar shell (see Section 4.2).

A number of molecules that are present at lower frequencies are notably absent from the 215–285 GHz spectral region, including the carbon chains HC$_3$N, HC$_7$N, HC$_5$N, C$_6$H, C$_5$H, C$_4$Si, and C$_3$S, and MgNC. The small rotational constants of these heavy molecules, combined with low excitation conditions, make their emission lines more prominent at 2 and 3 mm.

In VY CMa, 18 different chemical compounds have been identified, almost doubling the known chemical inventory in O-rich shells. For those with only one transition accessible in
Figure 1. Complete ARO SMT spectral survey of VY CMa and IRC +10216 (214.5–285.5 GHz). The intensity scale is the same for both sources and is truncated at $T_A^*$ = 0.1 K to show the weaker lines. The lower panel displays a 1 GHz section of the survey, centered at 267 GHz (smoothed to a resolution of 2 MHz per channel). The panel highlights molecular features common to both sources: HCN $v_2 = 1^{14}$ ($J = 3 → 2$), $^{32}$SiS ($J = 15 → 14$), Na$^{37}$Cl ($J = 21 → 20$), and HCO+ ($J = 3 → 2$). The IRC +10216 spectrum also contains PH$_3$ and various other vibrationally excited HCN lines that are notably missing from VY CMa. Assumed velocities are $v_{LSR} = -26$ km s$^{-1}$ (IRC +10216) and $v_{LSR} = 19$ km s$^{-1}$ (VY CMa).

the 1 mm band (e.g., CS, HNC, HCO+, and H$_2$S), confirming lines were measured at 2 and 3 mm (see Ziurys et al. 2007, 2009). Along with OH and NH$_3$ (Bowers et al. 1983; Monnier et al. 2000), this survey brings the total number of chemical species to 20 in this source, making it the most chemically complex circumstellar shell after IRC +10216, and comparable to CRL 618. Surprisingly, $^{32}$SO$_2$ and $^{34}$SO$_2$ are responsible for 35 of the total 130 observed emission lines. SiS is the next most prevalent species with 21 features, including isotopologues and vibrationally excited states. Of the 18 species found here, three are completely new molecules—PO, AlO, and AlOH (Tenenbaum et al. 2007; Tenenbaum & Ziurys 2009, 2010), and four have never been seen before in O-rich shells (NaCl, PN, NS, and HCO+). In addition, the line profiles in VY CMa exhibit complex velocity structures that cannot originate from a spherical circumstellar outflow, as found in IRC +10216 (see Ziurys et al. 2007, 2009).

4. DISCUSSION

4.1. Carbon-rich versus Oxygen-rich Circumstellar Chemistry

This survey has enabled a direct comparison to be made between O-rich and C-rich stellar envelopes in the 1 mm band. It is obvious that free radicals are produced in both types of sources. In IRC +10216, nine radicals are found: CN, CP, SiC, CCH, l-C$_3$H, c-C$_3$H, C$_3$N, SiN, and C$_4$H. Five radical species are present in VY CMa (SO, CN, NS, PO, and AlO). Of the 32 different compounds present in IRC +10216, 23 contain carbon, or 72%. Many of these species are acetylenic chains (C$_2$H, C$_3$H, C$_4$H, HCN, and SiC$_2$). VY CMa has six carbon-bearing molecules—33% of the total. Nine molecules in VY CMa contain oxygen (~50% of the total), while only four have this element in IRC +10216 (~12%). It is clear that the C/O ratio does not completely control the relative chemistries in these two objects.
While species with as many as seven atoms (CH₃CCH) were detected in IRC +10216, only diatomic and triatomic molecules are found in this spectral region in VY CMa. This result could simply be a question of sensitivity, or it could be chemistry. The more complex species in IRC +10216 contain carbon–carbon bonds, and are formed by neutral–neutral and ion–neutral reactions involving photodissociation products of “parent” species (Millar & Herbst 1994; Agúndez et al. 2008). It is not clear that an equivalent chemistry exists involving oxygen chains. Partly hydrogenated oxygen chain molecules are known to be weakly bound (e.g., Mckay & Wright 1998; Murray et al. 2009), in contrast with the strong C–C bonds in carbon-chain species. And while the rotational spectra of HO₂ (Saito 1977) and HO₃ (Suma et al. 2005) have been measured in the laboratory, there is no evidence for these molecules in the survey in VY CMa. Nevertheless, the bent-shaped radical HO₃ is a known intermediate species in the earth’s atmosphere (Murray et al. 2009), and it may be detectable in VY CMa at lower frequencies.

Sulfur chemistry appears to play an important role in VY CMa, with six sulfur-bearing molecules observed, and the ubiquitous presence of SO₂ and SO. In contrast, only two silicon-containing molecules, SiO and SiS, were detected in this source. Sulfur’s predominance may be a condensation effect. Three of the main dust constituents in VY CMa contain silicon (amorphous silicate, Mg₂SiO₄, and MgSiO₃), while none include sulfur (Harwit et al. 2001). Therefore, excess sulfur may be available for gas-phase molecule formation.

4.2. Discovery of Circumstellar CH₂NH in IRC +10216

Nine favorable rotational transitions of methylenimine (CH₂NH) were detected in IRC +10216. The six unblended lines are shown in Figure 2, and line parameters are listed in Table 2. The features have consistent line shapes and intensities, with no obvious “missing” transitions. Three of these lines were also observed by He et al. (2008), but were marked as unidentified. CH₂NH has previously been observed in dense clouds (Dickens et al. 1997) and in a galaxy (Salter et al. 2008), but never in a circumstellar envelope.

As Figure 2 illustrates, the CH₂NH features appear slightly U-shaped, indicating that the molecule is present in the outer envelope. Rotational diagram analysis of the emission yields an excitation temperature of $T_{\text{rot}} = 26$ K, consistent with outer envelope conditions, and a column density of $9 \times 10^{12}$ cm⁻², assuming a uniform filling factor. CH₂NH is likely formed via gas-phase neutral–neutral reactions. One plausible sequence for creating CH₂NH in IRC +10216 is the association of CH and NH₃, followed by rapid decomposition to CH₂NH and H. Experiments have shown this scheme to have appreciable rate constants at temperatures as low as 23 K (Bocherel et al. 1996). One of the reactants, NH₃, has been detected in IRC +10216 (Monnier et al. 2000). The other reactant, CH, is a likely photodissociation product in the outer envelope.

Other partially saturated molecules have recently been detected in IRC +10216, such as CH₂CN, CH₃CHCN, and CH₃CCH, also arising from the outer envelope (Agúndez et al. 2008). Column densities of these species fall in the range $(6–18) \times 10^{12}$ cm⁻², with excitation temperatures of 30–50 K, similar to the values found for CH₂NH. The detection of CH₂NH is additional evidence that partially saturated hydrocarbons are formed in C-rich shells. The equivalents have yet to be found in O-rich environments, but the “inorganic” molecules H₂SO₄ or ClO₂ may be viable candidates.

4.3. New Excited Vibrational States in VY CMa and IRC +10216

Table 2 summarizes the vibrationally excited states of CCH, NaCl, and H₂O identified for the first time in an astronomical source. The presence of these transitions offers chemical insight into the two sources as well.

4.3.1. The $v = 1$ Level of NaCl in VY CMa

In VY CMa, three rotational transitions of NaCl in the $v = 1$ state were detected at 245 GHz, 271 GHz, and 284 GHz, with
NaCl, CCH, NaCl has been identified in a number of C-rich and O- rich circumstellar envelopes, including VY CMa (Milam et al. 2007; Higuchi et al. 2003), the v = 1 level is newly detected. The observed lines all exhibit widths of ~15–22 km s^{-1} (see Table 2), similar to those of the v = 0 lines (ΔV_{1/2} = 13–24 km s^{-1}). Three other transitions of the v = 1 state lie in the survey region: the J = 20 → 19 transition is completely obscured by a strong SO feature, the J = 18 → 17 line is not observed due to insufficient sensitivity, and the J = 17 → 16 line is contaminated by image features.

The v = 1 level in NaCl lies ~250 K above the ground state, and therefore it is striking that lines originating in this state are only 2–3 times less intense than their v = 0 counterparts. The estimated vibrational temperature is T_v = ~300 K. NaCl is likely formed near the stellar photosphere (Tsuji 1973; Ziurys 2006); the presence of NaCl in both sources indicates that LTE chemistry is occurring near the stellar photosphere (Milam et al. 2007), where the gas is both hot (T ~ 3000 K) and dense, and may cause vibrational excitation. Radiative pumping at 3 µm could also contribute to populating the v = 1 level. In contrast, the v = 1 lines of NaCl in IRC +10216 were not observed down to upper limits of ~4–5 mK (2 MHz resolution), although the v = 0 transitions had intensities of ~20 mK. The presence of NaCl in both sources indicates that LTE chemistry is occurring near the stellar photosphere (Tsuji 1973; Ziurys 2006); the v = 1 level suggests that this chemistry is taking place at higher temperatures in VY CMa.

### 4.3.2. Vibrationally Excited CCH (v_2 = 1) in IRC +10216

Three rotational transitions originating in the v_2 = 1 bending mode of CCH (X^3Σ^+), located 530 K above ground state, were observed toward IRC +10216. These lines are the vibrational satellites of the N = 3 → 2 transition, which form a doublet of doublets from l-type and spin-rotation interactions. The proton hyperfine splitting is negligible. The fourth line at 261.2 GHz is obscured by an SiC_2 v_3 = 1 feature. Ground state CCH has been known to exist in space since 1974, but past searches for vibrationally excited CCH have been unsuccessful (e.g., Woodward et al. 1987).

The detected features appear slightly U-shaped with the typical line width of ~28 km s^{-1} (see Figure 3), indicating that the v_2 = 1 level of CCH must originate in the outer shell. Since thermal or radiative excitation to the v_2 = 1 level is improbable in the cool outer envelope, it is likely that the photodissociation of acetylene (C_2H_2) directly creates vibrationally excited CCH. Laboratory studies have shown that UV photodissociation of C_2H_2 favors formation of CCH in the v_2 bending mode (Morduant et al. 1998) or in the A^2Π electronic state (Lai et al. 1996). The rotational spectrum of 1A^2Π CCH has not been measured, but this state could contribute to the production of the v_2 bending mode.

### 4.3.3. A Remarkable New Water Maser: H_2O (v_2 = 2) in VY CMa

The most intense emission line observed in the 1 mm band of VY CMa is the T_A^* ~ 14 K feature arising from the v_2 = 2, J_{K_a,K_c} = 6_{5,2} → 7_{4,3} transition of water at 268149 MHz, displayed in Figure 3. Water has never been seen before in the v_2 = 2 state which has an E_u ~ 6040 K, though there have been many reports of lines in the v_2 = 1 state (e.g., Menten et al. 2006). The width of the line, ΔV_{1/2} = 4 km s^{-1}, is more narrow than typical VY CMa emission features. Observations over three epochs in 2008 (April–June) showed no variability in line intensity, and comparison of the orthogonal polarization data did not reveal significant differences. The substantial intensity of the line and the narrow width indicate maser action, and potential use for mm-wave VLBI. Two other water lines, both in the v_2 = 1 state, were detected in the VY CMa data: the J_{K_a,K_c} = 5_{5,0} → 6_{4,3} (232686 MHz) and the J_{K_a,K_c} = 7_{7,0} → 8_{6,3} (263451 MHz) transitions. The intensities of these features are T_A^* = ~0.02–0.04 K, and the emission appears to be broader with multiple peaks. Both of these lines have been previously observed in circumstellar envelopes (Menten & Melnick 1989; Alcolea & Menten 1993). The v_2 = 1 state has also been tentatively observed in the far-IR (Polehampton et al. 2010). These data are further evidence that in supergiants/hypergiants oxygen is primarily contained in H_2O. Therefore, the abundance of CO is low (Ziurys et al. 2009; Dinh-v-Trung et al. 2009) and
Figure 3. Spectra showing the detections of new vibrationally excited states in the survey data. The top panel displays a new water maser in VY CMa originating in the $v_2 = 1$ mode at 260448 MHz and 259152 MHz, respectively, observed toward VY CMa, which exhibits a very narrow line width. The third and fourth panels display two lines of CCH in the IRC +10216. The vibrationally excited CCH lines are U-shaped, indicating an upper state of the survey data. The top panel displays a new water maser in VY CMa originating in the $v_2 = 1$ mode at 260448 MHz and 259152 MHz, respectively, observed toward VY CMa, which exhibits a very narrow line width. The third and fourth panels display two lines of CCH in the IRC +10216. The vibrationally excited CCH lines are U-shaped, indicating an upper state.

There is carbon remaining to form other molecules. Despite the chemical richness of IRC +10216, oxygen-rich envelopes such as that of VY CMa offer a new perspective on circumstellar chemistry.

This research is supported by NSF grant AST-06-07803 and AST-09-06534. E.D.T. acknowledges support from an NSF graduate research fellowship.

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