Detection of C\textsubscript{3} in the Circumstellar Shell of IRC+10216

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Vibration-rotation lines of C\textsubscript{3} have been identified in the circumstellar spectrum of the obscured carbon star IRC+10216. This molecule is of interest in both the chemistry of flames, where it may be involved in the formation of soot, and in astrophysics, where it is a potential building block for carbonaceous grains. This high-resolution infrared detection of the pure carbon chain molecule C\textsubscript{3} allows the estimation of the equilibrium C–C bond length, 1.297 angstroms. Possible astrophysical formation and destruction mechanisms for C\textsubscript{3} are reviewed, including the relationship between C\textsubscript{3} and carbon clusters.

A unique group of spectral lines at 4050 Å was first detected in the spectrum of a comet in 1881 (1). It was not until 1951 that A. E. Douglas (2) was able to attribute the 4050 Å group to the C\textsubscript{3} molecule. The most thorough analysis of the A\textsuperscript{1}\Pi\textsubscript{u}–X\textsuperscript{1}\Sigma\textsuperscript{+} transition of C\textsubscript{3} was carried out by Gausset, Herzberg, Lagerquist, and Rosen (3). In addition to comets and electrical discharges, the C\textsubscript{3} molecule has been observed in flames (4) and explosions (5) and in the vaporization of carbon (6). There is some low-resolution evidence for the appearance of C\textsubscript{3} in the atmospheres of cool stars (7). In flames, C\textsubscript{3} may be a critical link in the formation of soot (4). In astrochemistry, pure carbon chains, including C\textsubscript{3}, have been linked to the formation of circumstellar grains (8) and may be involved in the formation of diffuse interstellar bands (9).

The detection of C\textsubscript{3} in carbon stars and in the interstellar medium is inhibited by lack of ultraviolet (UV) flux at 4050 Å. Because C\textsubscript{3} is linear (3) or quasilinear (10) there is neither a dipole moment nor strong microwave pure rotational transitions. There are three vibrational modes, \nu\textsubscript{1} the symmetric stretch (\sigma\textsubscript{s}) at 1224.5 cm\textsuperscript{-1} (11), \nu\textsubscript{2} the bending mode (\sigma\textsubscript{b}) at 63.1 cm\textsuperscript{-1} (3), and \nu\textsubscript{3} the antisymmetric stretch (\sigma\textsubscript{as}) at 2040 cm\textsuperscript{-1} (12). However, \nu\textsubscript{1} is Raman active, not infrared active, and \nu\textsubscript{2} occurs in the far infrared, which remains a difficult spectral region to observe. The antisymmetric stretch, \nu\textsubscript{3}, is ideal for monitoring C\textsubscript{3} because it has a remarkably strong transition dipole moment of 0.44 D (10) and occurs in a spectral region where the atmosphere is relatively transparent.

On 30 December 1987 spectra of the prototypical obscured carbon star IRC+10216 and the moon were observed with an apodized (13) resolution of 0.014 cm\textsuperscript{-1} (2 km s\textsuperscript{-1} full width at half maximum) by means of the Kitt Peak National Observatory 4-m telescope and the Fourier Transform spectrometer located at the coude focus (14). The 52-min integration on IRC+10216 resulted in a peak signal-to-noise (1 sigma) ratio of 112. The spectrum was limited to 1975 to 2050 cm\textsuperscript{-1} by a cold blocking filter. The moon is an intrinsically featureless source in the 2000 cm\textsuperscript{-1} region. After appropriately scaling the telluric line strengths to match the air mass of the IRC+10216 spectrum, the lunar spectrum was ratioed to the IRC+10216 spectrum to remove the telluric spectrum.

The goal of our observations was to detect the CN vibration-rotation fundamental (15). IRC+10216 is frequently used for high sensitivity searches of circumstellar molecules because it is a bright source and lines of circumstellar origin appear against a featureless continuum, not superposed on photospheric lines (16). Although the CN lines were not obviously present (17), a series of strong lines was observed (Fig. 1), which on the basis of combination differences (3) were identified as C\textsubscript{3}. More R branch lines were identified on an archival spectrum (18 October 1978, resolution 0.026 cm\textsuperscript{-1}, S/N = 95) that covered the 2040 to 2170 cm\textsuperscript{-1} region. Prior to the discovery reported in this paper of the C\textsubscript{3} \nu\textsubscript{1} band in the circumstellar envelope of the carbon star IRC+10216, no high resolution spectroscopic observations of the infrared spectrum of C\textsubscript{3} were available.

At the time this work was completed no laboratory frequencies were available for the 2040 cm\textsuperscript{-1} C\textsubscript{3} lines, thus the frequencies had to be derived from our spectrum. To do this we assumed that, in analogy to the other molecules observed in the infrared with similar line shape and excitation temperature...
(see below), the lines exist in the circumstellar shell at the terminal expansion velocity, \(-14\) km s\(^{-1}\) relative to the center of mass (16).

Assuming this velocity and correcting for a local standard of rest velocity of \(-26\) km s\(^{-1}\) for IRC+10216 (18) and for the earth’s velocity at the time of the observation, frequencies were measured. Telluric CO\(_2\) lines (19) gave the frequency zero point. Subsequent to the submission of this report, we have learned of two research groups reporting laboratory detections of the \(v_3\) band of C\(_3\) (20). The laboratory observations agree with the work reported here.

The observed line positions (Table 1) were reduced to the molecular constants by means of the customary (21) rotational energy level expression:

\[ F(J) = B(J + 1) - D[J(J + 1)]^2 \]

(1)

where \(B\) and \(D\) are constants, and \(J\) is the angular momentum quantum number. The constants obtained from this fit are reported in Table 2.

The high resolution detection of \(v_3\) completes the analysis of the C\(_3\) fundamental modes of vibration and allows the derivation of an equilibrium molecular structure. The vibrational dependence of the rotational constants can be represented by (3, 11, 21)

\[ B_{11,22} = 0.41767 - 0.0048(v_1 + \frac{1}{2}) \]

\[ + 0.01345(v_2 + 1) - 0.00071(v_2 + 1)^2 \]

\[ + 0.00510(v_3 + \frac{1}{2}) \]

(2)

where \(v_1\) is the vibrational quantum number of mode \(v_1\). From the value of \(B_{11}\) 0.41767 cm\(^{-1}\), the equilibrium C–C bond length (\(r_e\)) of 1.2968 Å was calculated. The total error in \(r_e\) is hard to assess because the extremely floppy C\(_3\) molecule executes large-amplitude bending motions (10), but \(\pm 0.001\) Å seems a reasonable assumption. The equilibrium bond length of a molecule is an easy quantity to compute by ab initio quantum chemical calculations. For example, Kraemer, Bunker, and Yoshimine (10) obtain 1.290 Å, whereas Peric-Radic et al. (22) obtain 1.308 Å, both in good agreement with experiment. The \(r_0\) value calculated from \(B_{110} = 0.43056\) cm\(^{-1}\) (Table 2) is 1.277 Å, rather different from the \(r_e\) value because of the large-amplitude vibrational motion.

One unusual feature of the \(v_3\) mode is the vibrational dependence of the rotational constant \(B_{11,22}\). For most linear molecules the rotational constants of the antisymmetric stretching mode decrease with increasing vibrational excitation but for C\(_3\) the opposite trend is observed. The nonrigid bender calculations of Kraemer, Bunker, and Yoshimine (10) predict this effect; \(\alpha_3\) (calculated) = \(-0.003\) cm\(^{-1}\) compared to \(\alpha_3\) (observed, this work) = \(-0.00510\) cm\(^{-1}\).

The C\(_3\) lines in the spectrum of IRC+10216 appear to be saturated and we have used an observer’s frame radiative transfer code to model the lines in the circumstellar shell (23). Lacking a detailed knowledge of the spatial distribution, we assume a \(r^{-2}\) density distribution truncated at some inner radius. The assumption of a continuous C\(_3\) distribution throughout the envelope, as if the C\(_3\) originated in the photosphere similar to CO, C\(_2\)H\(_2\), HCN, and CS (16, 23–25), results in synthesized line profiles that bear no resemblance to the observations. The line profiles of species with continuous distributions are strongly influenced by higher temperature (\(T > 100\) K) gas in the inner regions (26) (\(r < 300\) R\(_s\), where 1 R\(_s\) = 6.7 \times 10\(^{13}\) cm) of the circumstellar shell (23). Moreover, the (0,1,1) \(\longleftrightarrow (0,1,0)\) “hot” band, whose lower level lies only 63 cm\(^{-1}\) above the ground state, falls within our bandpass. It is not seen. For a continuous distribution of C\(_3\), the model’s warm gas results in synthetic hot band line strengths that start to rival the cold band line strengths.

The observed rotational distribution of C\(_3\) is inconsistent with a photospheric origin and widespread distribution similar to that of the molecules discussed above. Given the small rotational constant of \(\sim 0.43\) cm\(^{-1}\), the significant strength in the low \(J\) lines (unresolved and \(\sim 50\%\) deep) and the apparent lack of absorption for lines with \(J > 20\) imply that the C\(_3\) absorption arises well away from the photosphere. Using the undetected high excitation (\(J > 20\)) lines, we establish an upper limit on \(x(C_3)\) of \(1.5 \times 10^{-7}\) in the warm, inner envelope (\(<300\) R\(_s\)). With the assumption of an inner boundary at 350 R\(_s\), the radiation transport calculations require a range of temperature, from 70 K to \(<20\) K, and a C\(_3\) column density of \(1(\pm 0.15) \times 10^{15}\) cm\(^{-2}\). The strongest C\(_3\) lines have optical depths of about unity. The fractional abundance of C\(_3\) relative to molecular hydrogen, \(x(C_3)\), is 1.2 \times 10\(^{-6}\) in the region modeled. The strongest synthesized lines in the (0,1,1) \(\longleftrightarrow (0,1,0)\) hot band are ~2% deep, and are undetectable in our present spectrum. Higher signal-to-noise data will be very useful in further constraining the gas temperature. If the actual density distributions were more compact or peaked, then maintaining the same column density would require a larger fractional abundance. However, the range of temperature indicated by the transport calculations points toward an extended distribution.

The question arises as to the origin of the C\(_3\). The difficulty with a direct photolysis origin for C\(_3\) is the paucity of possible parent molecules. Methyl acetylene and its isomer allene, C\(_2\)H\(_4\), are suspected C\(_3\) photolysis parents in comets (27). It seems unlikely that such heavy molecules would be abundant enough in IRC+10216 (28) to account for the observed C\(_3\) and, indeed, this seems to be the case. Upper limits of 3 \times 10\(^{-7}\) have been found for the abundance of methyl acetylene (29), 2 \times 10\(^{-7}\) for allene (25), and 5 \times 10\(^{-7}\) for diacetylene (C\(_2\)H\(_2\)) (25). The cyanoacetylene (HC\(_3\)N) abundance is a few times 10\(^{-7}\) (30), subject to considerable uncertainty, making it difficult to rule out. However, laboratory studies of vacuum UV cyanoacetylene photolysis indicate the photodissociation daughters to be C\(_3\)H and CN (31).

In addition to direct photolysis, C\(_3\) could be the result of photolysis and subsequent neutral or ion gas phase chemistry. Ion-molecule reaction schemes to form C\(_3\) initiated by cosmic ray ionization of helium and (more importantly) acetylene photolysis have been suggested (32), but these manufacture C\(_3\) only in the cold outer envelope (\(r > 1000\) R\(_s\), \(T < 15\) K). The infrared (16) and microwave (33) C\(_3\)H observations are consistent with an outer envelope mother molecule abundance \(x(C_3H) = 3 \times 10^{-6}\). With this assumption, our chemical kinetics and radiation transport calculations indicate
| Table 2. Spectroscopic constants for the ν3 vibrational mode of C3. |
|---------------------------------------------------------------|
| Constant              | Value (cm⁻¹) |
|-----------------------|--------------|
| ν3                   | 2040.02113 (62)* |
| Bₜₙ₀,₀            | 0.430557 (37) |
| Dₜₙ₀,₀             | 1.415 (79) × 10⁻⁶ |
| Bₜₙ₀,₁           | 0.435654 (39) |
| Dₜₙ₀,₁             | 3.937 (88) × 10⁻⁶ |

*One standard deviation uncertainty in parentheses. These errors are determined by the least-squares fit of the 15 line positions of Table 1.

Table 2 shows spectroscopic constants for the ν₃ vibrational mode of C₃.

Of course, the C₃ could be formed on carbon-rich grains either through photolysis or, as is thought to be the case (25) for NH₃, CH₄, and SiH₄, catalytic reactions. With a standard model for the gas and dust density (26) and assuming a grain radius of 0.1 μm (16), and σ(C₃) = 10⁻⁶ at 400 Rₛ, we find that 10³ carbon atoms must be released per grain. Although this is only 0.1% of the grain mass, this assumes all carbon atoms are released as C₃. Note the relative abundance of the trace species NH₃, CH₄, and SiH₄ is 1 × 10⁻⁷ (25), similar to the C₃ abundance. However, these presumably catalytically produced species seem to leave the grains in a considerably warmer region (25). This still leaves photolytic interactions with the grains as a possibility.

In addition to the origin of C₃, its subsequent chemical behavior is potentially of great importance to the chemistry of the circumstellar shell. Because H₂, C₂H₂, and HCN are highly abundant at r < 100 Rₛ in the circumstellar shell of IRC+10216 and because many complex hydrocarbons are observed at r > 1000 Rₛ, (28), neutral gas phase reactions between H₂, C₂H₂, and HCN molecules, and C₃ are of potential importance. Studies (37) of ground-state C₃ reacting with other species indicate that the reaction rates are typically factors of 10² to 10⁴ slower than the gas kinetic collision rate. If this relatively slow reactivity applies to the molecular collision partners likely to be encountered in the circumstellar envelope then, with the possible exception of molecular hydrogen (because of its large relative abundance), neutral gas phase reactions with C₃ probably are not important on the time scales involved. The C₃ bond energy is 7.3 eV (31) and the ionization potential is 12.1 eV (38). These large values imply a relatively long life for C₃ against the eventual photodestruction into the more reactive species C₂ and C₂⁺.

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Solid-State Ice Volcanism on the Satellites of Uranus

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Voyager images of the uranian satellites Ariel and Miranda show flow features with morphologies indicating that ice has been extruded to the satellites' surfaces in the solid state. These images provide the first observational evidence for solid-state ice volcanism in the solar system. Topographic profiles have been measured across a number of flow features on Ariel. With a simple model of extrusion, spreading, and cooling of a viscous flow, the initial viscosity of the flow material is found to have been no more than about 10¹⁴ poise, far lower than expected for H₂O ice at the ambient surface temperatures in the uranian system. Sharply reduced viscosities may have resulted from incorporation of ices like NH₃ or CH₄ in the uranian satellites.

One of the most interesting results of the Voyager mission to Jupiter, Saturn, and Uranus has been the extent to which even small icy satellites of those planets have undergone geologic resurfacing (1–5). It generally has been uncertain, however, whether the resurfacing has taken place in the liquid or solid state. In the jovian system, buoyancy considerations seem to favor extrusion of warm, mobile ice rather than liquid water (6). However, no landforms clearly indicative of solid-state extrusion have been observed there. On the smaller saturnian satellites, mobility considerations favor extrusion of liquid (7), and the observed morphology is at least consistent with this interpretation. In the uranian system, there is morphologic evidence for extrusion in the solid state (5). In this report we consider this evidence, quantify the morphology of the flows, derive approximate viscosities at the time of extrusion, and consider the implications of these viscosities for the compositions and thermal histories of the uranian satellites.

The morphologic evidence for solid-state resurfacing on the uranian satellites is best developed on Ariel (Figs. 1 and 2). Much of the satellite's surface is transected by a pattern of linear graben-like canyons. On the floors of some of the grabens are deposits that have low crater densities compared to the rest of the satellite (8) and have topographic profiles that appear to be strikingly smooth and convex. They appear to steepen significantly at the margins, in what seem to be flow fronts. Some flows contain medial grooves running parallel to the graben walls. The convex topography and the concentration of the deposits in grabens strongly suggest that these deposits are materials that were extruded to the surface in the solid state, probably in an extensional environment.

In some cases, the flows appear to have been confined by graben walls. In others, however, they clearly have not. Figure 1 shows an instance where the lateral extent of a flow within a canyon remains relatively constant along the canyon's length, whereas the width of the canyon changes from that of the flow to roughly three times it. Figure 2 shows an instance where a flow has spread out across a plains unit, partially burying an impact crater.

It is likely that the sources of most flows were linear fracture systems on the graben floors. This interpretation is supported by (i) the likelihood that extensional fractures associated with grabens would parallel the graben walls; and (ii) the apparent steep flow fronts and limited lateral extent of some flows, indicating that they spread a short distance laterally rather than flowing long distances parallel to the graben walls. In large terrestrial grabens, volcanism is commonly concentrated along vents near the graben axis (9–11); such may also be the case on Ariel. At least some of the medial grooves may be the juncture of two independent flows that have been extruded from parallel fractures on a graben floor, have spread laterally and met, but have not completely coalesced.

Evidence for solid-state resurfacing is also observed on Miranda (Fig. 3). Miranda's surface consists of two types of materials: an old, heavily cratered terrain and a younger terrain transected by a complex pattern of subparallel bands, scarps, and ridges. Areas of this younger terrain are known as "coronae." In some places where corona materials come into contact with the ancient heavily...