

Microwave and laser spectroscopy of carbon chains and rings

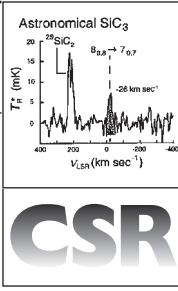
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The interstellar gas and the gas ejected into space by cool stars are now known to contain a rich collection of molecules. Most of these are organic compounds, some of which are familiar to the terrestrial chemist and can be found in a standard chemical stockroom, but many are entirely new molecules which have been detected and identified in space for the first time. Most of the nearly 100 polyatomic molecules so far detected in astronomical sources by radio telescopes are highly unsaturated carbon chains, a structure which is explosively unstable at even moderate density, and therefore difficult to study spectroscopically on Earth. For this reason laboratory detection has until quite recently lagged well behind the astronomical discovery of many carbon chains. The application of Fourier transform microwave and laser cavity ringdown absorption spectroscopy to supersonic molecular beams has largely overcome this difficulty, yielding in this laboratory during the past four years more than 75 new reactive molecules, including long carbon chains, chains attached to rings, silicon–carbon rings, and several protonated molecular ions. All or nearly all of these are candidates for astronomical discovery because they are highly polar and are close in structure and composition to molecules which have already been discovered in space. Seven have already been found with large radio telescopes, six as a result of the

laboratory work described here. These discoveries include the largest interstellar molecule HC₁₁N, the largest ring, SiC₃, and the largest positive ion, HC₃NH⁺. One of our most interesting recent laboratory discoveries is the laser detection of a strong molecular band at $\lambda 4429$, the wavelength of the strongest and best known diffuse interstellar band.

1 Introduction

In space as on Earth, the ambiguity of carbon in bonding and its unique ability to form both single and multiple bonds give rise to a chemistry of great subtlety and complexity. In the interstellar gas and in the gas being ejected into space from cool stars, 123 molecules have now been detected and identified (Fig. 1), mainly by radio telescopes with high spectral resolution receivers able to resolve the sharp rotational emission lines characteristic of molecules in cold, low density gas excited by collisional impact. The simple astronomical molecules are both inorganic and organic in composition, but all those with more than five atoms are organic, and the majority of these are carbon chains with linear heavy atom backbones of highly unsaturated carbon (generally unsymmetrical in structure, as Fig. 1 shows, to provide the permanent electric dipole moment

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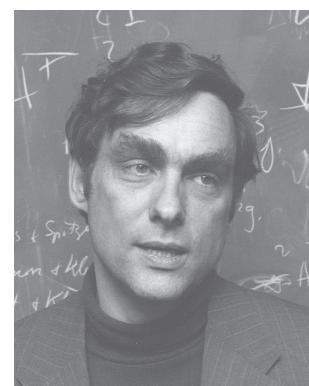
carbon clusters; the chemistry and physics of the interstellar medium; and molecular radio astronomy.



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required for radio detection). It is one of the paradoxes of interstellar chemistry that unsaturated carbon should be so conspicuous in a regime where hydrogen is the dominant chemically active element by more than three orders of magnitude.

It is thought that many of the molecules in Fig. 1 are produced by gas-phase ion-molecule reactions which occur rapidly even at the low temperature (less than 100 K) characteristic of the interstellar gas. Ion-molecule processes, for example, predict the existence of many reactive molecules and isomers whose abundances are far from those that would be predicted from equilibrium considerations alone, including polyatomic ions such as HCO^+ , and energetic isomers such as HNC and the cumulene carbene H_2C_4 . The abundance of carbon chains, in particular, is attributable to the formation of C^+ by the reaction $\text{CO} + \text{He}^+ \rightarrow \text{C}^+ + \text{O} + \text{He}$,¹ and by the ionization of atomic carbon by the hard UV photons from hot stars. Recent laboratory studies indicate that atomic carbon efficiently reacts with a variety of stable hydrocarbons at room temperature and below, implying that neutral-neutral reactions may also play a role in the formation of longer carbon chains.^{2,3}

Most of the polyatomic molecules in Fig. 1 have been discovered in molecular clouds, the dense component of the interstellar gas where the hydrogen is mainly H_2 , but a few have been found in the lower density so-called "diffuse" clouds which are mainly atomic H, and many others in circumstellar shells around evolved stars. Molecular clouds have densities from 10^2 to 10^6 cm^{-3} and temperatures that are generally under 50 K (although higher in the vicinity of newly formed hot stars); diffuse clouds have densities from 10 to 100 cm^{-3} and are generally hotter than molecular clouds, with temperatures from 50 to 150 K; the circumstellar ejecta where molecules can form and survive have densities of roughly 10^5 cm^{-3} and temperatures of 20 K. In all three types of objects dust grains formed from the cosmic nonvolatile elements are present in a

fairly constant proportion by mass. Molecular clouds, as a result, tend to be highly opaque, diffuse clouds fairly transparent, and circumstellar shells of intermediate opacity. In all three locations, many rotational levels of polyatomic molecules are generally populated, but the populations of excited vibrational and electronic levels are generally negligible.

An enigmatic family of optical diffuse interstellar bands (DIBs) have long been observed in the diffuse clouds.⁴ [There is an unfortunate ambiguity here: the bands have traditionally been termed 'diffuse' not because of the clouds in which they are observed, but rather because their profiles are wide and generally featureless, nearly all lacking appreciable rotational structure.] More than 125 are now known in the visual and near infrared,⁵ but despite much work over the past 50 years, the carrier of none has been positively identified. [A possible exception is the carbon chain anion C_7^- , which may be responsible for four or five diffuse bands in the region 560–630 nm,⁶ but recent astronomical observations by McCall *et al.*⁷ cast doubt on this identification.] The DIBs are almost exclusively seen in absorption against nearby fairly bright stars, but several may occur in emission toward one peculiar source, the Red Rectangle.⁸ Although in the past it has been argued that the DIBs originate in the interstellar dust grains, there is now much evidence that they are produced by molecules in the gas phase, some plausible carriers being carbon chains,⁹ polycyclic aromatic hydrocarbons,¹⁰ and fullerenes.¹¹ The conspicuous presence of linear carbon elsewhere in the interstellar gas in the dense molecular component is an obvious merit of the carbon chain hypothesis.

The first molecules detected in space with radio telescopes, OH , H_2O , NH_3 , and then H_2CO were well known to spectroscopists prior to their astronomical discovery. Many of the molecules subsequently detected in space, however, were highly reactive species, generally unknown or unfamiliar to the laboratory chemist or physicist. Because many of these are

Known Interstellar and Circumstellar Molecules (July 2000)

2		3		4		5		Number of Atoms		6		7		8		9	
H_2	H_2O	NH_3		SiH_4		CH_3OH		CH_3CHO		$\text{CH}_3\text{CO}_2\text{H}$		$\text{CH}_3\text{CH}_2\text{OH}$					
OH	H_2S	H_3O^+		CH_4		NH_2CHO		CH_3NH_2		HCO_2CH_3		$(\text{CH}_3)_2\text{O}$					
SO	SO_2	H_2CO		CHOOH		CH_3CN		CH_3CCH		$\text{CH}_3\text{C}_2\text{CN}$		$\text{CH}_3\text{CH}_2\text{CN}$					
SO^+	HN_2^+	H_2CS		$\text{HC}\equiv\text{CCN}$		CH_3NC		CH_2CHCN		C_7H		$\text{H}(\text{C}\equiv\text{C})_3\text{CN}$					
SiO	HNO	HNCO		CH_2NH		CH_3SH		HC_4CN		H_2C_6		$\text{H}(\text{C}\equiv\text{C})_2\text{CH}_3$					
SiS	$\text{SiH}_2?$	HNCS		NH_2CN		C_5H		C_6H				C_8H					
NO	NH_2	CCCN		H_2CCO		HC_2CHO		$\text{c-CH}_2\text{OCH}_2$									
NS	H_3^+	HCO_2^+		C_4H		$\text{CH}_2=\text{CH}_2$		$\text{C}_7^-?$									
HCl	NNO	CCCH		$\text{c-C}_3\text{H}_2$		H_2CCCC											
NaCl	HCO	c-CCCH		CH_2CN		HC_3NH^+											
KCl	HCO^+	CCCO		C_5		C_5N											
AlCl	OCS	CCCS		SiC_4		$\text{C}_5\text{S}?$											
AlF	CCH	HCCH		H_2CCC													
PN	HCS^+	HCNH^+		HCCNC													
SiN	c-SiCC	HCCN		HNCCC													
NH	CCO	H_2CN		H_3CO^+													
CH	CCS	c-SiC_3															
CH^+	C_3	CH_3															
CN	MgNC	$\text{CH}_2\text{D}^?$															
CO	NaCN																
CS	CH_2																
C_2	MgCN																
SiC	HOC^+																
CP	HCN																
CO^+	HNC																
HF	SiCN																
	$\text{KCN}?$																

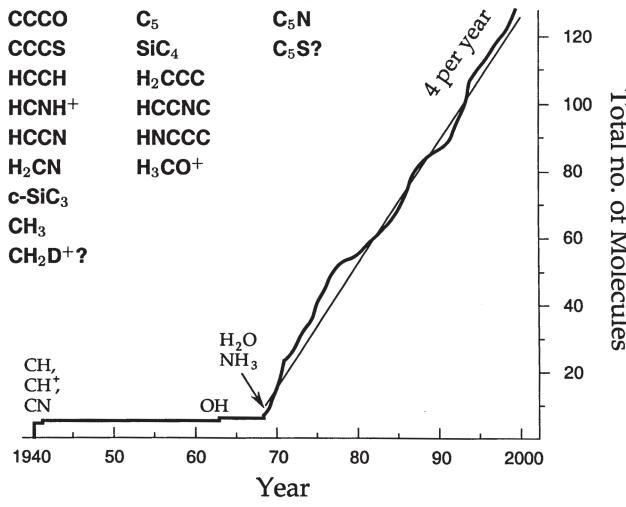


Fig. 1 Molecules identified in the interstellar gas and in circumstellar shells, ranked by number of atoms. Insert—Cumulative total by year since 1940.

carbon chains which are unstable at terrestrial densities, tending to explosively polymerize to disordered carbon with a more or less graphitic structure, laboratory detection has proved challenging, and, as a result, has often lagged rather than preceded astronomical discovery. Recent advances here and in other laboratories, however, suggest that the means are now at hand to overcome this difficulty, and that any polar molecule detected in space can now be found in the laboratory with present techniques or with a moderate refinement of them. Two have been found to be particularly powerful when applied to a supersonic molecular beam: Fourier transform microwave (FTM) spectroscopy and cavity ringdown absorption spectroscopy (CRDS). Together in our laboratory they have resulted in the detection of more than 75 reactive carbon molecules (Fig. 2), including chains, ring-chains, and rings; 13 are closed-shell polyyynes, 33 are radicals, 27 are carbenes, and two are ions. Of these, 71 are polar molecules whose rotational spectra have been detected by FTM spectroscopy at centimeter wavelengths, and four are non-polar molecules whose optical spectra have been detected by CRDS at visible wavelengths. As discussed below, a fifth molecule detected by CRDS, of still uncertain composition and structure, gives rise to a strong molecular band at 4429 Å, precisely the wavelength of the strongest and best known DIB.

For most of our new discoveries, the laboratory spectroscopy is now ahead of the observational astronomy, and astronomical searches, typically inefficient and costly in telescope time when frequencies are uncertain, can now be based on very precise spectral line frequencies. The large number of laboratory detections also provides much new data for the next generation of radio and optical astronomical investigations. Because of limited space it is not possible to give much here in the way of experimental details, or to present more than a brief survey of the flood of new data. Instead, we briefly describe the laboratory detection of several of the new molecules, and discuss joint astronomical and laboratory investigations that have led to recent astronomical discoveries.

2 Approach and experimental techniques

2.1 FTM spectroscopy

The application of FTM spectroscopy to supersonic molecular beams^{12,13} is particularly effective in the study of the large reactive carbon chains found in space, because the rotational spectra of these molecules are greatly simplified at the low rotational temperature of a few degrees Kelvin that is readily achieved in a supersonic expansion. In our spectrometer, as Fig. 3 shows, reactive molecules are created by a small low-current dc discharge in the throat of the expansion nozzle as a gas pulse consisting of a small amount of organic vapor heavily diluted (99% or more) in an inert gas (Ar or Ne) expands from a commercial pulsed valve. Free expansion from the nozzle forms in a short distance an approximately Mach 2 supersonic beam with a rotational temperature approaching 1 K. As the beam passes through a high-*Q* Fabry-Perot microwave cavity, a rotational transition resonant with one of the modes of the cavity is excited coherently by a short pulse of resonant microwave radiation; the microwaves almost immediately die away, and line radiation by the coherently rotating molecules is then detected by a sensitive microwave receiver. The Fourier transform of the free induction decay yields the power spectrum. For the axial beam illustrated in Fig. 3—the configuration adopted for nearly all our experiments because it gives the best signal-to-noise and resolution—the line shape is

double peaked, owing to the two Doppler components which result from decomposition of the standing mode of the Fabry-Perot cavity into two traveling waves, one parallel to the supersonic beam, the other antiparallel. In practice, this peculiar lineshape is usually only a minor inconvenience, and the effective spectral resolution of the spectrometer is determined by the small width of the individual Doppler peaks.

The success of our centimeter-wave device is principally the result of five factors: (1) the high intrinsic sensitivity of the technique, particularly when the molecular beam is directed along the axis of the Fabry-Perot cavity;¹⁴ (2) careful optimization of the geometry and electrical characteristics of the discharge and nozzle; (3) the general use of unstable and explosive precursor compounds; (4) refinements to the microwave receiver, including careful electromagnetic coupling of the receiver to the Fabry-Perot cavity and cooling of the cavity mirrors and the first-stage of the receiver amplifier to 77 K with liquid nitrogen; and (5) computer control which allows automatic scanning over wide frequency ranges and rapid data transfer and analysis. Together these factors have allowed us to attain an improvement in sensitivity of one to two orders of magnitude over that of the free-space millimeter-wave absorption spectrometer with which all our laboratory discoveries were made prior to 1996.

2.2 CRD spectroscopy

Many of the new laboratory molecules shown in Fig. 2 are plausible carriers of the diffuse interstellar bands, and it is for the optical study of the electronic spectra of those detected in the radio band and similar molecules that a laser spectrometer was recently constructed in this laboratory. The radio spectroscopy is complete in the sense that the identity of each molecule is quite secure and precise constants for the rotational spectra of each have been determined, but the electronic spectra of nearly all is unknown. For a given molecular density, laser spectroscopy is generally much more sensitive than rotational spectroscopy, so laser detection should be possible for many. (The red and violet bands of CN, for example, were first identified in 1932,¹⁵ but it was 45 years later that the rotational spectrum of this readily produced radical was observed by millimeter-wave absorption spectroscopy).¹⁶ Most of the molecules shown in Fig. 2 have conjugated structures, similar in their properties to organic dyes, with similarly strong electronic transitions that make them good candidates for the carriers of the DIBs. The specific abundances in our molecular beam of these molecules are known fairly accurately from the FTM measurements, and most are adequate for laser detection ($\sim 10^9 \text{ cm}^{-3}$).

CRDS is expected to be the technique of choice because most of the larger carbon molecules shown in Fig. 2 probably fail to fluoresce, or do so only weakly, so detection by the very sensitive technique of laser-induced fluorescence is prohibited. The same mechanism of rapid internal conversion which quenches fluorescence in these molecules may also provide for the wide, generally featureless absorption profiles of most diffuse bands.⁹ A schematic of our laser cavity ringdown spectrometer is shown in Fig. 3. The discharge source for reactive molecules is nearly identical to the one employed in the FTM experiment.

CRDS is long path, sensitive absorption spectroscopy^{17,18} achieved by measuring the rate of absorption of a light pulse confined within a highly reflective optical cavity. It has become a practical spectroscopic tool because of its ease and convenience, and because of the commercial availability of fairly inexpensive mirrors with reflectivities of order 99.99%, accomplished by the deposition of several tens of layers of dielectric

material; mirrors in the visual, several centimeters in diameter, typically cost \$1000–2000 a pair, and are highly reflective over a bandwidth of 15%. CRDS is more sensitive than conventional

absorption spectroscopy with a pulsed dye laser by about four orders of magnitude, meaning that relative absorptions as small as $\Delta I/I \sim 10^{-7}$ can be detected.

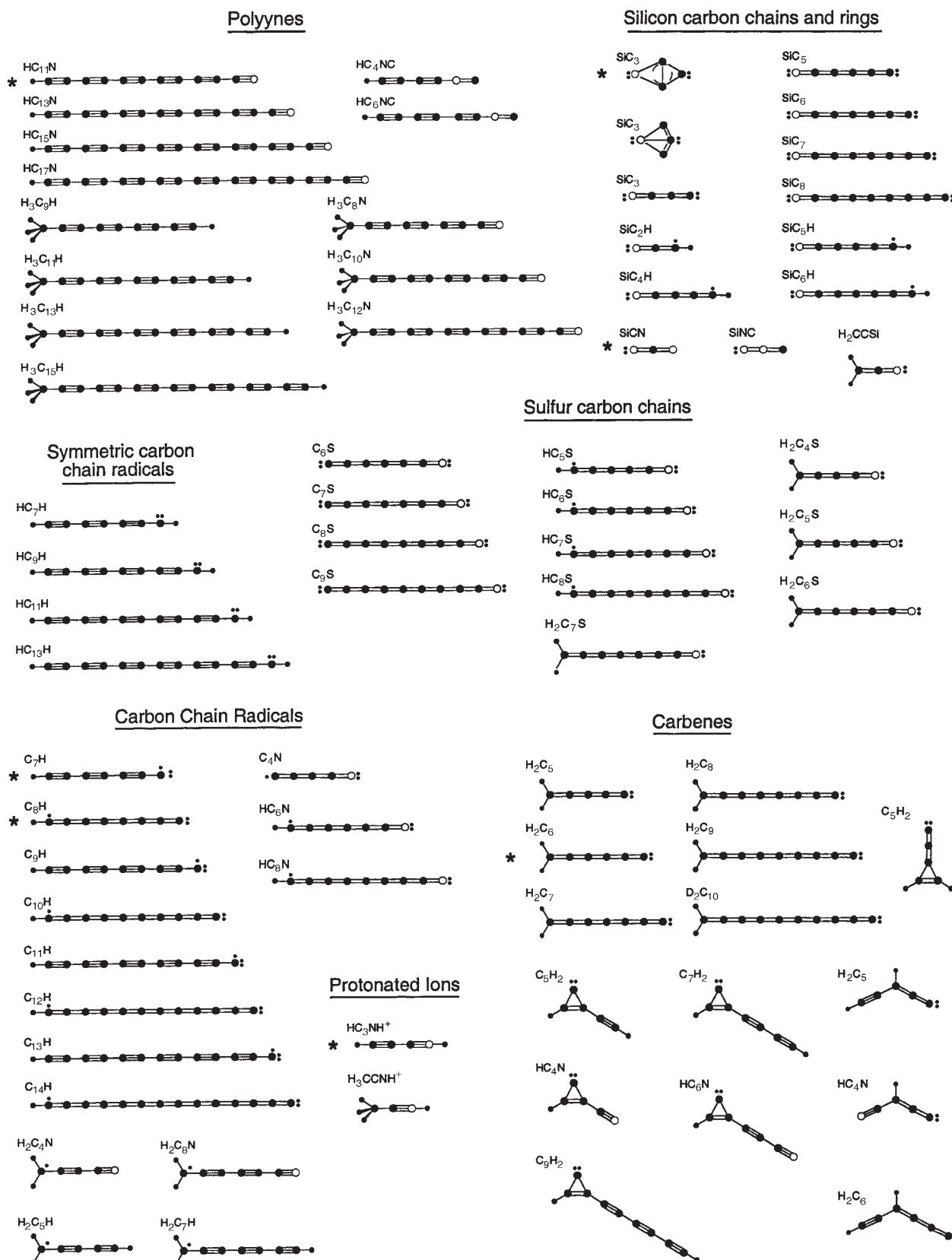


Fig. 2 The seventy-five molecules discovered here during the past four years. Open circles denote hetero atoms, either N, Si, or S. Asterisks (*) indicate those molecules already detected in space, all but one (HC_3NH^+) on the basis of the present laboratory work. The laboratory astrophysics of all is complete in the sense that the radio spectra (including hyperfine structure where it exists) have been measured directly or can be calculated to better than 1 ppm.

FTM Spectrometer

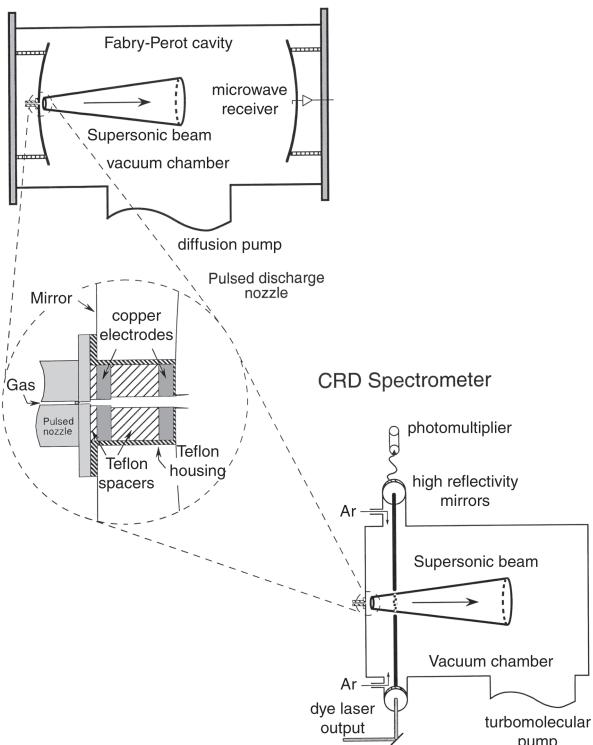


Fig. 3 Schematic diagram of the FTM and CRD spectrometers. In both experiments reactive molecules are produced in a small low-current dc discharge in the throat of a nozzle through a stream of a precursor vapor (diacetylene, cyanoacetylene, acetylene, silane, etc., diluted 99% or more with Ne or Ar), just prior to supersonic expansion to about Mach 2 in a large vacuum chamber. The stagnation pressure of the gas behind the valve is 1–3 atm, the discharge potential is 1000–1800 V, and the length of the gas pulse is typically 200–350 μ s. The diameter of the opening orifice of the nozzle immediately following the valve is 1 mm. A pulsed valve working 6–10 Hz, open less than 1% of the time, is required to keep the pressure in the chamber low enough to form a good molecular beam.

3 Recent results

3.1 The long cyanopolyyne chain HC_{17}N

The longest carbon chain so far detected in our laboratory is a large molecule by the standards of known astronomical chains: HC_{17}N with 19 atoms and a molecular weight of 219 amu,¹⁹ nearly three times the molecular weight of glycine, the simplest amino acid. HC_{17}N and other long chain cyanopolynes are produced best in our discharge with a mixture of cyanoacetylene (HC_3N) and diacetylene (HC_4H) in Ne. Like other closed-shell linear molecules, the radio spectrum of HC_{17}N can be calculated to high precision from two free parameters: $\nu_{J \rightarrow J-1} = 2BJ - 4DJ^3$, where J is the angular momentum quantum number for the upper level of the transition, and B and D are the rotational constant and the leading centrifugal distortion constant. Shown in Fig. 4 is an energy level diagram of the lower rotational levels of HC_{17}N and the transitions that have been measured, along with a sample line. The lower-lying rotational transitions below 1 GHz are expected to have resolvable nitrogen quadrupole hfs, but for the high- J transitions we have observed this hyperfine structure (hfs) has collapsed and is too small to observe.

As found for other closed-shell chains, the rotational constants of the longer cyanopolynes are remarkably well predicted by extrapolation.²⁰ The predicted constants agree with those measured to within a few parts in 100,000 for both HC_{15}N and HC_{17}N , so that at 5 GHz (where HC_{17}N has its most intense rotational transitions in our 3 K molecular beam) a frequency search of 1 MHz or less was required. The empirical predictions are at least an order of magnitude better than the best theoretical

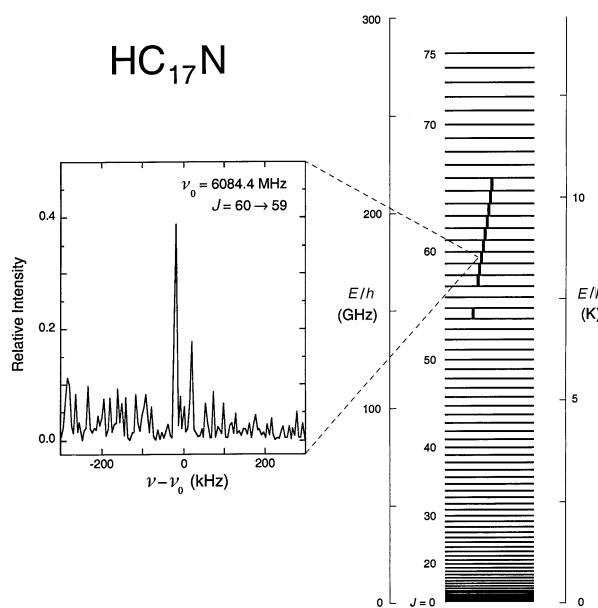


Fig. 4 Lower rotational levels of HC_{17}N with observed transitions indicated (vertical bars). Insert—Sample line of HC_{17}N , obtained with an integration time of 60 min. The double peaked line shape is instrumental in origin: it results from the Doppler shift of the supersonic molecular beam relative to the two traveling waves that compose the confocal mode of the Fabry-Perot cavity.

ab initio predictions, which are no better than 0.1% in accuracy. The close agreement of extrapolation with experiment suggests that the moment of inertia of these long chains is quite insensitive to structural details such as the rotation-vibration interaction which are important for small molecules. Little frequency search should therefore be required to detect HC_{19}N and HC_{21}N , whose rotational constants are predicted to be only 37.069(2) MHz and 29.919(3) MHz, respectively.

The detection of HC_{17}N illustrates why it is worth refining the sensitivity of FTM spectroscopy. The lines of HC_{17}N are nearly an order of magnitude stronger than predicted by the nearly constant decrement in intensity observed for HC_3N to HC_9N , and there is apparently almost no decrement in the actual number density of the longer chains in our beam—as Fig. 5 shows, HC_{17}N is about as abundant as HC_{15}N . The longest cyanopolynes are evidently more abundant and more easily detected than might have been expected, and still longer ones are probably within our grasp with slight improvement in sensitivity. In the interstellar gas, as in our molecular beam, one suspects that long chains because of their stability may be similarly more abundant than extrapolation from the shorter ones suggests.

An interesting and useful property of carbon chains is their extremely simple and predictable behavior under centrifugal distortion. Most polyatomic molecules deform on rotation in a fairly complicated way, characterized by a series of centrifugal distortion parameters which are not readily calculated from the structural parameters of the molecule, but must be empirically determined. We find in contrast that the cyanopolynes and other carbon chains deform under centrifugal distortion like thin classical rods, with a Young's modulus that is independent of length.²¹ All carbon chains we have studied apparently distort under rotation in this simple way, regardless of either terminal groups or the low-lying vibrational structure of the individual molecules, and with a Young's modulus that is about the same for all. One might expect such classical behavior for long chains, but it is somewhat surprising that it holds for quite short ones, where quantum effects and the details of the vibrational structure of the molecule might be thought to be important.

Astronomical detection of molecules as large as HC_{17}N and perhaps even larger is now possible. Larger and better telescopes, such as the Green Bank 100 meter telescope and the

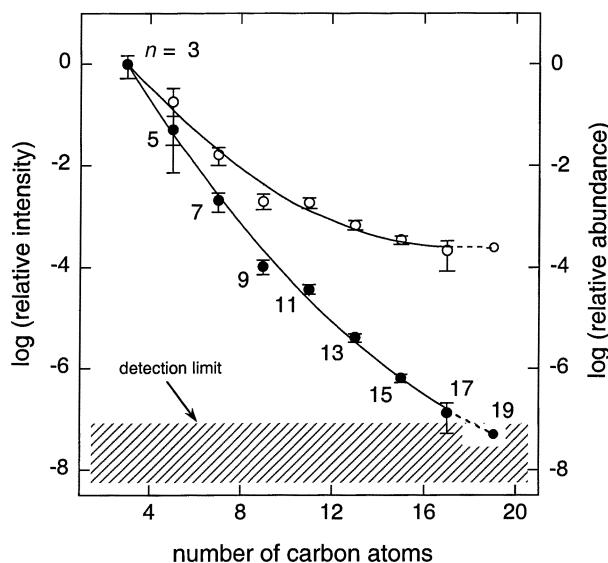


Fig. 5 Relative intensity of the strongest rotational lines of the cyanopolyyne (filled circles) and their relative abundance (open circles) in the FTM spectrometer, as a function of the number of carbon atoms in the chain. The error bars are estimated 2σ uncertainties. Relative abundances are obtained from line intensities by taking into account the dependence on the chain length of the rotational partition functions and dipole moments. The limit of the detection sensitivity is approximately that achieved in a total observation time of 3 h.

resurfaced Arecibo 305 meter telescope, will soon be available in the 1–10 GHz frequency range where the most intense astronomical lines of the longer chains lie. Although many hours of integration were required to detect lines of HC_{11}N in a particularly rich molecular source (the molecular cloud TMC-1 in the Taurus cloud complex),²² considerably less time may be necessary to detect other long chains in this source with these next generation telescopes. Because small-scale unresolved structures may possess the highest column density of molecules in TMC-1,²³ the new large telescopes with higher angular resolution may be considerably more efficient for astronomical detection.

Detection of the lowest frequency bending modes of long conjugated carbon chains may provide another way to observe molecules as large as HC_{17}N in astronomical sources. This approach has already been used with good success for short, non-polar chains such as C_3 which have been detected in the laboratory²⁴ and in the circumstellar shell of the evolved carbon star IRC+10216 with the Infrared Space Observatory.²⁵ The frequencies of the bending modes of a long chain such as HC_{17}N can be estimated to an uncertainty of about 15% from a semi-classical calculation in which bending modes scale in frequency as the inverse square of the chain.²¹ Applied to the two longest cyanopolyne chains here, such scaling predicts 14 cm^{-1} (420 GHz) for the lowest bending mode of HC_{15}N and 11 cm^{-1} (330 GHz) for that of HC_{17}N . Both frequencies are well within the range of existing high frequency radio telescopes, and the atmosphere is fairly transparent at these wavelengths. Precise laboratory measurements of the bending frequencies and accurate calculations of the transition moments are needed before undertaking such searches.

3.2 Experimental structures of HC_7N , HC_9N , and HC_{11}N

The refinements in instrumental sensitivity and production that were required to detect HC_{17}N and other long polyyne chains now permit shorter ones to be observed with very high signal-to-noise, such that all the isotopic species with a single carbon-13 or nitrogen-15 are readily detected in natural abundance or with slight isotopic enrichment. For the cyanopolyne series, these refinements have enabled us to determine precise effective

(r_0) structures for HC_7N , HC_9N , and HC_{11}N —the largest reactive molecules to our knowledge for which accurate structures have been empirically derived. The structures of HC_3N (ref. 26) and HC_5N (ref. 27) were determined by isotopic substitution some time ago, so a detailed comparison of five successive cyanopolyyne can now be made to study how the chemical bonding and electronic structure vary as a function of chain length. For HC_7N and HC_9N , *ab initio* values of the individual bond lengths have been calculated by Botschwina and co-workers²⁸ allowing a direct comparison of experiment with theory.

For each cyanopolyne, effective structures (Fig. 6) were determined from a least-squares fit of all the bonds in the

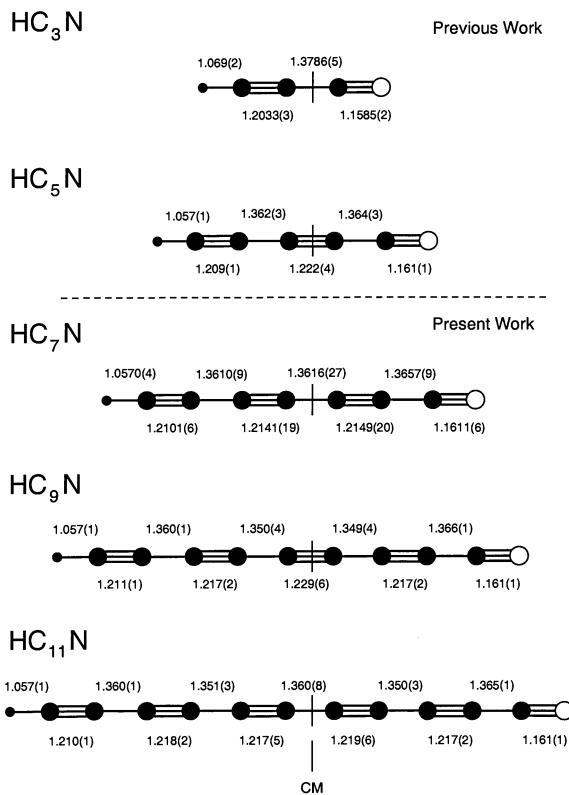


Fig. 6 Effective (r_0) structures of HC_3N and cyanopolyynes up to HC_{11}N obtained by isotopic substitution. Uncertainties are in the units of the last significant digit.

molecule to the measured rotational constants (*i.e.*, those of all the rare isotopic species plus the normal), on the assumption that each molecule is strictly linear. Toward the terminal atoms of each chain the bonds have been determined to remarkably high accuracy for molecules so large: of order 0.001 Å or 0.1%. Because the rotational constant of a linear chain is relatively insensitive to isotopic substitution near the center of mass, the central bonds are not so well determined, but are still good to about 0.01 Å or 1.0%. The experimental structures are in excellent agreement with recent high-level theoretical calculations, or, in the case of HC_{11}N , with extrapolation from HC_9N .

These structural determinations provide the first empirical evidence that well-defined bond alternation, as predicted by theory, exists throughout a long polyyne chain. There is no evidence in HC_{11}N , for example, of a tendency of the central bonds to even out, approaching those of a cumulenic, double bonded structure, as observed for example in the shorter cumulenic chains such as H_2CCCC ,²⁹ and predicted for longer members of that series.³⁰ Presumably bond alternation persists in the limit of the infinite polyyne chain, as it does in the polyenes, the somewhat similar stable carbon chains with alternating single and double bonds, whose structures have been studied extensively by X-ray diffraction.³¹ With little or no

additional effort, similar structural investigations to those described here could probably be undertaken for other polyyne chains such as methylpolyynes up to $\text{H}_3\text{C}_{11}\text{H}$ and methylcyano-polyynes up to $\text{H}_3\text{C}_9\text{CN}$. It is worth noting that although HC_{11}N was entirely unknown in the laboratory a short time ago, its ^{13}C isotopic species, less abundant relative to the normal species by a factor of 89, can now be detected without isotopic enrichment.

3.3 Reactive rings: rhomboidal SiC_3

A good example of the close interplay between laboratory astrophysics and astronomical observations is the recent discovery of rhomboidal SiC_3 , a highly polar, planar ring. Rhomboidal SiC_3 is one of five known interstellar rings. Three of the four others (C_3H_2 , C_3H , and SiC_2) are also highly reactive molecules generally unfamiliar to the laboratory chemist or physicist; the remaining ring, ethylene oxide ($\text{C}_2\text{H}_4\text{O}$), is a stable molecule. In the laboratory, as in the interstellar gas, the detection of rings has lagged behind detection of chains of similar size and composition in part because cyclic molecules lack simple harmonically-related rotational transitions that are readily spotted. The detection of new rings is worth pursuing because these molecules provide quite novel information on the rich and largely unexplored transition of carbon from chains to the two-dimensional graphitic lattice.

Rotational transitions of rhomboidal SiC_3 and its rare isotopic species were first observed with our FTM spectrometer³² with a discharge through a dilute mixture of diacetylene and silane—a very efficient method of production, it turns out, which yields high concentrations of SiC_3 and longer linear silicon carbides up to SiC_8 . At most, four rotational transitions (Fig. 7) of each isotopic species lie within the frequency range of our spectrometer, but this number alone is sufficient to unambiguously establish the existence of this exotic ring, and to allow a precise determination of its geometry. If SiC_3 were strictly planar and rigid, two parameters would suffice to determine the entire spectrum: three moments of inertia constrained by the Pythagorean theorem, but to describe the actual deformable molecule to the accuracy needed to conduct a radio astronomical search requires the inertial defect and several centrifugal distortion constants as well. Using the free-space millimeter-wave absorption spectrometer in this laboratory, a number of the higher rotational transitions of SiC_3 were subsequently measured to within a few parts in 10^7 up to 300 GHz, allowing the determination of the inertial defect and the six leading centrifugal distortion constants.

With the help of laboratory data, a number of millimeter-wave rotational transitions of SiC_3 have now been detected in IRC+10216 (Fig. 7) using the 12 meter NRAO telescope on Kitt Peak.³³ The lines are fairly weak, but all have precisely the same radial velocity found for other molecules in this source, so the identification is beyond doubt. The rotational excitation of SiC_3 is similar to that of SiC_2 , with a low rotational temperature (10–20 K) within the K -stacks, and a high rotational temperature (roughly 50 K) across the K -stacks. The column density of SiC_3 is perhaps 50% larger than that of SiC_4 .

Photochemical models of IRC+10216³⁴ predict that, as observed, SiC_3 and SiC_4 are more than two orders of magnitude less abundant than either SiC and SiC_2 . Some SiC_3 is predicted from the photodissociation of SiC_4 . The implication is that the total amount of SiC_3 cannot exceed that of SiC_4 . If SiC_3 is found to be more abundant than SiC_4 , however, other reactions may be required to explain the observed abundance. To clarify the formation of SiC_3 and to see if rhomboidal SiC_3 is actually produced *via* photodissociation of linear SiC_4 , it would be desirable to detect additional SiC_3 isomers in this astronomical source, and to compare their abundances. Two other low-lying, fairly polar SiC_3 isomers, a triplet chain and second rhomboidal

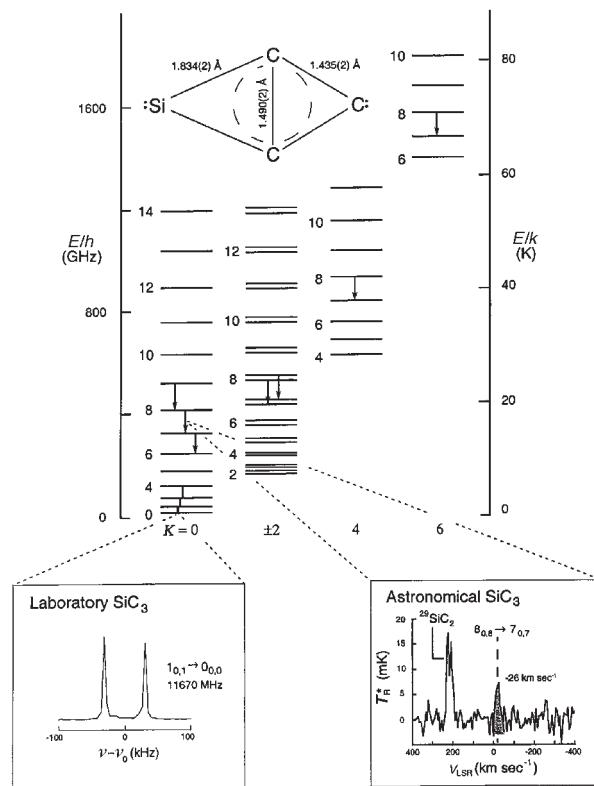


Fig. 7 Lower rotational levels of SiC_3 showing the three transitions measured with the FTM spectrometer (vertical bars) and the seven transitions detected in IRC+10216 (lines with arrows). The effective (r_0) structure obtained from isotopic substitution is shown above the energy level diagram. Insets: (left) laboratory spectrum of the $1_{01} \rightarrow 0_{00}$ transition at 11,670 MHz, observed with a single gas pulse and an integration time of 0.2 ms. The double peaked line shape as in Fig. 4 is instrumental in origin. (right) Radio spectrum of IRC+10216 near 91,845 MHz showing the $8_{08} \rightarrow 7_{07}$ transition. The spectral resolution is 2 MHz and the integration time is 7 h.

isomer, have recently been detected in this laboratory, so the data exists for a sensitive astronomical search.

3.4 Nonpolar chains: linear triplet HC_7H , HC_9H , HC_{11}H , and HC_{13}H

The first carbon chains detected with our CRD apparatus were the nonpolar radicals HC_7H and HC_9H .³⁵ For both the wavelengths of the strongest optical bands have been measured to an accuracy of about 1 part in 10^6 , and at least one vibronic band of each chain has also been measured to about the same level of accuracy. Because the origin bands of the two radicals have nearly the same intensity, and because the wavelengths of the strongest bands of each member in this homologous series are known fairly precisely from matrix spectra,³⁶ it has now been possible to detect the gas-phase spectra of the next two odd-numbered chains HC_{11}H and HC_{13}H .³⁵ Sample spectra of each are shown in Fig. 8. For all four molecules, internal conversion seems to be much more rapid than radiative decay, and laser-induced fluorescence is not observed. For HC_9H , the origin band is close in wavelength to a weak diffuse band at $\lambda 5818$, but recent astronomical observations by McCall *et al.*³⁷ indicate that the difference in wavelength between the two is too large to establish an identification.

Even though there is yet no evidence that these symmetric hydrocarbon radicals are carriers of the DIBs, they remain good candidates for astronomical detection in both the diffuse gas and in cool stellar atmospheres or circumstellar shells. The wavelength of the origin band of each chain can be determined very accurately from the laboratory data. High accuracy is possible because $\Sigma-\Sigma$ transitions lack both spin-orbit splitting

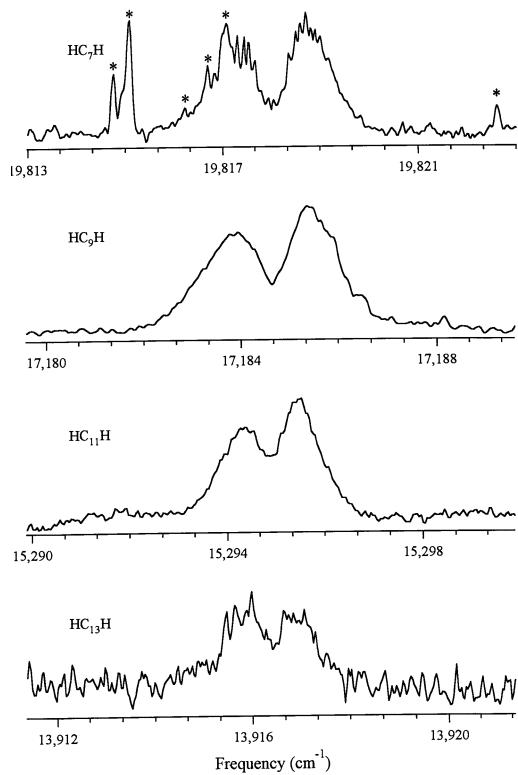


Fig. 8 Origin bands of HC_7H , HC_9H , HC_{11}H and HC_{13}H . Features marked with an asterisk in the HC_7H data indicate unrelated molecular lines, probably of C_2 , which appear in both normal and deuterated samples.

and red-shaded R -heads which tend to shift the wavelengths of electronic transitions by 0.05 nm or more depending on the rotational temperature either in the molecular beam or along different lines of sight in space. Since neither complication exists here, the band contours of the $\Sigma-\Sigma$ transitions are essentially insensitive to rotational temperature, and, as a result, the wavelengths of the origin bands can be determined about an order of magnitude more precisely than most $\Pi-\Pi$ transitions.³⁸ If transitions of the symmetric chains can eventually be found in space, confirmation of the assignment might then come from detection of the characteristic P - and R -branches in Fig. 8, or by detection of the somewhat weaker vibronic bands.

3.5 A laboratory band at $\lambda 4429 \text{ \AA}$

Very recently a fairly strong molecular absorption band at $4429 \pm 0.04 \text{ \AA}$, closely centered on the strongest diffuse interstellar band at $4428.9 \pm 1.4 \text{ \AA}$ has been detected. The laboratory band was found first in our supersonic molecular beam among the products of a discharge through benzene and toluene, then somewhat less intensely through diacetylene and other carbon chain sources.³⁹ We have not yet been able to determine the exact elemental formula or structure of the carrier of the laboratory band, nor have we been able to demonstrate with certainty that the laboratory band is the same as that observed in space, but the agreement in wavelength between the two is so good (to a few parts in 10^4) that a chance coincidence would seem unlikely. As Fig. 9 shows, the width of the laboratory band is significantly less than that of the interstellar diffuse band, but this difference is plausibly the result of the very low rotational temperature in the supersonic beam, possibly as low as 2 K, relative to that of a nonpolar or weakly polar molecule in the diffuse interstellar gas (100–200 K).

The carrier of the laboratory band is almost certainly a hydrocarbon because the band is produced with different inert carrier gases, and is absent in all discharges studied so far through molecules containing oxygen, nitrogen, silicon, and sulfur. From the observed deuterium isotopic shifts we have

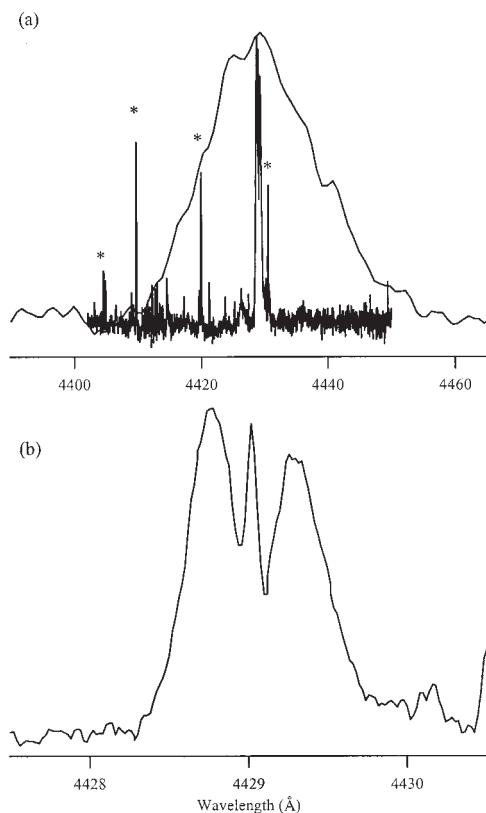


Fig. 9 (a) New laboratory molecular band, superposed on the strongest and best known interstellar band $\lambda 4429$, as observed towards a distant hot star. (b) The same laboratory band plotted on an expanded wavelength scale, displaying (from left to right) apparent P -, Q -, and R -branches. Features marked with an asterisk denote unassigned lines of light hydrides.

established that the carrier probably has the elemental formula C_nH_5 , and that the hydrogen atoms consist of two pairs of symmetrically-placed equivalent atoms plus a lone atom. The number of carbon atoms is likely to be in the 3–6 atom range because no plausible candidate carrier exists with two carbon atoms or less, and because we have found from our FTM studies that benzene discharges do not readily produce molecules with more than six carbon atoms. The number of plausible molecules (Fig. 9) in that mass range with the elemental formula of C_nH_5 is fairly small (Fig. 10), but includes at least two carbon chains,

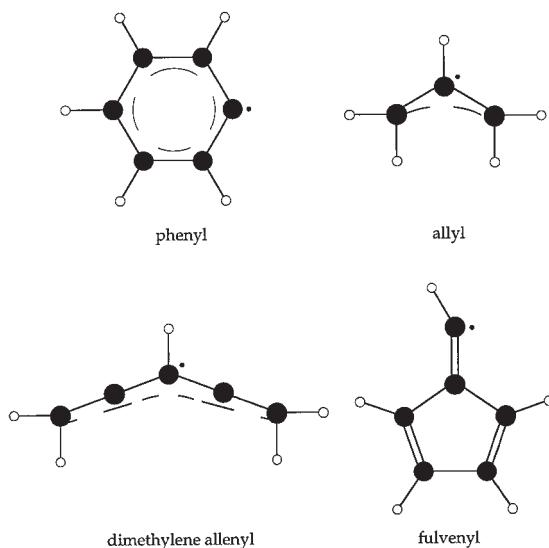


Fig. 10 Selection of hydrocarbon molecules with the elemental formula C_nH_5 and the right symmetry to explain laboratory $\lambda 4429$.

allyl and dimethyleneallenyl radicals, and two cyclic aromatic hydrocarbons, the phenyl and fulvenyl radicals. Neutral allyl

and phenyl would seem to be ruled out because their optical spectra are known,^{40,41} but the remaining two neutral radicals or positive or negative ions of all four can not be excluded. One of the more promising candidates is the dimethylene allenyl radical, C₅H₅, a slightly bent carbon chain which may be close enough to linear to reconcile the puzzling appearance of *P*-, *Q*-, and *R*-branches in the laboratory band with the five hydrogen atoms suggested from the isotopic shifts.

If the astronomical and laboratory bands are indeed the same, the present detection should constitute a substantial step towards the solution of the long standing problem of $\lambda 4428$. The array of laser, mass spectrometric, microwave, and theoretical techniques which can now be brought to bear on a problem of this kind is formidable, so an unambiguous assignment of the carrier of $\lambda 4428$ may now be possible on a fairly short time scale.

4 Outlook

In the radio band the laboratory astrophysics of molecular spectra is at last ahead of the radio astronomy, allowing new astronomical molecules to be found without searches in frequency that with large telescopes can be prohibitive in time and cost. Although many new chains and rings have been found with our present instrumentation, we are probably still very far from the optimal production efficiency for many of them and from the fundamental limits on the instrumental sensitivity. Continued experimentation with new precursor gases and different production methods such as laser ablation might yield significantly higher concentrations of the molecules of interest. Liquid helium cooling of the optics and first-stage of receiver amplification promises to improve the sensitivity by at least an order of magnitude, and a further improvement by a factor of perhaps five might be gained for molecules with ten or more heavy atoms by lowering the frequency of operation to the low-GHz range, where lines are strongest at a rotational temperature of a few Kelvin. With modest and systematic improvements in both production and instrumental sensitivity, appreciably larger chains, rings, and molecular ions than those here may be within reach. The recent laser experiments here suggest that detection of the optical spectra of many of the radio molecules shown in Fig. 2 may now be possible; by extension, the same may be true for other known and postulated astronomical species. Such studies should provide a critical test of the hypothesis that carbon chains and other large organic molecules are the carriers of the optical diffuse interstellar bands, a problem in astronomical spectroscopy that has defied solution for over 60 years.

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