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Carbon chains and rings in the laboratory and in space

P. Thaddeus [a,b,*], M.C. McCarthy [a,b]

[a] *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA*
[b] *Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA*

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Abstract

Seventy-seven reactive organic molecules of astrophysical interest have been identified in a supersonic molecular beam, 73 in the radio band by Fourier-transform microwave spectroscopy, four in the optical by laser cavity ringdown spectroscopy. Most are linear carbon chains, but six consist of carbon chains attached to the compact, highly polar C_3 ring, and two are rhomboidal cyclic configurations of SiC_3. The laboratory astrophysics of the radio molecules is complete for the time being, in the sense that essentially all the rotational transitions of current interest to radio astronomy (including hyperfine structure when present) can now be calculated to a small fraction of 1 km s^{-1} in equivalent radial velocity; six of the radio molecules have already been detected in space on the basis of the present data. The FTM spectrometer employed in this work is far from fundamental limits of sensitivity, so many more molecules can probably be found by refinements of present techniques. The density of reactive molecules in our supersonic beam is generally high by the standards of laser spectroscopy, and many of the radio molecules probably have detectable optical transitions which we are attempting to find, largely motivated by the long-standing problem of the diffuse interstellar bands. Our most interesting result to date is the detection of a fairly strong molecular band at 443 nm in a benzene discharge, in exact coincidence with the strongest and best known interstellar band. Isotopic shifts measured with partially and totally deuterated benzene suggest that the carrier of the laboratory band is a hydrocarbon molecule with the elemental formula C_nH_5, with n most likely in the range 3–6. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The identification with radio telescopes of the hydroxyl radical in 1963 [1] and ammonia [2] and water [3] 5 years later opened a largely unanticipated new field of astrophysics, starting a process of discovery which after more than 30 years shows no sign of flagging. As Fig. 1 shows, the total number of molecules identified in the interstellar gas and in circumstellar shells is currently 123, and the rate of discovery, averaging about four per year since 1968, may be slightly on the rise. Like hydroxyl, ammonia and water, most of these molecules are polar compounds which have been detected in the radio band, but there are also

* Corresponding author.
E-mail address: pthaddeus@cfa.harvard.edu (P. Thaddeus).

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several non-polar molecules such as CO_2, C_2H_2, and CH_3 which have been identified in the infrared, either from the ground or with telescopes in space. A few have also been found in the optical or near UV with large telescopes on the ground, including the first three interstellar molecules CH, CH^+, and CN; very recently the carbon chain ion C_7^- has been tentatively identified [4] as the carrier of several of the mysterious optical diffuse interstellar bands (DIBs).

It is interesting to note that there is no science fiction chemistry in Fig. 1: in space as on earth, Nature exploits the remarkable flexibility of the carbon bond in the synthesis of large compounds. About two-thirds of the diatomic molecules are inorganic, and one-third of the triatomics, but only one of the 16 molecules with five atoms; all the heavier astronomical molecules are organic compounds in the technical sense of the term. It is, however, somewhat peculiar organic chemistry, familiar compounds found in any chemical stock room, like formaldehyde, ethanol, and methyl formate, coexisting with a somewhat larger number of reactive organic compounds which are unfamiliar and generally highly unstable in the terrestrial laboratory, but which in space are often comparable in abundance with stable compounds of the same size. A number of these 'non-terrestrial' molecules were detected in space before being identified in the laboratory, just as helium was observed in the solar spectrum over a century ago before being identified in natural gas from terrestrial wells.

Because much of the molecular gas in space is cold and quiescent, spectra can often be measured to an accuracy which is very high by astronomical standards and good even by those of the laboratory; as a consequence there are very few questionable identifications in Fig. 1. The main reason for this high specificity is the very sharp lines characteristic of interstellar molecules, and the remarkable precision with which the astronomical

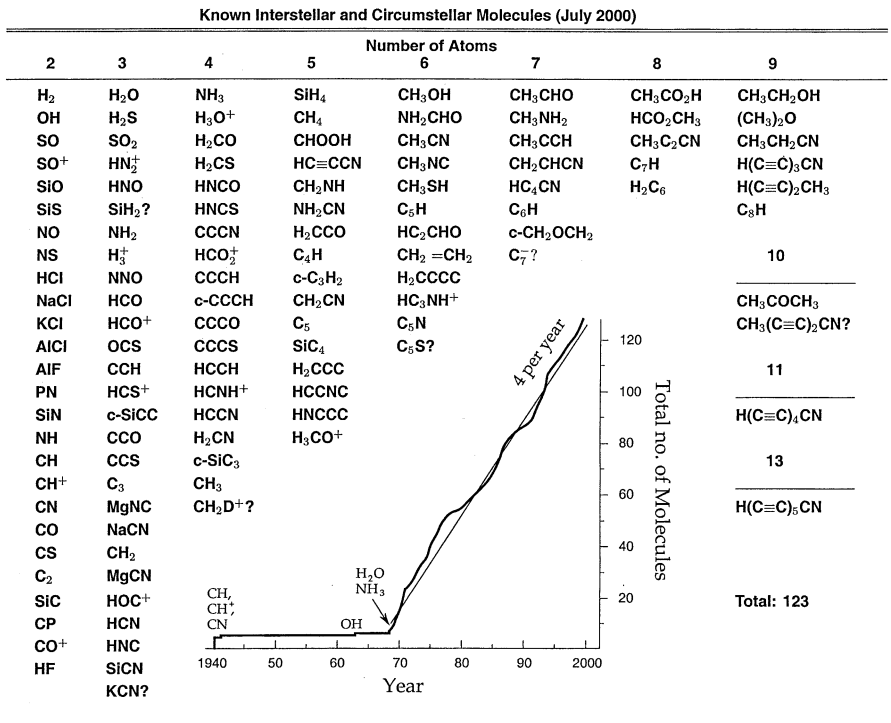

Fig. 1. Molecules identified in the interstellar gas and in circumstellar shells, ranked by number of atoms. Insert: cumulative total by year.

frequencies can be matched to laboratory data. Pressure broadening is entirely negligible in even the densest interstellar clouds, and in the radio band the same is true of natural line widths; molecular radio lines in space instead are Doppler broadened, the result of the thermal motion of the molecules and the internal turbulence of the clouds in which they exist. In the coldest clouds, line widths are less than 1 km s^{-1} in equivalent radial velocity ($c\Delta v/v$), or 3 ppm, and correspond to effective kinetic temperatures as low as 15–20 K, a temperature at which all the molecules in Fig. 1 except H_2 freeze out in the laboratory. With the high signal-to-noise often achieved it is possible to measure line frequencies to one part in 10^7, and to match these to laboratory lines to comparable accuracy. It is this specificity which allows the molecular composition of distant astronomical objects to be established with a certainty usually reserved for matter studied in the terrestrial laboratory.

The discovery of molecular clouds, a largely unsuspected new class of astronomical objects, is one of the most important results of the detection of molecules in space. The interstellar medium in a spiral galaxy like ours consists mainly of hydrogen and helium, which constitute about 75% and 24%, respectively, of the total interstellar mass. All the other chemical elements comprise the residual 1%, and C, N, and O, the key elements of organic chemistry, are the greater part of that, about 80%. The interstellar dust grains, small particles of the non-volatile elements Si, Ca, Mg, Fe, etc. represent a significant fraction of the remaining 0.2%, and may contain as well some C, N, and O in the form of ices, graphite, silicon carbide, and various organic compounds. Most of the visible mass of the Milky Way, (90–95%), is contained in small stable stars like the Sun which by stellar winds or infall exchange little material with the interstellar gas, and are highly inert (the energy output of the Sun per unit mass and time, for example, is only about 10^{-4} that of the human body). There is also evidence from the anomalously large rotation rate of gas and stars in the outer Galaxy of a large amount of invisible or 'dark' galactic matter, but whether that is stellar or interstellar is unknown. It is almost certainly not molecular in composition, but may consist of a myriad of faint 'brown dwarf' stars (though that seems increasingly unlikely), heavy neutrinos, or exotic new fundamental particles.

As a chemically inert element, helium always exists in interstellar space as free atoms, and in low density clouds the hydrogen is also mainly atomic, where it has been extensively studied since the 1950s by means of its 21-cm radio hyperfine line. When atomic gas in interstellar space is compressed by gravity or some other mechanism such as shock waves or stellar winds, a fairly rapid conversion of atoms to molecules takes place at a density in the vicinity of 50–100 H atoms per cm^3. Atomic hydrogen is efficiently converted to H_2 on the surfaces of the cosmic dust grains, and little H remains; much or most of the chemically active atoms then react with H_2 and each other, to form by a complex web of reactions the many observed molecules. As discussed below, in this synthetic process ions produced by cosmic rays are thought to play a key role. A chemical change of phase from largely atomic to largely molecular gas has taken place, and the boundary between the two phases is usually fairly sharp. Molecular clouds typically possess a wealth of internal structure, but their edges are generally about as well defined as clouds in the earth's atmosphere (Fig. 2).

Although H_2 is the dominant molecule by far in molecular clouds, it is extremely difficult to observe directly because it has no radio spectrum, and is generally too obscured by dust or too cold for the spectral lines which it does possess in the infrared and ultraviolet to be detected. However, radio lines from abundant polar molecules such as CO, CS, HCN, and H_2CO are readily observed throughout the Milky Way and in spiral galaxies similar to ours, and it is with these that molecular clouds have been discovered and studied in great detail over the last 30 years. The distribution of the more complex molecules remains largely unknown; many have been observed in only a single source or a few (Fig. 2), owing to the many hours required for detection in even the best locations. But there is no evidence that the locations so far studied are unique, and it can probably be assumed that all of the known interstellar molecules

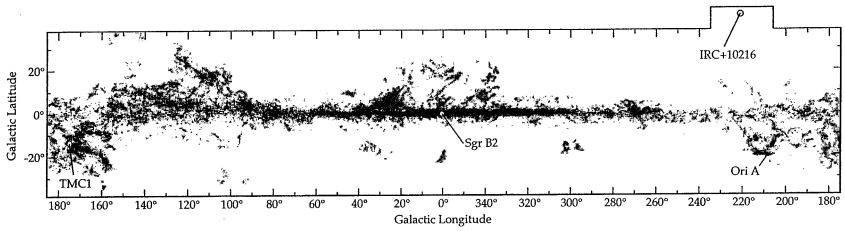

Fig. 2. The molecular clouds in the plane of the Milky Way, as seen in the 1–0 rotational transition of CO, the best tracer of the largely invisible H_2 which constitutes most of the interstellar molecular mass. Most of the molecular clouds are contained in the distant spiral arms within 40° of the Galactic Center; the large clouds well off the galactic plane are very close to the Sun, typically only a few per cent of the way to the Center. Other simple molecules like CS and HCN have also been observed in many molecular clouds, but most of the 123 astronomical molecules in Fig. 1 have been detected so far in a only a small number of locations, sometimes only one or two, because of the long integration times (up to 30 h) required to detect a single line. Because the interstellar dust grains correlate well with the CO and the H_2, it is likely that even the large molecules in Fig. 1 are very widely distributed, and may ultimately be detectable.

are widely distributed, and that many could be detected throughout the Milky Way with more sensitive telescopes.

Of the abundant molecules, the most easily detected is CO, which is so stable and readily formed that it contains a significant fraction, roughly 15%, of the carbon in molecular clouds. Its ratio to H_2 and He appears to be fairly constant under a wide range of conditions, and it has therefore been widely used to trace the total mass in molecular regions. As good a working definition as any of a molecular cloud is: a dense concentration of interstellar gas with fairly distinct boundaries that is detectable in the radio spectral lines of CO.

Thanks to large scale CO surveys which have been done in the US and Chile over the past 20 years (Fig. 2), the distribution of molecular gas in the Milky Way is now well understood. Molecular clouds have been shown to be excellent tracers of the overall spiral structure of the Galaxy, delineating its spiral arms with remarkable clarity. Although there are many molecular clouds near the Sun, some associated with well known bright stars such as those in Orion, or visible to the naked eye as large dark nebulae and rifts in the Milky Way, most of the clouds and most of the molecular mass of the Galaxy lie far from the Sun in the distant inner arms of the Milky Way, peaking in a broad, irregular annulus roughly half way between the Sun and the Galactic Center. Like the Sun and stars, the clouds in this ring and outward to the edge of the Galaxy are in approximately circular motion about the Galactic Center.

The early molecular discoveries were observationally driven, motivated mainly by curiosity and the availability of a few radio telescopes with spectral line capabilities — there was very little encouragement from theory. Molecular clouds were almost entirely unsuspected in 1968; from the early studies of the 21-cm line of atomic hydrogen, the standard interstellar cloud was thought to have a density of only a few atoms per cm^3 and a temperature of 100–200 K, and to be fairly transparent to starlight. It was readily calculated that polyatomic molecules subject to the hard UV interstellar radiation field penetrating such clouds would rapidly photodissociate, and astronomers were at a loss at that low density to find a comparably rapid process of formation. It was therefore widely supposed that the abundance of all but the simplest molecules in space would be nil. The early optical observations of CH, CH^+, and CN, which indicated that the abundances of these simple diatomics relative to hydrogen was very small (10^{-7}), served to reinforce this unfortunate conclusion.

2. Molecular spectroscopy in this laboratory

With the discovery of ammonia, and especially the very strong line emission of water at 22 GHz,

soon shown to result from maser amplification, the prejudice against polyatomic molecules in the interstellar gas quickly vanished. Because technological developments had outpaced scientific understanding, it was found at first that discovering new molecules was fairly easy — requiring little more than tuning one of the few existing high-frequency radio telescopes with spectral line receivers to the lines of a plausible astronomical molecule, and pointing the telescope toward a dense pocket of gas in a region of star formation, such as that associated with the Orion Nebula (cf. Fig. 2). A significant number of lines kept turning up however, some surprisingly strong, which could not be found in the spectral line catalogs. It was suspected that these were produced by exotic species so unstable that they had eluded laboratory detection, and that has been shown repeatedly by laboratory work to be the case. It was largely to unravel the identity of these tantalizing unidentified 'U' lines that the present program of molecular spectroscopy in this laboratory was started ca 1975. The accurate measurement of centrifugal distortion of known molecules at high frequency was a secondary motive; centrifugal shifts, sometimes amounting to many line widths in the millimeter-wave band, were often poorly predicted on the basis of the available data, and without knowledge of these, line misidentifications were a serious hazard.

Our first spectrometer was an early version of the present instrument shown schematically in Fig. 4. Reactive molecules are made in a large glass absorption cell by a d.c. gas discharge through a flowing mixture of an inert buffer gas (usually argon) and an organic vapor (e.g., acetylene, allene). A millimeter-wave carrier signal is generated by a Gunn oscillator or a frequency multiplier fed by a Gunn, which after passing twice through the discharge cell is detected by a low noise liquid-helium-cooled InSb detector. To double the path length, the carrier after passage through the cell is reflected back by a roof reflector at 45°, rotating the plane of polarization by 90° and causing the beam after its second passage to be deflected to the side by a fine wire grid, a polarization-dependent mirror almost totally transparent on the first passage. Important refinements which have been added over the years [5,6] include (i) liquid nitrogen cooling of the cell walls to as low as 120 K to enhance line strengths (typically by a factor of 3–4), and (ii) numerical on-line filtering of spectra to remove standing waves, typically the limiting factor in detecting weak lines of reactive molecules in gas discharges, where Stark modulation, the standard microwave technique for suppressing standing waves, cannot be applied. Zeeman modulation however does work for open shell molecules, and is sometimes employed.

A number of the most interesting 'non terrestrial' molecules in space were first detected in the laboratory with this instrument, which sometimes worked extremely closely with radio telescopes in joint investigations of new lines or the search for new molecules. These discoveries include the ethynyl radical CCH, the carbon chain radicals C_3N and C_4H, the first interstellar organic ring C_3H_2, the SiC radical, which had defied gas phase detection for over 50 years, and the carbene chains H_2CCC and H_2CCCC. New detections were not made quickly with this instrument, however, and there were frustrating failures. After H_2CCC and H_2CCCC were detected in rapid succession in both the laboratory and space, it seemed likely that longer carbene chains of this kind could be found, but several astronomical and laboratory searches drew a complete blank. Similarly, after C_3H_2 was found a series of hypothetical ring-chain molecules was proposed, constructed by substituting carbon chains for one of the hydrogen atoms of this highly polar carbene. Again, repeated laboratory searches turned up nothing. The fear arose that something was fundamentally wrong — that the molecules we hoped to find were abnormally unstable, or were not produced at all in a gas discharge source of the kind employed. The rate of discovery too, although steady, was painfully slow, only one or two new molecules being detected per year. The goal of detecting new molecules first in the laboratory so astronomical searches with large telescopes could be done efficiently proved elusive.

2.1. FTM spectroscopy

In nearly every case the problem with the molecules which we had hoped to find turned out to be simply signal-to-noise. Late in 1995 we constructed the Fourier-transform microwave (FTM) spectrometer shown schematically in Fig. 5, and to our delight achieved at least an order of magnitude improvement in sensitivity for most reactive species. The rate of discovery increased by a corresponding factor, and a number of the hypothetical molecules which we had failed to find, including carbenes and rings, fell into place in a flood of new discoveries. The 77 new

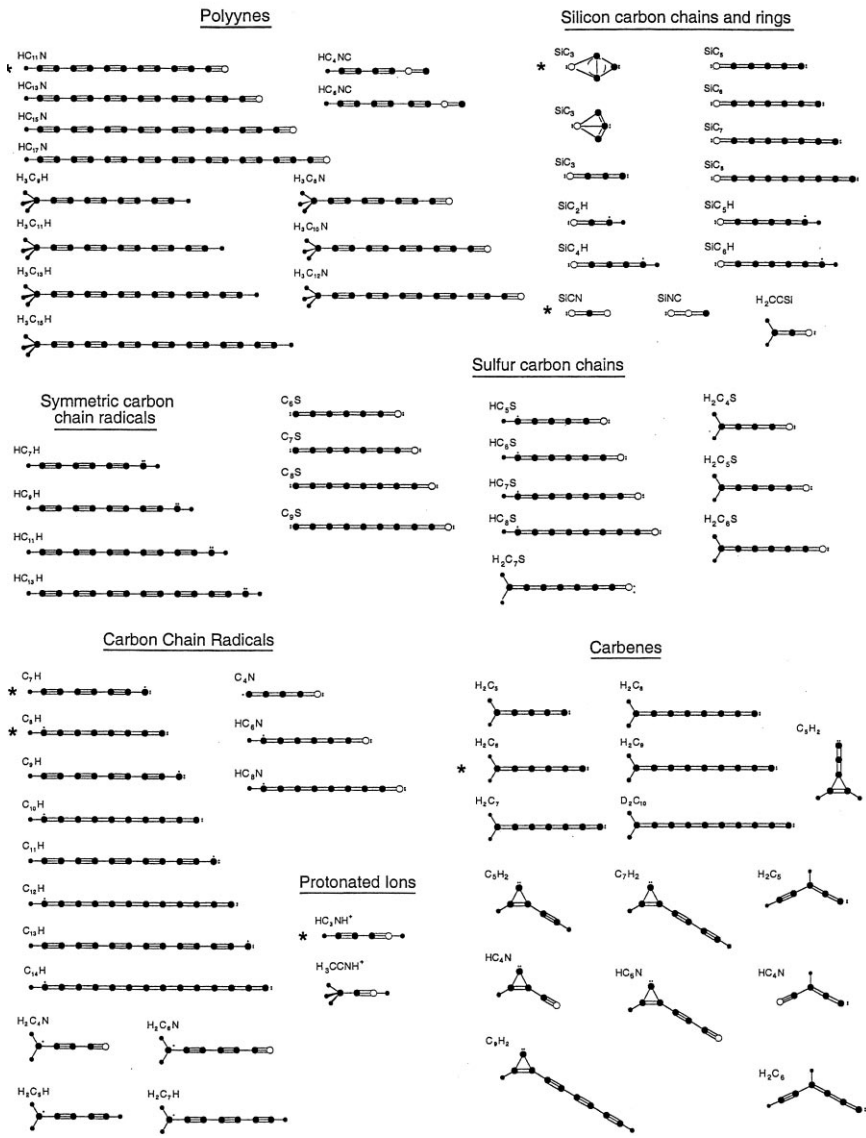

Fig. 3. The 77 reactive molecules discovered in this laboratory over the past 4 years. Open circles denote hetero atoms, N, Si, or S, asterisks those molecules already detected in space, all but one on the basis of the laboratory work described here. The laboratory astrophysics of the radio molecules is complete in the sense that the lines of astronomical interest have either been measured directly or can be calculated to high precision.

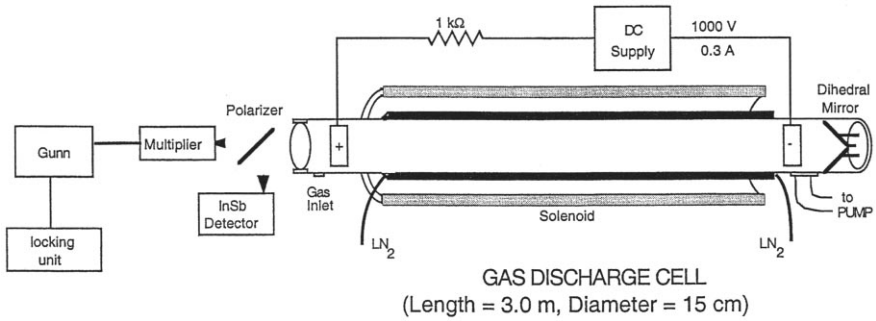

Fig. 4. Schematic diagram of the millimeter-wave free space spectrometer.

molecules detected as of July 2000 are shown in Fig. 3. Most have already been described in the literature in some 50 papers; two summary articles [7,8] and four reviews [9–12] of this work have also appeared, where many specific references can be found. Essentially all the molecules in Fig. 3 are candidates for detection in the interstellar gas or in circumstellar shells, and, as indicated in that figure, six have in fact already been detected on the basis of the laboratory data. Because of limited space, it is not possible to give here a detailed spectroscopic description of the unpublished new chains or much in the way of experimental details. We will instead make some general observations about the whole set, and will discuss the prospects for further laboratory and astronomical detections.

2.1.1. Spectroscopic characterization

The spectroscopy of all the radio molecules in Fig. 3 is complete, in the sense that the astronomically-relevant rotational transitions have either been measured to high precision, or are readily calculated from the derived spectroscopic constants to an accuracy approaching that of the measurements. In addition to the rotational constants, these generally include (i) the leading centrifugal distortion constants required to predict frequencies to quite high J, (ii) for radicals like C_8H and SiC_4H with doublet ground states, the several constants which characterize the hfs and lambda doubling caused by the unpaired electron, and (iii) for triplet radicals like SiC_3 and C_6S, the spin–spin and spin–rotation constants which describe the magnetic interaction between the two unpaired electrons.

Carbon chain radicals such as $SiC_{n+1}H$, $HC_{n+2}S$, and $C_{n+4}H$ ($n \geq 1$) and longer chains within each family have $^2\Pi$ states, with inverted fine structure (negative fine structure constant A) when n is even, but normal fine structure (A positive) when n is odd. At the low rotational temperature of our molecular beam, only the lowest lying of the two fine structure ladders in the ground state is populated: the $^2\Pi_{3/2}$ ladder when n is even and the $^2\Pi_{1/2}$ ladder when n is odd. As a result, A cannot be determined from our FTM data alone. For several radicals such as SiCCH, SiCN, SiNC, C_7H and C_8H, however, we were able to detect both fine structure ladders in the free space spectrometer of Fig. 4, where T_{rot} is of order 200 K. Since A is readily determined when the rotational constants in both ladders are known [via the relation $B_{1/2,3/2} = B_0(1 \pm B_0/A)$], we were therefore able to obtain accurate values of A for these radicals.

Gas discharges through an organic vapor typically produce a rich brew of molecules, and a daunting thicket of rotational lines. In spite of that, there are good reasons to be fairly certain that there are no misidentifications in Fig. 3. First is the simplicity and symmetry of the rigid body Hamiltonian. Rotational spectra can usually be estimated to about 1% from general principles of valence and standard bond lengths and angles, and that estimate can typically be refined by a factor of three or more by current ab initio numerical calculations of molecular structure; very large searches in frequency therefore are not generally required to identify a new molecule, and within the search range there are not usually too

large a number of unrelated lines to serve as decoys. Most of the molecules in Fig. 3 are linear or are highly prolate asymmetric tops, with rotational transitions forming tight harmonic sequences readily distinguished even in the presence of a dense thicket of unrelated lines. Determining the existence of these harmonic ladders with high confidence is a crucial first step in most identifications, and to do that many more lines are usually measured than the two needed to determine the two constants B_{eff} and D_{eff} required to fit the line frequencies to high accuracy (typically 1 ppm or

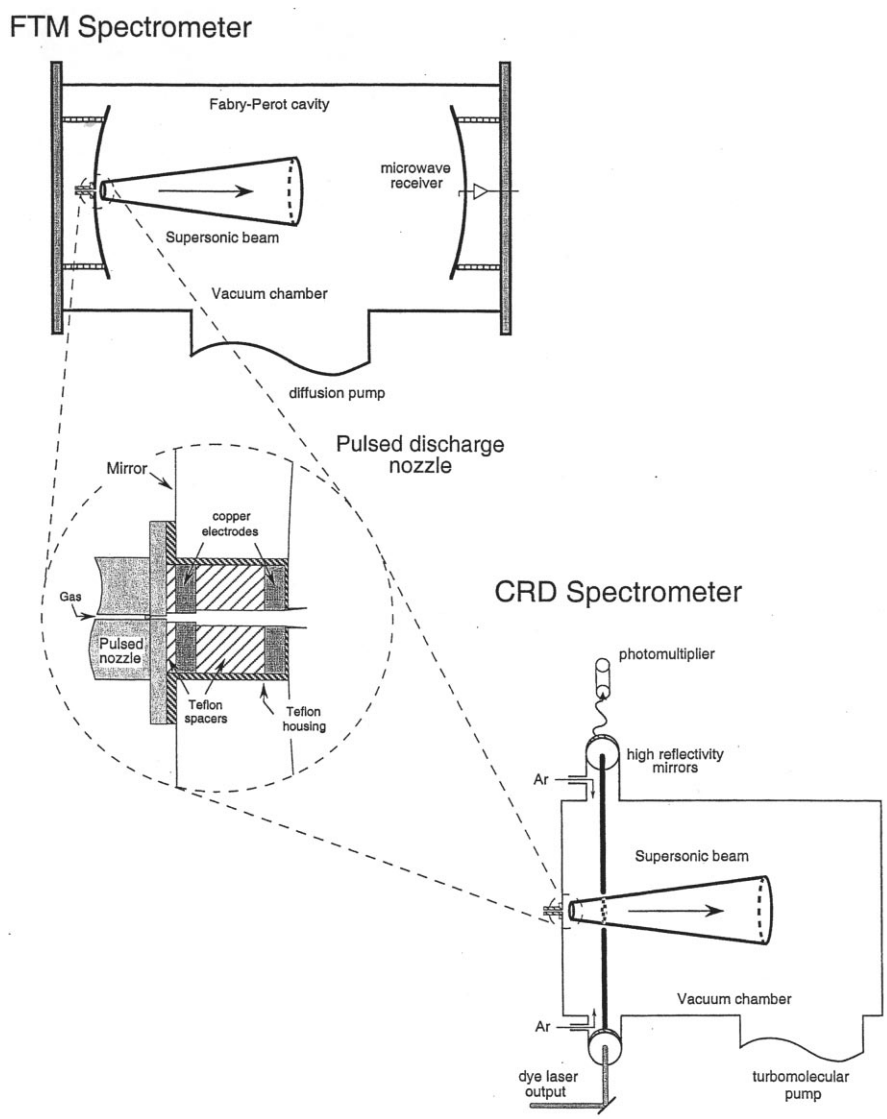

Fig. 5. Schematic diagram of the FTM and CRD spectrometers. In both, reactive molecules are produced in a small d.c. electric discharge in the throat of a nozzle through a stream of a precursor vapor (e.g. acetylene or diacetylene or silane, diluted 99% or more with Ne or Ar), just prior to supersonic 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 gas pulse is typically 200–350 μs. The diameter of the nozzle immediately following the valve is 1 mm. To keep the pressure in the chamber low enough to form a good molecular beam, the pulse repetition rate is kept fairly low: 6–10 Hz, so the valve is open less than 1% of the time.

better). Isotopic shifts are crucial checks on an identification, and are usually measured, either in natural abundance or with isotopically enriched samples, from the D, ^{13}C, ^{15}N, etc. species of a given molecule. Additional checks are provided by the appearance of hyperfine structure, and the strong Zeeman effect exhibited by lines of an open shell molecule when a strong permanent magnet is held near the molecular beam. The identifications are about as secure as ones can be which are based largely on spectroscopic evidence, and we would be surprised if Fig. 3 contains a single mistake.

2.1.2. Dipole moments

Unsymmetrical carbon chains tend to be extremely polar molecules, which is one of the reasons why they are readily detected in the laboratory and in space. Dipole moments have not been measured for any of the chains in Fig. 3, but ab initio calculations which are probably accurate to a few percent or better have been done for most of the shorter members in each homologous series of carbon chains, including the cumulene carbenes [13–15], acetylenic radicals [16], cyanopolyynes [17,18], and silicon carbides (C.M.L. Rittby, private communication). In each series the dipole moment is found to increase steadily with chain length; the cumulene carbenes H_2C_n and silicon carbides SiC_n are the most polar. The dipole moment rises, for example, from 6 D for H_2C_5 to over 10 D for H_2C_{10} — a remarkably high polarity for hydrocarbons. A similarly rapid increase is found in the silicon carbides, from a moment of 5.7 D for SiC_4 to 10 D for SiC_8. The acetylenic radicals C_nH and the cyanopolyynes HC_nN also exhibit an increase in polarity with length, but are less polar than the cumulenes by about 20% and 40%, respectively. For the longest cyanopolyynes we have so far detected, the dipole moment is apparently leveling off (P. Botschwina, private communication).

2.1.3. Sensitivity far from fundamental limits

The largest member of each family of chains in Fig. 3 is close to the limit of detectability of the present liquid-nitrogen-cooled FTM spectrometer, but the sensitivity of this instrument is far from

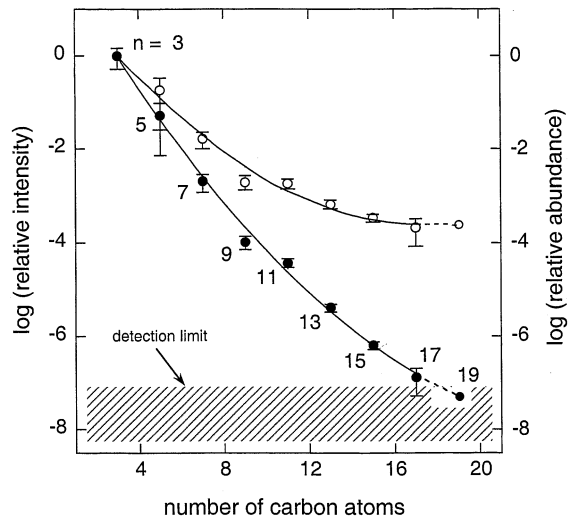

Fig. 6. Relative intensities of the strongest rotational lines of the cyanopolyynes (filled circles) and relative abundances (open circles) from the FTM spectrometer, as a function of the number of carbon atoms in the chain. Error bars are estimated 2σ uncertainties. The indicated detection limit is that achieved in an integration of about 3 h.

fundamental limits. Liquid helium cooling of the optics and the first stage of receiver amplification might improve the sensitivity by nearly an order of magnitude, and a further improvement by a factor of about 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 the rotational temperature of 1–3 K characteristic of our supersonic molecular beam. While technically challenging, both improvements are feasible, particularly if a closed resonant cavity is used instead of the large open Fabry–Perot resonator of the present device. Another factor favors the detection of large molecules: with our discharge source the line intensity and abundance decrement of the cyanopolyynes markedly flatten beyond about nine carbon atoms, as Fig. 6 shows; $HC_{17}N$ for example turned out to be much easier to detect than was expected by extrapolation from the short members of the series [19]. If a similar effect exists for the other types of chains in Fig. 3, and liquid helium cooling can be exploited, much larger chains than those here (and their isomers) may be within reach.

2.1.4. Production of carbon chains

Most of the molecules in Fig. 1 were produced when simpler molecules such as acetylene, diacetylene, and silane, heavily diluted in an inert gas, were subject to a small d.c. discharge in the throat of the supersonic nozzle of our molecular beam spectrometer. The choice of the precursor and inert gases, the dilution factor, and the parameters of the electrical discharge are all highly empirical, guided largely by trial and error, since no good theoretical model of the synthetic process exists. In the past, simple unsaturated compounds like acetylene and allene were shown here and elsewhere to be a good source of carbon chains and the C_3H_2 ring in the large glow discharges used in millimeter-wave free space spectrometers, and these were employed in the present FTM instrument with some success. Better results were achieved however with diacetylene, which to avoid explosions was synthesized in small quantities, and immediately diluted in Ne or Ar. Cyanoacetylene was also synthesized, and proved to be an almost equally good source of nitrogen-containing chains. Silane has been the key raw material for the production of the silicon molecules in Fig. 3; the small amount of gas consumed by the FTM machine relative to that required for the millimeter-wave instrument in Fig. 4, greatly alleviates the precautions required in the handling of silane. Further details on the particular sources used for each chain can be found in the articles cited.

It bears emphasis that our production techniques are still fairly primitive, and with systematic investigation may be subject to considerable improvement. Only a few have been tried among the large number of possible production schemes, and it is likely that ones we have not yet employed, such as laser ablation or discharges through even more unstable precursor gases, will yield significantly higher concentrations of carbon chains and rings than any of the methods so far adopted. A systematic theoretical investigation of the problem is needed, but we have no illusions that that would be easy, or would quickly yield results to guide experiment.

2.1.5. Astronomical detections

Many of the first carbon chains (e.g., the sequence of free radicals CCH, CCCH…C_6H) were identified in astronomical sources before being detected on earth, but with the work here, laboratory spectroscopy is now well ahead of radio astronomy, allowing new astronomical molecules to be found without searches in frequency that with radio telescopes are often prohibitive in time and cost. Any carbon chain which can be observed in space can probably be detected in the laboratory with the present techniques, or extensions of these which are planned.

All or most of the chains in Fig. 3 are candidates for astronomical detection, because at least one shorter member of each series has already been detected in space, and, as mentioned, five of the present chains were quickly found once laboratory frequencies were in hand. With existing telescopes, detecting the larger ones will be difficult or impossible in even the best presently known astronomical sources — integrations of roughly 30 h per line were required to detect $HC_{11}N$ with modest signal-to-noise [20] — but larger and better telescopes (e.g., the Green Bank 100 m telescope and the resurfaced Arecibo 305 m telescope) will soon be available to work in the 1–10 GHz band where the larger molecules in Fig. 3 are expected to have their strongest astronomical lines.

There is, moreover, the possibility that significantly better astronomical sources of large molecules will be found. Molecule-rich circumstellar shells of stars as close as IRC + 10216 are rare, and it is quite likely that this object is the best of its kind. TMC-1 is a different matter; it is merely one rather undistinguished molecular clump among many in the extensive collection of dark nebulae in Taurus covering some 150 square degrees, which is one of the closest regions of molecular gas and star formation to the sun (Fig. 2). Very few of the many other molecular cores in Taurus have been studied in any molecule heavier than HC_3N, and there are comparably extensive molecular regions elsewhere in the sky which have been even less studied, although not much further away than those in Taurus — e.g., the well known molecular complexes associated with the

dark nebulae in Auriga, Perseus, Aquila, and Ophiuchus. More distant molecular clouds are almost entirely terra incognita with respect to large molecules. CO has been detected in over one-half of the 3600 square degrees of the sky that lies within 5° of the Galactic plane, but almost none of the hundreds or thousands of dense, generally distant molecular clouds which lie in this wide band have been studied in any molecule larger than HC_3N. Once a few good sources were in hand, the radio astronomers simply returned to these locations again and again in their search for still larger molecules, unwilling to devote scarce telescope time to slow and frustrating attempts to find better locations.

2.1.6. Geometrical structures

In our search for new reactive molecules, ab initio theoretical calculations have been of considerable value. By providing structures that sometimes approach 0.1% in accuracy, they have helped us to find the rotational spectra of new molecules without excessively large searches in frequency, and by providing fairly reliable isomeric energies, they have guided us in the search for astronomically interesting rearrangements of known astronomical molecules. Although radio astronomers are often satisfied with the rotational constants of the normal isotopic species of a molecule, the quantum chemist usually wants the individual bond lengths and angles for comparison with theory, and for that knowledge of the rare isotopic species is required. The high sensitivity of our FTM spectrometer often allows the determination of the rotational constants of rare species in natural abundance without isotopic enrichment, particularly those for the crucial carbon-13 species, allowing a fairly rapid determination of structures to the accuracy achieved by ab initio theory.

The molecules whose structures have been determined in this laboratory are H_2C_3 and H_2C_4 [21], C_3N and C_4H [22], the SiC_3 rhomboids [23,24], the silicon–carbon chains SiC_4 and SiC_6 [25],and the cyanopolyynes HC_7N through $HC_{11}N$ [26] (Fig. 7). The latter, to our knowledge, are the largest molecules whose detailed structures have been determined by isotopic substitution; they provide the best existing evidence that the predicted single–triple bond alternation actually exists throughout the length of a long polyyne carbon chain. There is no evidence that the central bonds even out, approaching the double bond structure observed in cumulenic chains like H_2C_4. Presumably bond alternation persists in the limit of the infinite polyyne lattice as the result of a Peierl's instability.

2.1.7. Isomers

With increasing number of atoms, the number of low lying isomers of a molecule which one might hope to detect in the laboratory and in space tends to increase very rapidly. The C_7H_2 ring-chain has been calculated ab initio to be the most stable isomer with that elemental formula, but five others have been calculated to lie within 1 eV [27], and there are still others which may be comparably stable, or only slightly less so. Two of these have now been found: a cumulene carbene chain and a linear nonpolar triplet found in our laboratory by laser spectroscopy (see below). As Fig. 8 shows for C_5H_2, four polar isomers calculated ab initio to lie within 1 eV [28] have been detected with our FTM spectrometer [29]: the ground state ring-chain, a cumulene chain, a bent-chain, and new type of ring-chain where a cumulenic C_2 unit is added to the apex carbon of c-C_3H_2. An unsuccessful optical search for a fifth isomer, the low-lying linear nonpolar triplet, was attempted with our laser spectrometer. Similarly, we have also detected three isomers of SiC_3: two planar singlet rhomboids and a triplet linear chain.

The existence of fairly energetic molecular isomers in regions of the interstellar gas where the kinetic and rotational temperature is not much larger than 10 K is striking evidence of how far the chemical processes in space depart from thermal equilibrium. HNC for example is more energetic than HCN by 0.6 eV, and in thermal equilibrium at the temperature of a typical cold molecular cloud, say 15 K, the abundance of HNC relative to HCN is entirely negligible: $\sim \exp(E/kT) \sim 10^{-200}$. The observed ratio actually approaches unity in some locations, because the ion-molecule reactions which make both isomers

couple the chemistry to the very high effective temperature reservoir of the cosmic rays which permeate the interstellar gas.

Little is known about isomeric systems containing more than six or seven carbon atoms. Ab initio calculations to our knowledge have not been done for C_9H_2 or the longer carbon chains in Fig. 3, but by analogy with C_5H_2 and C_7H_2, these must all possess a large number of low-lying isomers, many of which are probably fairly stable, and candidates for laboratory and astronomical detection. Cyclic or ring-chain isomers of C_5H

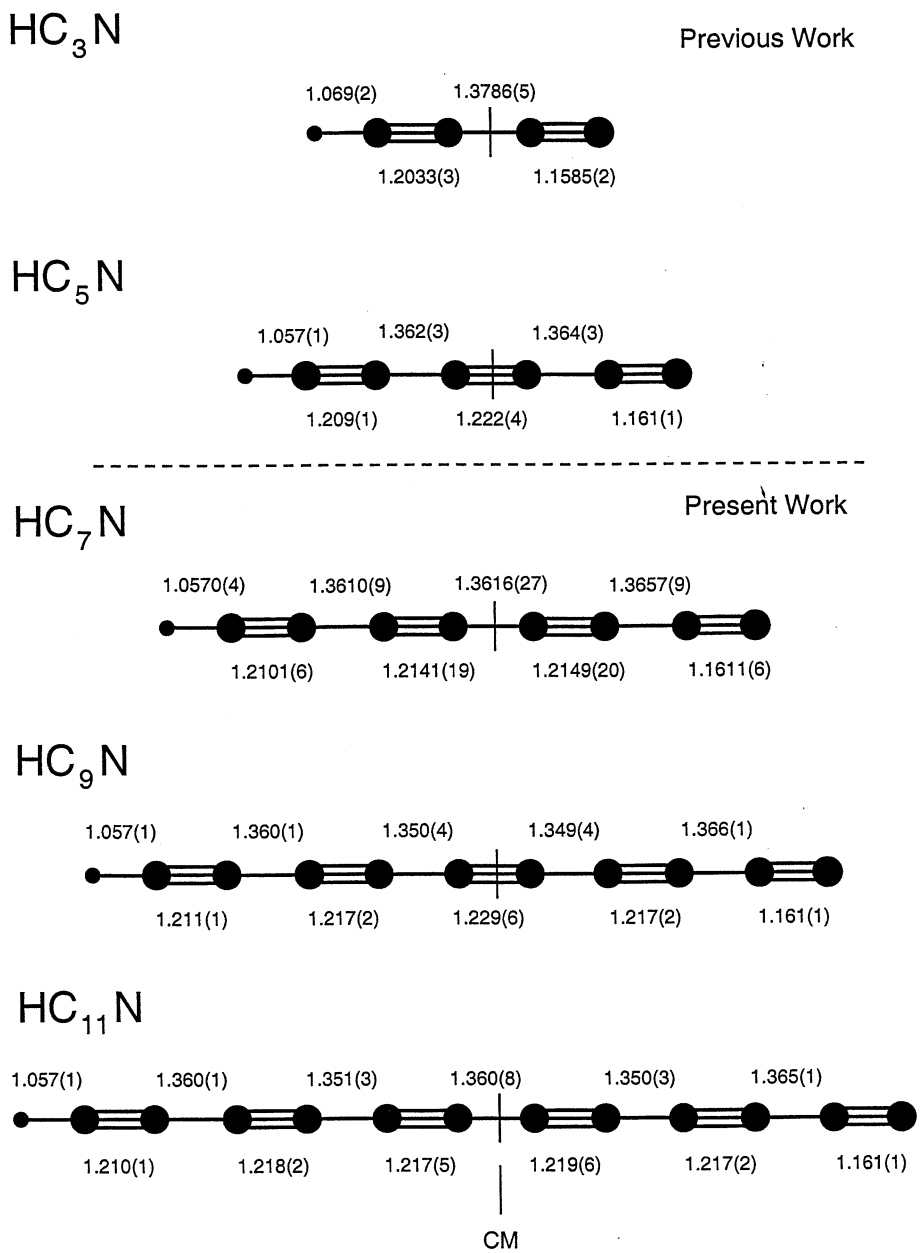

Fig. 7. Structures of cyanopolyynes determined by isotopic substitution.

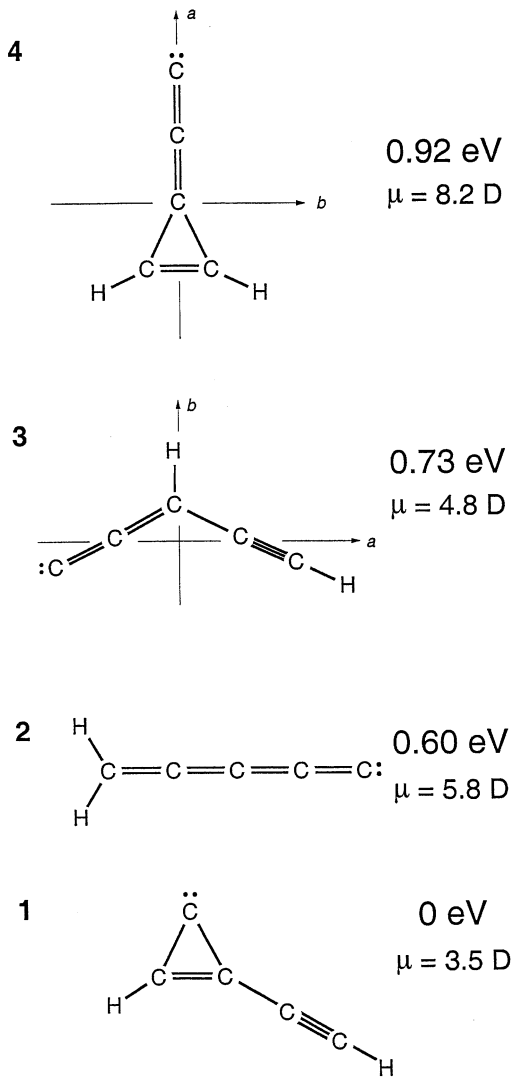

Fig. 8. Isomers of H_2C_5 now detected, with ab initio dipole moments and energies.

[30] and SiC_5 [31] and longer chains would appear to be particularly favorable for detection because lines of the linear isomers are strong in our molecular beam, and because linear C_5H through C_8H and rhomboid SiC_3 have all been found in space.

2.1.8. Molecular ions

Once H_2 forms on the dust grains mixed throughout the interstellar medium, gas phase reactions fairly rapidly build up larger molecules. As mentioned above, ion-molecule reactions are especially important because their reaction cross section may be hundreds or thousands of times larger than the geometrical cross section of the molecules involved, and because such reactions typically have no activation barrier, and so remain very rapid at temperatures close to absolute zero where most neutral molecule reactions are frozen out [16]. A long chain of reactions begins with the ionization of H_2 by cosmic rays: $H_2 + CR \rightarrow H_2^+ + e$, where the most important cosmic rays are the low energy primary protons produced in supernova explosions which uniformly fill the galactic plane and readily penetrate into even dense molecular clouds. The resulting H_2^+ ion rapidly reacts with a second H_2 to form the highly reactive H_3^+ ion: $H_2^+ + H_2 \rightarrow H_3^+ + H$.

H_3^+ has a low proton affinity, and on the first encounter with any one of a number of stable molecules it will give up its proton to form a more stable molecular ion: $H_3^+ + X \rightarrow HX^+ + H_2$, starting a diverging sequence of ion-molecule reactions [32]. The widely distributed HCO^+ and HNN^+ ions are formed in this way from CO and N_2, and there are several other observed but less abundant ions which may be formed similarly, including H_3O^+ from water, H_3CO^+ from formaldehyde, and HC_3NH^+ from cyanoacetylene. Other ion-molecule reactions of importance start with the cosmic ray ionization of helium. At least eleven positive molecular ions have now been detected in space (Fig. 1), and probably many more will be found when laboratory rest frequencies are in hand.

We have recently undertaken a concerted search for molecular ions with our FTM spectrometer, and have now found two: protonated cyanoacetylene, HC_3NH^+, and protonated methyl cyanide, CH_3CNH^+. Both had been previously observed spectroscopically in the infrared; a third ion, protonated cyanogen, $NCCNH^+$, has also been detected, but is not included in Fig. 3 because its rotational spectrum had previously been detected in the millimeter-wave band. For all three molecular ions, the frequencies of the rotational lines of astronomical interest are now determined to the same accuracy as those of the neutral molecules in Fig. 3, i.e., to 1 km s^{-1} or

better in equivalent radial velocity. In the course of this work it was found that using H_2 instead of Ne or Ar as the buffer gas in our discharge source yielded an order of magnitude improvement in signal strength, a finding likely to be of considerable value in the search for larger ions.

The $C_3H_3^+$ ion, familiar in the laboratory as the mass 39 peak in mass spectrometers, is almost certainly present in the interstellar gas, where it is thought to be the main source of cyclic C_3H_2 via dissociative recombination. Owing to its planarity and D_{3h} symmetry, however, it possesses no electric dipole moment, and no microwave spectrum (although $C_3H_2D^+$ has a weak rotational spectrum which we might be able to detect in the laboratory). On substituting carbon chains for one of the H atoms, however, the symmetry is broken, and one obtains a family of ring-chain ions analogous to the carbene ring-chains of Fig. 3. Because these too are likely to be highly polar, and because positive ions are readily formed in the interstellar gas, this so-far-unobserved sequence is of considerable astronomical interest. Laboratory detection is again a prerequisite for an astronomical search, and there does not appear to be any fundamental reason why this cannot be accomplished.

2.1.9. Carbon chains as classical elastic rods

In our Faraday Discussion review [10] it is shown that the centrifugal distortion of carbon chains like those here is remarkably simple, and readily understood in terms of a semi-classical model. On the assumption that the chain is a uniform, thin elastic rod of length L, cross sectional area σ, density per unit length ρ, and with a Young's modulus E that is independent of length and type of chain, it is found that the ratio of the centrifugal distortion constant to the rotational constant is inversely proportional to the inverse fourth power of L. Specifically $D/B = (18h^2/5\pi^2 E\sigma\rho)L^{-4}$. As a semi-classical model, one might expect it to hold only in the limit of long chains, or that the stiffness would depend on the type of chain, i.e., the various end groups and valence structures in Fig. 3, but that is not observed. Instead, the model seems to hold to the very shortest chains studied, and to fit all types of chains equally well.

The practical value of this relation is considerable when it comes to identification. It allows a true chain to be distinguished from less stiff weakly-bonded complexes which are readily formed in molecular beams such as ours (e.g., $HCCCCH–H_2O$), and by making a specific prediction of the centrifugal distortion once the rotational constant is determined, it simplifies the process of identification — i.e., it reduces the number of parameters required to fit the rotational spectrum of a linear chain from two to one.

2.1.10. Low frequency bends at radio frequencies

Long carbon chains are difficult to stretch but easy to bend, and the lowest frequency bends of the two longest chains in Fig. 3, $HC_{15}N$ and $HC_{17}N$, are expected to lie in the submillimeter band, where they are within range of existing high frequency radio telescopes. An estimate of the frequencies is again provided by a semi-classical calculation. The bending modes of a thin elastic rod scale in frequency as the inverse square of the rod's length, so one expects the more 'classical' of the transverse vibrations of a long chain, the lowest frequency bend especially, to scale with length in approximately that way. The low frequency bends measured for HCN and HC_3N, and those calculated ab initio for HC_5N and HC_7N, fit this scaling law to about 15%. Extended to the chains here, such scaling predicts that the frequency of the lowest frequency bend of $HC_{15}N$ should be 16 times less than that of HC_3N, which is at 220 cm^{-1}. It should therefore lie at about 14 cm^{-1}, or 420 GHz. Similarly, that of $HC_{17}N$ should be 20 times less than that of HC_3N, and should lie at about 11 cm^{-1}, or 330 GHz.

Both these frequencies are accessible to existing radio telescopes, such as the Caltech Submillimeter Telescope and the UK James Clark Maxwell Telescope on Mauna Kea. Precise laboratory measurements of these vibrational transitions are a prerequisite for an astronomical search, because the estimated frequencies are probably uncertain to about 15%. The transition dipole moments for these low frequency bends are even more uncertain than the frequencies. Estimates differ by an order of magnitude (A. Cooksy, private communication), from about 1.3 D to 0.1 D, the uncer-

tainty resulting from the largely unknown distribution of the dipole moment along the long conjugated chain. Ab initio calculations of the structures of $HC_{15}N$ and $HC_{17}N$ might yield considerably better transition moments, and it would be desirable to have these in hand before attempting to observe the undoubtedly weak bends in astronomical sources.

2.2. Laser spectroscopy

Carbon chains because of their conjugated electrons are similar to organic dye molecules, and they are similarly expected to possess strong electronic optical transitions which move to the red as the chain length is increased. Many of the carbon chains in Fig. 3 therefore are likely to possess intense optical transitions, but with the exception of C_8H, $C_{10}H$, and $C_{12}H$ [33], none of these has been observed in the gas phase. At the densities which we have been able to produce, almost all are probably detectable with modern laser techniques, LIF spectroscopy, for example, for those transitions which fluoresce, and cavity ringdown and REMPI spectroscopy for those which do not. Carbon chains like $HC_{17}N$ at the limit of detection of the present FTM spectrometer (at an integration time of order 1 h) have a density of about 10^8 cm^{-3} in our molecular beam, which is well above the threshold of detection by either laser technique. Aside from the interest to radio astronomy, a major motivation of the present work has been to learn how to produce and to identify large carbon chains, preparatory to optical experiments designed to identify the carriers of the diffuse interstellar bands.

It was clear with our first FTM discoveries that exotic new molecules were being produced at a density high by the standards of laser spectroscopy ($\sim 10^9$ cm^{-3}). To exploit this finding the spectrometer shown in Fig. 4 was constructed three years ago, a flexible instrument capable of two of the most sensitive laser techniques: laser-induced fluorescence (LIF) for those molecules which fluoresce, and cavity ringdown spectroscopy (CRDS), a very long-path absorption technique, for those molecules which fail to fluoresce. The main scientific motivation for this new instrument was to identify the carriers of the famous diffuse interstellar bands (DIBs), a long-standing enigma widely considered the outstanding unsolved problem in astrophysical spectroscopy. It is likely that solution of the problem of the DIBs will open a new and possibly unique window into the organic chemistry of the material in interstellar space that ultimately forms stars and planets. The diffuse bands are not generally observed in the dense molecular clouds where the radio molecules are found; they have been telling us for nearly 80 years that even in the diffuse interstellar gas there exists a remarkably rich chemical specificity.

The first success with this laser spectrometer was achieved last year with the detection of the four symmetric carbon chains HC_7H through $HC_{13}H$ shown in Fig. 3 [34,35], linear radicals with triplet electronic ground states previously studied in rare gas matrices [36], but not previously detected in the gas phase. Because carbon chains are ubiquitous in molecular clouds (Fig. 1), these are DIB candidates, but they are not particularly good ones, since they may have more stable cyclic isomers; we were therefore disappointed but not surprised to find that none of the bands of these carbon chains coincided with known DIBs [in the most recent tabulation: [37]]. However a search by C. D. Ball of our group for molecular bands in the vicinity of the strongest and best known DIB at 4429 Å turned up the remarkable candidate shown in Fig. 9 — a molecular band with well developed *P*, *Q*, and *R* branches at precisely the wavelength of the astronomical band [38]. No comparably good laboratory match has been found since this archetypal DIB was discovered in the 1930s by Merrill.

Laboratory λ4429 was discovered in a discharge through benzene, but subsequently observed in ones through toluene and, at reduced intensity, through diacetylene and acetylene, our best carbon chain sources, which yielded most of the molecules in Fig. 3. Deuterium isotopic shifts then established that the carrier of this band is (i) a hydrocarbon with the probable elemental formula C_nH_5, and (ii) that the five H atoms probably consist of two pair of symmetrically-placed 'equivalent' H atoms plus one lone H. Unfortu-

nately, it has not been possible to determine the number or symmetry of the carbon atoms by carbon-13 substitution, because the band shifts produced by this isotope are too small to resolve (as demonstrated with 100% carbon-13 benzene). Because we have found from our FTM studies that benzene discharges do not readily produce molecules with more than six carbon atoms, and because no plausible candidate carrier exists with

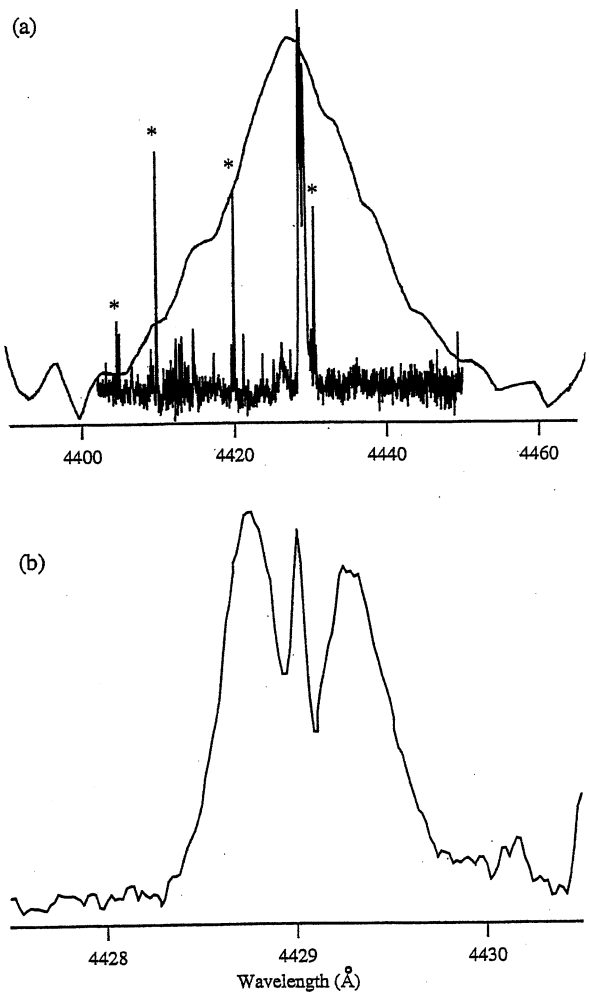

Fig. 9. (a) New laboratory molecular band from a benzene discharge, superposed on the diffuse interstellar band at 443 nm observed toward a hot distant star in the Galactic plane. (b) The laboratory band on an expanded wavelength scale, displaying (from right to left) apparent *P*, *Q*, and *R* branches. Features marked by an asterisk are lines of light hydrides.

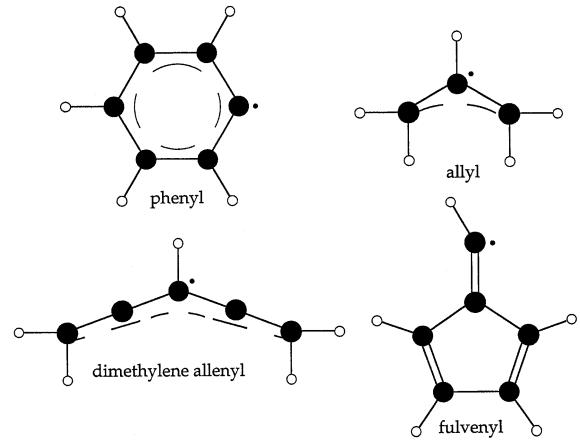

Fig. 10. Four hydrocarbon molecules with elemental formula C_nH_5 and the right symmetry to explain the D isotope shifts in the laboratory band at 443 nm.

two or less, we conclude that n is probably in the range 3–6, inclusive. This is not a very firm conclusion, and we are prepared to abandon it and consider larger molecules if those in this range ultimately fail as candidates.

The number of plausible molecules in that mass range with the elemental formula C_nH_5 is fortunately fairly small; four of the better candidates are shown in Fig. 10. Of the various types of molecules which have been proposed as carriers of the diffuse bands, carbon chains [39] and polyaromatic hydrocarbons [40] have long been among the leading contenders. It is therefore noteworthy that two of the candidates in Fig. 10 are carbon chains — the allyl and dimethylene allenyl radicals — and two are cyclic aromatic hydrocarbons — the phenyl and fulvenyl radicals. The neutral phenyl radical can probably be ruled out because its optical spectrum has long been known, and it contains no strong band at λ4429; the same is true of neutral allyl, but the remaining two neutral radicals and the ions of all four — the positive ions are the more plausible — can not be ruled out. Determining which of these, if any, is the carrier of λ4429 is now our highest priority.

As Fig. 9 shows, our laboratory band is considerably sharper than the astronomical one at 4429 Å, but that may simply be the result of the large difference in rotational temperature between our

Table 1
Summary of recent detections

Molecules	Reference
$C_{10}H$, $C_{12}H$, $C_{13}H$, $C_{14}H$	[41]
H_2C_7, H_2C_8, H_2C_9, D_2C_{10}	[42]
H_2C_5H	[43]
HC_4N, HC_6N ring chains	[44]
HC_4N bent-chain carbene	[45]
HC_3NH^+, CH_3CNH^+	[46]
SiC_3, SiC_5, SiC_6, SiC_7, SiC_8	[47]
triplet HC_6N	[48]
SiCCH, SiCN, SiNC	[49]

rotationally cold supersonic beam ($T_{rot} = 3–10$ K) and that of a non-polar or weakly polar molecule in the diffuse interstellar gas ($T_{rot} = 125–300$ K). H. Linnartz of Maier's group has recently shown in a hollow cathode discharge that at several 100 K the laboratory band broadens considerably as the result of rotational excitation and possibly the excitation of hot bands. At the very low density characteristic of the interstellar gas, some vibrational levels excited in the hollow cathode discharge will radiatively relax to the vibrational ground state, and the profile of hot bands may change markedly. Until the precise composition and structure of our molecule are determined and some knowledge of its vibrational spectrum inferred, it is not possible to calculate the shape of its optical bands under interstellar conditions, and premature to attempt a precise fit of the profile of the astronomical band. For the present we conclude simply that there is empirical evidence that our band broadens at higher temperature by roughly the required amount; ultimately of course when more is known about the carrier molecule the exact shape of astronomical λ4429 must be explained in detail.

Appendix A

Many of the 77 molecules shown in Fig. 3 have already been described in the literature. For those detected before 1998, specific citations can be found in our 1998 review [10], or in either of our two supplemental articles [7,8]. For those detected since 1998 which are not cited here, references to published papers are summarized in Table 1.

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