

Figure 21 The i.r. spectra obtained (a) for CF_3PH_2 , (b) by passing CF_3PH_2 through a tube packed with KOH, (c) by double passage over KOH.⁷⁹ The strong band at ca. 1170 in (a) is the C–P stretch of CF_3PH_2 . In (b) both $\text{CF}_2=\text{PH}$ and FCP appear and in (c) FCP is more intense relative to $\text{CF}_2=\text{PH}$, and CF_3PH_2 has been almost completely eliminated. In (b) the stronger $\text{CF}_2=\text{PH}$ features are ν_1 (PHstr), ν_2 (C=Pstr), ν_3 (CF_2 asym str) and ν_5 (CF_2 sym str). In (c) the FCP features ν_1 , $2\nu_2$, and ν_3 are identified: ν_1 appears to be an antisymmetric stretching frequency and ν_3 a symmetric stretching frequency. Fermi resonance with ν_3 enhances $2\nu_2$. Note the correlation with the microwave spectrum in Figure 17

4 Poly-yne

A. Introduction.—Linear molecules present some most interesting problems in molecular dynamics. If they are very long they flex like a cane and one can visualize rotational energy transfer or vibrational energy transfer depending on whether a collision is near an end or near the chain centre respectively. In general they possess the most simple spectra and the longer they are, the higher is the number of bending vibrations excited at room temperature. These types of intrinsically interesting physical ideas initiated a programme with David Walton aimed at spectroscopic study of poly-yne. This involved the preparation of a range of simple poly-yne, some of which are rather unstable, by a combination of traditional synthesis and novel reactions.

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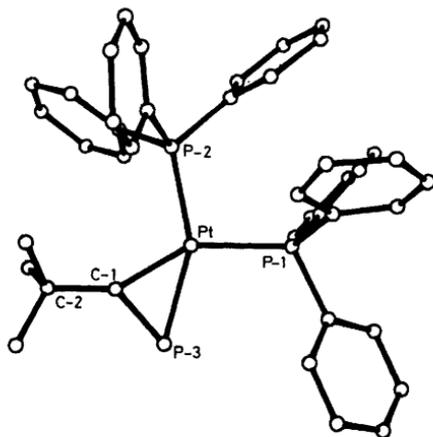
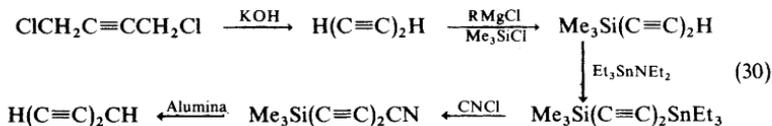


Figure 22 The results of an X-ray analysis of the $t\text{-BuC}\equiv\text{PPt}[\text{P}(\text{Ph})_3]_2$ π complex.⁹⁸ $\angle\text{CCP}$ has changed from 180° in the free $t\text{-BuCP}$ molecule to 132° in the complex

A number of alkynes and polyalkynes were produced and their microwave spectra, and in some cases also their photoelectron, n.m.r., and i.r. spectra, were measured.¹⁰⁰ The length of these molecules gives rise to extended vibrational satellite structure in their microwave spectra enabling detailed rotation-vibration studies to be made.

The study of these species, in particular $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$, coincided with the exciting breakthrough in detection of interstellar molecules by radio-astronomy¹⁰¹⁻¹⁰³ and the microwave measurements initiated a search for interstellar poly-yne which has led to exciting and perplexing discoveries whose implications have still to be explained.

B. Microwave Spectra of Polyacetylenes.—In a typical synthesis, $\text{HC}_3\text{N}^{104}$ was made as shown in equation (30)



The triethyl tin group is preferentially replaced in step 4 resulting in $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_2\text{CN}$. This molecule is a symmetric rotor and its microwave spectrum is shown in Figure 23.¹⁰⁵ In this case there are so many lines, due to not

¹⁰⁰ A. J. Alexander, 'Spectroscopic Studies', B.Sc. Thesis, University of Sussex, 1975.

¹⁰¹ G. Winnewisser, E. Churchwell, and C. M. Walmsely in 'Modern Aspects of Microwave Spectroscopy', ed. G. Chantry, Academic Press, London, 1979, p. 313.

¹⁰² H. W. Kroto, 'Chemistry between the Stars', *New Scientist*, 1978, **79**, 400.

¹⁰³ H. W. Kroto, 'The Spectra of Interstellar Molecules', *Int. Rev. Phys. Chem.*, 1981, **1**, 309.

¹⁰⁴ A. J. Alexander, H. W. Kroto, and D. R. M. Walton, *J. Mol. Spectrosc.*, 1976, **62**, 175.

¹⁰⁵ A. J. Alexander, H. W. Kroto, and D. R. M. Walton, to be published.

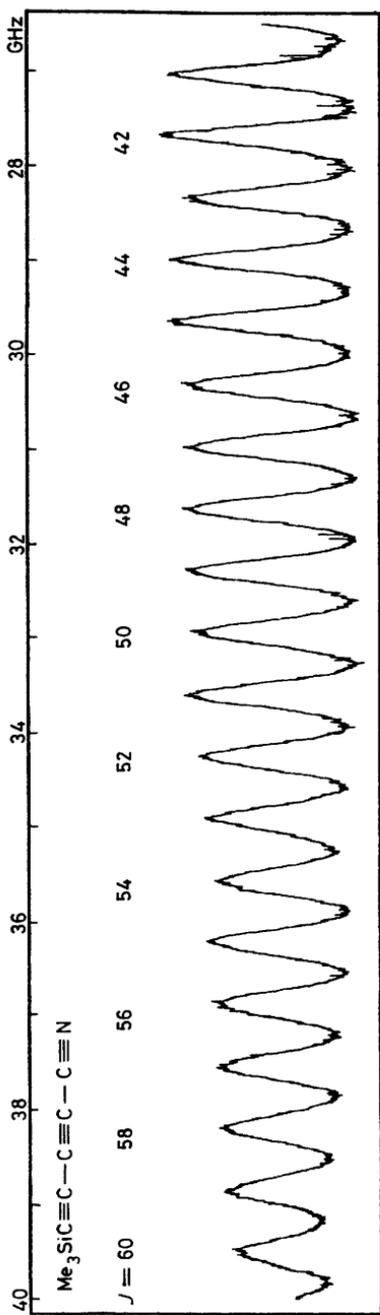


Figure 23 The wide-scan microwave spectrum of $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CN}$.¹⁰⁵ Each of the bands for a given J consists of a multitude of unresolved lines for the various bending and torsional satellites as well as K components

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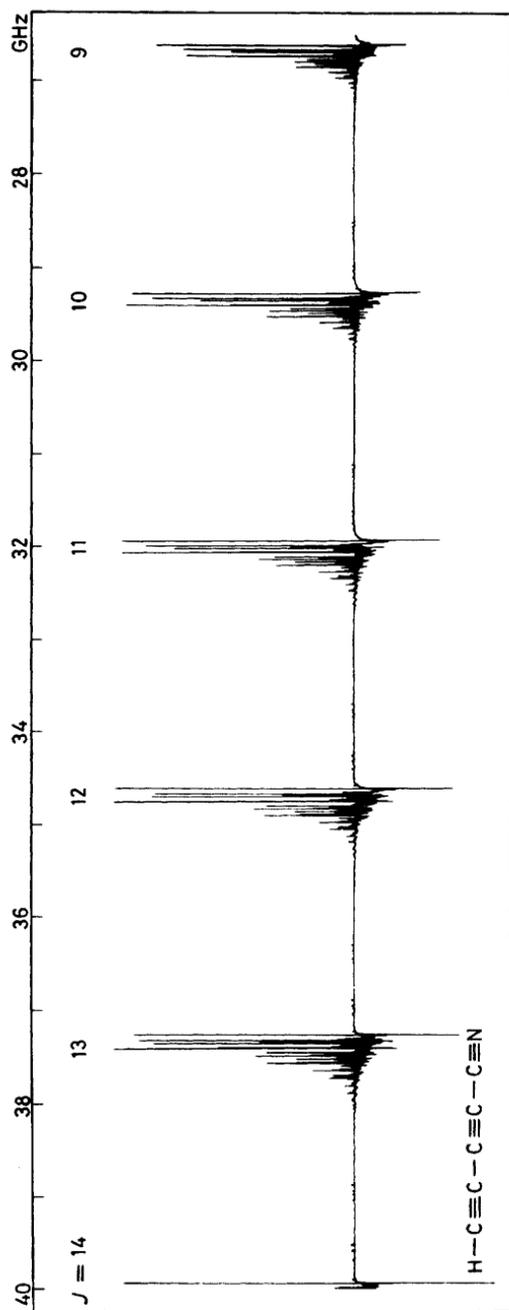


Figure 24 The wide-scan microwave spectrum of $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}\equiv\text{N}$.¹⁰⁴ Each J transition consists of the ground state line with an entourage of vibrational satellites. These are shown in more detail for this $J = 14 \leftarrow 13$ transition in Figure 25

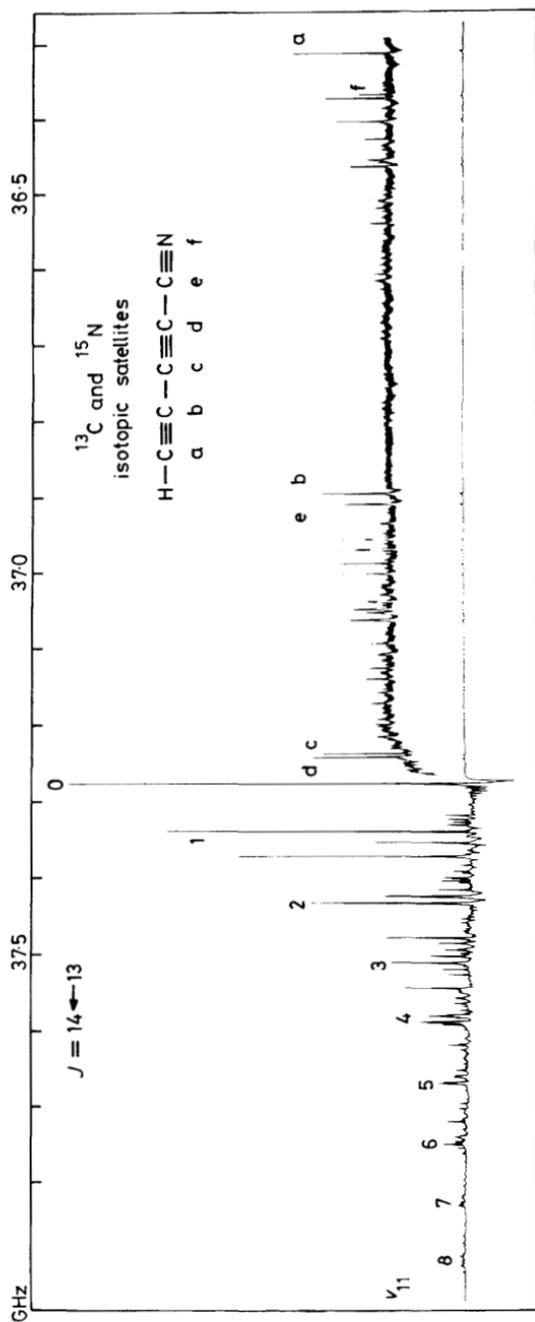


Figure 25 The $J = 14 \leftarrow 13$ transitions of HC_3N under moderate resolution.¹⁰⁴ The bending vibrational satellites march out with exponential intensity to high frequency. On bending the molecule shortens, decreasing the moment of inertia and consequently increasing the average B_0 value causing the shift to high frequency. The various singly substituted isotopic modifications are also observed, being heavier they lie to low frequency. As the moment of inertia is a function of m^2 the shift is roughly proportional to the square of the distance of the substituted atom from the centre of mass. To see that this is roughly correct one can assume all the bonds are the same length and that the c. of m. is in the middle of the central triple bond. The distances of atoms d and c, e and b, and f and a are then in the ratio 1 : 3 : 5 respectively. This should result in isotope shifts in the ratio 1 : 9 : 25. From the above spectrum one can see that this is roughly correct as the ratios are ca. 1 : 10.3 : 26.6. The correct analysis is discussed in the text and in Table 6. The ground state lines for the isotopically substituted species are identified

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only $|K|$ degeneracy but also bending vibrational satellites as well as Me_3Si group torsional satellites, that each $J + 1 \leftarrow J$ transition is a very broad band, composed of many hundreds of unresolved lines.

The trimethylsilyl group can be readily hydrolysed off to produce cyano-butadiyne $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ whose broad-band microwave spectrum is shown in Figure 24.¹⁰⁴ The spectrum is so strong, mainly due to the large dipole moment ($\mu = 4.33$ Debye), that naturally occurring ^{13}C and ^{15}N isotopically substituted analogues can be seen even though they are only present in *ca.* 1% abundance. The structure of the $J = 14 \leftarrow 13$ transition is presented in Figure 25 so that the isotopic satellites and the roughly exponentially decaying vibrational satellites can be seen in more detail. In fact, a very accurate structure determination can be made simply and directly from measurement of these lines alone using the Kraitchman relations.^{3,106,107} In the simple case of a linear molecule, the Kraitchman relation shows that, if I is the moment of inertia of a particular species (mass M) and I^* is that for a *singly* substituted species (mass $M + \Delta m$) then the distance of the substituted atom from the c. of m. of the parent species (r_s) is given by equation (31)

$$r_s = [\mu^{-1}(I^* - I)]^{1/2} \quad (31)$$

where $\mu = M\Delta m/(M + \Delta m)$. The Kraitchman analysis yields substitution (r_s) co-ordinates, and for the transitions shown in Figure 25 is given in Table 6. The reason for giving a detailed analysis is that this is a very good example of what is arguably the most important structure determination procedure for small molecules and does not appear to be well known outside the field of microwave spectroscopy. The standard method, given in all spectroscopy textbooks, involves the solution of sets of complex quadratic equations, a method which in fact gives relatively poor results as discussed by Costain.^{3,107} The resulting structural parameters are compared with those of HC_3N ¹⁰⁸ in Table 6.

The vibrational satellites of HC_5N can also be analysed in detail on the basis of vibration-rotation theory of linear molecules. This has been carried out to as high as eight quanta of the lowest frequency bending vibration.¹⁰⁹

A symmetric top has a much more complicated spectrum as shown in Figure 26 for $\text{CH}_3-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$.¹¹⁰ Instead of a single line, as in the linear case, the ground state transition is, as discussed in Section 2A, split into $K + 1 |K|$ components, Figure 27. The vibrational satellite structure is more complex and difficult to unravel. The same type of l -type doubling occurs as in $\text{CH}_3\text{C}\equiv\text{P}$, Figure 16, except that here there are many more contributing low-frequency vibrations to confuse the issue.

¹⁰⁶ J. Kraitchman, *Am. J. Phys.*, 1953, **21**, 17.

¹⁰⁷ C. C. Costain, *J. Chem. Phys.*, 1958, **29**, 864.

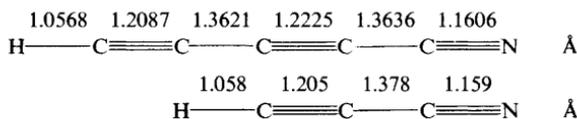
¹⁰⁸ J. K. Tyler and J. Sheridan, *Trans. Faraday Soc.*, 1963, **59**, 2661.

¹⁰⁹ M. Hutchinson, H. W. Kroto, and D. R. M. Walton, *J. Mol. Spectrosc.*, 1980, **82**, 394.

¹¹⁰ A. J. Alexander, H. W. Kroto, M. Maier, and D. R. M. Walton, *J. Mol. Spectrosc.*, 1978, **70**, 84.

Table 6 Determination of the substitution bond lengths (r_s) of cyanobutadiyne $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}^a$

Species ^b	$\Delta E(13)^c$ / MHz	B^d / MHz	I^e / amu \AA^2	ΔI^f / amu \AA^2	μ^g	$r_s^h/\text{\AA}$
$\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$	37 276.99	1331.321	379.6162	—	—	—
$\text{D}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$	35 589.32	1271.047	397.6179	18.0017	0.992956	4.2579
$\text{H}-\overset{*}{\text{C}}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$	36 306.63	1296.665	389.7622	10.1460	0.990111	3.2011
$\text{H}-\text{C}\equiv\overset{*}{\text{C}}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$	36 894.99	1317.678	383.5467	3.9305	0.990111	1.9924
$\text{H}-\text{C}\equiv\text{C}-\overset{*}{\text{C}}\equiv\text{C}-\text{C}\equiv\text{N}$	36 238.39	1329.943	380.0095	0.3933	0.990111	0.63026
$\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\overset{*}{\text{C}}-\text{C}\equiv\text{N}$	36 242.92	1330.104	379.9635	0.3473	0.990111	0.59226
$\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\overset{*}{\text{N}}\equiv\text{N}$	36 908.73	1318.169	383.4038	3.7876	0.990111	1.9559
$\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\overset{*}{\text{N}}$	36 361.62	1298.629	389.1727	9.5565	0.983955	3.1165



(a) This calculation has been simplified by neglecting centrifugal distortion so the B values in this table are not quite correct (see ref. 104). However, because the structure calculation utilises ΔI the discrepancies cancel out and yields a very good structure. (b) * Indicates substituted nucleus. (c) Measured frequency of $J = 14 \leftarrow 13$ transition, Figure 25. (d) B obtained neglecting centrifugal distortion, i.e. $B = \Delta E(J)/2(J+1)$. (e) $I/\text{amu } \text{\AA}^2 = 505391/B(\text{MHz})$. (f) $\Delta I = I^* - I(\text{H}^{12}\text{C}_3^{14}\text{N})$. (g) $\mu = M\Delta m/(M + \Delta m)$; M = total mass; masses are: 1.007825, 2.014102, 12.0, 13.00335, 14.00307, and 15.00011 for H, D, ^{12}C , ^{13}C , ^{14}N and ^{15}N respectively. (h) $r_s = (\Delta I/\mu)^{1/2}$.

C. Interstellar Molecules.—In the period since 1968 when Townes and colleagues¹¹¹ discovered NH_3 emission by radioastronomy from the direction of Orion, there has been a rapid development in the study of interstellar molecules with numerous exciting and surprising results.^{101–103} The black clouds which congregate in the plane of the galaxy have now been shown, by spectroscopy, to harbour vast quantities of molecules. As these clouds are the raw material from which stars and planets form, molecular spectroscopy is the medium through which the earliest stages of star formation can, for the first time, be observed. The field of interstellar molecules has made a significant contribution not only to astronomy through its impact on the Big Bang Theory, the evolution of galaxies, and the birth of stars but also to Chemistry, Physics, and Biology. New types of chemical reactions must now be considered involving the new types of molecules which are now known to exist under the unusual

¹¹¹ A. C. Cheung, D. M. Rank, C. H. Townes, D. C. Thornton, and W. J. Welch, *Phys. Rev. Lett.*, 1968, **21**, 1701.

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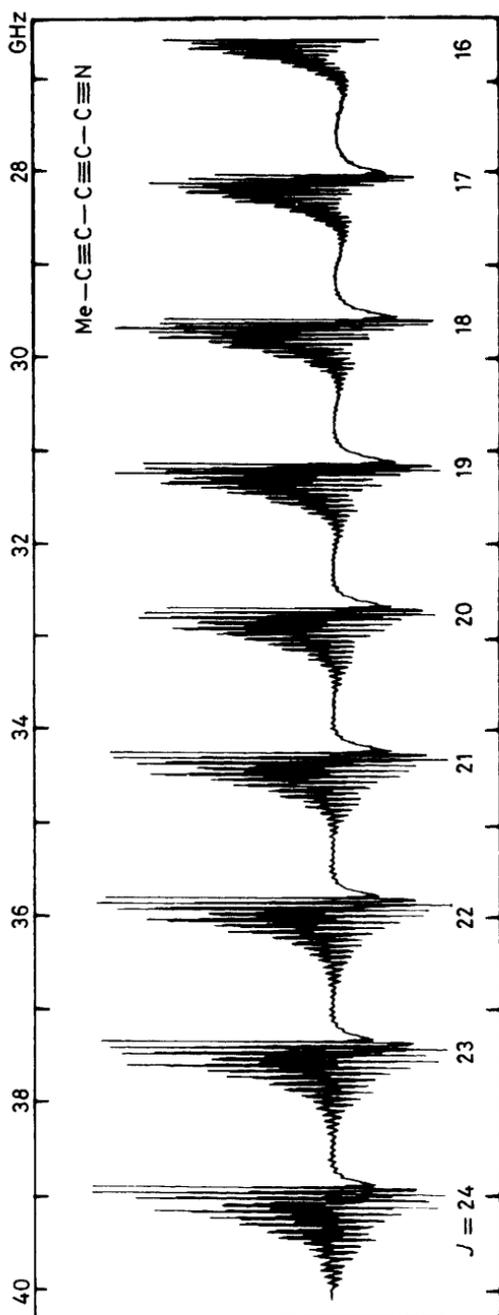


Figure 26 Wide-band scan of the microwave spectrum of $\text{CH}_3\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$.¹¹⁰ As in the case of HC_3N the first line at the RH end of each J group belongs to the vibrational ground state and the rest to bending vibrational satellites. The ground state lines can be resolved into $|K|$ multiplets under high resolution as shown in Figure 27

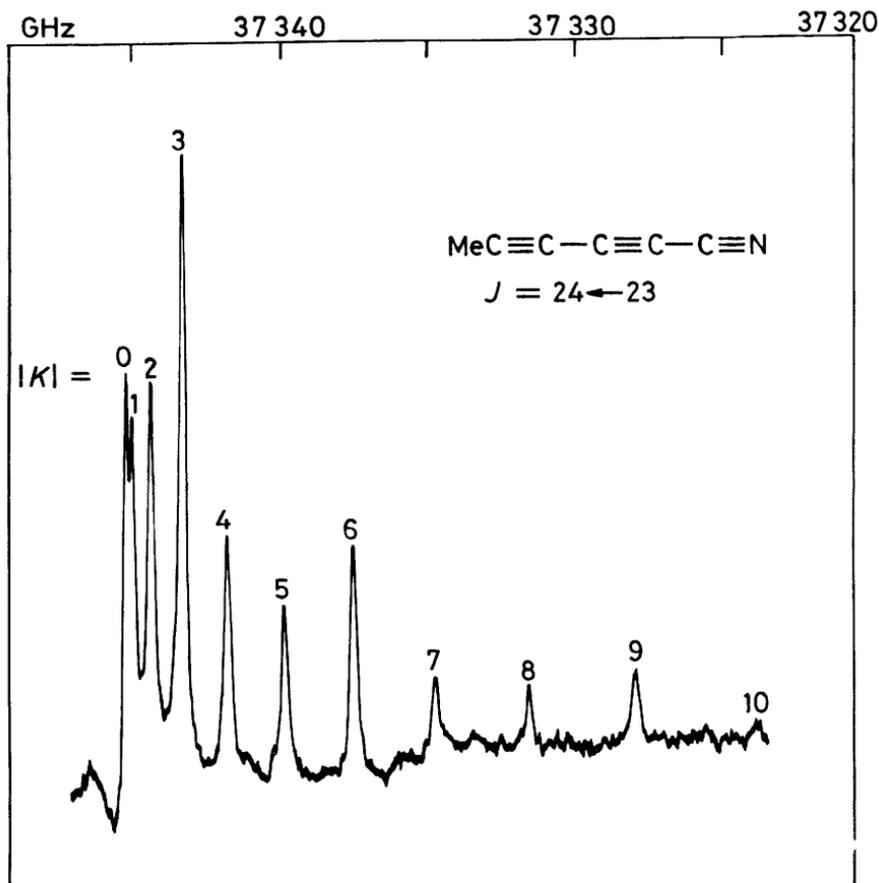


Figure 27 Part of the $|K|$ structure of the $J = 24 \leftarrow 23$ transition of $\text{CH}_3(\text{C}\equiv\text{C})_2\text{CN}$.¹¹⁰ The higher $|K|$ levels are not sufficiently populated so the structure peters out at $|K| > 10$. Note the increased intensity of lines for $|K|$ a multiple of 3 in agreement with C_{3v} statistical weights³

conditions in space. Perhaps the most interesting aspect of these new findings lies in the light that is shed on the origin of the biosphere.

The beautiful photograph by Murdin, Allen, and Malin¹¹² shown in Figure 28 gives a nice feel for what a small region in the Constellation of Orion looks like; a conglomeration of stars and nebulae either cold and black or heated to incandescence by nearby hot stars.

The dark areas are very important from our point of view. It was only in

¹¹² P. Murdin, D. Allen, and D. Malin, 'Catalogue of the Universe', Cambridge University Press, Cambridge, Massachusetts, 1979, p. 131.

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this century that these regions were shown to be clouds of opaque material rather than, as had been thought in ancient times, holes in the star fields through which one could see deep into space. Rather frail circumstantial evidence indicates that the blackening is caused by micron or submicron sized particles of unknown constitution which scatter light at optical wavelengths. The assignment is frail because it is based on very rough scattering data whose characteristics cannot be ascribed to any other entities. The full importance of the scattering constituent has still to be determined though one thing seems clear, the scattering of starlight protects the molecules in the clouds from photodissociation by the starlight that pervades the rest of space.

Although the hot regions have been studied for years by optical spectroscopy it is only since 1968 that analysis of rotational radio or microwave emission from molecules has been able to show that the vast black clouds which litter the space between the stars are full of compounds. In fact, to date, more than 50 different molecules have been detected varying from H_2 , the most abundant, and CO, the next most abundant, through such species as CH_3NH_2 and OCS to species such as CH_3CH_2OH and HC_9N .

Radio telescopes are essentially glorified radios with large steerable highly directional aerials. The sensitive detectors and amplifiers can tune in to very weak, narrow-frequency signals. In general a search is made by tuning the radio-telescope to the same frequency* as that determined by the laboratory study, pointing the telescope at a suitable interstellar source and integrating the incoming signal to see whether a molecule is emitting the same frequency or preferably set of frequencies.

The first experiments were, of course, searches for common molecules whose microwave lines had already been measured. Occasionally during these experiments, lines were detected which corresponded to no known laboratory frequency. One of the most prominent of these unidentified lines (U lines), detected by Buhl and Snyder,¹¹³ was assigned by Klemperer to HCO^+ (protonated CO).¹¹⁴ The assignment was confirmed in laboratory measurements by Woods and co-workers.¹¹⁵ This and other similar results showed that molecules were important probes of the conditions in interstellar molecular clouds and that, in particular, species such as molecular ions and radicals were relatively stable and abundant in the rarified environment and non-equilibrium conditions that existed. Indeed, the detections indicated that the special conditions in space stabilize some molecules that are very difficult indeed to study in the laboratory. A particular example of this is the case of the interstellar poly-yne, discovered as a result of the laboratory experiments discussed in the previous section which were, of course, initiated for quite a different purpose.

* The frequency is usually adjusted slightly to make due allowance for the Doppler shifts arising from the relative motion of the earth and the celestial object being observed.

¹¹³ D. Buhl and L. E. Snyder, *Nature*, 1970, **228**, 267.

¹¹⁴ W. Klemperer, *Nature*, 1970, **227**, 1230.

¹¹⁵ R. C. Woods, T. A. Dixon, R. J. Saykally, and P. G. Szanto, *Phys. Rev. Lett.*, 1975, **36**, 1269.

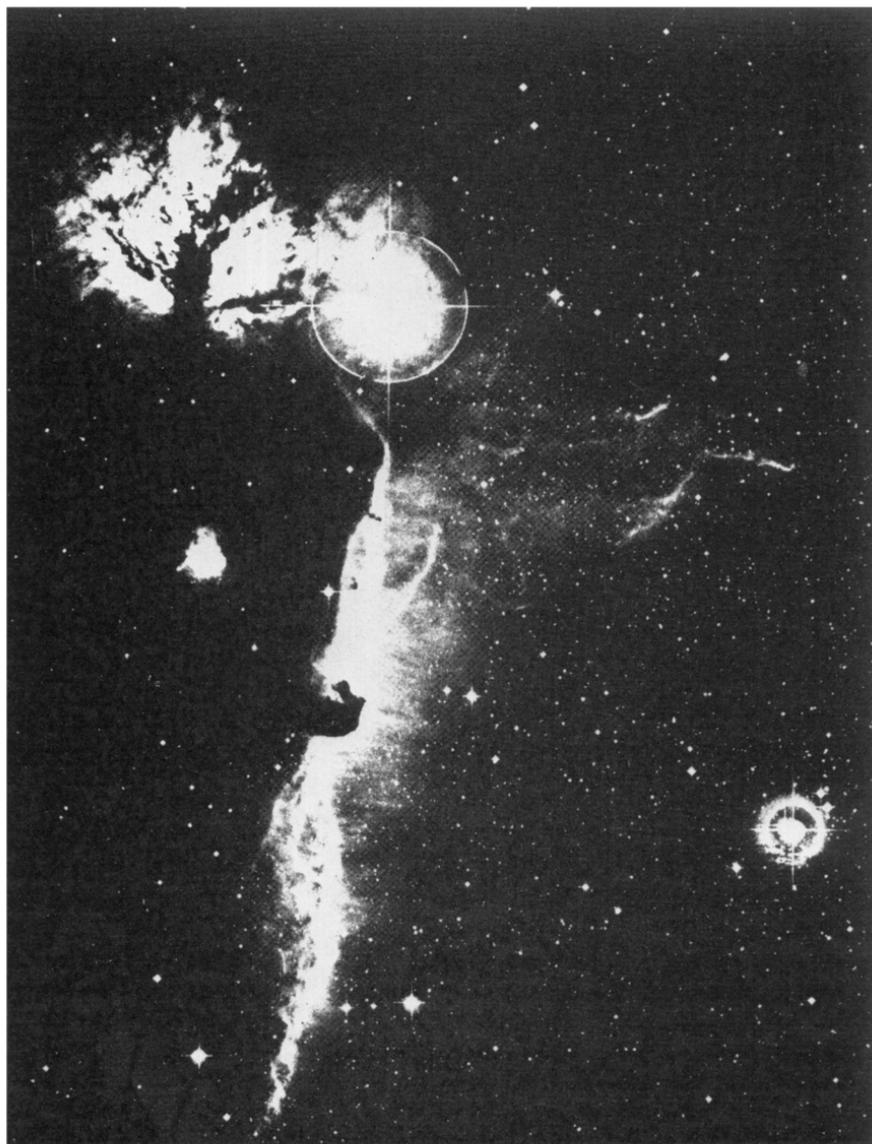


Figure 28 The long bright emission nebula IC434 silhouetting the well known Horsehead dark cloud in the constellation of Orion (taken from Murdin, Allen, and Malin¹¹² UKSTU). North is up and East is left in this photograph. The bright star at the top end of IC434 is ζ Orionis, the left-hand star of the three in Orion's belt. The nebula NGC2024 lies just to the East (left) of ζ Orionis. IC434 glows due to the photoionization by σ Orionis which is the bright star near the Western (L.H.) edge of the picture

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Figure 29 The dark clouds in Taurus from Barnards 1927 Survey. The TMC region is near the LH (SE) corner and the co-ordinates are marked on the edge of the picture

D. Interstellar Poly-yne $\cdots \text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}\cdots$?—As it happened, the study of the poly-yne, in particular cyanobutadiyne $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$, coincided with the exciting breakthrough in detection of interstellar molecules by radioastronomy discussed above. The observation and analysis of the spectrum of HC_5N seemed particularly significant when connected with the roughly simultaneous realization that the previous member of the family, cyanoethyne $\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$, was a relatively abundant interstellar species. This abundance and the knowledge of the radio frequencies obtained from the spectrum in Figure 24 suggested that HC_5N might be detectable by radioastronomy and prompted an enquiry to Takeshi Oka, who had been a former colleague at N.R.C. Ottawa, to see whether he was interested in collaborating in such a search.*

* He wrote back to say that he was 'very, very, very, very, very much interested'.

The $J = 4 \leftarrow 3$ transition was subsequently detected in collaboration with Lorne Avery, Norm Broten, and John MacLeod¹¹⁶ using the N.R.C. 46 metre telescope in Algonquin Park in Canada.

At the time the detection of HC_5N was very exciting as it had six heavy atoms, two more than any molecule previously detected (such as HC_3N). A semi-quantitative view of the chemical situation at the time (1976) indicated that small molecules with one or two heavy atoms (C, N, or O) tended to be fairly abundant and that after two, each successive heavy atom tended to reduce the abundance by a factor of *ca.* 10. This rough rule seemed to make sense in the light of some vague statistical reasoning based on the apparent molecular composition of the interstellar medium. Some doubts, however, about the applicability of this rule to the HC_nN ($n = 1, 3, \text{ or } 5$) family began to creep in. Indeed, searches for these types of molecule (Morris *et al.*,¹¹⁷ Churchwell *et al.*,¹¹⁸ and Little *et al.*,¹¹⁹) indicated that there were clouds, such as TMC1 (Taurus Molecular Cloud 1) with very high HC_3N and HC_5N abundances. This cloud is in the LH bottom (SE) corner of the photograph (Figure 29) published by Barnard¹²⁰ in 1927. In this beautiful picture dark clouds, which contain molecules, streak across the sky obscuring the myriads of background stars.

The detection of HC_5N together with the unexpectedly high abundance clearly promised the possibility of detecting the next poly-yne, HC_7N , and urged us accordingly to attempt its synthesis and analysis, which turned out to present some difficulties. The main problem lay in the last step in which the rather involatile and reactive HC_7N had to be vapourized into the microwave cell. It was essentially a nip-and-tuck situation in which the sample holder temperature was raised enough to obtain a sufficient cell vapour pressure but not so high that the sample decomposed completely. This turned out to be just feasible. The resulting spectrum, of which part is shown in Figure 30, was in fact decaying because of sample decomposition during this run. The spectrum shows three $J + 1 \leftarrow J$ transitions consisting of distinct bunches of lines. The strong ground-state lines stand isolated to the RH (low frequency) side of the rest, which are the multitude of bending vibrational satellites. Because the molecule is so long there are several very low frequency bending modes which give rise to satellites with ν (and associated combinations) as high as 15. A good estimate of the B_0 value can be obtained from the spacing between adjacent ground state lines and a rather better value by dividing a given $J + 1 \leftarrow J$ frequency by $2(J + 1)$, neglecting centrifugal distortion corrections which are relatively small. The accurate analysis allowed a successful search for the

¹¹⁶ L. W. Avery, N. W. Broten, J. M. MacLeod, T. Oka, and H. W. Kroto, *Astrophys. J.*, 1976, **205**, L173.

¹¹⁷ M. Morris, B. E. Turner, P. Palmer, and B. Zuckerman, *Astrophys. J.*, 1976, **205**, 82.

¹¹⁸ E. Churchwell, G. Winnewisser, and C. M. Walmsley, *Astron. Astrophys.*, 1978, **67**, 139.

¹¹⁹ C. T. Little, G. H. Macdonald, P. W. Riley, and D. M. Matheson, *Mon. Not. R. Astron. Soc.*, 1978, **183**, 45.

¹²⁰ E. E. Barnard in 'Atlas of Selected Regions of the Milky Way', ed. E. B. Frost and R. Calvert, Carnegie Institute of Washington, 1927.

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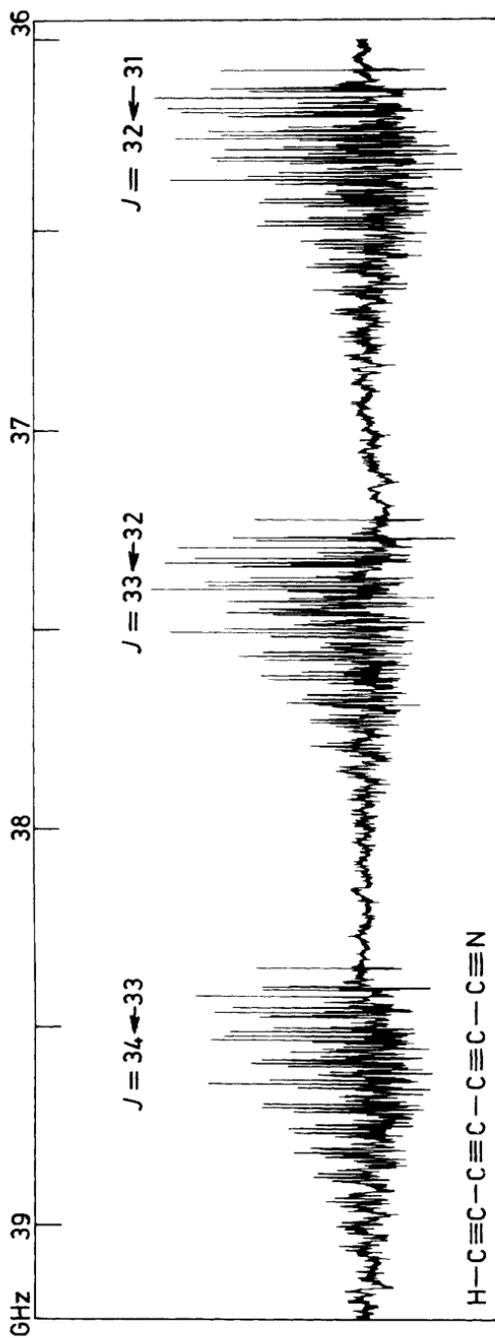


Figure 30 Three $\Delta J = +1$ transitions in the microwave spectrum of HC_7N .¹²¹ The RH line in each group belongs to the vibrational ground state; the rest are bending vibrational satellites and there are many of them because the molecule is long and readily flexes. In the cold clouds the temperature is so low that the vibrational states are not populated and all the intensity crowds into the ground state lines

¹²¹ C. Kirby, H. W. Kroto, and D. R. M. Walton, *J. Mol. Spectrosc.*, 1980, **83**, 261.

H. W. Kroto

$J = 10 \leftarrow 9$ line to be made.*¹²² The first oscilloscope trace of this detection is shown in Figure 31. Not only had HC_7N been detected but again the intensity was high, suggesting that perhaps there was something special about the chemistry that gave rise to these species. Of course, the next step, the quest for HC_9N was obvious though the route to detection much less so. A synthetic scheme could be worked out but the problems which beset us with the last step for HC_7N could surely only be compounded for HC_9N . Just as the initial synthetic

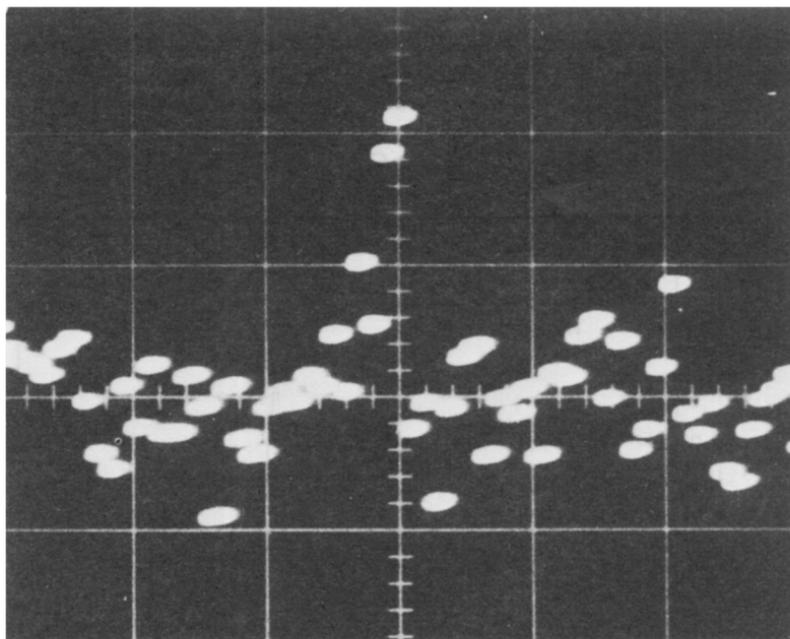


Figure 31 A photograph of the raw data for the initial detection of interstellar $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$.¹²² Each dot represents data in a 10 kHz wide channel. The spectrum was observed from the cold cloud TMC1 which yields very narrow lines no more than 10 kHz wide. The range was centred so that the line should lie in one or two of the central three channels. The high signals in the central two channels indicate that radiation at the expected frequency has been detected

* Because of the above experimental snags, the experiment to observe the microwave spectrum at Sussex had still not been successful when the earmarked observing session at the Algonquin Observatory started. However, about half-way through the session Colin Kirby back at Sussex finally succeeded and analysed the spectrum to obtain the rotational constants. He telephoned my wife, she telephoned a friend in Ottawa, and he telephoned the observatory and so the priceless B_0 and D_0 values were transferred (without error). Together with my Canadian collaborators, we tuned the telescope to a possible frequency and the observing session began. At 01.00 after some six hours of integration during which time only the results of individual 10 minute integrations had been available the signal shown in Figure 31 appeared, for the first time, on the oscilloscope screen. The circumstances had made the experiment exciting.

¹²² H. W. Kroto, C. Kirby, D. R. M. Walton, L. W. Avery, N. W. Broten, J. M. MacLeod, and T. Oka, *Astrophys. J.*, 1978, **219**, L133.

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steps were initiated Takeshi Oka discovered a neat, simple, and surprising empirical technique which enabled the B_0 value of HC_9N to be predicted with quite remarkable accuracy by extrapolating from the known values of HC_nN with $n = 1, 3, 5,$ or 7 .¹²³ The $J = 18 \rightarrow 17$ (Figure 32) and $J = 25 \rightarrow 24$ lines were detected and indicated that $B_0 = 290.5185 \pm 0.002$ as compared with the predicted value of 290.523 MHz!¹²⁴ The ratios of HC_nN species with $n = 3, 5, 7, 9$ turned out to be 10:5.0:1.2:0.32 respectively.¹²⁴ HC_9N has still not been observed in the laboratory nor is it probably worth the effort as its spectrum is measurable more readily and with higher accuracy by Radioastronomy.

It is now clear that even longer species can now be searched for using the extrapolation technique and indeed HC_{11}N has been detected by Bell *et al.*¹²⁵ and there may be no obviously foreseeable limit, though the available signal to noise may provide the most immediate stop. This technique should also work for the related radicals such as C_6H and C_5N since C_2H , C_4H , CN , and C_3N

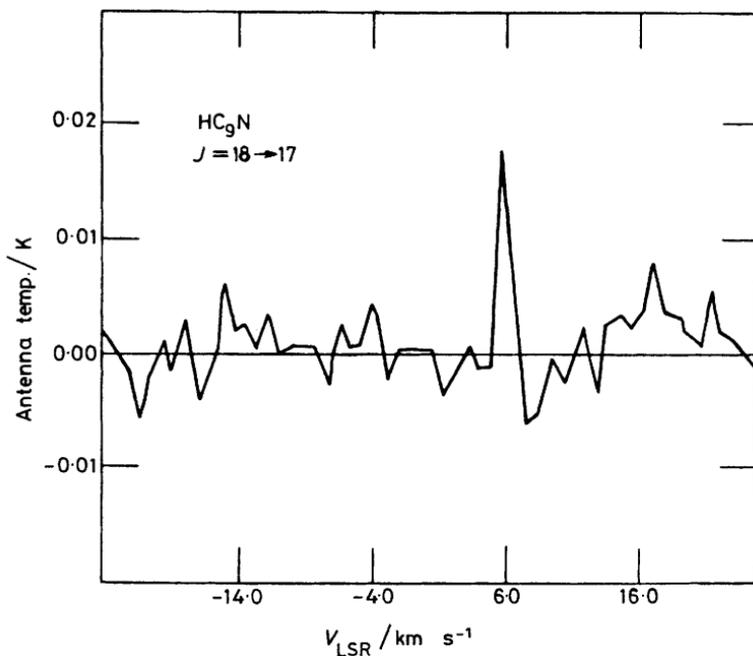


Figure 32 The spectrum of HC_9N detected by radioastronomy. In astronomy the intensity is usually given in terms of the Antenna temperature. The abscissa indicates that the frequency of the signal differs from that in the laboratory by an amount (the Doppler Shift) consistent with a 5.9 km s^{-1} relative velocity of the source and the earth. All signals from TMC1 show exactly the same Doppler Shift so the frequency adjustment is known

¹²³ T. Oka, *J. Mol. Spectrosc.*, 1978, **72**, 172.

¹²⁴ N. W. Broten, T. Oka, L. W. Avery, J. M. MacLeod, and H. W. Kroto, *Astrophys. J.*, 1978, **223**, L105.

¹²⁵ M. B. Bell, S. Kwok, P. A. Feldman, and H. E. Matthews, *Nature*, 1982, **295**, 389.

have all been observed. An important aspect of the recent studies is that the polyynes as well as C_3N and C_4H seem to be particularly abundant in the expanding gaseous envelope which surrounds the cool carbon star IRC + 10216.¹⁰³

5 Discussion

There are a few general points that seem to be worth making in this summary.

Microwave spectroscopy is a technique which has in the past been rather difficult to apply* and in general has been used by chemical physicists to make detailed studies of molecular structure and other molecular parameters such as those obtainable from vibration-rotation analysis. It is, however, a very flexible technique and in recent years a few groups have used it to make significant contributions to other areas: Oka to collisional energy transfer,¹²⁶ Legon and Millen to the study of weakly bound complexes,¹²⁷ Johnson and Lovas⁵⁶ as well as Hirota, Saito, and co-workers¹²⁸ to unstable molecules. Cross-field application of expertise is in general valuable. In this work the main philosophy has been to study problems of intrinsic chemical interest; essentially to use microwave spectroscopy, backed up synergistically by other techniques such as photoelectron spectroscopy, to carry out main group chemistry on compounds not accessible by standard chemical techniques. It has been traditional to hang on heavy groups in order to stabilize elusive moieties and *then* use the entity in further reactions. In the present approach, however, the aim has been to find a route to semi-stable species, characterize them and develop techniques for further reaction. The last aim is now being developed as shown by reactions such as (28) in which NCCP was made from HCP *on line*. It is probably worth noting that the very properties that are smothered by substituent group stabilization may be the most valuable that these moieties have. Indeed, it is probably the differences between related species rather than their similarities that are most important and likely to lead to new chemistry. To force them into some pre-ordained mould may by-pass important features.

The low-pressure operational conditions of the microwave and photoelectron techniques have been critical in slowing down the polymerization or decomposition rates sufficiently to facilitate detection. In retrospect there has been a subconscious tendency to avoid modifying the equipment and instead tailor experiments by, for instance, aposite precursor synthesis to exploit those virtues of the basic instrument that experience has uncovered. For instance, the microwave cell which consists of a 1 metre metal tube allowing (rather difficult) access only at the ends offers outstanding sensitivity. Although it is poor for the

* It will again become difficult to apply since Hewlett Packard, the only firm to market, successfully, a commercially viable instrument, no longer makes it.

¹²⁶ T. Oka, *Adv. At. Mol. Phys.*, 1973, **9**, 127.

¹²⁷ J. W. Bevan, Z. Kisiel, A. C. Legon, D. J. Millen, and S. C. Rogers, *Proc. R. Soc. London, Ser. A*, 1980, **372**, 441.

¹²⁸ E. Hirota, S. Saito, *et al.*, Annual Review, Institute for Molecular Science, Okazaki National Research Institutes, Japan, 1980, pp. 38–51; 1981, pp. 29–46.