TILDEN LECTURE*

Semistable Molecules in the Laboratory and in Space

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1 Introduction

This article deals with the production, detection and application of new, unstable or semistable (or perhaps semi-unstable?) molecules. The lifetimes are usually of the order of 1 s under the conditions of the experiments, sufficiently long that extensive modifications of standard equipment can often be avoided but usually too short to allow isolation. In some cases, however, the work has shown that certain species are somewhat more stable than previously expected. The instability usually arises because they are unsaturated and in the main contain second- (or sometimes third-) row elements of the periodic table, elements which exhibit a well known reluctance to participate in $p\pi$–$p\pi$ bond formation. This antipathy is perhaps most clearly manifested by the fact that so few such molecules are known and the instability of those that are known. The reason is probably the small contribution to the binding energy obtainable by $p\pi$–$p\pi$ overlap. This tends to be an optimum at the distances which characterize bonds between first-row atoms, becoming less and less favourable when second- or third-row atoms participate and the interatomic distance increases.

Not only are the precepts which initiated and governed the experiments explored but so also are some diverse applications to other areas such as mainstream chemistry and radioastronomy. Although the main experimental technique used has in general been microwave spectroscopy, backed up by photoelectron measurements, in several cases nuclear magnetic resonance, infrared spectroscopy, mass spectrometry, *X*-ray crystallography, and theoretical calculations have been invaluable.

There are a few basic ground rules that have governed the research detailed here. The most important come under the three headings

A) Chemical Relationships
B) Experimental Synergy
C) General Implications

A. Chemical Relationships.—There are several types of relationship which can usefully be used to extrapolate or interpolate and so conjecture that a certain

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* This is an expanded version of a lecture that was first presented at a meeting of the Faraday Division of the Royal Society of Chemistry at the Scientific Societies' Lecture Theatre, London, on 29 October 1981.

molecule or group of molecules might exist. In fact it is likely that almost any cluster of atoms one can think of may exist for some period of time, albeit short; it is just a matter of catching it unawares. For our purposes we are interested in species which are not to be found in the average chemist's bucket, but also not so elusive that we need to use very fast techniques, *i.e.* not, for instance, free radicals. The relationships which have proven most valuable are

i) Mendeleevian or Periodic relationships
ii) Isoelectronic relationships
iii) Analogous and Homologous relationships

To give a feeling for the interplay of these relationships a diagram which shows the family related *via* i), ii), and iii) to formaldehyde CH_2O is given in Figure 1.

On this CH_2O cube Mendeleevian relationships are represented by vertical steps, isoelectronic ones by steps to the right, and analogous/homologous ones by steps to the left. Isovalent relationships can be represented by diagonal steps

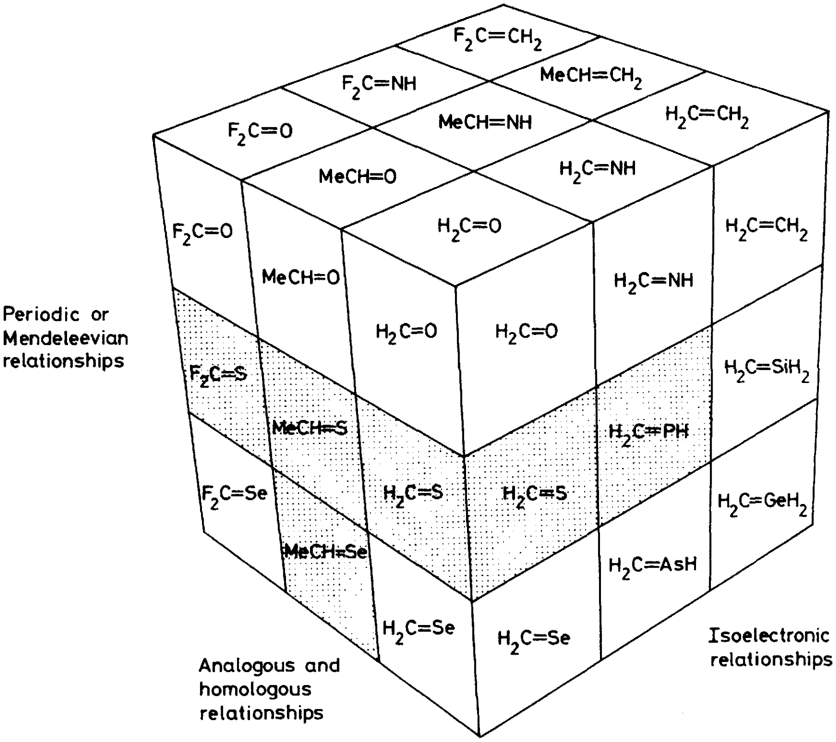
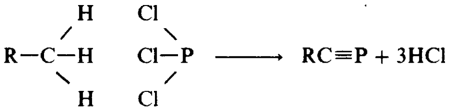


Figure 1 *Chemical cube showing some molecules related to formaldehyde* $H_2C{=}O$. *Periodic group relationships are given by vertical steps, steps to the left are possible analogously and homologously related species, and steps to the right are isoelectronically related species. The molecules shaded have been studied in this work*

on the right face *etc.* It is almost certain that, since the time of Mendeleev, chemists must have at least ruminated about various possibilities. Could for instance Si analogues of ethene such as $CH_2{=}SiH_2$ be made? Not only that, could $CH_2{=}PH$ the P analogue of $CH_2{=}NH$ be made, or for that matter, $CH_2{=}S$ the S analogue of formaldehyde?

One can obviously play similar games with other molecules and, in fact, a good deal of the work presented here results from relationships which can be catalogued on the CH_2O and HCN cubes. It is likely that games such as these lie at the base of most scientific research whatever the field, and chemists in particular use related concepts to develop new chemistry. One also needs, in good measure, an inalienable faith that should relationships point to a species, then it can be formed.

A childish naivety is useful. As an example, after a lesson on the periodic table and one on the nitriles at school one would be quite happy to extrapolate and assume that $CH_2C{\equiv}P$ would be similar to the well known molecule $CH_3C{\equiv}N$. A more knowledgeable chemist might be aware of the difficulty of forming $p\pi{-}p\pi$ bonds involving second-row elements and subconsciously aware that he had almost never come across a $C{\equiv}P$ group and take its non-existence for granted. Early chemists must have attempted to make such compounds and ended up with polymeric products. Some sort of naivety is also useful in developing routes to such species. As an example, it is likely that only a school student would suggest that the reaction (1) might be worthy of study.



$$\mathrm{R{-}\overset{H}{\underset{H}{C}}{-}H \qquad Cl{-}\overset{Cl}{\underset{Cl}{P}}} \longrightarrow \mathrm{RC{\equiv}P + 3HCl} \qquad (1)$$

One aim of this review is to show that these simple ideas are not entirely naive and that one must always take care that the more knowledge of chemistry one has the less adventurous one can become because of the hang-ups this knowledge invariably generates.

B. Experimental Synergy.—Combining two or more disparate, though complementary, techniques can be very rewarding. Although microwave spectroscopy is a very high resolution technique (linewidths *ca.* $100\,\mathrm{kHz} \sim 0.33 \times 10^{-5}\,\mathrm{cm^{-1}}$) its application in this work has often been facilitated by photoelectron studies where features seldom have bandwidths less than $20\,\mathrm{meV} \sim 160\,\mathrm{cm^{-1}}$ ($1\,\mathrm{eV} \equiv 8065\,\mathrm{cm^{-1}}$). The interaction has often been two-way and synergistic. The value has been mainly experimental in that a particular molecule may be more readily detectable by one technique and once detected the conditions can be optimized to facilitate detection by the other.

C. General Implications.—Spectroscopy has an inherent charisma not only in the beauty of the patterns often produced, but also in the deep insight it gives at the molecular level and the degree of certainty which it can often bestow on the conclusions. The analysis of microwave spectra can give the most positive molecule identification and some of the most accurate structural data. In addition it can yield: dipole moments, quadrupole moments, vibration–rotation parameters, and associated force-field data such as internal rotation barrier heights. It has been used to further our understanding of maser processes, collisional energy transfer, and interstellar chemistry. Photoelectron spectroscopy yields ionization potentials and, through these, information about the electronic structure of molecules and their associated ions.

Apart from these specific virtues of the two techniques, their more general value as probes to initiate new areas of basic chemistry has been the most important factor in this work. Indeed, the major aim has been to show that microwave spectroscopy in particular need not be an esoteric technique whose sole value to chemists is the elucidation of structural information. It can and has been a powerful tool in the development of new areas of organic, inorganic, organometallic, and interstellar chemistry.

2 Experimental Techniques

The method used to produce semistable molecules is extremely simple in that a suitable precursor molecule is passed through an 8 mm i.d. quartz tube, heated for about 10 cm of its length, to a suitable temperature (up to *ca.* 1100 °C), and the resulting products flow directly into the cell of a microwave or photoelectron spectrometer, Figure 2. In general the rate of loss of the new species by further reactions is slowed considerably because of the low pressures used for these two spectroscopic techniques (*ca.* 1—100 μHg).

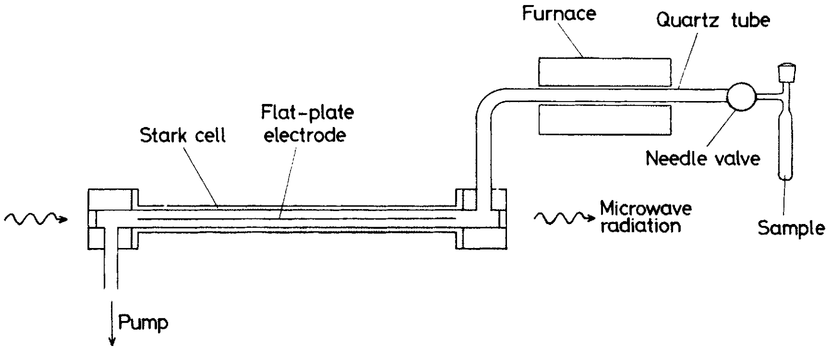


Figure 2 *Schematic diagram of the main production and detection technique. The quartz tube is* ca. 0.8 cm *i.d. and heated for some* 10 cm *of its length. The distance between the furnace and the cell is about* 10 cm. *The cell is made from rectangular cross-section wave guide which has a septum held half way between the two broad faces by a teflon spacer/insulator. This allows Stark modulated signals to be observed. In general the spectrum is displayed so that a positive signal is the field free frequency, and the negative signal that in the presence of the field. See Figure* 17

A. Microwave Spectroscopy.—In general microwave spectroscopy is used to observe the rotational spectra of molecules.[1-3] The very high resolution available, together with the high degree of pattern specificity allows such moderately complex molecules as ethanol EtOH, glycine NH_2CH_2COOH and cyanoethene $CH_2{=}CHC{\equiv}N$ to be unequivocally identified in extremely complex mixtures. To confirm this one only has to note that some 50 molecules and numerous isotopically substituted modifications have been identified by radio astronomical detection of microwave radiation from the molecular soups which exist in interstellar space (Section 4).

The advent of the Hewlett Packard 8460A microwave spectrometer, alas no longer available, for the first time enabled the research worker to obtain microwave spectra which were not only linear in frequency but also obtainable over a wide bandwidth, with high sensitivity. The instrument obviated the technical problems that beset previous microwave research, particularly frequency sweep problems and frequency calibration. At a stroke it was possible to transfer from the technical problem of obtaining spectra and concentrate on the chemical problems involved in producing the species to be studied. As some of the results obtained during this programme display many of the merits of the microwave technique, such as spectroscopic patterns, in a way that hitherto has not been possible a short general introduction to the most important features is given.

As in all spectroscopic studies one must use quantum mechanics to develop the energy levels and in this case one can start from the Hamiltonian for a rigid rotating molecule (a very good first approximation in general) given in equation (2)

$$H_r = AJ_A^2 + BJ_B^2 + CJ_C^2 \tag{2}$$

where J_A, J_B, and J_C are the components of overall rotational angular momentum (in units of $\hbar$) along the molecule-fixed principal axes and A, B, and C are rotational constants related to the principal moments of inertia I_A, I_B, and I_C by $A = 1/2I_A$ . . . *etc.** By convention $I_A \leqslant I_B \leqslant I_C$ and therefore $A \geqslant B \geqslant C$. The solution of H_r depends on the type of molecule and the results can be summarized as follows:[3] *Linear molecules* such as CO, OCS, and $HC{\equiv}C{-}C{\equiv}N$ have $B = C$ and $J_A \rightarrow 0$ and the resulting energy is given by the familiar expression (3)

$$E(J) = BJ(J+1) \tag{3}$$

where J is the overall angular momentum quantum number.† *Symmetric tops*

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* $I_A = \sum_n m_n(r_B^2 + r_C^2)_n$, $I_B = \cdots$ *etc.* where m_n are atomic masses and r_A *etc.* are co-ordinates relative to the principal axes of the molecule[3] $A\,(\text{MHz}) = 505391/I_A\,(\text{amu Å}^2)$ or $A\,(\text{cm}^{-1}) = 16.858/I_A\,(\text{amu Å}^2)$

† The units of E (and ΔE for a transition) will be governed in these expressions by the units of the rotational constant, usually Hz or cm^{-1}

[1] C. H. Townes and A. L. Schawlow, 'Microwave Spectroscopy', McGraw-Hill, 1955.

[2] W. Gordy and R. L. Cook, 'Microwave Molecular Spectra', Interscience, 1970.

[3] H. W. Kroto, 'Molecular Rotation Spectra', John Wiley, London, 1975.

such as $CH_3C{\equiv}N$ or SF_5Cl which are prolate (*i.e.* cigar-shaped) have $A > B = C$, can spin about their symmetry axes with associated quantum number K, and the energy is given by equation (4).

$$E(J, K) = BJ(J + 1) + (A - B)K^2 \qquad (4)$$

The energy levels for a linear molecule are shown in Figure 3a and those for a prolate symmetric top in Figure 3b.

A similar expression to (4), in which $A \rightarrow C$ and $C \rightarrow A$, applies to oblate (discus-shaped) tops such as NH_3 and C_6H_6. Spherical tops such as CH_4 and SF_6 which have $A = B = C$ are rather complicated and will not be dealt with here as their spectra[4] are difficult to detect. Their levels are also governed by equation (3).

Asymmetric top molecules are most important, they have $A > B > C$ and their

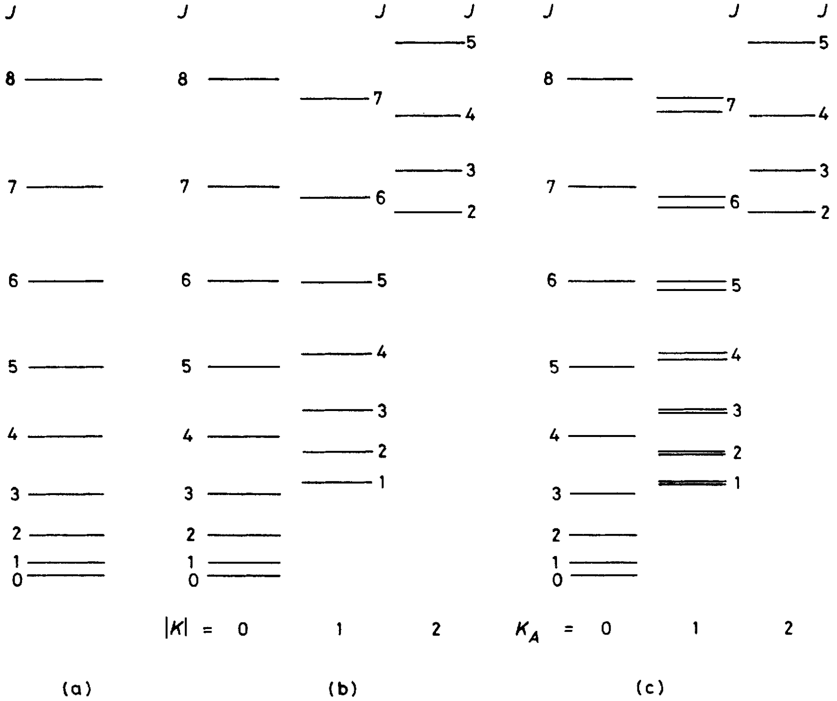

Figure 3 *The rotational levels of* (a) *a linear molecule,* (b) *a prolate symmetric top, and* (c) *a prolate slightly asymmetric rotor. For this diagram* $A \sim 38$ GHz, $B \sim C \sim 3.06$ GHz *and* $B - C \sim 0.25$ GHz. *In all cases vertical transitions between adjacent levels in a given manifold may occur* ($\Delta J = \pm 1$) *depending on the dipole moment conditions. In such cases the transitions give rise to equidistantly spaced lines in the linear case or groups of lines in the non-linear case*

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[4] J. K. G. Watson, *J. Mol. Spectrosc.*, 1971, **40**, 536.

energy levels follow much more complicated expressions. These will not be discussed in detail but one can get some feel for the spectral patterns by summarizing the approximate results that apply in the case of molecules which are not too asymmetric. We will also restrict ourselves to *near* prolate molecules which are the most common, at least in the work studied here. In a near prolate molecule $A > B \sim C$ and perturbation theory yields the relation (5)[3]

$$E(J, K_A) = \bar{B}J(J+1) + (A - \bar{B})K_A^2 \pm \tfrac{1}{4}\delta_{K_A,1}(B - C)J(J+1) \cdots \qquad (5)$$

where $\bar{B} = \frac{1}{2}(B + C)$ and K_A is a *good enough* quantum number $\equiv |K|$, which for a symmetric top is *almost* perfect. An understanding of what the ephemeral 'good' quantum number is demands a deeper study of quantum mechanics than is possible here. The first two terms are very closely related to the symmetric top expression, equation (4). The third has a Kronecker delta coefficient which indicates that *only* the $|K| = 1$ levels, in the symmetric rotor, limit are split by this factor which is proportional to $(B - C)$—which is of course a rough asymmetry gauge. Smaller, second-order, terms which shift and/or split other levels have been truncated. They become less important as K increases (for a given value of J), *i.e.* as the top spins more and more quickly about its symmetry axis. The resulting levels are shown in Figure 3c.

If a molecule is very asymmetric, the energy level pattern can be very complicated, as can the resulting spectrum. For the asymmetric molecule it is useful to further specify the levels for, as can be seen in Figure 3c, levels of a given $|K|$ or K_A are no longer degenerate. It is usual to add also the value of $|K|$ with which the level correlates in the oblate limit, *i.e.* K_C. Thus a given level is characterized by $J_{K_A K_C}$.

For a linear molecule the expression which governs the spectroscopic patterns can be derived from equation (3) using the electric dipole selection rule $\Delta J = \pm 1$ to yield equation (6).

$$\Delta E(J) = 2B(J+1) \qquad (6)$$

This gives rise to a set of equally spaced lines separated by $2B$. In the symmetric top case the rules $\Delta J = \pm 1$ and $\Delta K = 0$ apply and result in the same expression for transitions. Lines with a given $|K|$ have the same frequency and pile up on top of each other. They are, however, usually split apart by centrifugal distortion effects which are observed under high resolution.

For asymmetric rotor molecules the most frequently observed transitions often occur for near prolate molecules with dipoles oriented roughly along the long A axis. In this case the main selection rules that apply are $\Delta J = \pm 1$ and $\Delta K_A = 0$. Applying these to equation (5) for this slightly asymmetric case yields equation (7).

$$\Delta E(J, K_A) = 2\bar{B}(J+1) \pm \tfrac{1}{2}\delta_{K_A,1}(B - C)(J+1) + \cdots \qquad (7)$$

As $\bar{B} \gg (B - C)$ we can see that the transitions tend to bunch together, in this case, at $2\bar{B}$ $(= B + C)$ intervals but with an added factor that each J group is symmetrically flanked by the two $K_A = 1$ lines, which are separated from the main bunch by $\frac{1}{2}(B - C)(J + 1)$. This splitting of the $K_A = 1$ lines is the quantum mechanical equivalent of classical wobbling which occurs for an object which is not a good top. Under high resolution this type of splitting is seen to occur also, but to a smaller extent, for $K_A > 1$ lines. It increases with asymmetry and decreases with K_A, *i.e.* as the molecule spins more rapidly about its axis it becomes a better top.

A good example of the power of microwave spectroscopy is shown in Figure 4 where the spectra of EtNO are presented.[5] The bands of *two* conformers are readily distinguished because the spectroscopic patterns depend so strongly on the moments of inertia and they are very different for the two conformers. The conformers are both eclipsed, and one, the *gauche* conformer, much closer to the prolate symmetric rotor limit than the other, *cis* conformer. It is this type of enormous change in pattern, as a function of a parameter which does not readily affect other properties, that makes this technique such a powerful structural and also analytical tool. Examples of spectra of linear and symmetric rotors as well as other asymmetric rotors will be presented.

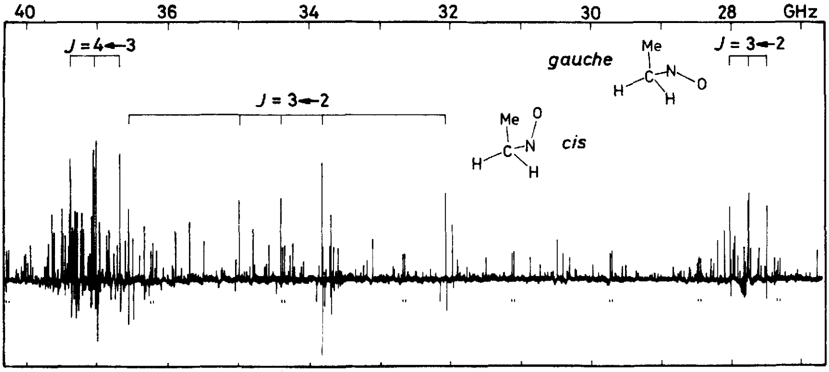

Figure 4 *The microwave spectra of* EtNO.[5] *Two sets of spectra are identified. One set, belonging to the* gauche *isomer, shows two groups of transitions each with a typical triplet pattern. The outer members of the triplet are the* $K_A = 1$ *lines and the central member a composite of lines belonging to* $K_A \neq 1$ *lines. The central line is usually resolved under high resolution. The second set belongs to the* cis *isomer which is very asymmetric and the resulting pattern rather more complex and spread out as indicated (compare with Figure* 15b). *There are many other lines belonging to vibrationally excited molecules and transitions for which* $\Delta K_A \neq 0$, i.e. *cross-stack transitions in Figure* 3c. *Positive-going lines are zero field frequencies, negative-going lines are Stark shifted frequencies*

B. Photoelectron Spectroscopy.—Photoelectron spectra are obtained by analysing the kinetic energy of electrons (E_{kin}) ejected by molecules irradiated by a

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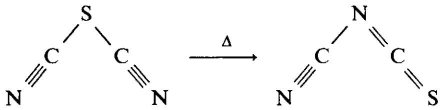
[5] A. P. Cox, J. A. Hardy, H. W. Kroto, M. Maier, and D. R. J. Milverton, to be published.

monochromatic beam of ionizing photons. If the photon energy is $E = h\nu$ then the ionization energy ($E_{\text{ionization}}$) is given by expression (8).

$$E_{\text{ionization}} = h\nu - E_{\text{kin}} \tag{8}$$

The electrons tend to bunch together (in energy) giving rise to several bands which often can be identified with electron ejection from individual molecular orbitals. To a first, and often satisfactory, approximation the resulting ionization potentials can be directly equated to molecular orbital energies derived from theoretical calculations, and so this technique yields some of the most valuable information about the electronic structures of molecules from a molecular orbital viewpoint. Perhaps the most important point is that the separations between various bands yield the transition energies of the associated electronic states of the *molecular ion*. In fact, the technique tends to tell us about the ion rather than the molecule, a fact that should not be overlooked. The application of photoelectron spectroscopy to the study of unstable species has recently been reviewed by Dyke, Jonathan, and Morris.[6]

C. Combined Application of Microwave and Photoelectron Techniques.—A good example of the synergistic aspects of combining techniques is evidenced in some recent work on high temperature reactions involving $S(CN)_2$. In these experiments a new microwave spectrum (Figure 5) was detected.[7] The spectrum consists of bunches of lines at intervals of roughly 3.25 GHz. Under high resolution the bunches show $K_A = 1$ flanking lines consistent with an asymmetric top and also additional features due to vibrationally excited molecules which complicate the spectrum. After a few guesses and trial moment of inertia calculations it became clear that a thermal rearrangement of the form given in scheme (9) had taken place.



(9)

The NCNCS molecule is V-shaped as shown in Figure 6 and a good rough estimate of I_B and therefore also B can be made from the approximate scale diagram and dimension shown. The molecule is planar which means that $r_C = 0$ for all atoms and thus the B moment of inertia, summed over all atoms, n, is given by equation (10).

$$I_B = \sum_n m_n(r_A^2 + r_C^2)_n = \sum_n m_n(r_A^2)_n \tag{10}$$

According to the approximate dimensions in Figure 6 we see that:

$$I_B = 14(3.0)^2 + 12(2.0)^2 + 14(0.5)^2 + 12(0.5)^2 + 32(2.0)^2 = 308.5\,\text{amu}\,\text{Å}^2$$

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[6] J. M. Dyke, N. Jonathan, and A. Morris, *Int. Rev. Phys. Chem.*, 1982, **2**, 3.

[7] M. A. King and H. W. Kroto, *J. Chem. Soc., Chem. Commun.*, 1980, 606.

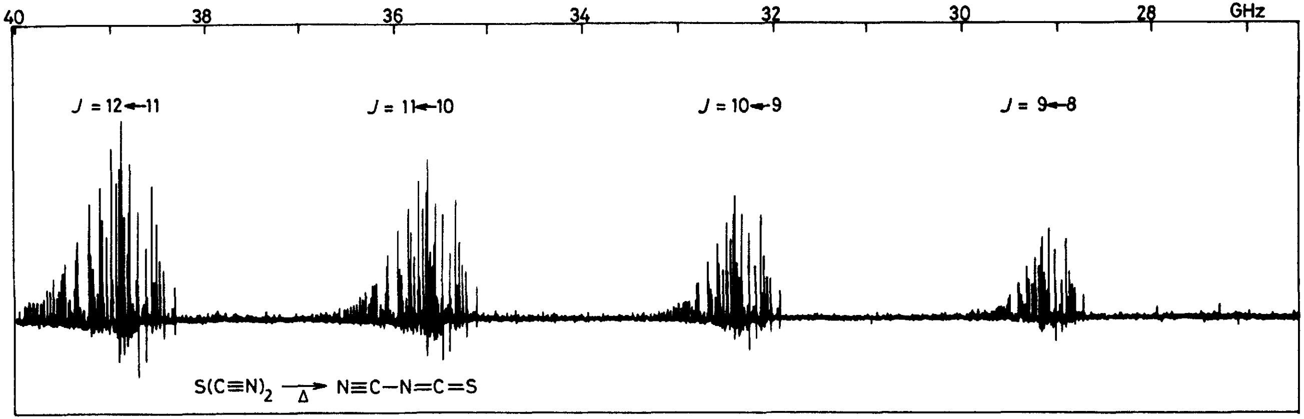

Figure 5 *The microwave spectrum of* NCNCS.[7] *This spectrum is characteristic of a slightly asymmetric rotor in that strongest lines lie in bunches at almost equidistant intervals of* ca. $2\bar{B} = B + C$. *Under high resolution the lines resolve into a complex pattern for a molecule which is rather flexible and so has many excited vibrational states*[8]

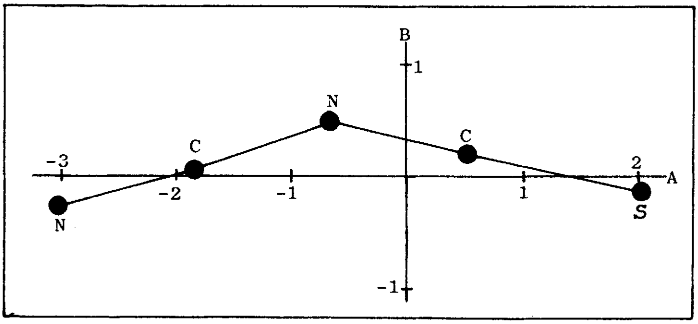

Figure 6 *The structure of* NCNCS *relative to the* A *and* B *principal axes (scale in* Å *units). The molecule is planar with an angle at the central nitrogen of* ca. 150°. I_B, *the moment of inertia about the B axis, is determined by* $\sum_n m_n(r_A^2)_n$ *as discussed in the text*

The B rotational constant can now be calculated as $B = 505.391/308.5 = 1.638$ GHz and compared with the rough value of $\bar{B} = \frac{1}{2}(B + C) = \frac{1}{2}(3.25) = 1.625$ GHz obtained from the spectrum shown in Figure 6. A more accurate analysis shows that the observed value of $B_0 = 1.628$* and the preliminary structure yields $B_{\text{calc}} = 1.623$ GHz. The fine details of the analysis show that NCNCS has a rather unusual spectrum in that the molecule shows quasi-linear behaviour. Essentially the molecule does not know whether it is linear or bent and this ambivalence is exhibited in the spectroscopic patterns observed under high resolution.[8]

The initial attempt to detect NCNCS by photoelectron spectroscopy (Figure 7b) was unsuccessful, resulting in product peaks which were readily identified with CS_2 and C_2N_2, neither of which have permanent dipole moments and are therefore not detectable by our microwave spectrometer. Parallel experiments using a small quadrupole mass spectrometer confirmed this. The photoelectron and mass spectroscopic data thus immediately indicated that at *ca.* 1000 °C very little NCNCS is produced, even though under similar conditions the microwave experiments showed extremely strong lines of NCNCS. As NCNCS was known, from the microwave experiments, to be present, the temperature and flow conditions were varied until new peaks, consistent with NCNCS were found. These are identified in Figure 7c. The products of pyrolysing under the new conditions were trapped and the spectrum of essentially pure NCNCS shown in Figure 7d was obtained on re-vaporization.[9] In this way the microwave detection had identified, with ease, a species which was much more difficult to observe by the photoelectron technique. The microwave technique had, however,

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* The rotational constants of a real molecule, which is not of course rigid, depend on vibrational state. The experimentally determined constants for the ground vibration state are labelled by a subscript zero, *i.e.* A_0, B_0, and C_0.

[8] M. A. King, H. W. Kroto, and B. M. Landsberg, to be published.

[9] M. A. King and H. W. Kroto, to be published.

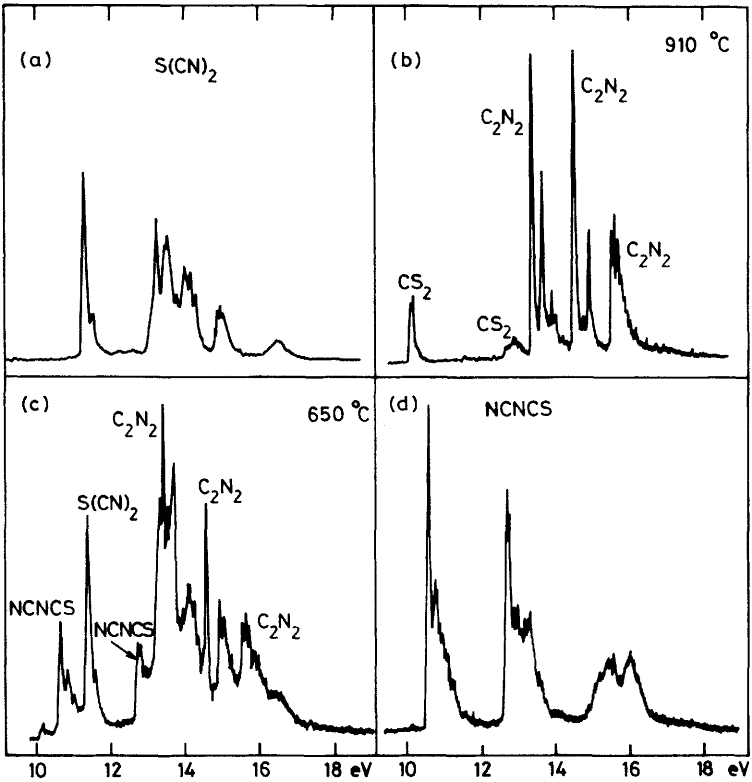

Figure 7 (*a*) *The p.e. spectrum of* $S(CN)_2$. (*b*) *The p.e. spectrum of* $S(CN)_2$ *pyrolysed at* 910 °C. (*c*) *The p.e. spectrum of* $S(CN)_2$ *pyrolysed at* 650 °C. (*d*) *The p.e. spectrum obtained by revaporizing* NCNCS *from a sample produced under the conditions of* (*c*) *and trapped*[9]

overlooked some other important reaction pathways. In the next sections similar situations are discussed, some of which show the rôles reversed in that the p.e. technique has spearheaded microwave detection.

3 Studies of Semistable Molecules

A. Thiocarbonyls and Selenocarbonyls.—It was work on some small thiocarbonyls which originally highlighted the value of joint microwave and photoelectron experiments as general readily applicable techniques for detecting moderately unstable species. There must have been many attempts in the past to make sulphur analogues of formaldehyde, acetaldehyde, and acetone. Indeed Noller[10]

[10] C. R. Noller, Chemistry of Organic Compounds', W. B. Saunders Co., Philadelphia, 1957, p. 282.

notes that 'the odour of thioacetone is so obnoxious that Baumann and Fromm had to abandon their work because of the protests of the City of Freiburg'. This anecdote conjures up a vision of the smell wafting gently over the city fathers as they, holding their noses, march towards the laboratory to find Baumann and Fromm working without a fume cupboard and oblivious to the odour.

The present work has its origins in a number of experiments. During flash photolysis experiments on dimethyl peroxide aimed at the detection of the methoxy-radical, MeO, the spectrum of formaldehyde $H_2C{=}O$ was detected (unpublished results). Subsequent experiments aimed at detecting the sulphur analogue, $H_2C{=}S$, by photolysing MeSSMe proved unsuccessful because the S—S bond was more difficult to break photolytically and the electronic transition sought is very weak. Some experiments by Callear *et al.*[11] did, however, detect a transient spectrum at around 2100 Å. The first clear spectroscopic identification was made by Johnson *et al.*[12] using flow pyrolysis of MeSSMe and microwave detection. The value of photoelectron spectroscopy, which is also a low pressure (1—50 μHg) technique, for detecting such molecules became clear after experiments on CS produced by a discharge in CS_2[13-15] as well as experiments on H_2CS.[16] Lifetime data for CS had previously been obtained by Dyne and Ramsay[17] and the microwave spectrum by Kewley *et al.*[18] The *synergistic* value of combining the two techniques was evidenced by work on F_2CS, a molecule which had originally been made by Middleton, Howard, and Sharkey[19] by pyrolysing the dimer $(CF_2S)_2$. Several attempts to detect the microwave spectrum by myself and others had failed although the molecule was isolable. Subsequent photoelectron detection of the species in a flow-pyrolysis system[20] showed that the molecule was readily formed by this technique and, using an essentially identical set-up and optimized conditions for production, the microwave spectrum of F_2CS was finally observed.[21] The spectrum was very weak because the dipole moment μ (on which rotational intensity depends as μ^2) was only 0.08 Debye. In addition F_2CS reacts very quickly (in the metal waveguide microwave cell) with adsorbed water to form HF, F_2CO, HFCO, and OCS, whose lines are very strong. The flow technique flushes the cell and after a while the strong lines of by-products can be almost eliminated allowing the search for weak lines to proceed efficiently. A very similar two pronged approach finally succeeded in detecting the elusive mixed halide BF_2Cl, which is in fact isoelectronic with CF_2S. Photoelectron experiments showed clear evidence for the mixed

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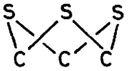
[11] A. B. Callear, J. Connor, and D. R. Dickson, *Nature*, 1969, **221**, 1238.
[12] D. R. Johnson, F. X. Powell, and W. H. Khirchhoff, *J. Mol. Spectrosc.*, 1971, **39**, 146.
[13] G. H. King, H. W. Kroto, and R. J. Suffolk, *Chem. Phys. Letts.*, 1972, **13**, 457.
[14] N. Jonathan and M. Okuda, *Faraday Discuss. Chem. Soc.*, 1972, **54**, 67.
[15] D. C. Frost, S. T. Lee, and C. A. McDowell, *Chem. Phys. Lett.*, 1972, **17**, 153.
[16] H. W. Kroto and R. J. Suffolk, *Chem. Phys. Letts.*, 1972, **15**, 545.
[17] P. J. Dyne and D. A. Ramsay, *J. Chem. Phys.*, 1952, **20**, 1055.
[18] R. Kewley, K. V. L. N. Sastry, M. Winnewisser, and W. Gordy, *J. Chem. Phys.*, 1963, **39**, 2856.
[19] W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, 1965, **30**, 1375.
[20] H. W. Kroto and R. J. Suffolk, *Chem. Phys. Letts.*, 1972, **17**, 213.
[21] A. J. Careless, H. W. Kroto, and B. M. Landsberg, *Chem. Phys.*, 1973, **1**, 371.

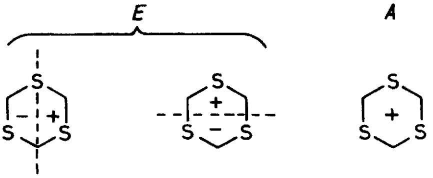
species BF_2Cl and $BFCl_2$ in BF_3–BCl_3 mixtures,[22] and reproducing the flow conditions using microwave detection resulted in the observation of some very weak lines of BF_2Cl which proved very difficult to detect.[23]

The studies on CS, CH_2S, and F_2CS, all of which were known compounds, showed how well microwave and photoelectron techniques could be used to mutual benefit and in particular should enable the detection of new molecules—most obviously new thiocarbonyls. In general, attempts to prepare the smaller thiocarbonyls result in the production of trithianes which are ring trimers, $(R_2CS)_3$. For instance, the reaction of acetaldehyde, CH_3CHO, with H_2S in acid solution yields 1,3,5-trimethyltrithiane $(CH_3CHS)_3$ which has a crown shaped skeleton (1).



(1)

This compound is sufficiently volatile to allow its photoelectron spectrum to be observed Figure 8a. The sulphur *p* orbitals overlap to give rise to *E* and an *A* highest occupied molecular orbitals with the nodal characteristics [(2)–(4)].



(2) (3) (4)

The degenerate combination is less bonding, possessing a node, and gives rise to the broad first IP at 8.39 eV. The more bonding *A* orbital is more stable and is associated with the second IP at 8.91 eV. The intensities are roughly 2:1, in line with the degeneracies. On pyrolysis this spectrum is completely eliminated and replaced by the more simple spectrum of monomeric $CH_3CH{=}S$[24] as shown in Figure 8b. The spectrum of CH_3CHS has a single peak at 8.98 eV which can be assigned to ionization from a single sulphur lone-pair orbital and a second band at 10.87 eV which corresponds to ionization from the C=S π bonding orbital. The spectra given in Figures 8a and b show how efficient and complete is the formation of the monomer from the trimer. On the

[22] H. W. Kroto, M. F. Lappert, M. Maier, J. B. Pedley, M. Vidal, and M. F. Guest, *J. Chem. Soc., Chem. Commun.*, 1975, 810.

[23] H. W. Kroto and M. Maier, *J. Mol. Spectrosc.*, 1977, **65**, 280.

[24] H. W. Kroto, B. M. Landsberg, R. J. Suffolk, and A. Vodden, *Chem. Phys. Letts.*, 1974, **29**, 265.

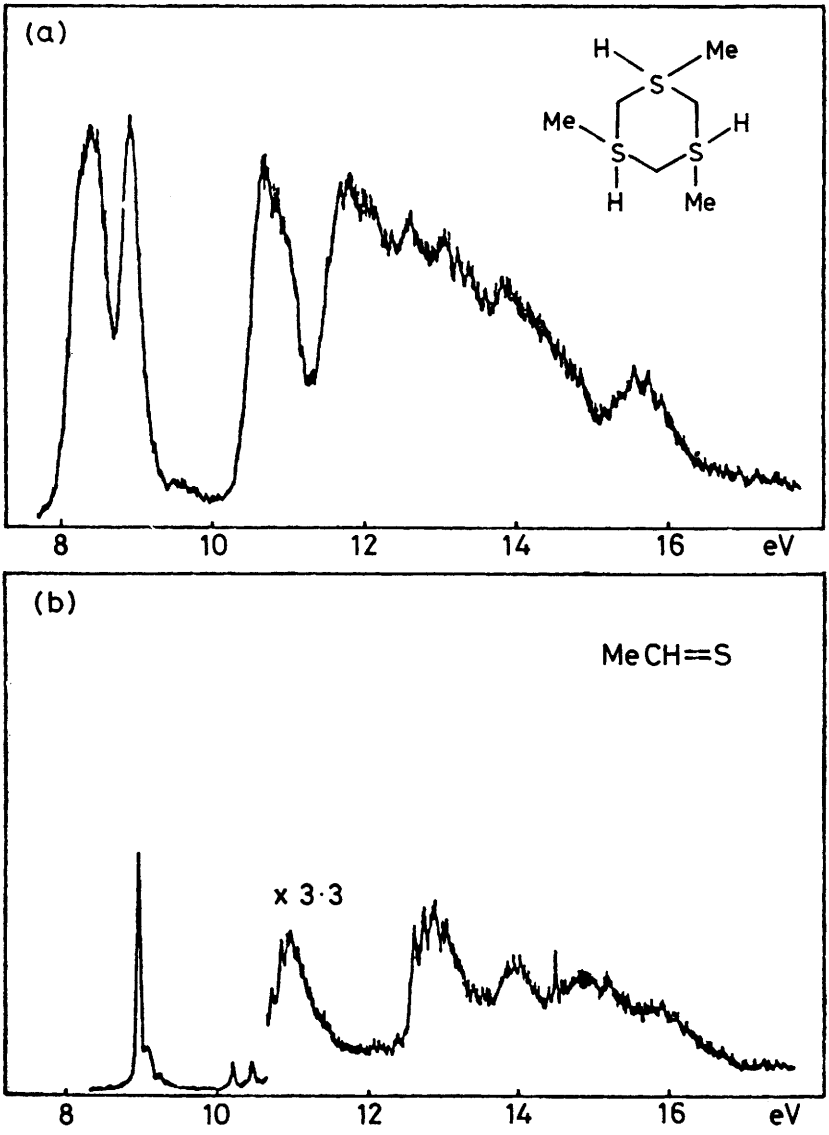


Figure 8 (*a*) *The p.e. spectrum of* $(CH_3CHS)_3$. (*b*) *The p.e. spectrum of monomeric* $CH_3CH{=}S$ *produced by pyrolysing the trimer at* 600 °C. *The first and second bands correspond to ionization of electrons from the* n(S) *and* π(C=S) *orbitals respectively*[24]

basis of these experiments a microwave search for CH_3CHS was carried out successfully[25] and the spectrum of the $J = 3 \leftarrow 2$ transition is shown in Figure 9. The pattern has the classic structure of a bunch of centrally placed $K_A \neq 1$ lines flanked by two $K_A = 1$ lines. Here the $K_A = 1$ lines are split by methyl group internal rotation tunnelling into doublets. From these splittings the barrier height $V_3 = 6.578\,\mathrm{kJ\,mole^{-1}}$ was determined.

In a similar way the photoelectron and microwave spectra of $(CH_3)_2CS$ were observed in the pyrolysis of the trimer $(Me_2CS)_3$.[24]

These experiments were refined still further in an attempt to detect thioketene $CH_2{=}C{=}S$. Some evidence for this species as an intermediate had been presented previously by Howard during the pyrolysis of $Me_3SC{\equiv}C{-}H$.[26] In our experiments[27,28] this species was positively identified by microwave spectroscopy in the pyrolysis of $(Me_2CS)_3$ at 1000 °C. Krantz and Laureni[29] also detected this molecule by i.r. spectroscopy by a neat route involving the pyrolysis of the thiadiazole, $\overline{CH{=}CH{-}S{-}N{=}N}$. Krantz and Laureni also detected $CH_2{=}C{=}Se$ by an analogous route.[30] This route is more efficient and has allowed photoelectron spectra to be observed.[31,32] The microwave spectrum of CH_2CSe has also been studied using this route[33].

As well as thioketene, a second new species was identified when thioacetone trimer was pyrolysed at 1000 °C. This was finally identified as propenethial, $CH_2{=}CHCH{=}S$,[34] which had formed by skeleton rearrangement from thioacetone. This molecule had originally been identified by Bailey and Isogawa[35] in the pyrolysis of diallylsulphide $(CH_2{=}CHCH_2)_2S$ from which it is more efficiently produced.

Some preliminary experiments aimed at developing analogous selenocarbonyl species have been carried out. These are much more difficult to handle (i) because there is an ever-present tendency for elemental Se to deposit and (ii) there is a psychosomatic response at the mere hint that such experiments are being carried out. Before the latter problems halted the present work the microwave spectrum of selenoacetaldehyde CH_3CHSe was detected and studied[36] and some circumstantial photoelectron evidence for CH_2Se obtained. Some synthetic studies of $(CH_2Se)_3$ have been discussed[37] and these methods were modified, with difficulty, to make $(MeCHSe)_3$ which was successfully pyrolysed to produce CH_3CHSe. This species was found to be much less stable and more difficult to

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[25] H. W. Kroto and B. M. Landsberg, *J. Mol. Spectrosc.*, 1976, **62**, 346.

[26] E. G. Howard, *Chem. Absr.*, 1962, **57**, 13617*f.*

[27] K. Georgiou, H. W. Kroto, and B. M. Landsberg, *J. Chem. Soc., Chem. Commun.*, 1974, 739.

[28] K. Georgiou, H. W. Kroto, and B. M. Landsberg, *J. Mol. Spectrosc.*, 1979, **77**, 365.

[29] A. Krantz and J. Laureni, *J. Am. Chem. Soc.*, 1974, **96**, 6768.

[30] A. Krantz and J. Laureni, *J. Am. Chem. Soc.*, 1977, **99**, 4843.

[31] H. Bock, B. Solouki, G. Bert, and P. Rosmus, *J. Am. Chem. Soc.*, 1977, **99**, 1663.

[32] H. Bock, S. Aygen, P. Rosmus, and B. Solouki, *Chem. Ber.*, 1980, **113**, 3187.

[33] B. Bak, O. J. Nielsen, and H. V. Svanholt, *Chem. Phys. Lett.*, 1978, **53**, 374.

[34] K. Georgiou and H. W. Kroto, *J. Mol. Spectrosc.*, 1980, **83**, 1.

[35] W. J. Bailey and M. Isogawa, *Polym. Prep. Am. Chem. Soc., Div. Polym. Chem.*, 1973, **14**, 300.

[36] M. Hutchinson and H. W. Kroto, *J. Mol. Spectrosc.*, 1978, **70**, 216.

[37] H. J. Bridger and R. W. Pittman, *J. Chem. Soc.*, 1950, 1371.

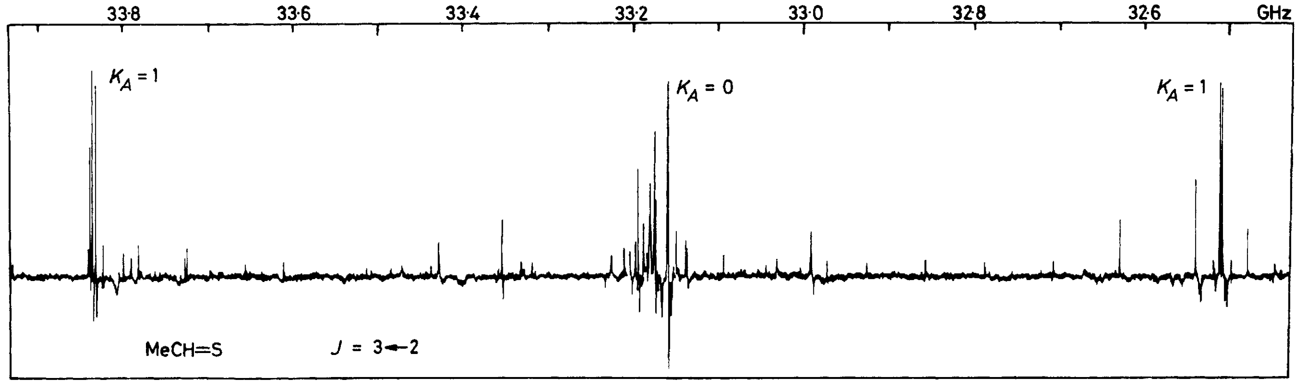

Figure 9 *The* $J = 3 \leftarrow 2$ *microwave transition of* $CH_3CH{=}S$.[25] *The outer* $K_A = 1$ *lines are split into doublets by the effects of methyl group internal rotation. The central group consisting of the* $K_A = 0$ *and* $K_A = 2$ *lines are also split by these effects. The other lines belong to torsional satellites*

detect than CH_3CHS. Attempts to produce selenoacetone compounds appear to lead to the deposition of elemental Se.[38]

Data on various thio- and seleno-carbonyls have been collected together in Table 1.

Table 1 *Collected data for thio- and seleno-carbonyls*

	r(C=S) / r(C=Se) /Å	μ/Debye	*Ionization Potentials*/eV	*Other data*
$CH_2{=}S$	1.611[12]	1.6474[12]	9.34 11.78[16]	
$CH_3CH{=}S$	1.610[25]	2.33[25]	8.90 10.87 12.74[24]	$V_3 = 6578 \text{ J mole}^{-1}$ [25]
$(CH_3)_2C{=}S$	—	—	8.60 10.46 12.40[24]	$V_3 = 5440 \text{ J mole}^{-1}$ [24]
$CH_2{=}CHCH{=}S$	1.61[34]	2.61[34]	—	$r(C{=}C) = 1.341$[34] $r(C{-}C) = 1.46$ Å
$F_2C{=}S$	1.59[21]	0.080[21]	10.45 11.34 14.87[20] 17.65	∠(FCF) = 107.1°[21] $r(C{-}F) = 1.315$ Å
$CH_2{=}C{=}S$	1.554[28]	1.02[28]	8.9 11.3 12.1[31]	$r(C{=}C) = 1.314$ Å[28]
$CH_3CH{=}Se$	1.758[36]	—	—	$V_3 = 6859 \text{ J mole}^{-1}$ [36]
$CH_2{=}C{=}Se$	1.702[33]	0.9[33]	8.7 10.7 11.6[32]	$r(C{=}C) = 1.313$[33]

B. Sulphidoboron and Selenidoboron Species.—A family of molecules related to HCN can be assembled and the resulting cube would have HCN, HBO, and CO along the isoelectronic top edge. The second layer beginning with HC≡P, together with the third layer, is shown in Figure 10. The isoelectronically related molecule HB=O has not been detected spectroscopically although the halide ClB=O has been observed by Kawaguchi, Endo, and Hirota in an O_2–BCl_3 discharge.[39] HBS, the sulphur analogue of HBO, was detected by Kirk and Timms in the products of a high temperature reaction (*ca.* 1000 °C) between H_2S and crystalline boron using a mass spectrometer[40] and further confirmation has come from microwave work by Pearson and McCormick[41,42] and photoelectron work.[43,44] In Figure 11 the spectrum observed using a fast-flow photoelectron instrument (of the type developed at Southampton by Dyke, Jonathan, and Morris[45]) is shown.[46]

The original detection of HB=S initiated a programme to produce substituted analogues by various sensible, though unsuccessful, routes such as the thermal elimination of HCl from BCl_2SH. Finally, a simple modification of the original Kirk and Timms route to HBS was attempted which at the time did not seem likely to be fruitful. In the event it worked beautifully. In the first experiment

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[38] D. S. Margolis and R. W. Pittman, *J. Chem. Soc.*, 1957, 799.
[39] K. Kawaguchi, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.*, 1982, **93**, 381.
[40] R. W. Kirk and P. L. Timms, *Chem. Comm.*, 1967, 18.
[41] E. F. Pearson and R. V. McCormick, *J. Chem. Phys.*, 1973, **58**, 1619.
[42] E. F. Pearson, C. L. Norris, and W. H. Flygare, *J. Chem. Phys.*, 1974, **60**, 1761.
[43] H. W. Kroto, R. J. Suffolk, and N. P. C. Westwood, *Chem. Phys. Letts.*, 1973, **22**, 495.
[44] T. P. Fehlner and D. W. Turner, *J. Am. Chem. Soc.*, 1973, **95**, 7175.
[45] J. M. Dyke, N. Jonathan, and A. Morris, *Electron Spectrosc.*, 1979, **3**, 189 (Academic Press).
[46] T. A. Cooper and H. W. Kroto, to be published.

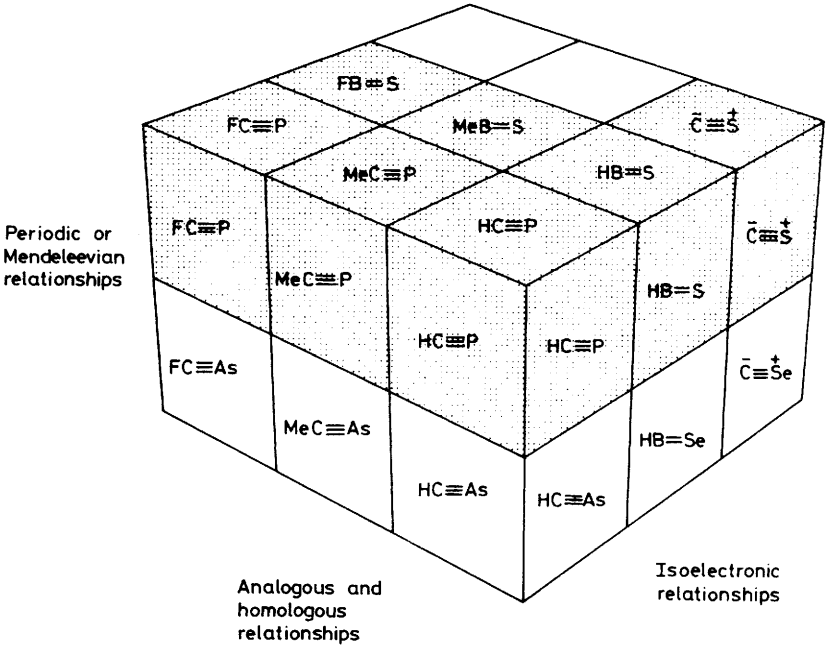

Figure 10 *The* HC≡N *cube with the top layer removed. All the molecules shaded in the second-row layer have been studied in the work discussed in this review*

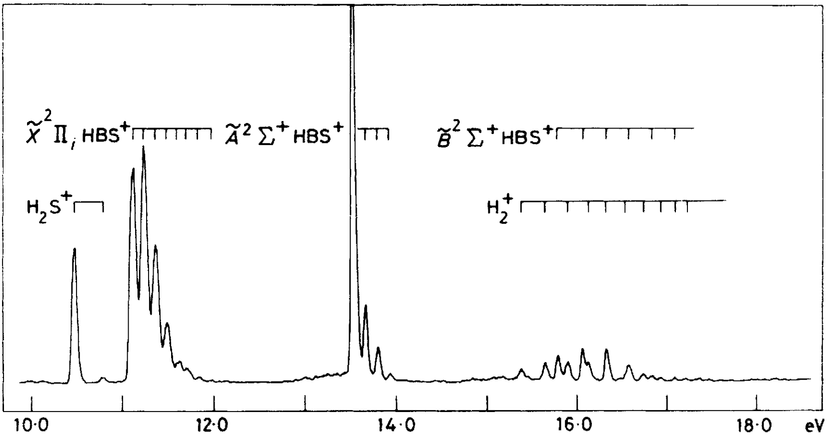

Figure 11 *The p.e. spectrum of* HB=S *detected during fast flow pyrolysis of* H_2S *over solid boron*[46]

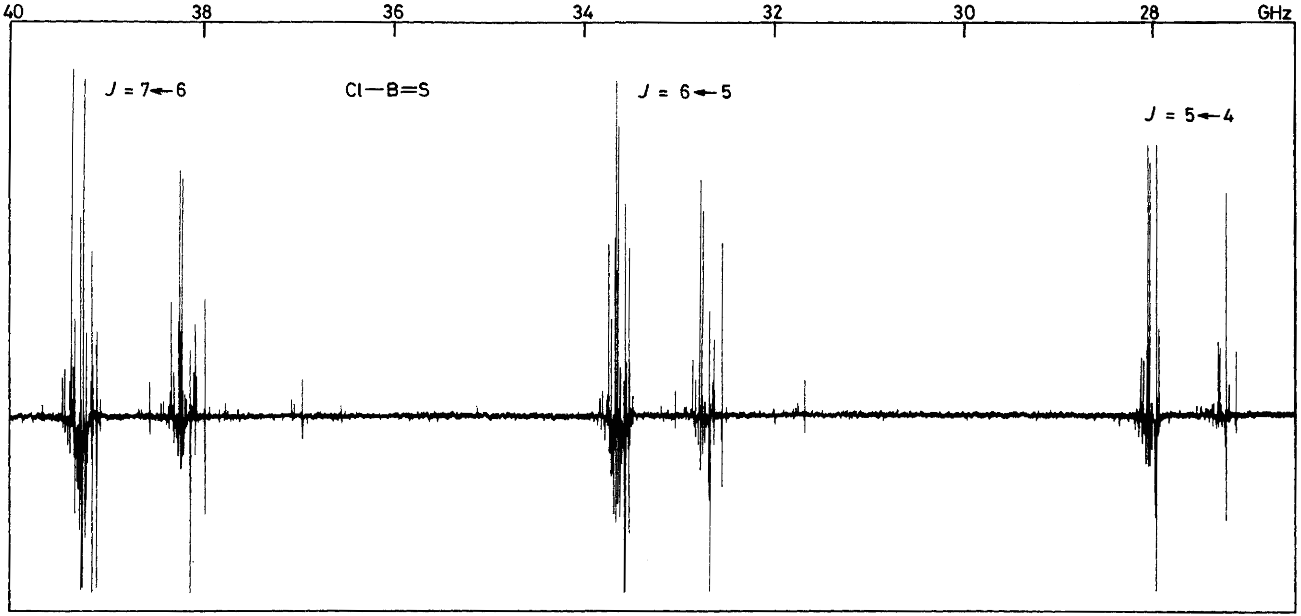

Figure 12 *The wide band scan of* ClB=S.[49] *There are 12 possible isotopic variants involving* ^{35}Cl, ^{37}Cl, ^{10}B, ^{11}B, ^{32}S, ^{33}S, *and* ^{34}S. *Lines of all twelve appear in the spectrum together with associated vibrational satellites. As the most abundant species* ^{35}Cl^{11}B^{32}S *and* ^{37}Cl^{11}B^{32}S *give rise to the most prominent lines each J transition appears to be split into two bunches. The higher frequency bunch associated mainly with* ^{35}Cl *variants, the lower frequency bunch with* ^{37}Cl *variants. The intensities bear a very poor relationship with abundance due to modulation effects*

the reaction of MeSSMe with crystalline boron at *ca.* 1000 °C was investigated and the new molecule $CH_3B{=}S$ was readily identified by microwave measurements.[47,48] Of course, with hindsight, a logical mechanism can be formulated such as equation (11)

$$CH_3SCH_3 \xrightarrow{\Delta} CH_3S\cdot \xrightarrow[B]{\Delta} CH_3SB \longrightarrow CH_3BS \qquad (11)$$

where the electron deficient boron surface is attacked by $CH_3S\cdot$ radicals following the readily accomplished thermal breakage of the S—S bond. The feasible CH_3SB species may then isomerize to the more stable methyl sulphidoboron, $CH_3B{=}S$. The process is probably more complex than this, involving solid products. Photoelectron studies have not detected this species, indicating that in this case the process produces very small amounts of CH_3BS which is detected because microwave spectroscopy is very sensitive to symmetric tops with large dipole moments ($\mu = 2.573$ Debye).

These experiments led naturally on to the study of the halides by essentially the same technique using disulphur dihalides, equation (12).

$$X_2S_2 \xrightarrow[B]{1000\,°C} XB{=}S\ (X = Hal) \qquad (12)$$

In Figure 12 the microwave spectrum of ClBS[49] is shown. Here the wide band scan shows the profusion of isotopic transitions which can be used to obtain accurate structural data. The photoelectron spectrum of ClBS is shown in Figure 12. In the original photoelectron work on HBS[43] and ClBS[50] a modified Perkin Elmer P.S.16 spectrometer was used which allowed only modest flow rates to be achieved. With very fast flow rates the much improved data in Figures 11 and 13[46] are obtained which indicate that reaction (12) yields a remarkably high conversion rate in these cases. This really seems quite surprising considering all the other possible reactions that might be expected to occur.

This work has been extended to the detection of monomeric FBS and BrBS by both photoelectron[46,51] and microwave spectroscopy.[46] The trimers of the sulphidoboron species are quite well known, and in fact, some interesting results on the FBS system have been obtained using combined microwave, photoelectron, and mass spectrometric techniques. These have shown that under the right conditions the spectra of FBS, $(FBS)_2$, and $(FBS)_3$ can be identified in the gas phase.[51] Such species can be formed by high temperature reactions involving SF_4–B, SF_6–B, or BF_3–B_2S_3 as well as the F_2S_2–B.[51]

The sulphidoboron data are collected together in Table 2 and the photoelectron data correlated in Figure 14.

This work has recently been extended to the bottom layer of Figure 10 by the detection of ClBSe[52] using a modification of reaction (12) in which Cl_2Se_2

[47] C. Kirby, H. W. Kroto, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1978, 19.

[48] C. Kirby and H. W. Kroto, *J. Mol. Spectrosc.*, 1980, **83**, 1.

[49] C. Kirby and H. W. Kroto, *J. Mol. Spectrosc.*, 1980, **83**, 130.

[50] C. Kirby, H. W. Kroto, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1978, **100**, 3766.

[51] T. A. Cooper, C. Kirby, H. W. Kroto, and N. P. C. Westwood, to be published.

[52] T. A. Cooper, M. A. King, H. W. Kroto, and R. J. Suffolk, *J. Chem. Soc., Chem. Commun.*, 1981, 354.

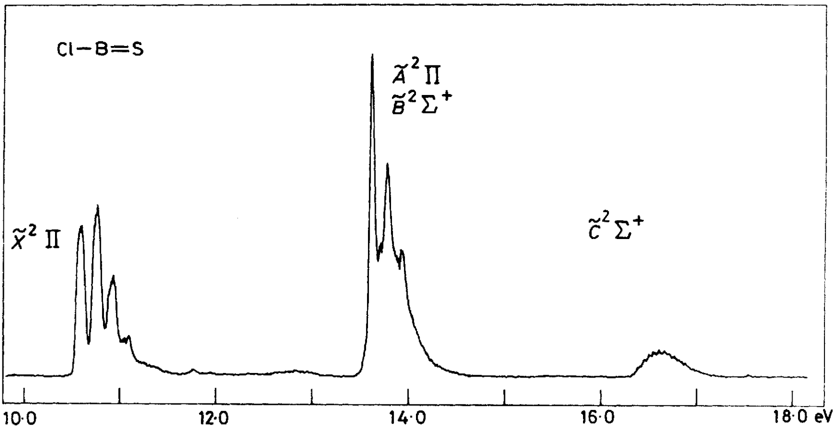

Figure 13 *The fast flow p.e. of* ClB=S.[46] ClBS *is produced by passing* Cl_2S_2 *over solid boron at* 1100 °C *and this spectrum indicates that the resulting vapour phase product is essentially pure* ClBS. *Note that the* 2nd *and* 3rd *ionization potentials coincide closely*

Table 2 *Spectroscopic data on sulphidoboron and selenidoboron species*

Species	r(X−B)/Å	r(B=S)/Å	μ/Debye	*Ionization Potential*/eV	*Ref.*
HB=S	1.169	1.599	2.098	11.1 13.55 15.84	41—44
FB=S	1.284	1.606	1.086	10.9 14.2 17.2 19.62	46, 51
ClB=S	1.681	1.606	1.45	10.57 13.55 13.63 16.36	49, 50
BrB=S	1.831	1.608	—	10.42 12.77 13.43	46
CH_3B=S	1.535	1.603	2.573	—	48
ClB=Se	1.664	1.751	—	—	52

is passed over B at 1100 °C. The spectrum is much more difficult to detect than that of ClBS. This is the first example of a selenidoboron compound and there is no obvious reason why other analogues should not be detectable.

C. Carbon–Phosphorus Multiple Bonds.—*Phospha-alkenes and Phospha-alkynes.* In 1961 Gier at Du Pont showed that phosphaethyne, HC≡P, the phosphorus analogue of HCN is produced when PH_3 is passed through a carbon arc discharge.[53] Subsequently Tyler at NRC studied the microwave spectrum[54] and the optical spectrum with Johns and Shurvell.[55] The existence of this molecule immediately suggested various possible consequences. Could analogues be made and might there be an associated chemistry parallel to that of the nitriles? The chemistry of the C≡P group might be equally, if not even more,

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[53] T. E. Gier, *J. Am. Chem. Soc.*, 1961, **83**, 1769.
[54] J. K. Tyler, *J. Chem. Phys.*, 1964, **40**, 1170.
[55] J. W. C. Johns, H. F. Shurvell, and J. K. Tyler, *Can. J. Phys.*, 1969, **47**, 893.

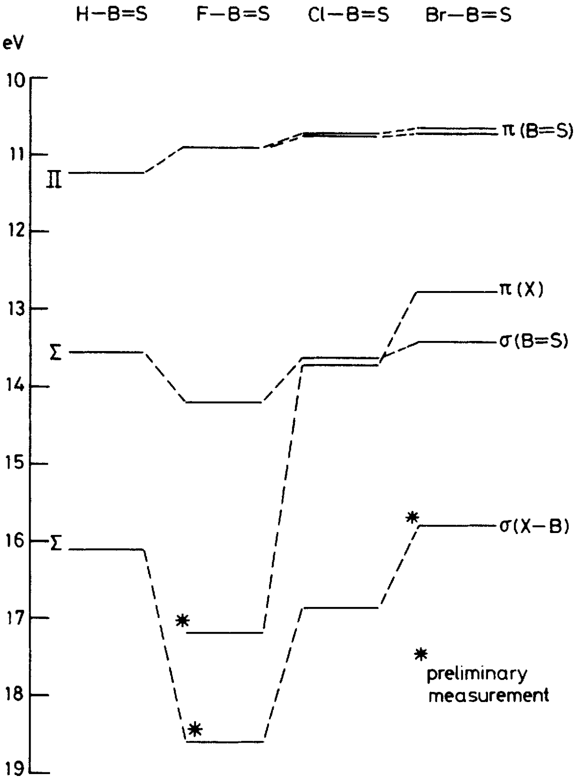

Figure 14 *Correlation diagram showing the variation in observed ionization energy*[46] *for the various molecular orbitals of the sulphidoboron halides*

diverse and important relative to that of the nitriles. The possibilities for reactions such as condensation reactions, polymerization processes, inorganic and organometallic complex formation seemed endless. The questions were clear but the techniques for solving them much less obvious.

Although nitriles are well known stable systems the doubly bonded imino $>C{=}N\diagup$ species are much less so, indeed it is only fairly recently that Johnson and Lovas[56] succeeded in identifying the simplest molecule $CH_2{=}NH$ by microwave spectroscopy in the products of pyrolysing CH_3NH_2. This experiment together with the existence of $HC{\equiv}P$ point to the distinct possibility that phosphaethene $CH_2{=}PH$ might be detectable in the pyrolysis of such species as CH_3PH_2 *etc.* Indeed some work by Haszeldine and co-workers[57,58] postulated

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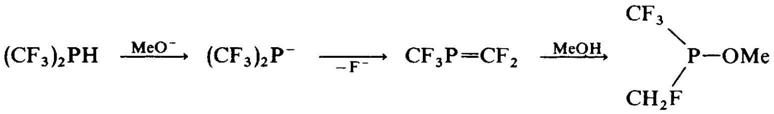
[56] D. R. Johnson and F. J. Lovas, *Chem. Phys. Lett.*, 1972, **15**, 65.
[57] H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, *J. Chem. Soc.*, 1965, 6875.
[58] M. Green, R. N. Haszeldine, B. R. Iles, and D. G. Rowsell, *J. Chem. Soc.*, 1965, 6879.

that species of the type $R_2C{=}PX$ were intermediates in the reactions of certain perfluoroalkylphosphines with bases, in for instance scheme (13).



$$(CF_3)_2PH \xrightarrow{MeO^-} (CF_3)_2P^- \xrightarrow[-F^-]{} CF_3P{=}CF_2 \xrightarrow{MeOH} (CF_3)(CH_2F)P{-}OMe \qquad (13)$$

The combined microwave and photoelectron technique which had already been successful in studying such species as $CH_2{=}S$[16] and $CF_2{=}S$[20,21] (isoelectronic with the feasible species $CH_2{=}PH$ and $CF_2{=}PH$ respectively) as well as CS[13] and $HB{=}S$[43] (both isoelectronic with $HC{\equiv}P$) thus seemed ideally suited to the detection of the hitherto *unknown* phospha-alkenes as well as *new* phospha-alkynes related to the lone species $HC{\equiv}P$. Accordingly some exploratory microwave investigations were initiated at Sussex together with John Nixon. These met with immediate success in that three members of the phospha-alkene family, a new structural type, including the simplest, $CH_2{=}PH$, were produced and characterized.[59] In addition the first substituted phospha-alkyne, $CH_3C{\equiv}P$, the phosphorus analogue of acetonitrile was produced.[60] At the same time, Becker[61] observed a rearrangement in a P-silylated acyl phosphine to form $PhP{=}C(Bu^t)OSiMe_3$.

In the first experiment attempted, the pyrolysis of dimethyl phosphine Me_2PH, a microwave transition of the species $CH_2{=}PH$[59] was detected according to equation (14).

$$(CH_3)_2P \xrightarrow[\Delta]{} CH_2{=}PH + CH_4 \qquad (14)$$

Further evidence for the assignment came with the detection of the same transition in the pyrolysis of CH_3PH_2 and subsequently, more efficiently, of $Me_3SiCH_2PH_2$.[62,63] Furthermore this detection was immediately followed[59] by the identification of $CH_2{=}PCl$ in the reaction (15)

$$CH_3PCl_2 \xrightarrow[\Delta]{} CH_2{=}PCl + HCl \qquad (15)$$

and the molecule $CF_2{=}PH$[59] in the reaction (16)

$$CF_3PH_2 \xrightarrow[\Delta]{} CF_2{=}PH + HF \qquad (16)$$

The microwave spectra for the pyrolysis of CH_3PCl_2 are shown in Figure 15. A second and very important result is also to be found in this spectrum in that at 39.952 GHz the $J = 1 \leftarrow 0$ transition of $HC{\equiv}P$ is readily detectable.

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[59] M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Chem. Soc., Chem. Commun.*, 1976, 513.

[60] M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *Chem. Phys. Lett.*, 1976, **42**, 460.

[61] G. Becker, *Z. Anorg. Allg. Chem.*, 1976, **423**, 242.

[62] H. W. Kroto, J. F. Nixon, K. Ohno, and N. P. C. Simmons, *J. Chem. Soc., Chem. Commun.*, 1980, 709.

[63] H. W. Kroto, J. F. Nixon, and K. Ohno, *J. Mol. Spectrosc.*, 1981, **90**, 367.

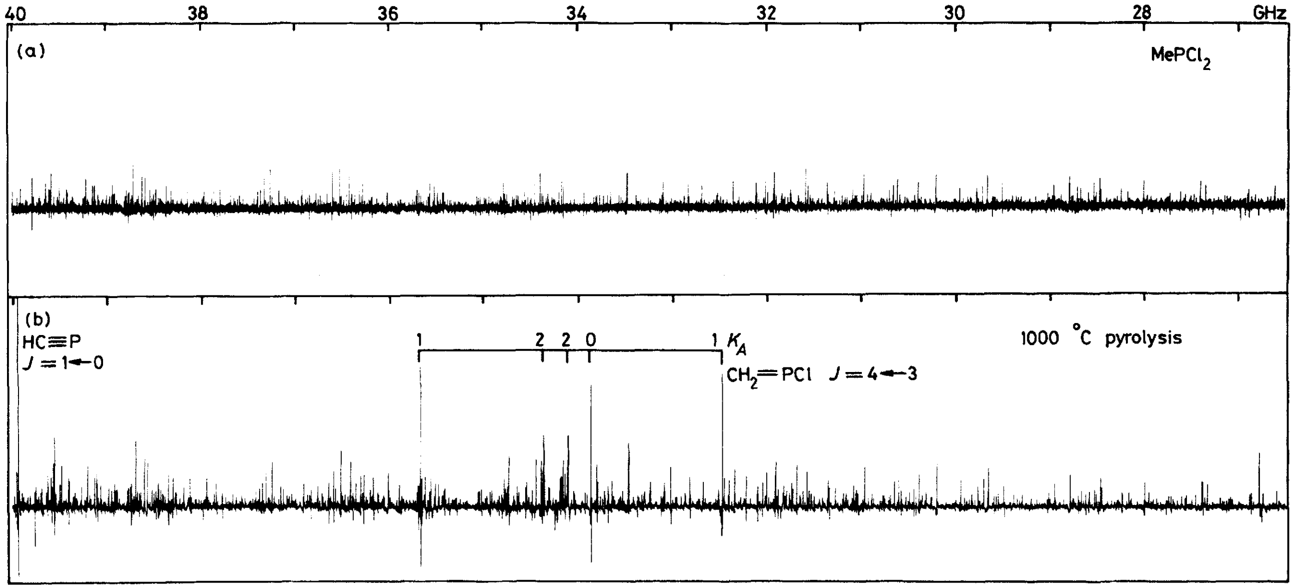

Figure 15 (*a*) *The wide band scan of the microwave spectrum of* CH_3PCl_2. *This molecule is fairly asymmetric and gives rise to a very complicated multitude of weak rotational lines which fall into few, if any, recognisable patterns.* (*b*) *On pyrolysis of* CH_3PCl_2 *a new group of lines appears which is readily assigned to the* $J = 4 \leftarrow 3$ *transition of* $CH_2{=}PCl$. *In addition the strong* $J = 1 \leftarrow 0$ *line of* $HC{\equiv}P$ *appears at* 39.952 GHz *indicating that two* HCl *fragments have been eliminated*

The second part of these initial investigations relating to the phospha-alkynes was now clear and pyrolysis of the species $EtPCl_2$ according to equation (17)

$$CH_3CH_2PCl_2 \xrightarrow{\Delta} CH_3C{\equiv}P + 2HCl \tag{17}$$

was immediately confirmed by microwave[60,64] and photoelectron [65] investigations. The microwave spectrum is shown in Figure 16.

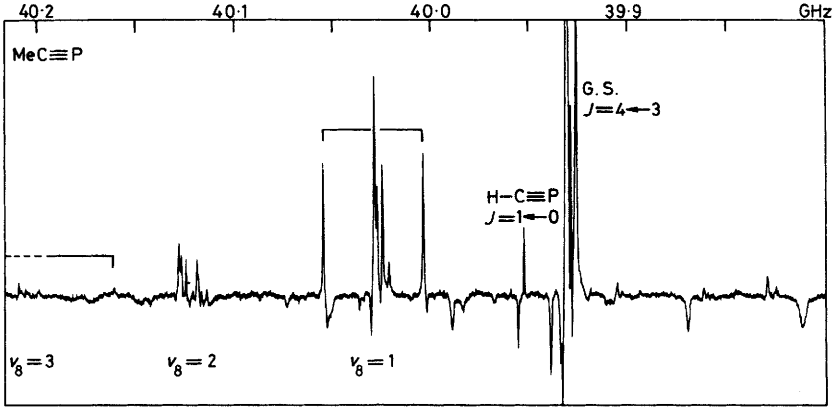

Figure 16 *The* $J = 4 \leftarrow 3$ *transition of* MeC≡P *produced by pyrolysing* $EtPCl_2$. *The ground vibrational state lines for this symmetric top molecule with* $K = 0$—3 *bunch together at* ca. 39 930 MHz. *When the lowest vibrational mode, the* C—C—P *bend, is excited the molecule changes from a symmetric to an asymmetric rotor and the* $v = 1$ *vibrational satellite shows a pattern which has characteristics similar to those of a slightly asymmetric rotor. The* $J = 1 \leftarrow 0$ *line of HCP is also in this region and it shows a nice example of a simple Stark modulated microwave line. The positive line is the zero-field frequency and the negative lobe is the frequency in the presence of the perturbing field. For the simple* $J = 1 \leftarrow 0$ *case one only observes a Stark shift. In general one observes splittings when higher values of* J *are involved (see Figure* 17)

A careful search for FCP formed by thermally eliminating two HF fragments from CF_3PH_2 continuing equation (16) was also carried out and the $J = 3 \leftarrow 2$ transition, Figure 17, was identified even though it was rather weak.[66] When this experiment was modified to prevent the possible back reaction of HF with FCP, by passing the pyrolysed products over solid KOH, it was discovered that HF could be eliminated directly by a reaction between the precursor CF_3PH_2 and KOH—no heating was necessary,[66] Figure 17. The reaction (18)

$$CF_3PH_2 \xrightarrow[KOH]{-HF} CF_2{=}PH \xrightarrow[KOH]{-HF} FC{\equiv}P \tag{18}$$

takes place at room temperature. These techniques have also confirmed the importance of phospha-alkenes as intermediates in reactions between primary

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[64] H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Mol. Spectrosc.*, 1979, **77**, 270.

[65] N. P. C. Westwood, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Chem. Soc., Dalton Trans.*, 1979, 1405.

[66] H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Mol. Spectrosc.*, 1980, **82**, 185.

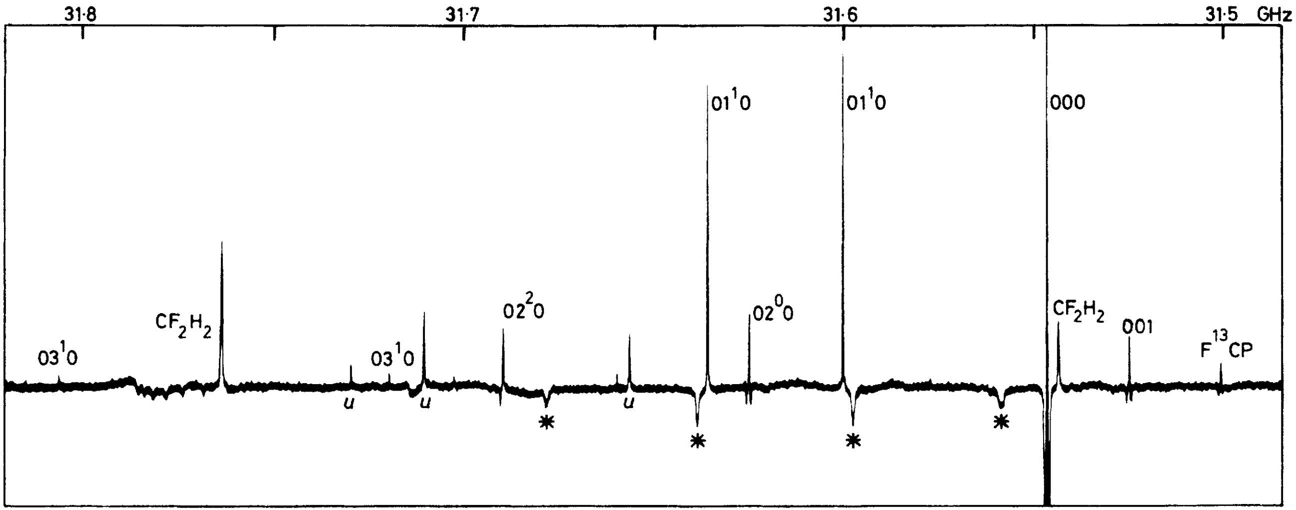

Figure 17 *The $J = 3 \leftarrow 2$ microwave transition of* FC≡P *is a beautiful example of a linear molecule rotational spectrum. The ground vibrational state line is assigned* (000) i.e. ($v_1 = 0$, $v_2 = 0$, $v_3 = 0$)*. The bending vibration ν_2 is doubly degenerate and the satellite splits into two lines by an interaction called l-type doubling. The effect is loosely related to the asymmetry splitting of $K_A = 1$ lines in asymmetric tops due to the fact that on bending the molecule is no longer linear and $B \neq C$. These are the two lines labelled* (01^10)*. The superscript indicates the quantum number for vibrational angular momentum, l. The $2\nu_2$ state gives rise to a state with $l = 2$,* i.e. (02^20) *and a state with $l = 0$* (02^00)*. The 02^00 state is shifted by a Fermi resonance with the ν_3 state* (001)*, see Figure* 21*. The asterisks indicate Stark lobes belonging to the two* (01^10) *lines. The* U*-lines are unidentified and belong to another species*

or secondary polyfluoroalkyl phosphines with nucleophiles such as alkoxides and amines. In particular the species $CF_3P{=}CF_2$, postulated as an intermediate in the methanolysis of $(CF_3)_2PH$, equation (13), has been trapped and identified by n.m.r.[67] The obvious step of treating $CF_3CF_2PH_2$ with KOH to observe $CF_3C{\equiv}P$ was not successful, though this species has been detected in the pyrolysis products of the precursor in rather low yield.[68]

Having detected the phospha-alkenes $CH_2{=}PH$, $CH_2{=}PCl$, $CF_2{=}PH$, and $CF_3P{=}CF_2$ and the phospha-alkynes $FC{\equiv}P$, $CH_3C{\equiv}P$, and $CF_3C{\equiv}P$ in these preliminary experiments, the programme was developed in wider and more general directions. Not only were new members of these two groups sought but more efficient synthetic routes and new chemical applications, for instance as ligands in transition-metal complexes, were explored. In addition, the chemistry of these species is now being studied by several other groups such as those of Becker, Appel, Bickelhaupt, and Issleib. Below, the contributions made by this research programme in collaboration with John Nixon are summarized, with contributions from other groups included where appropriate. Reviews of these systems are now beginning to appear.[69–72]

(i) *Production of Phospha-alkenes.* As indicated above, the thermal elimination route has proven very successful, especially for spectroscopic purposes. Thus, the general scheme shown in equation (19)

$$\mathrm{RCX_2PY_2} \xrightarrow[\Delta]{} \mathrm{RCX{=}PY + XY} \qquad (19)$$

has led to $CH_2{=}PH$, $CF_2{=}PH$, and $CH_2{=}PCl$[59] and Klebach *et al.*[73] have shown that a phospha-alkene is produced according to equation (20).

$$\mathrm{RPCl_2} \longrightarrow \mathrm{RPClCHPh_2} \longrightarrow \mathrm{RP{=}CPh_2}\ (\mathrm{R} = \text{mesityl}) \qquad (20)$$

where the resulting compound is stabilized by the substituents. The elimination step can, in the case of CF_3PH_2 and $(CF_3)_2PH$, be carried out by treatment with base to form $CF_2{=}PH$ and $CF_3P{=}CF_2$ respectively (previous Section). Studies, together with David Walton, of routes involving silyl substituted phosphines are in progress and have resulted in phospha-alkenes by equations (21)—(24)

$$\begin{tikzcd}
 & \mathrm{CH_2{=}PCl} & & (21) \\
\mathrm{Me_3SiCH_2PCl_2} \arrow[ur, "\Delta"] \arrow[r, "\mathrm{SbF_3}"] \arrow[dr, "\mathrm{LiAlH_4}"'] & \mathrm{Me_3SiCH_2PF_2} \arrow[r, "\Delta"] & \mathrm{CH_2{=}PF} & (22) \\
 & \mathrm{Me_3SiCH_2PH_2} \arrow[r, "\Delta"] & \mathrm{CH_2{=}PH} & (23) \\
\mathrm{Me_3SiCH_2PBr_2} \arrow[r, "\Delta"] & \mathrm{CH_2{=}PBr} & & (24)
\end{tikzcd}$$

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[67] H. Eshtiagh-Hosseini, H. W. Kroto, J. F. Nixon, and O. Ohashi, *J. Organomet. Chem.*, 1979, **181**, C1.

[68] N. P. C. Simmons, H. W. Kroto, and J. F. Nixon, to be published.

[69] H. W. Kroto and J. F. Nixon in 'Phosphorus Chemistry', ed. L. D. Quin and J. Verkade, A.C.S. Symposium Series 171, American Chemical Society, 1981, p. 283.

[70] J. C. T. R. Burckett-St. Laurent, T. A. Cooper, H. W. Kroto, J. F. Nixon, O. Ohashi, and K. Ohno, *J. Mol. Struct.*, 1982, **79**, 215.

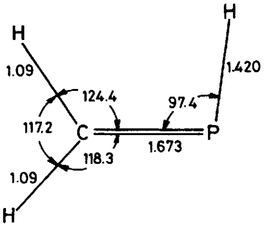
[71] R. Appel, F. Knoll, and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731.

[72] H. W. Kroto and J. F. Nixon, to be published.

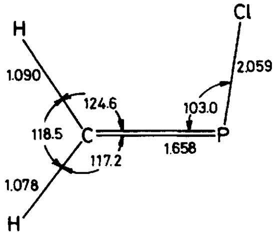
[73] T. C. Klebach, R. Lourens, and F. Bickelhaupt, *J. Am. Chem. Soc.*, 1978, **100**, 4886.

The route (23) to $CH_2{=}PH$ is more efficient than the original one, equation (14), and has allowed an accurate structural study to be made.[63] Since this work, $CH_2{=}PCl$ has also been detected in the pyrolysis of CH_3OPCl_2.[74] The review by Appel *et al.*[71] contains details of other phospha-alkenes.

(ii) *Spectroscopic Data on Phospha-alkenes.* From the microwave studies accurate structures for the two phospha-alkenes $CH_2{=}PH$[63] and $CH_2{=}PCl$[74,75] have been determined (5) and (6) where the bond lengths are in Å and angles in degrees.



(5)



(6)

In addition to $CH_2{=}PH$ and $CH_2{=}PCl$, microwave studies have also been carried out on $CH_2{=}PF$,[76] $CH_2{=}PBr$,[77] and $CF_2{=}PH$.[59,78] The rotational constants of some of the species studied are given in Table 3 and some of the more important structural parameters (some of which are preliminary) are collected in Table 4. Some dipole moment data are also included in this Table. Ohno *et al.*[79] have obtained vibrational frequencies from an i.r. study of $CF_2{=}PH{:}\nu_1$(PH stretch) = 2326.9 and ν_2(C=P stretch) = 1349.5 cm^{-1} (see Section 3Cii). This system has also been studied by n.m.r. (see Section 3Cii).

Table 3 *Rotational constants of phospha-alkenes*

*Species**	A_0/MHz	B_0/MHz	C_0/MHz	*Ref.*
$CH_2{=}PH$	138 503.2	16 418.105	14 649.084	62, 63
$CH_2{=}PD$	93 513.75	16 098.885	13 701.898	
$CH_2{=}PF$	28 454.9	8890.30	6760.13	76
$CH_2{=}P^{35}Cl$	22 712.5	4667.318	3865.535	59, 75
$CH_2{=}P^{37}Cl$	22 657.0	4539.161	3735.677	
$CH_2{=}P^{79}Br$	21 608.48	2904.010	2586.750	77
$CH_2{=}P^{81}Br$	21 603.06	2879.260	2537.48	
$CF_2{=}PH$	11 107.108	4766.393	3330.787	59, 78
$CF_2{=}PD$	10 676.036	4672.806	3246.213	

* Species containing ^{12}C, ^{31}P, and ^{19}F

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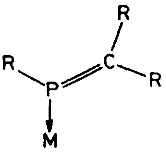
[74] B. Bak, N. A. Kristiansen, and H. Svanholt, *Acta Chem. Scand., Ser A*, 1982, **36**, 1.
[75] H. W. Kroto, J. F. Nixon, O. Ohashi, K. Ohno, and N. P. C. Simmons, to be published.
[76] H. W. Kroto, J. F. Nixon, K. Ohno, and D. R. M. Walton, to be published.
[77] H. W. Kroto, J. F. Nixon, and K. Ohno, to be published.
[78] H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, to be published.
[79] K. Ohno, H. Matsuura, H. W. Kroto, and H. Murata, *Chem. Letts.*, 1982, 981.

Table 4 *Structural and dipole moment data for phospha-alkenes*

	$r(CP)$/Å	$r(PX)$/Å	∠(CPX)/°	μ_A	μ_B/Debye	μ	*Ref.*
$CH_2{=}PH$	1.673	1.420	97.4	0.731	0.470	0.869	63
$CH_2{=}PF$	1.67[a]	1.58[a]	104.0	—	—	—	76
$CH_2{=}PCl$	1.658	2.059	103.0	—	—	—	75
$CH_2{=}PBr$	1.65[a]	2.22[a]	104	—	—	—	77
$CF_2{=}PH$	1.67[a]	1.42[a]	(100)	0.705	0.533	0.884	78

(*a*) preliminary data

(iii) *Phospha-alkene Complexes.* On production of the first phospha-alkenes the possibility of their use as ligands with transition metals was investigated. This has resulted in the synthesis of several organometallic complexes of the form (7).



(7)

The complexes which have been made[80] are ($L = MesP{=}CPh_2$):

cis-$M(CO)_4L_2$ (M = Cr, Mo, or W)

$M(CO)_5L$ (M = W)

$RhCl(PPh_3)L$, $RhCl(CO)L_2$, $Rh(C_9H_7)L_2$, PtX_2L_2 (X = Cl, I, or Me)

$PtCl_2(PEt_3)L$

The last compound has been the subject of an *X*-ray structure analysis,[81] from which the main structural parameters are: $r(C{=}P) = 1.668$ Å, ∠$(C{=}P{-}C) = 112°$, $r(Pt{-}P) = 2.193$ Å, ∠$(C{=}P{-}Pt) = 120.2°$.

(iv) *Production of Phospha-alkynes.* The original Gier method[53] required a rather complicated cooled carbon arc device to be made and the reaction between graphite and PH_3 produced a mixture of *ca.* 4:1 C_2H_2:HCP. It appears to be almost impossible to separate these two as their physical properties are very similar.

The method of production that has been most fruitful has been the thermal elimination route (25)

$$RCX_2PY_2 \xrightarrow[\Delta]{-2XY} RC{\equiv}P \quad (XY = HCl \text{ or } FH) \qquad (25)$$

Using this straightforward method at temperatures of *ca.* 1000 °C or so, the

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[80] H. Eshtiagh-Hosseini, H. W. Kroto, J. F. Nixon, M. J. Maah, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1981, 199.

[81] H. W. Kroto, J. F. Nixon, M. J. Taylor, A. A. Frew, and K. W. Muir, *Polyhedron*, 1982, **1**, 89.

molecules $HC{\equiv}P$,[59] $FC{\equiv}P$,[66] $CH_3C{\equiv}P$,[60,64,65] $CF_3C{\equiv}P$,[68] and $CH_2{=}CHC{\equiv}P$[82] have all been detected by microwave spectroscopy. Photoelectron studies indicate that the yield is good in the case of HCP,[83] fair for CH_3CP,[65] and poor for the rest. Pure HCP can now be produced from CH_3PCl_2 by titrating off the HCl with NH_3.[83] FCP can be produced in good yield by treating CF_3PH_2 with KOH (see Section 3Cv).

During experiments aimed at detecting $HC{\equiv}C{-}C{\equiv}P$ which involved an attempted synthesis of $HC{\equiv}CCH_2PCl_2$, the sought species was detected.[84] To produce the precursor, the Grignard of $HC{\equiv}CCH_2Cl$ was treated with PCl_3 and the resulting products flow pyrolysed, which gave rise to a weak but readily identifiable spectrum of HC_3P. The precursor was not, however, $HC{\equiv}CCH_2PCl_2$, which did not appear to be formed, but the original starting materials $HC{\equiv}CCH_2Cl$ and PCl_3. In fact the strongest spectrum was observed using a 10:1 $PCl_3{:}HC{\equiv}CCH_2Cl$ mixture. This result suggested that HC_3P might be formed in reaction (26),

$$HC{\equiv}C{-}CH_3 + Cl_3P \xrightarrow{\Delta} HC{\equiv}C{-}C{\equiv}P + 3HCl \qquad (26)$$

which indeed turned out to be the case. In fact the reaction, equation (1), has now been generalized with $R = HC{\equiv}C$, $N{\equiv}C$, and Ph to produce not only $HC{\equiv}C{-}C{\equiv}P$ but also $N{\equiv}C{-}C{\equiv}P$, and $PhC{\equiv}P$. Most recently the molecule NC_5P has been detected by equation (27) the first new species to be detected by this route.[85]

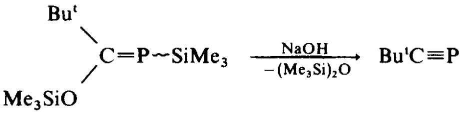
$$N{\equiv}C{-}C{\equiv}C{-}CH_3 + Cl_3P \xrightarrow{\Delta} N{\equiv}C{-}C{\equiv}C{-}C{\equiv}P + 3HCl \qquad (27)$$

$N{\equiv}C{-}C{\equiv}P$ had originally been detected by co-pyrolysing HCP with NCN_3,[86] equation (28).

$$N{\equiv}CN_3 + HC{\equiv}P \xrightarrow{\Delta} N{\equiv}C{-}C{\equiv}P + \cdots \qquad (28)$$

The PCl_3/CH_3CN route is at least as good for spectroscopic purposes.

The molecules $SiMe_3C{\equiv}P$ and $PhC{\equiv}P$ have been produced by pyrolysis of $ClP{=}C(SiMe_3)_2$ and $ClP{=}C(SiMe_3)Ph$ respectively by Appel and Westerhaus,[87,88] Becker *et al.*[89] have shown that the *stable* molecule $Bu^tC{\equiv}P$ can be produced by equation (29)



$$(Bu^t)(Me_3SiO)C{=}P{\sim}SiMe_3 \xrightarrow[-(Me_3Si)_2O]{NaOH} Bu^tC{\equiv}P \qquad (29)$$

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[82] K. Ohno, H. W. Kroto, and J. F. Nixon, *J. Mol. Spectrosc.*, 1981, **90**, 507.
[83] M. A. King, H. W. Kroto, and J. F. Nixon, unpublished.
[84] H. W. Kroto, J. F. Nixon, and K. Ohno, *J. Mol. Spectrosc.*, 1981, **90**, 512.
[85] M. Durrant, H. W. Kroto, D. McNaughton, and J. F. Nixon, to be published.
[86] T. A. Cooper, H. W. Kroto, J. F. Nixon, and O. Ohashi, *J. Chem. Soc., Chem. Commun.*, 1980, 333.
[87] R. Appel and A. Westerhaus, *Tetrahedron Lett.*, 1981, 2159.
[88] R. Appel and A. Westerhaus, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 197.
[89] G. Becker, G. Gresser, and W. Uhl, *Z. Naturforsch, Teil B*, 1981, **36**, 16.

(v) *Spectroscopic Data on Phospha-alkynes.* Using Gier's original method of producing HC≡P numerous spectroscopic investigations were made. The microwave spectrum was studied by Tyler,[54] the electronic spectrum by Johns *et al.*,[55] the n.m.r. spectrum by Anderson *et al.*,[90] the i.r. by Garneau and Cabana,[91] and the p.e. spectrum by Frost *et al.*[92] In some cases, particularly the last two, the acetylene contaminant obscured regions of the spectrum. This problem is obviated by producing HCP from CH_3PCl_2, allowing a p.e. spectrum of pure HCP to be observed.[83] It has also enabled the electronic fluorescence spectrum of the HCP^+ ion, excited by slow electron bombardment, to be observed, Figure 18.[93]

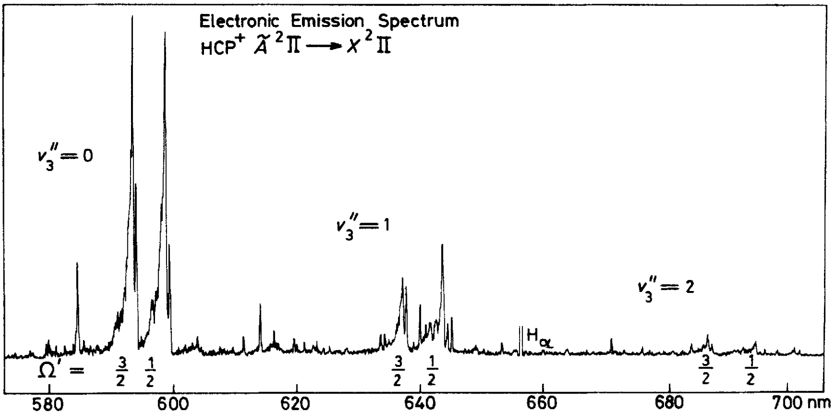

Figure 18 *The electronic emission spectrum of* HCP^+ *excited by slow electron bombardment of* HCP[93]

So far, CH_3CP,[60,64] FCP,[65] CF_3CP,[68] NCCP,[86,85] HC≡CCP,[84,85] NCC≡CCP,[85] CH_2=CHCP,[82] and PhCP[85,94] have all been studied by microwave spectroscopy. Indeed, all but the last compound were first identified by this technique. The more important data are collected in Table 5.

The discovery of reaction (18) enabled a thorough analysis of the microwave spectrum of FCP shown in Figure 17 to be carried out.[66] It also enabled the

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[90] S. P. Anderson, H. Goldwhite, D. Ko, A. Letson, and E. Esparza, *J. Chem. Soc., Chem. Commun.*, 1975, 744.

[91] J. M. Garneau and A. Cabana, *J. Mol. Spectrosc.*, 1980, **79**, 502.

[92] D. C. Frost, T. Lee, and C. A. McDowell, *Chem. Phys. Lett.*, 1973, **23**, 472.

[93] M. A. King, H. W. Kroto, J. F. Nixon, D. Klapstein, J. D. Maier, and O. Marthaler, *Chem. Phys. Lett.*, 1981, **82**, 543.

[94] J. C. T. R. Burckett-St. Laurent, H. W. Kroto, J. F. Nixon, and K. Ohno, *J. Mol. Spectrosc.*, 1982, **92**, 158.

Table 5 *Spectroscopic data on phospha-alkynes*

	B_0/MHz	μ/ Debye	$r(X{-}C)$/ Å	$r(C{\equiv}P)$/ Å	*Ionization Potentials*/ eV	*Ref.*
$HC\equiv P$	19973.67	0.39	1.0667	1.5421	10.79 12.86	54, 92
$HC\equiv P^+$			1.11	1.596		93
$CH_3C\equiv P$	4991.339	1.499	1.465	1.544	9.89 12.19	64, 65
$FC\equiv P$	5257.80	0.279	1.285	1.541	10.57 13.55	66, 96
$CF_3C\equiv P$	1668.5644	—	1.460	1.542		68
$N\equiv C{-}C\equiv P$	2704.4803	3.44	1.382	1.547		86
$H{-}C\equiv C{-}C\equiv P$	2656.3944	0.754	1.382	(1.544)		84
$N\equiv C{-}C\equiv C{-}C\equiv P$	873.4803	—	1.382	(1.544)		85
$CH_2{=}CHC\equiv P$	2726.773	1.183	1.432	(1.544)		82
$PhC\equiv P$	867.6925	—	1.467	(1.544)	8.68 9.60 9.87 10.79	97
$t\text{-}BuC\equiv P$	—	—	—	—	9.61 11.44	97

p.e. spectrum shown in Figure 19 and the n.m.r. data in Figure 20 to be obtained.[95] The i.r. data of Ohno *et al.*[79] in Figure 21 give a particularly useful insight into the overall efficiency of this reaction.

As well as the earlier p.e. work on HCP,[92] CH_3CP,[65] and FCP,[96] more

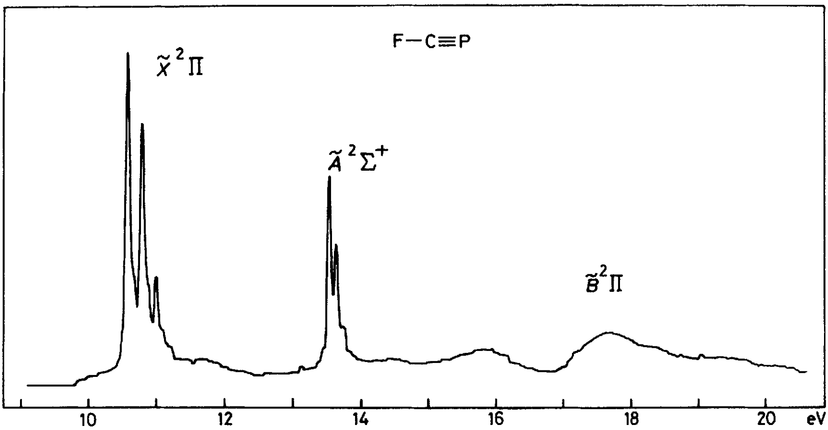

Figure 19 *The p.e. spectrum of* $FC\equiv P$ *produced by flowing gaseous* CF_3PH_2 *over solid* KOH. *The first and second bands correspond to ionizations from the* $\pi(C\equiv P)$ *and* $n(P)$ *orbitals respectively*[96]

[95] H. E. Hosseini, J. F. Nixon, H. W. Kroto, S. Browstein, J. R. Morton, and K. F. Preston, *J. Chem. Soc., Chem. Commun.*, 1979, 653.

[96] H. W. Kroto, J. F. Nixon, N. P. C. Simmons, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1978, **100**, 446.

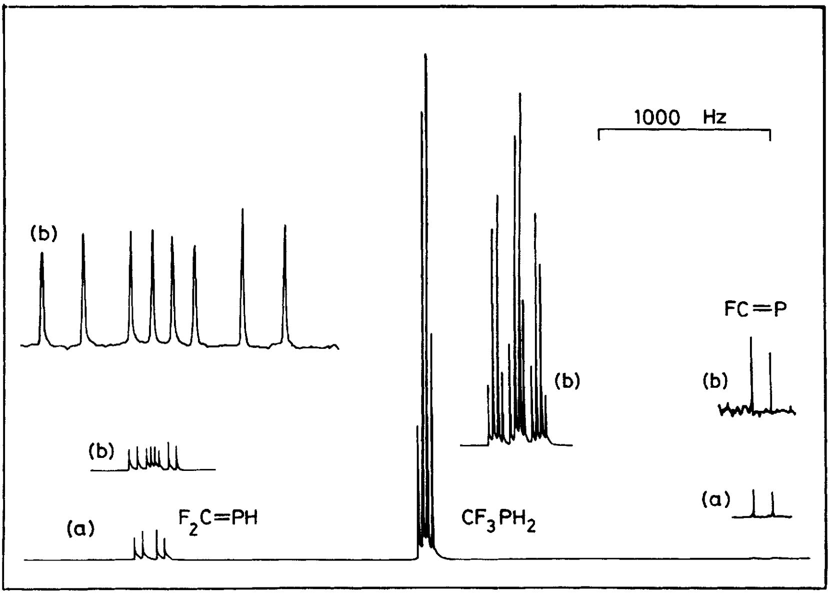

Figure 20 ^{31}P (ca. −80 °C) *n.m.r. spectra of the products of the reaction of* CF_3PH_2 *with* KOH *at room temperature.*[95] (*a*) ^{1}H *decoupled,* (*b*) ^{1}H *undecoupled*

recently PhCP and t-BuCP[97] have been studied, yielding useful information on the electronic behaviour of the C≡P group. In particular, it is worth noting that the n and π ionization energies for HCN are almost identical, whereas for HCP the π(C≡P) is the first at 10.79 eV and the P lone pair is the second at 12.86 eV.[92] Some ionization potential data are also collected in Table 5.

(vi) *Phospha-alkyne Complexes.* One of the more exciting prospects with phospha-alkynes is the possibility of making transition-metal complexes. A Pt complex of Bu^{t}C≡P has been made and its structure, as determined by *X*-ray analysis, is shown in Figure 22.[98] It is noteworthy that the angle ∠CCP has bent from 180° → 132° and the C≡P bond length has increased from *ca.* 1.544 Å (as in $CH_3C{\equiv}P$) in the free molecule to 1.672 Å in the complex reflecting the effects of back-bonding from the zero-valent platinum. The n.m.r. spectrum has also been measured.[98] Seyferth and Henderson have observed dechlorination of $RCCl_2PCl_2$ by $Co_2(CO)_8$ to form a phospha-alkyne complex.[99] A similar complex can be formed from $Co_2(CO)_8$ and free t-BuCP.[98]

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[97] J. C. T. R. Burckett-St. Laurent, M. A. King, H. W. Kroto, J. F. Nixon, and R. J. Suffolk, to be published.

[98] J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1981, 1141.

[99] D. Seyferth and R. S. Henderson, *J. Organomet. Chem.*, 1978, **162**, C35.

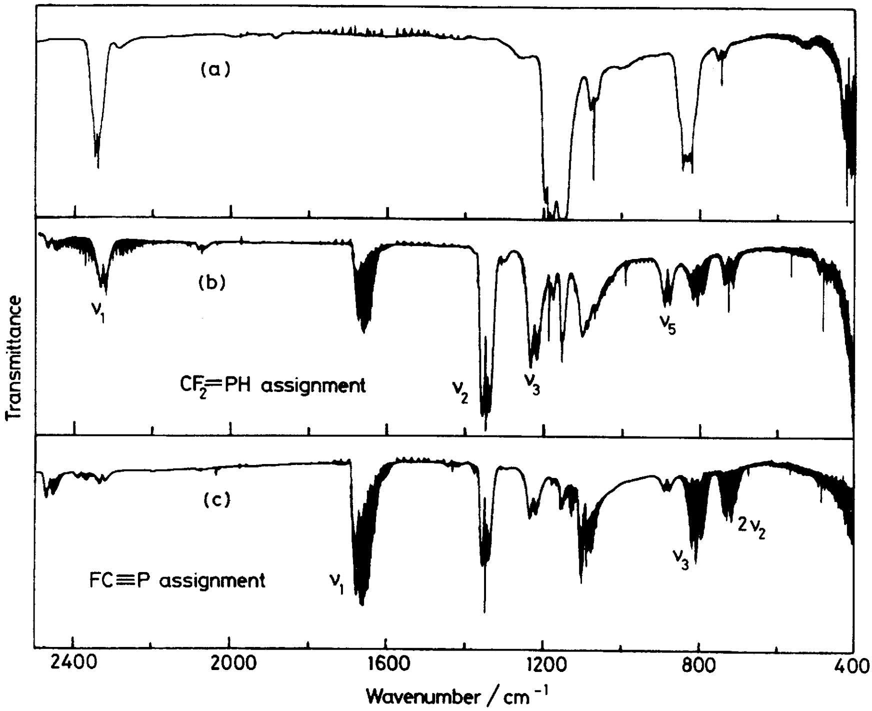

Figure 21 *The i.r. spectra obtained (a) for* CF_3PH_2, *(b) by passing* CF_3PH_2 *through a tube packed with* KOH, *(c) by double passage over* KOH.[79] *The strong band at* ca. 1170 *in (a) is the* C—P *stretch of* CF_3PH_2. *In (b) both* $CF_2{=}PH$ *and* FCP *appear and in (c)* FCP *is more intense relative to* $CF_2{=}PH$, *and* CF_3PH_2 *has been almost completely eliminated. In (b) the stronger* $CF_2{=}PH$ *features are* ν_1(PHstr), ν_2(C=Pstr), ν_3(CF_2asym str) *and* ν_5(CF_2sym 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-ynes

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-ynes. This involved the preparation of a range of simple poly-ynes, some of which are rather unstable, by a combination of traditional synthesis and novel reactions.

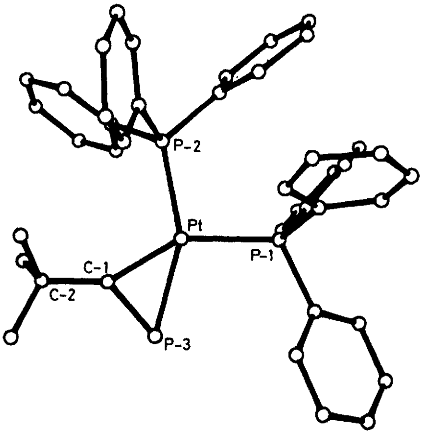

Figure 22 *The results of an* X*-ray analysis of the* t-BuC≡PPt[P(Ph)$_3$]$_2$ π *complex.*[98] ∠CCP *has changed from* 180° *in the free* t-BuCP *molecule to* 132° *in the complex*

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 HC≡C—C≡C—C≡N, coincided with the exciting breakthrough in detection of interstellar molecules by radio-astronomy[101–103] and the microwave measurements initiated a search for interstellar poly-ynes which has led to exciting and perplexing discoveries whose implications have still to be explained.

B. Microwave Spectra of Polyacetylenes.—In a typical synthesis, HC_5N[104] was made as shown in equation (30)

$$\begin{tikzcd}
\mathrm{ClCH_2C{\equiv}CCH_2Cl} \arrow[r, "\mathrm{KOH}"] & \mathrm{H(C{\equiv}C)_2H} \arrow[r, "\mathrm{RMgCl}", "\mathrm{Me_3SiCl}"'] & \mathrm{Me_3Si(C{\equiv}C)_2H} \arrow[d, "\mathrm{Et_3SnNEt_2}"] \\
\mathrm{H(C{\equiv}C)_2CH} & \mathrm{Me_3Si(C{\equiv}C)_2CN} \arrow[l, "\mathrm{Alumina}"'] & \mathrm{Me_3Si(C{\equiv}C)_2SnEt_3} \arrow[l, "\mathrm{CNCl}"']
\end{tikzcd} \qquad (30)$$

The triethyl tin group is preferentially replaced in step 4 resulting in $Me_3Si(C{\equiv}C)_2CN$. 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

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[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.

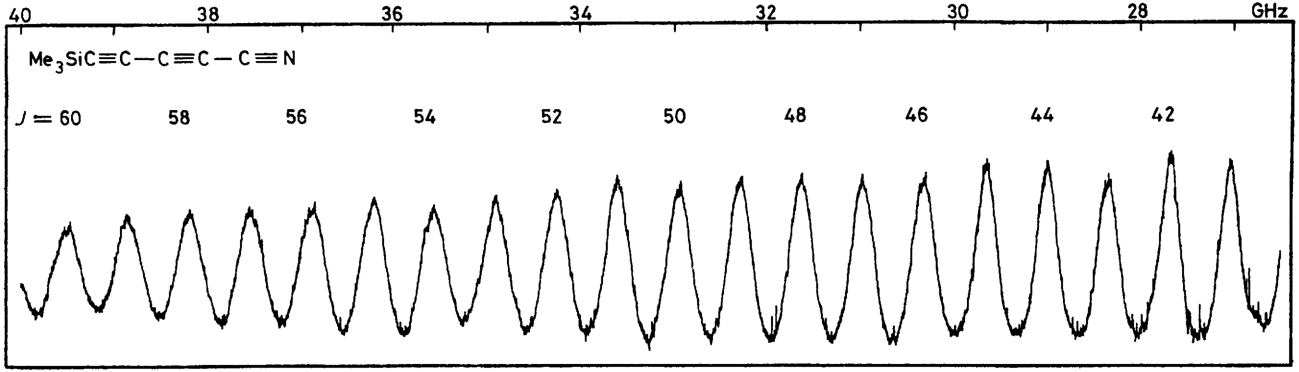


Figure 23 *The wide-scan microwave spectrum of* $Me_3SiC{\equiv}C{-}C{\equiv}C{-}CN$.[105] *Each of the bands for a given J consists of a multitude of* unresolved *lines for the various bending and torsional satellites as well as K components*

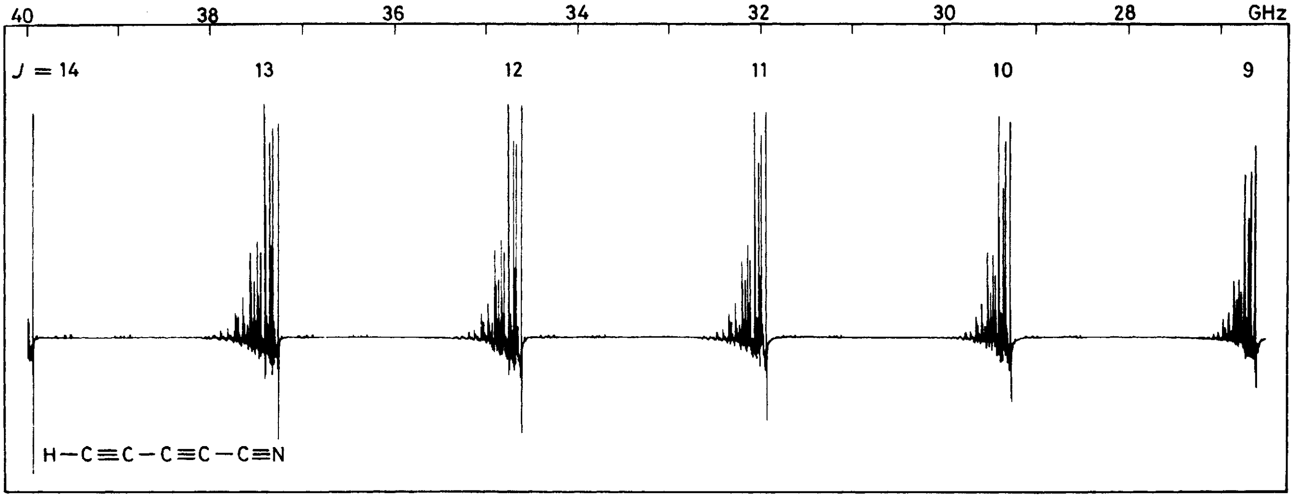


Figure 24 *The wide-scan microwave spectrum of* $HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$.[104] *Each J transition consists of the ground state line with an entourage of vibrational satellites. These are shown in more detail for this* $J = 14 \leftarrow 13$ *transition in Figure 25*

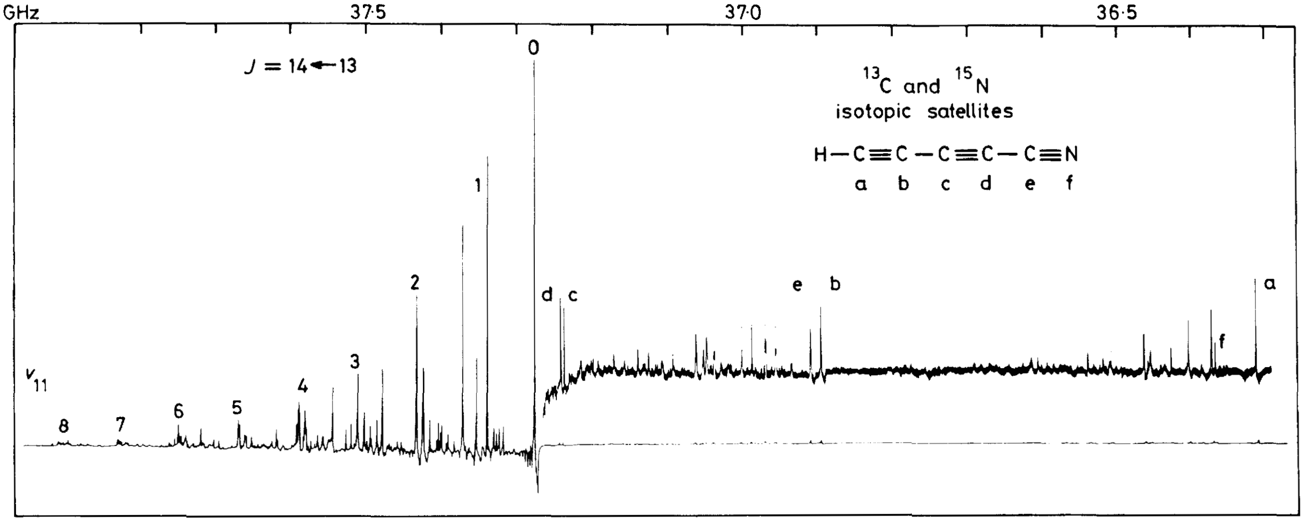


Figure 25 *The* $J = 14 \leftarrow 13$ *transitions of* HC_5N *under moderate resolution.*[104] *The bending vibrational satellites march out with exponential intensity to high frequency. On bending the molecule shortens, decreasing the moment of inertia and consequently increasing the average* B_0 *value 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* mr^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*

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 cyanobutadiyne $HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$ 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)

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

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.

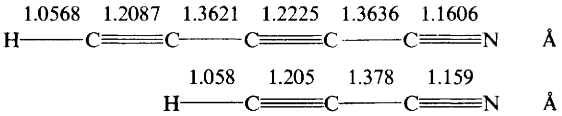
The vibrational satellites of HC_5N can also be analysed in detail on the basis of vibration–rotation theory of linear molecules. This has been carried out to as high as eight quanta of the lowest frequency bending vibration.[109]

A symmetric top has a much more complicated spectrum as shown in Figure 26 for $CH_3{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$.[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 $CH_3C{\equiv}P$, 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* $H-C\equiv C-C\equiv C-C\equiv N^a$

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



$$H\overset{1.0568}{-\!-\!-}C\overset{1.2087}{\equiv\!\equiv}C\overset{1.3621}{-\!-\!-}C\overset{1.2225}{\equiv\!\equiv}C\overset{1.3636}{-\!-\!-}C\overset{1.1606}{\equiv\!\equiv}N \quad \text{Å}$$

$$H\overset{1.058}{-\!-\!-}C\overset{1.205}{\equiv\!\equiv}C\overset{1.378}{-\!-\!-}C\overset{1.159}{\equiv\!\equiv}N \quad \text{Å}$$

(*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/amu Å^2 = 505391/B(MHz). (*f*) $\Delta I = I^* - I(H^{12}C_5{}^{14}N)$. (*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 colleagues[111] 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

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

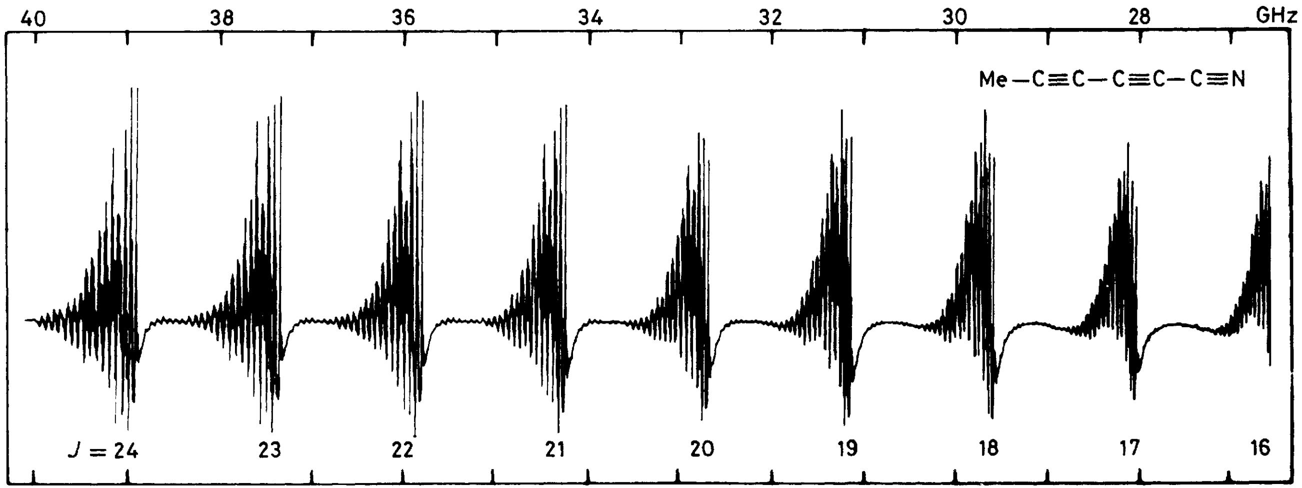

Figure 26 *Wide-band scan of the microwave spectrum of* $CH_3C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$.[110] *As in the case of* HC_5N *the first line at the RH end of each J group belongs to the vibrational ground state and the rest to bending vibrational satellites. The ground state lines can be resolved into* $|K|$ *multiplets under high resolution as shown in Figure 27*

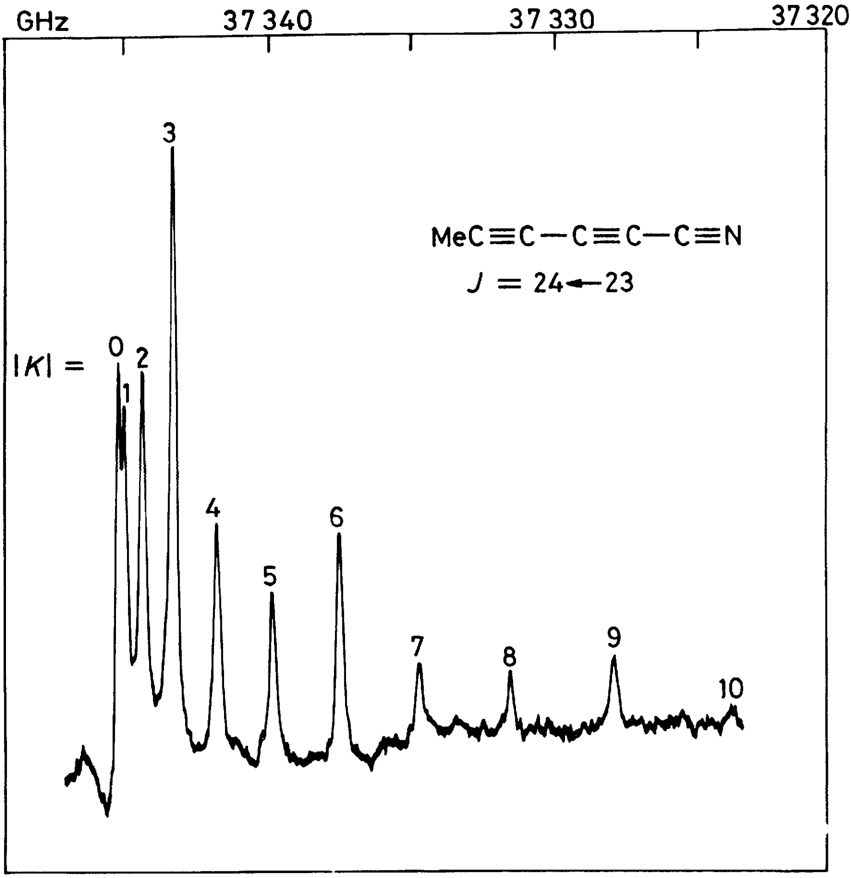

Figure 27 *Part of the* $|K|$ *structure of the* $J = 24 \leftarrow 23$ *transition of* $CH_3(C{\equiv}C)_2CN$.[110] *The higher* $|K|$ *levels are not sufficiently populated so the structure peters out at* $|K| > 10$. *Note the increased intensity of lines for* $|K|$ *a multiple of* 3 *in agreement with* C_{3v} *statistical weights*[3]

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 Malin[112] 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

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

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 radiotelescope 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-ynes, discovered as a result of the laboratory experiments discussed in the previous section which were, of course, initiated for quite a different purpose.

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* 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.

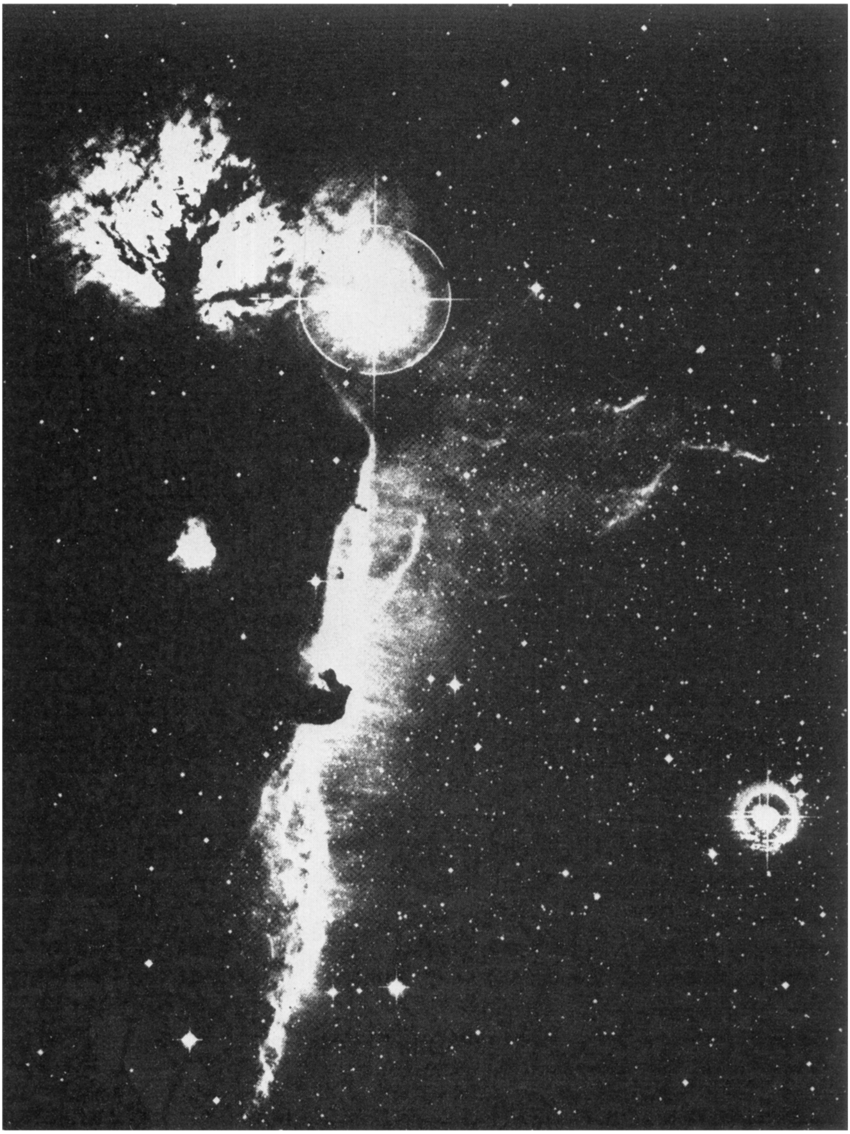

Figure 28 *The long bright emission nebula* IC434 *silhouetting the well known Horsehead dark cloud in the constellation of Orion (taken from Murdin, Allen, and Malin*[112] *UKSTU). North is up and East is left in this photograph. The bright star at the top end of* IC434 *is ζ Orionis, the left-hand 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*

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-ynes $\cdots C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C\cdots$?—As it happened, the study of the poly-ynes, in particular cyanobutadiyne $HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$, 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 $HC{\equiv}C{-}C{\equiv}N$, 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.*

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* 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 MacLeod[116] 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, 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 Barnard[120] 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 v (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

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[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.

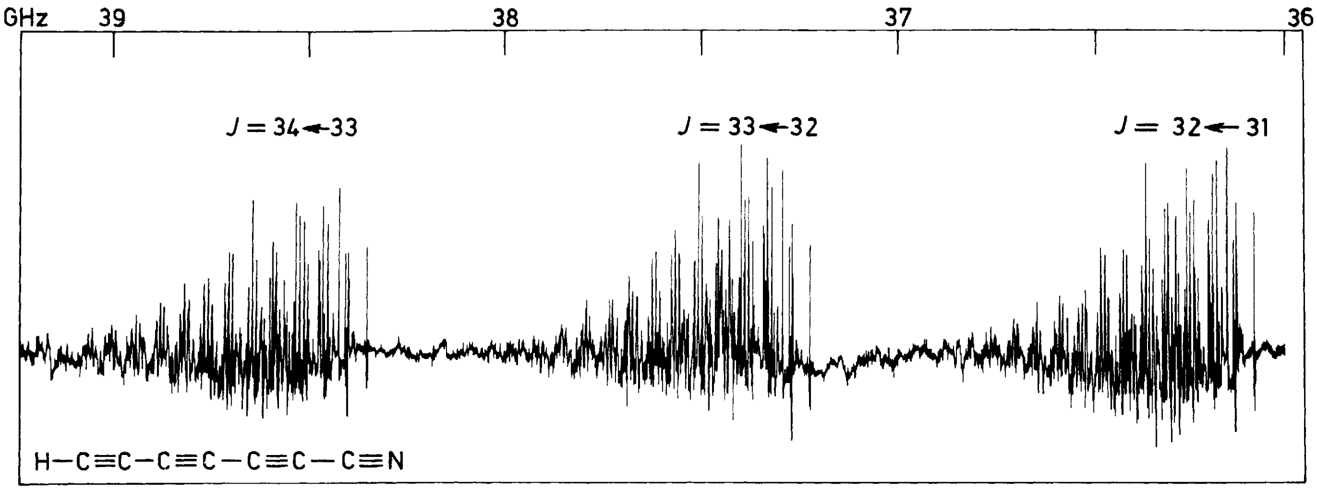

Figure 30 *Three* $\Delta J = +1$ *transitions in the microwave spectrum of* HC_7N.[121] *The RH line in each group belongs to the vibrational ground state; the rest are bending vibrational satellites and there are many of them because the molecule is long and readily flexes. In the cold clouds the temperature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

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

$J = 10 \leftarrow 9$ 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

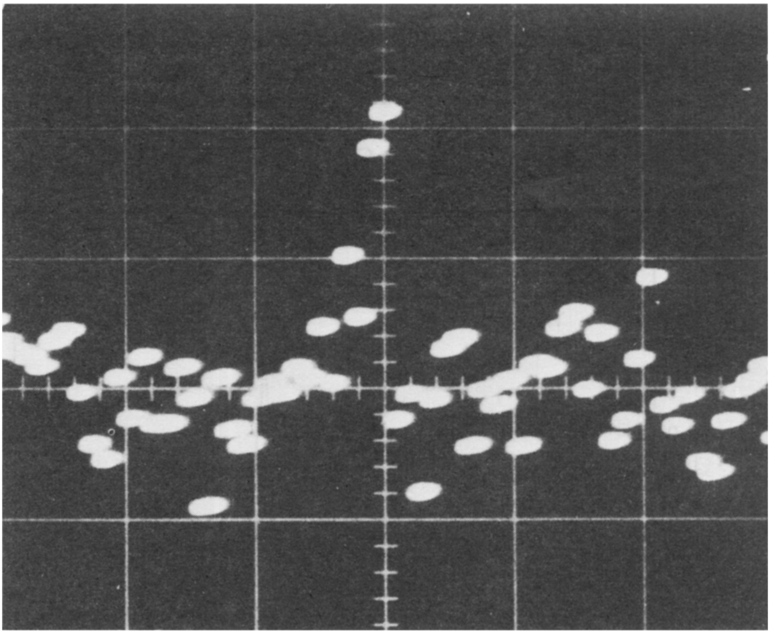

Figure 31 *A photograph of the raw data for the initial detection of interstellar* $HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$.[122] *Each dot represents data in a* 10 kHz *wide channel. The spectrum was observed from the cold cloud* TMC1 *which yields very narrow lines no more than* 10 kHz *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*

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* 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 Algonguin 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.

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

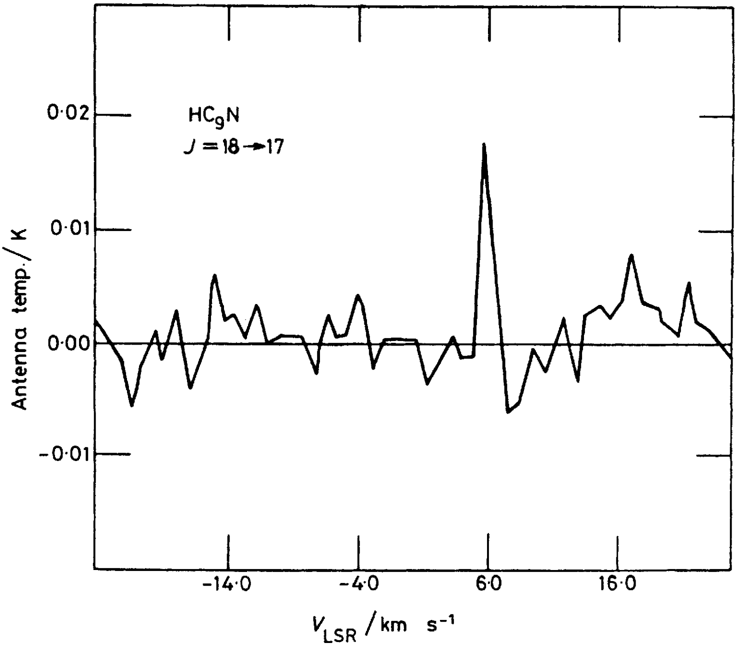

Figure 32 *The spectrum of* HC_9N *detected by radioastronomy. In astronomy the intensity is usually given in terms of the Antenna temperature. The abscissa indicates that the frequency of the signal differs from that in the laboratory by an amount (the Doppler Shift) consistent with a* 5.9 km s^{-1}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

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[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 poly-ynes 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 Lovas[56] as well as Hirota, Saito, and co-workers[128] 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, apposite 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

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* 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.

detection of free radicals, which decay too quickly, it is excellent for species of intermediate stability which last long enough effectively to fill a 1—2 metre active length at moderate flow rates.

Technical reasons have prevented the beautiful spectroscopic patterns from being displayed in early microwave studies. The data have, in the past, been presented as inedible tabulations of relatively large numbers which mask the patterns and preclude recognition. Indeed, it is the initial observation, together with abstract pattern recognition, which is the cathartic experience that drives this and many other types of research. As a consequence it has been a very important objective in this work that these patterns be displayed in the literature and in this review a range of textbook examples has been presented.

The general result of this work is that the chemistry of: $>C=S$, $>C=Se$, $-B=S$, $-B=Se$, $>C=P-$, and $-C\equiv P$ containing species has been either extended or initiated so that they can now take their place beside their well-studied first row counterparts, the carbonyls, imines, and nitriles and be considered as viable functional groups in their own right.

Some *specific* points about the various groups of molecules studied are discussed below.

A. Thiocarbonyls and Selenocarbonyls.—As far as thiocarbonyls are concerned they were the first group to be studied and were used to hone the experimental techniques. They were also rather easily handled, after all OCS is a well known species being, apart from the smell, rather well-behaved. Thiocarbonyls seem to be sufficiently close in stability to carbonyls that traditional chemistry can handle them except for the simplest ones such as $CH_2=S$. Even $Me_2C=S$ seems to be relatively stable. As well as the thiocarbonyls, the selenocarbonyls can also be studied though with somewhat more difficulty. The major technical problem is probably the incredible persistence of the smell and the apprehension with regard to selenium's reputation as a poison, a reputation almost entirely based on the properties of H_2Se. It is probably the close similarity between Se and S in organic configurations that is responsible for the blocking of metabolic pathways.

The results do indicate that with some modification of technique such molecules as $CH_2=S$ and $MeCH=S$ could be useful reactants with parallel chemical behaviour to the aldehydes and ketones.

B. Sulphidoboron Compounds.—It seems curious that oxoboron molecules seem to be *less* stable than the analogous sulphidoboron molecules. This is based on the circumstantial evidence that they have not been detected by the techniques that produced the sulphidoborons. The yields of the halides, especially ClBS, are excellent as witnessed by the p.e. data, but rather poor in the case of MeBS which presumably reflects the alternative reactions which the precursor may follow.

The structural data indicate that the $B=S$ bond length is relatively constant at 1.604 ± 0.004 Å for the analogues studied. The nitriles show a similar degree of bond length inflexibility. MeBS presents the first example of a bond between sp^3 hybridized carbon and sp hybridized boron. An increase of 0.066 Å occurs in r(C—B) between MeBS and $MeBF_2$ where it is 1.534 Å and 1.60 Å respectively. This is in good agreement with the ClBS/$ClBF_2$ system where it increases from 1.681 Å in ClBS by 0.047 Å to 1.728 Å in $ClBF_2$.

The mechanism for producing sulphidoborons is probably complicated. Detailed searches have not yielded any evidence for XSB isomers which, if formed, would probably be too short-lived for our detection techniques. An alternative mechanism follows from known reactions of Cl_2S_2 and boron. Cl_2S_2 decomposes above 300 °C to form Cl_2 and sulphur, and boron reacts with Cl_2 and sulphur at elevated temperatures to form BCl_3 and B_2S_2. Further, it is known that BCl_3 reacts with B_2O_3 to form ClBO.[129] Thus, an alternative reaction, equation (32), is possible.

$$Cl_2S_2 \xrightarrow{\Delta} Cl_2 + S \xrightarrow[\Delta]{B} BCl_3 + B_2S_3 \xrightarrow{\Delta} ClBS \qquad (32)$$

The photoelectron data on ClBS have provided circumstantial evidence for such a scheme in that large quantities of BCl_3 are produced at temperatures below those needed to form ClBS.

From the analysis of the quadrupole structure of ClBS an estimate of the character of the Cl—B bond can be obtained. This indicates that the bond has 0.5 σ character, 0.23 π character, and 0.27 ionic character.[48]

An almost complete, apart from IBS, photoelectron correlation diagram can now be drawn as shown in Figure 14. This shows that for the π(B=S) system there is a gradual destabilization with substituent. The order of stability is: H > F > Cl > Br in line with an increase in electron density due to the effects of hyperconfiguration. In the σ(B=S) system the introduction of F stabilizes this orbital in line with the expected withdrawing inductive effects. The effect of Cl and Br in this case is negligible.

Preliminary theoretical calculations indicate some interesting features about the XB=S system which relate to the question of whether there is a double or triple bond between boron and sulphur. There are two electrons in the σ(BS) orbital and four in the degenerate π(BS) orbitals, so one might expect a major contribution from a valence configuration such as $X\overset{-}{B}\equiv\overset{+}{S}$ implying a build-up of charge on the boron. This does not appear to be the case as the boron, at least according to preliminary Gaussian 70 calculations, is effectively uncharged. It turns out that the electron density in the π orbitals resides mainly on the sulphur atom and the two π bonds are roughly half-strength. The initial indication is that the net effect is roughly that of a double bond because the π orbitals have 50:50 bonding:non-bonding character.

C. Phospha-alkenes and Phospha-alkynes.—The results on phospha-alkenes and phospha-alkynes have shown that the family resemblance between P and N in multiple bond configurations is considerably closer than chemists realised. In fact

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[129] J. Blauer and M. Forber, *Trans. Faraday Soc.*, 1962, **58**, 2090.

it is somewhat surprising, in the light of such results as the ease of production of FCP and the stability of t-BuCP as well as the big hints implicit in the existence of HC≡P and phosphabenzene, that the field did not open up much sooner. The reason for the lack of awareness was probably the fact that these compounds are *just* past the threshold of attack by traditional chemical techniques. They are *only just* past this threshold as such molecules as MeCP can be retrieved after trapping, but this is not the case for the sulphidoborons which appear to form trimers before revaporizing.

In these experiments there has also been no evidence for isomers of the form XPC analogous to the isonitriles.

From the general structural study one can obtain the following covalent radii for phosphorus.

	P	C	Sum		
sp	0.94	0.60	1.54	Å	$CH_3C{\equiv}P$
sp^2	1.00	0.67	1.67	Å	$CH_2{=}PH$
aromatic sp^2	1.03	0.70	1.73	Å	C_5H_5P
sp^3	1.07	0.77	1.84	Å	CH_3PH_2

The photoelectron data indicate that the $\pi(C{\equiv}P)$ orbital is the HOMO which fits in nicely with the fact that π-complexes such as the Pt compound, Figure 22, can be made. In the case of HCN the σ and π orbitals have almost identical ionization energies in line with the co-ordinating properties of nitriles. In some respects, particularly in its co-ordinating ability, HC≡P behaves more like HC≡CH than HC≡N.

D. Multiply Bonded Si.—An important series of molecules represented on the CH_2O cube in Figure 1 has not featured in the experimental work summarized in previous sections. The sila-alkene family related to $CH_2{=}SiH_2$ is absent, though not for want of trying. As pointed out in Section 1, the techniques applied have not in general involved the custom construction of equipment designed to catch very elusive species (*i.e.* species with lifetimes of *ca.* 10^{-3}—10^{-6} s) but rather are aimed at those which are just fickle (*i.e.* lifetimes of *ca.* 1 s). Our experiments on Si=X species have indicated that they have very elusive spirits indeed, with reactivities comparable with those of small free radicals.

The family resemblance between C and Si is very much less obvious and the generation gap that exists is perhaps most spectacularly exemplified by the difference between a sample of CO_2 and a sample of SiO_2.

The reluctance of Si=X species to submit to the techniques of Section 2 led to a theoretical study of the problem as a last resort.[130,131] This showed that Si has a strong tendency to remain *divalent* which manifests itself critically during attempts to produce multivalent configurations. This tendency is experimentally apparent in the relative stability of SiF_2 compared with that of CF_2, which readily forms $CF_2{=}CF_2$.

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[130] J. N. Murrell, H. W. Kroto, and M. F. Guest, *J. Chem. Soc., Chem. Commun.*, 1977, 619.

[131] H. W. Kroto, J. N. Murrell, A. Al-Derzi, and M. F. Guest, *Astrophys. J.*, 1978, **218**, 886.

Some early results of Gusel'nikov and Flowers[132] presented circumstantial evidence for $>Si=C<$ type intermediates in pyrolysis experiments on cyclic silaethenes. More recently Brookes *et al.*[133] have succeeded in using large stabilizing groups to form such molecules as $(Me_3Si)_2Si=C(OSiMe_3)$adamantyl which has been characterized by *X*-ray analysis. A very interesting result was obtained by Leclercq and Dubois[134] who detected the transient species $CH_2=Si$ during flash discharge experiments in $MeSiH_3$. This observation is in circumstantial agreement with the theoretical prediction that Si prefers to be divalent and that in this case $CH_2=Si$ is much more stable than $HC\equiv SiH$.[130] This study also indicates that $HN=Si$ is much more stable than $HSi\equiv N$, which is of course a reversal of the HNC/HCN situation.[130,131]

E. Poly-ynes.—The original reason for studying the poly-ynes lay in their simplicity and the consequent tractability of their rotational spectra. In addition their dynamic behaviour should be simpler than that manifested by other molecules. The spectra and the basic analysis have already been discussed and the resulting data show some interesting points. The accurate structural study Table 6 provides a textbook example of delocalization in extended conjugated systems. As the conjugated system extends from HC_3N to HC_5N delocalization *increases* the lengths of the triple bonds and *decreases* the lengths of the single bonds, expecially near the middle of the chain. For instance $r(C\equiv C)$ increases from 1.205 Å for HC_3N to 1.2225 Å for HC_5N. The bond lengths show a general trend which is manifested by the success of the extrapolation technique used by Oka to estimate the B_0 values (previous section). A second indicator of good behaviour is the excellent transferability of structural data. This has recently been shown by $N\equiv C-C\equiv C-C\equiv P$ whose experimental B_0 value was found to be 873.480 MHz.[85] This can be compared with an estimated value of 873.66 MHz based on $[N\equiv C-C\equiv C]$ lengths taken directly from the appropriate part of HC_5N and a $[C-C\equiv P]$ structure taken from that of $N\equiv C-C\equiv P$.

The vibration-rotation analysis for such species is clearly quite severe as indicated by Figures 25 and 30. An analysis for HC_5N has been carried out which has shown that the transitions involving highly excited vibrational modes are well explained by the standard theory which governs general vibration-rotation behaviour.[109] This was a little surprising as the instinctive feeling is that molecules in such states are very bent systems on average, and that a theory based, as this was, on a small amplitude approximation might show signs of breakdown.

F. Interstellar Poly-ynes.—The origin of interstellar molecules has been the subject of numerous studies and radio observations have instigated much

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[132] L. E. Gusel'nikov and M. C. Flowers, *J. Chem. Soc., Chem. Commun.*, 1967, 864.

[133] A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, and R. K. Kallury, *J. Chem. Soc., Chem. Commun.*, 1981, 191.

[134] H. Leclercq and I. Dubois, *J. Mol. Spectrosc.*, 1979, **76**, 39.

recent work. In particular, gas phase ion-molecule reactions and grain surface catalysis have been invoked. The detection of long chains, however, has presented severe problems to the acceptance of these processes. It is certainly not clear that ion-molecule reactions can build up such chains preferentially with respect to branched species, especially as branched ions are generally expected to be more stable. Indeed, if there are analogous, branched hydrocarbon species in commensurate numbers with the C_n chain molecules, the clouds must contain significantly more molecules than ever considered possible. It is also not at all clear that the chains can be formed on grains as it is seemingly impossible for them to desorb at the low temperatures that exist in clouds such as TMC1 (*ca.* 10—30 K). The chemistry is not clear but the most recent results do indicate that some molecules are formed in the envelopes of cool stars. The cool star IRC+10216, which has a high carbon to oxygen ratio, has now been shown to be pumping out molecules, in particular the chains. In addition, it seems to be pumping out grains. It may well be that in these stars grains and chains are formed at roughly the same time but whether there are enough of these stars to account for the colossal quantities of molecules now known to exist is not clear.

Suffice it to say, the interstellar studies have shown that some very long molecules exist in the space between the stars. They may be very long indeed and their relationship with grains is far from being understood. In fact, it is only now that a possible relationship can even be contemplated.[103] The long chains may be an intermediate form of carbon, between atoms and small molecules such as C, C_2, and C_3, which are well known, and particles with high carbon content such as soot. Another factor is that chains of this length must be good scatterers of radiation due to their electronic properties and so it is even possible that they *are* the grains.[103] Douglas has suggested that the chains give rise to the so-called Diffuse Interstellar Lines.[135] These are a set of some 40 broad interstellar features in the visible spectroscopic region which have perplexed astronomers for nearly 50 years.

The latest data indicate that some new experimental and theoretical work on the mechanism of precipitation of particles from carbon vapour is necessary. The interaction of radiation with these chains also should be studied to see how it might relate to the quantitative interstellar scattering characteristics.

Finally, the interesting general point is that these molecular clouds are the raw material out of which stars and particularly planets form. The mechanism of planet formation is still far from clear and indeed the relationship of the molecules in these clouds with those in the earth's atmosphere is even less clear. We now know that molecules are formed in stars and pushed out into space. There are now, therefore, three known ways in which bio-emotive molecules, such as glycine, can be formed: (1) in the biosphere by Urey-Miller type processes; (2) in the cold interstellar clouds by ion-molecule reactions and perhaps also by grain catalysed processes; (3) in reactions in circumstellar shells.

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[135] A. E. Douglas, *Nature*, 1977, **269**, 130.

There is clearly an inexorable drive to form the molecules that are the building blocks of life. Indeed, the new results suggest that one should consider whether the circumstellar molecules might actually have survived the transition from circumstellar shell to the molecular cloud, protected from photolysis by starlight in a symbiotic relationship with the grains, and perhaps accreted into planetary atmospheres more or less intact during a later cooler phase of planet formation. The new results herald a new look at not only the origin of the biosphere but also a new look at the mechanism of grain formation and grain identity, as well as the formation of larger objects such as planets.

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