

## 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

\* 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.

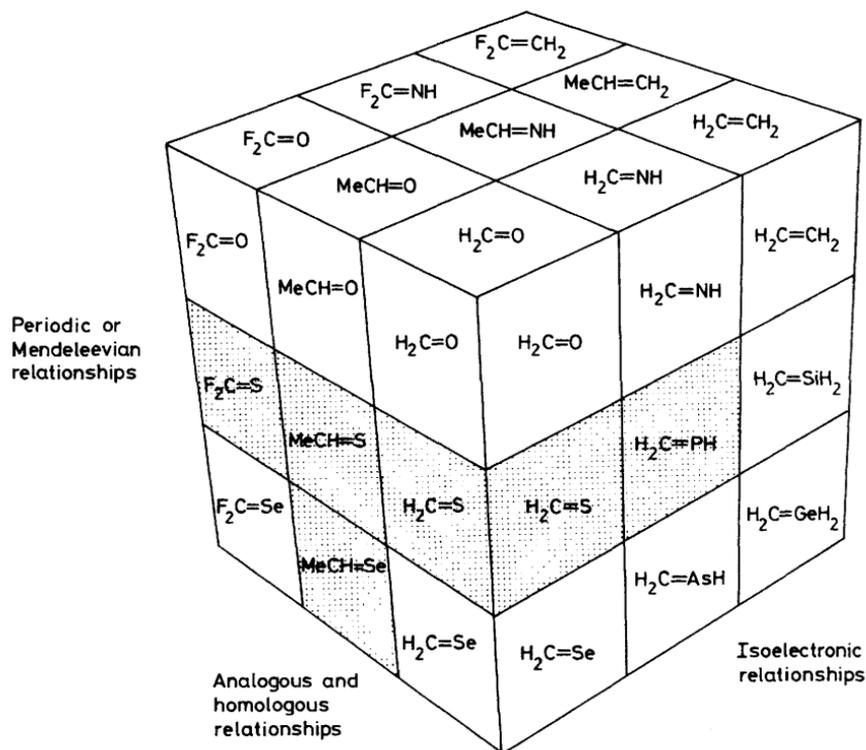
## Semistable Molecules in the Laboratory and in Space

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  $\text{CH}_2\text{O}$  is given in Figure 1.

On this  $\text{CH}_2\text{O}$  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

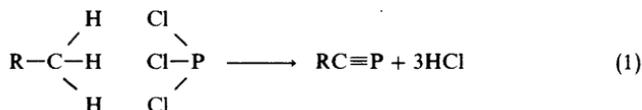


**Figure 1** Chemical cube showing some molecules related to formaldehyde  $\text{H}_2\text{C}=\text{O}$ . Periodic group relationships are given by vertical steps, steps to the left are possible analogously and homogeneously related species, and steps to the right are isoelectronically related species. 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  $\text{CH}_2=\text{SiH}_2$  be made? Not only that, could  $\text{CH}_2=\text{PH}$  the P analogue of  $\text{CH}_2=\text{NH}$  be made, or for that matter,  $\text{CH}_2=\text{S}$  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  $\text{CH}_2\text{O}$  and  $\text{HCN}$  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  $\text{CH}_2\text{C}\equiv\text{P}$  would be similar to the well known molecule  $\text{CH}_3\text{C}\equiv\text{N}$ . 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  $\text{C}\equiv\text{P}$  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.



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.*  $100\text{ kHz} \sim 0.33 \times 10^{-5}\text{ cm}^{-1}$ ) its application in this work has often been facilitated by photoelectron studies where features seldom have bandwidths less than  $20\text{ meV} \sim 160\text{ cm}^{-1}$  ( $1\text{ eV} \equiv 8065\text{ cm}^{-1}$ ). 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

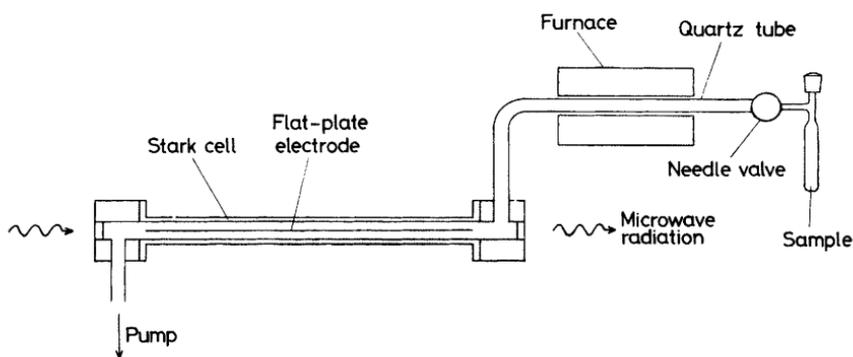
## Semistable Molecules in the Laboratory and in Space

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  $\mu$ Hg).



**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.<sup>1-3</sup> The very high resolution available, together with the high degree of pattern specificity allows such moderately complex molecules as ethanol EtOH, glycine NH<sub>2</sub>CH<sub>2</sub>COOH and cyanoethene CH<sub>2</sub>=CHC≡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)

$$H_r = AJ_A^2 + BJ_B^2 + CJ_C^2 \quad (2)$$

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  $A = 1/2I_A \dots$  etc.\* By convention  $I_A \leq I_B \leq I_C$  and therefore  $A \geq B \geq C$ . The solution of  $H_r$  depends on the type of molecule and the results can be summarized as follows:<sup>3</sup> *Linear molecules* such as CO, OCS, and HC≡C—C≡N have  $B = C$  and  $J_A \rightarrow 0$  and the resulting energy is given by the familiar expression (3)

$$E(J) = BJ(J + 1) \quad (3)$$

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

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

† The units of  $E$  (and  $\Delta E$  for a transition) will be governed in these expressions by the units of the rotational constant, usually Hz or cm<sup>-1</sup>

<sup>1</sup> C. H. Townes and A. L. Schawlow, 'Microwave Spectroscopy', McGraw-Hill, 1955.

<sup>2</sup> W. Gordy and R. L. Cook, 'Microwave Molecular Spectra', Interscience, 1970.

<sup>3</sup> H. W. Kroto, 'Molecular Rotation Spectra', John Wiley, London, 1975.

## Semistable Molecules in the Laboratory and in Space

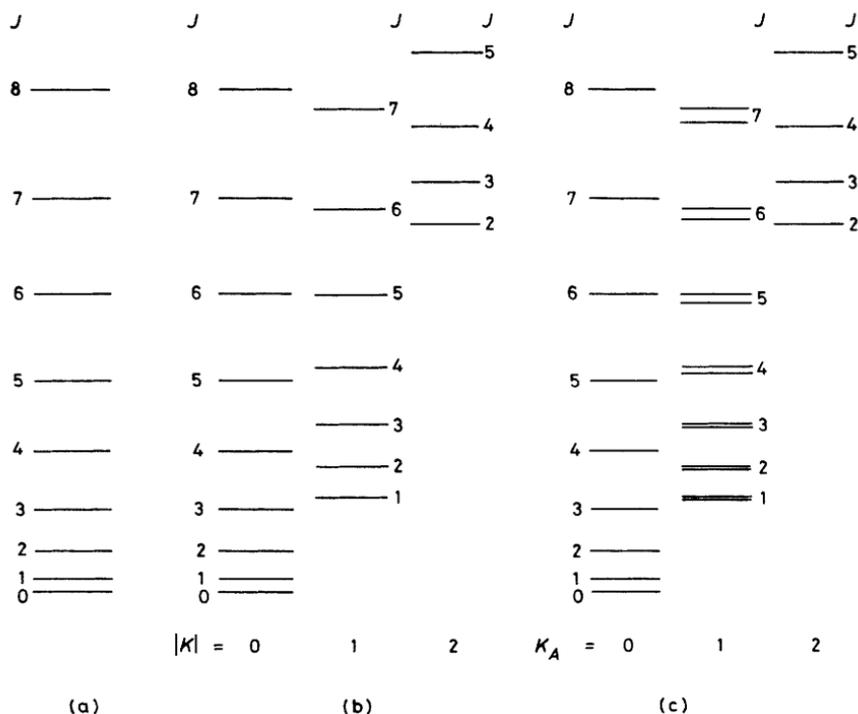
such as  $\text{CH}_3\text{C}\equiv\text{N}$  or  $\text{SF}_5\text{Cl}$  which are prolate (i.e. cigar-shaped) have  $A > B = C$ , can spin about their symmetry axes with associated quantum number  $K$ , and the energy is given by equation (4).

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

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  $\text{NH}_3$  and  $\text{C}_6\text{H}_6$ . Spherical tops such as  $\text{CH}_4$  and  $\text{SF}_6$  which have  $A = B = C$  are rather complicated and will not be dealt with here as their spectra<sup>4</sup> 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

<sup>4</sup> 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)<sup>3</sup>

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

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).

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

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).

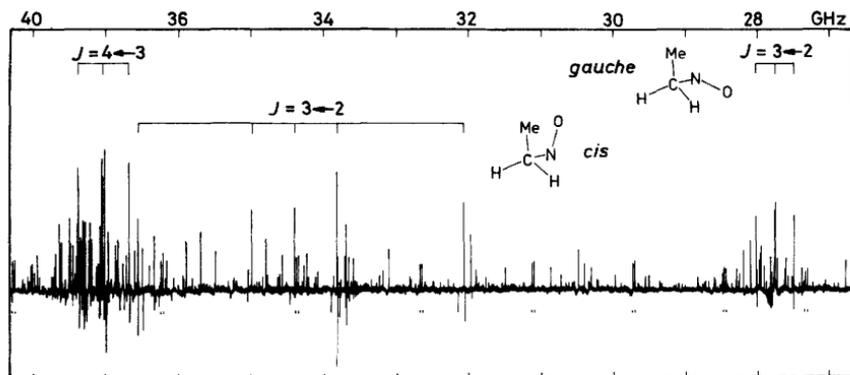
$$\Delta E(J, K_A) = 2\bar{B}(J+1) \pm \frac{1}{2}\delta_{K_A,1}(B - C)(J+1) + \cdots \quad (7)$$

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

## Semistable Molecules in the Laboratory and in Space

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.<sup>5</sup> The bands of two conformers are



**Figure 4** The microwave spectra of EtNO.<sup>5</sup> 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 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

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.

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

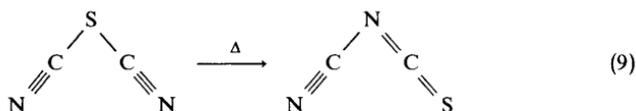
<sup>5</sup> A. P. Cox, J. A. Hardy, H. W. Kroto, M. Maier, and D. R. J. Milverton, to be published.

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).

$$E_{\text{ionization}} = h\nu - E_{\text{kin}} \quad (8)$$

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.<sup>6</sup>

**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  $\text{S}(\text{CN})_2$ . In these experiments a new microwave spectrum (Figure 5) was detected.<sup>7</sup> 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.



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).

$$I_B = \sum_n m_n (r_A^2 + r_C^2)_n = \sum_n m_n (r_A^2)_n \quad (10)$$

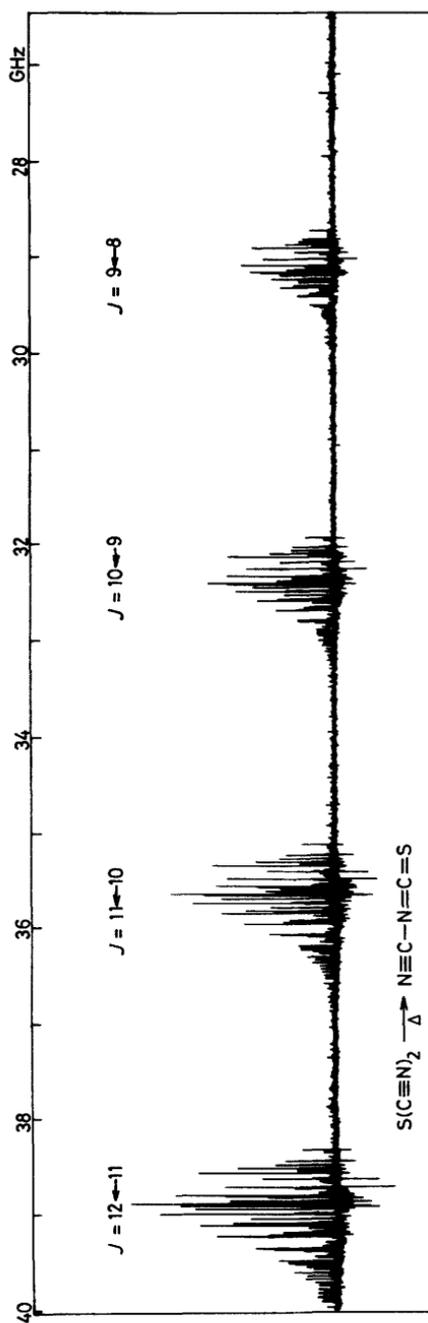
According to the approximate dimensions in Figure 6 we see that:

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

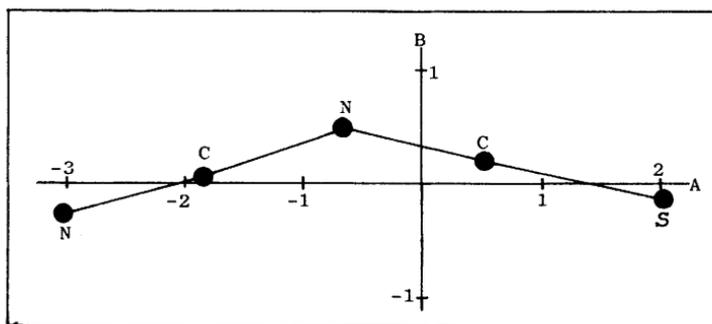
<sup>6</sup> J. M. Dyke, N. Jonathan, and A. Morris, *Int. Rev. Phys. Chem.*, 1982, 2, 3.

<sup>7</sup> M. A. King and H. W. Kroto, *J. Chem. Soc., Chem. Commun.*, 1980, 606.

## Semistable Molecules in the Laboratory and in Space



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



**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.  $150^\circ$ .  $I_B$ , the moment of inertia about the B axis, is determined by  $\sum_n m_n (r_A^n)^2$  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.<sup>8</sup>

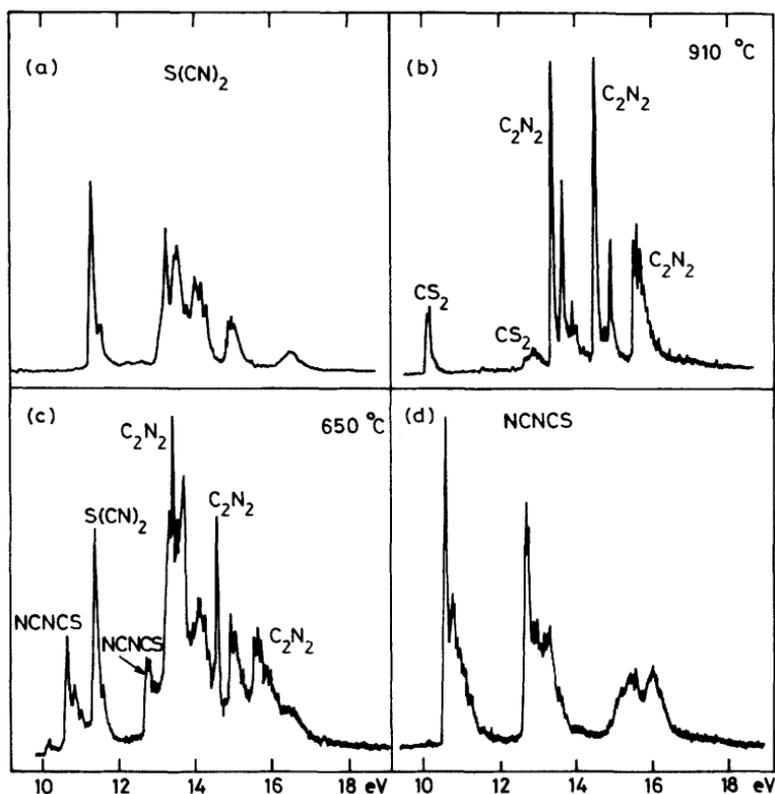
The initial attempt to detect NCNCS by photoelectron spectroscopy (Figure 7b) was unsuccessful, resulting in product peaks which were readily identified with  $\text{CS}_2$  and  $\text{C}_2\text{N}_2$ , neither of which have permanent dipole moments and are therefore not detectable by our microwave spectrometer. Parallel experiments using a small quadrupole mass spectrometer confirmed this. The photoelectron and mass spectroscopic data thus immediately indicated that at ca.  $1000^\circ\text{C}$  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.<sup>9</sup> 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,

\* 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  $C_0$ .

<sup>8</sup> M. A. King, H. W. Kroto, and B. M. Landsberg, to be published.

<sup>9</sup> M. A. King and H. W. Kroto, to be published.

## Semistable Molecules in the Laboratory and in Space



**Figure 7** (a) The p.e. spectrum of  $S(CN)_2$ . (b) The p.e. spectrum of  $S(CN)_2$  pyrolysed at  $910^\circ C$ . (c) The p.e. spectrum of  $S(CN)_2$  pyrolysed at  $650^\circ C$ . (d) The p.e. spectrum obtained by reevaporizing NCNCS from a sample produced under the conditions of (c) and trapped<sup>9</sup>

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<sup>10</sup>

<sup>10</sup> C. R. Noller, *Chemistry of Organic Compounds*, W. B. Saunders Co., Philadelphia, 1957, p. 282.