

# RECENT RESULTS AND FUTURE TRENDS IN MICROWAVE SPECTROSCOPY

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## INTRODUCTION

Microwave spectroscopy, as a means of precise study of free molecules, has of course been a mature field for some time. The assignment of the rotation spectrum of the ground state of an abundant isotopic form of a substance has long ceased to be regarded as anything more than a preliminary to a laborious, but often very rewarding, elucidation of various types of detailed molecular information. The recognition of this maturity has however been especially noticeable in the past two or three years. In particular, the contributions of microwave spectroscopy to our knowledge of intramolecular motions have become so significant that the method is now accepted as a powerful means of studying the internal mechanics of molecules, in addition to their geometry and electronic structure. These advances have naturally occurred through simultaneous refinements in the experimental, theoretical and computational methods. Some of the most important phases of development are now well-known, and it would be inappropriate to repeat details of them here. I shall attempt rather to indicate those aspects of technique and interpretation which are particularly important for the present and the immediate future, and to illustrate them from recent work.

## EXPERIMENTAL ASPECTS

### Frequency range

While the extension of microwave methods towards shorter wavelengths is always important, I shall not discuss it in detail, not least because the paper by Gordy<sup>1</sup> at this meeting will cover recent developments far better than I could. Perhaps I could be allowed to comment that spectroscopically useful radiation at over a million megacycles has been obtained in Great Britain by Froome and Bradsell<sup>2</sup> using high-pressure arc harmonic generators, and that the paper by Knapp and Martin<sup>3</sup> at this meeting will have told us more about work by this promising technique. In keeping with the now considerable overlap of the microwave and infrared ranges, we may anticipate more use of detectors developed from the infrared side, such as the indium antimonide photodetector<sup>4</sup> with its very short response time.

Although rotation spectra can now be studied in absorption by radio methods over at least ten octaves, most of the important results are obtained in the so called conventional range of the radar bands. This, however, also involves a widening span of frequency, commonly now about 8–80 Gc/s, as component development continues. Increasing use is made of backward wave oscillators as sources. These tubes have been strikingly developed<sup>5</sup>, and, though often costly, have advantages over reflex klystrons.

Emission spectroscopy by beam-maser techniques now also covers a very large frequency range, extending studies of rotation spectra down to a few megacycles<sup>6</sup>.

### **Spectrometer sensitivity**

The immense sensitivity which can now be attained with absorption spectrometers in the conventional range is the most important feature of the techniques for present and future studies. Stark effect modulation and phase-sensitive detection with very narrow band-pass have for some time enabled many workers to detect lines with absorption coefficients as low as about  $10^{-9}$   $\text{cm}^{-1}$ , and with frequency-stabilized sources and scanning speeds reduced to a megacycle per hour or less, sensitivities 10–100 times greater have been attained for special purposes. Such sensitivities, allowing detection of transitions which would only produce a few per cent absorption in thousands of miles of path, are a remarkable and invaluable result of the electronic nature of microwave methods. Component development, particularly in the field of frequency control, where we can now choose from several commercial instruments, has permitted such extreme sensitivities to be available as a routine in the future. The potentialities of this type of development have been demonstrated in particular by Gwinn *et al.*<sup>7,8</sup>. The retention of the high resolution in the study of weak lines is an important feature.

The tediousness of slow scanning work and the risk of destructive interference by non-stochastic noise will be lessened in the future by the use of "spectrum accumulators", of which there are several variously named commercial models. In these, the averaged results of repeated faster scans are observed until the necessary enhancement of signal-to-noise ratio is obtained<sup>9</sup>. Source stabilization will still be necessary and the total time required to obtain a spectrum will remain large. Since, however, individual scans can be fast, the method is attractive for short-lived molecular species.

Tobler and Bauder<sup>10</sup>, show, at this meeting, how extreme sensitivities were necessary for the work on azulene.

### **Intensity measurements**

As a result of a considerable period of work, particularly at Harvard<sup>11</sup> and at Utrecht<sup>12</sup>, microwave intensity measurements have achieved the status of reliability. Their use in assigning spectra and in other ways, which is already growing, will clearly become a regular feature. Esbitt and Wilson<sup>11</sup> showed that straightforward refinements of conventional spectrometers, particularly the use of ferrite isolators to limit standing wave effects, can permit relative intensity measurements accurate to a few per cent, and several later publications have shown the value of this facility.

Intensity work is inevitably associated with the possibility of chemical analysis by means of microwave spectroscopy, the potentialities and limitations of which have been frequently discussed. Perhaps it will be easier to interest our commercial colleagues in this practical aspect of microwaves, now that a commercial microwave spectrometer has been placed on the market. This very welcome and important development we owe to the

Hewlett-Packard Company<sup>13</sup>, and features of the instrument will be discussed by Harrington<sup>14</sup> at this meeting. I shall merely note here that this is a very stable and sensitive spectrometer, incorporating novel features, and that its capabilities for identification and estimation of substances, or indeed for purely spectroscopic studies, look very impressive.

### Double-radiation methods

Closely associated with intensity studies are investigations of changes in strengths and shapes of lines caused by simultaneous irradiation with a second frequency which corresponds to another transition involving one of the levels concerned with the line. Early work in this field was carried out by Battaglia, Gozzini, and Polacco<sup>15</sup> in Pisa, and by Shimoda and Yajima<sup>16</sup>, who emphasize that detection of certain transitions can be facilitated in such ways. Cox, Flynn and Wilson<sup>17</sup> have now published a systematic study of such effects and established the reliability of experimental methods for such work. While details of the line shapes are important and follow expectations from the theory<sup>18</sup> of three-level systems subjected to double radiation, the main interest for microwave spectroscopists springs from the fact that the levels involved in transitions in complex spectra can be checked by such methods. Several applications to confirm (or reject) assignments are described by Cox, Flynn and Wilson<sup>17</sup>, and an application of this type in the case of methyl vinyl ether will be discussed at this meeting by Cahill, Gold and Owen<sup>19</sup>. Like intensity studies, double resonance methods are likely to become common practice.

Double resonance experiments with selected *M*-components of Stark patterns<sup>17</sup> give interesting information on collisional transitions of molecules. Similar experiments have been conducted<sup>20</sup> with selected nuclear quadrupole components of spectra. Thus here also, a variety of new possibilities for study has become evident.

### Other special techniques

After earlier discouragements, work on unstable species is enjoying better success. At this meeting Lide and Powell<sup>21</sup> will describe studies of free radicals<sup>22</sup>. High-temperature work by Lide, Cahill and Gold<sup>23</sup> has also succeeded with cells of simple structure. Special cells for accurate studies of dipole moments and molecular polarizabilities will be discussed at this meeting by Laurie and Muenter<sup>24</sup>. There seems a general need in the future for improvements in the uniformity and range of Stark fields employed in regular spectral measurements.

## INTERPRETATION OF SPECTRA

The accumulation of spectroscopic measurements and derived data is now so great that we welcome the publication of the first volumes of the compilation of such data by the National Bureau of Standards<sup>25</sup>. Other compilations, from the University of Freiburg<sup>26</sup> and by Favero<sup>27</sup>, continue to be very valuable.

If we ignore the purely practical aspect of identification of substances by their lines, whether assigned or not, the primary objective of all micro-

wave studies is the assignment of rotational constants for the ground state of the substance concerned. A variety of special aspects then come into consideration depending on the molecule studied. In surveying some recent investigations, I have adopted this approach, which is essentially that of the experimentalist.

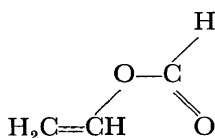
### Ground state constants

There continue to be a small proportion of cases where assignments can be made immediately and from which structural information can be derived. A simple example is  $\text{XeOF}_4$ <sup>28</sup> which gives symmetric-top spectra in agreement with  $C_{4v}$  symmetry.

In the paper by Gerry, Sugden and Thompson<sup>29</sup>, at this meeting,  $C_{3v}$  symmetry is proved by the observation of a symmetric-top spectrum for silyl isocyanate. In all such cases, however, the problem at once becomes one of more detailed analysis.

With asymmetric rotors, the assignment for the ground state of the main species, while often a longer process, can still frequently provide at once useful structural information. The computational aids which often make the assignment a relatively straightforward task are now well-known. Attention may be directed to the very extensive  $E_\kappa$  tables published by the Grumman Aircraft Corporation<sup>30</sup>, now extending to  $J = 18$  at intervals in  $\kappa$  of 0.001. The tables from the University of Freiburg<sup>31</sup> are also very valuable, containing some additional useful quantities such as  $\partial E_\kappa / \partial \kappa$ . There are, of course, a number of computer programmes for the general solution of the asymmetric rotor problem. While such facilities no doubt contribute to the increasing rate of assignment of new asymmetric rotor spectra, and to the fact that many spectra now assigned are of quite complicated molecules, containing 10–15 atoms, we are by no means yet at the stage where assignment can be predicted with absolute confidence. Well-known limiting factors, however, such as multiple nuclear quadrupole effects, or excessive molecular flexibility, are less decisive than formerly and it is common for spectra of molecules with two quadrupole nuclei, or with many low-frequency vibrational modes, to be assigned. Sometimes the situation is such that acceptable predicted structures do not allow the asymmetry parameter, or the dipole moment components, to be estimated at all well. In our laboratory we have found isoxazole to be such a case, it being finally established<sup>32</sup> that this planar ring structure has  $\kappa = 0.9146$  and dipole components of 1.98D and 2.12D in the  $A$ - and  $B$ -axes respectively.

A principal result of the primary assignment of asymmetric rotors is the establishment of general aspects of molecular geometry, particularly the presence of certain geometric isomers or rotamers. For example 2-fluoro<sup>33</sup>, 2-methyl<sup>34</sup>, and 1,1-difluoro<sup>35</sup>-butadiene have all been shown to possess planar *trans*-configurations. Constants for vinyl formate<sup>36</sup> are consistent with the planar form



Cahill, Gold and Owen<sup>19</sup> show that methyl vinyl ether has a planar *cis*-form. Demonstration of the presence of stable rotamers in alkyl derivatives has continued, following the success of such microwave studies of *n*-propyl derivatives<sup>37</sup>. Notable examples in which the presence of *cis*- and *gauche*-rotamers has been demonstrated are propionaldehyde<sup>38</sup> and 3-fluoropropene<sup>39</sup>, which I shall mention further below. Cyclobutene<sup>40</sup> has constants consistent with a planar C<sub>4</sub>-ring, and the non-planarities of rings in 1,3-cyclohexadiene<sup>41</sup> and 1,3,5-cycloheptatriene<sup>42</sup> have been discussed on the basis of their moments of inertia.

### Arrays of constants for one molecular species

The above term means arrays of constants for isotopic forms of a particular molecular species, or for different vibrational levels of such a species. The securing of such information is a vital part of the development of a structural study. The assignment of spectra for numerous isotopic forms permits calculation of  $r_s$ -structure parameters, which are often the closest estimates we can hope to obtain at present of the true equilibrium molecular geometry. Vibrational state assignments hold the key to investigations, which have been remarkably active, of how the effects of vibrations on rotational constants should be allowed for. When we recall the vital parts which must be played by isotopes in small natural concentration and by molecules in weakly populated excited levels, the importance of work at highest sensitivities is apparent. The work I am about to mention already shows much varied activity in these fields and by no means all of it was done with instruments of the highest sensitivity. There is, therefore, much more to be done along these lines.

Several papers at this meeting deal with determinations of  $r_s$ -structures. These include studies of methyl keten (Nygaard and Kunstmann<sup>43</sup>), pyridine (Sorensen, Nygaard and Mahler<sup>44</sup>), B<sub>2</sub>H<sub>3</sub>O<sub>3</sub> (Brooks, Costain and Porter<sup>45</sup>), (CH<sub>3</sub>)<sub>3</sub>CCCCl (Bodensch *et al.*<sup>46</sup>), silyl isocyanate (Gerry, Sugden and Thompson<sup>29</sup>), 2-chloropropene (Good and Bauder<sup>47</sup>) and our own work on derivatives of methyl acetylene and methyl cyanide<sup>48</sup>. The work on pyridine extends the outstanding series of accurate studies of cyclic structures made by Bak's group here in Copenhagen. Costain's molecule, B<sub>2</sub>H<sub>3</sub>O<sub>3</sub>, is also an interesting ring compound; boron derivatives at least make up for some of their chemical awkwardness by offering good isotopic arrays. Thus, information has similarly been obtained on the cage-like molecule C<sub>2</sub>B<sub>5</sub>H<sub>7</sub><sup>49</sup>.

Some of the simplest systems studied by substitution are HCP<sup>50</sup>, HN<sub>3</sub><sup>51</sup>, HNCO and HNCS<sup>52</sup>. The structures of both isomers of S<sub>2</sub>F<sub>2</sub> are reported<sup>53</sup>. Other recent studies using isotopic arrays are those of nitric acid<sup>54</sup>, cyclopropyl chloride<sup>55</sup>, 2-chloropropane<sup>56</sup>, sulphur dicyanide<sup>57</sup>, and 1,2,5-oxadiazole<sup>58</sup>. This work continues to produce new intriguing information about molecular structures, such as the very short S—S distance in FSSF, discussed by Kuczkowski<sup>53</sup> in relation to the other parameters and the FOOF structure. Among other refined features demonstrated is a tilting of the NO<sub>2</sub> group in nitric acid away from the hydrogen atom<sup>54</sup>. Such deductions will continue to be eagerly sought, for fortunately few microwave

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spectroscopists are content to regard the object of a research as the mere assembly of accurate spectroscopic constants.

There are now many examples of rotational assignments for vibrationally excited states of molecules. These even underlie the determinations of precise equilibrium parameters in diatomic molecules by waveguide methods<sup>23,59</sup> and from molecular beam experiments<sup>60</sup>, although in some cases, such as SO<sup>22</sup>, it is necessary to use optical spectroscopic data to correct the ground state constants. The general effects of vibration on rotational constants are obviously very complex and even for simple polyatomic molecules it has been by no means easy to achieve the corrections needed to obtain the equilibrium structures. The work of Morino and his group has been outstanding in this field. A very notable achievement has been their assignment of spectra of molecules in the first excited levels of all the modes of sulphur dioxide<sup>61</sup> and the derivation of the equilibrium structure

as S—O =  $1.4308 \pm 0.0002\text{\AA}$ ,  $\angle\text{OSO} = 119^\circ 19' \pm 2'$ . It is encouraging that this is very close to the  $r_s$ -structure. Important extensions of this work<sup>3</sup> are referred to in the abstract of Morino's paper<sup>62</sup>.

This is an appropriate point at which to refer to the growing volume of work on the various averages of structure parameters obtained from spectroscopic and diffraction studies and their relation to the equilibrium structure. There is now an extensive literature on the theoretical treatment<sup>63</sup>, which naturally makes use of numerous vibrational data. In particular, Herschbach and Laurie<sup>64</sup> indicate how in molecules with a plane of symmetry the vibrational corrections to rotational constants can be largely assessed by means of simple approximations depending mainly on the lowest frequency modes. At the present time there is a marked increase in the number of precise electron diffraction studies of internuclear distances<sup>65</sup> and it may well soon be profitable to make more exact comparisons between spectroscopic and diffraction parameters. Secondary isotope effects on averaged distances, which it is believed may occur in ethane<sup>65</sup>, have been treated theoretically<sup>66</sup>. Such effects on carbon-halogen  $r_s$ -distances have been demonstrated in CH<sub>3</sub>Cl, CD<sub>3</sub>Cl, CH<sub>3</sub>Br and CD<sub>3</sub>Br<sup>67</sup> and it would no doubt be easy to add quickly to this type of information.

Microwave spectroscopy now makes many contributions to our knowledge of molecular vibrations. Some examples occur again in Morino's paper<sup>62</sup>, where revision of the vibrational assignment for ClNO<sub>2</sub><sup>68</sup> and the establishment of that for FNO<sub>2</sub> are mentioned. The same group have also made a close study of vibration states of formaldehyde<sup>69</sup>. Similarly, microwave and infrared studies have been combined to decide fundamentals of sulphuryl fluoride<sup>70</sup> and sulphur dicyanide<sup>67</sup>. In such studies the importance of reliable intensity measurement is obvious. In cyclopentene<sup>71</sup> the interaction of out-of-plane bending with rotation was detected and analysis made in terms of rigid rotor constants for the lowest four levels of this mode. We are to hear from Gwinn at this meeting<sup>72</sup>, about microwave studies of rather similar ring-puckering vibrations, which have been notably successful.

The paper in this meeting by Lafferty<sup>73</sup> is an example of further work on vibrationally excited molecules, and has extended somewhat the measure-

ments (Tyler and Sheridan<sup>74</sup>) for the  $v_2 = 1$  state of fluorine cyanide. Lafferty and Lide have reported similar work on nitrous oxide<sup>75</sup>. Much work on vibrational states is known to be in progress, especially at Tokyo and the National Bureau of Standards. It will frequently be found necessary to distinguish and assign vibration state spectra in order to obtain ground state constants for rarer isotopic forms. In our laboratory it was possible to assign constants for seven vibrationally excited states of trifluoroethylene<sup>76</sup>, involving four modes, while distinguishing the lines due to natural carbon-13 species. With the help of intensity data it is possible to obtain the inertial defect contributions for different modes, and to use these<sup>64,77</sup> to check the vibrational assignment and Coriolis factors. It is possible that the final assessment of these results will suggest a reassignment of the lowest mode of trifluoroethylene.

Burden and Millen<sup>78</sup> show how anharmonic potential constants for HCN and OCS can be obtained from vibration-rotation interaction constants ( $\alpha$ ) derived from microwave or vibrational spectra, and they are to discuss this at this meeting<sup>79</sup>. Similar work on OCS and N<sub>2</sub>O is reported by Dorman and Lin<sup>80</sup>. Work has continued on force-field calculations from centrifugal distortion corrections, an example of which is the paper in this meeting by Mirri and Mazzariol<sup>81</sup> on nitrosyl chloride and bromide. Cook<sup>82</sup> reports similar force constant determinations for nitrosyl fluoride from millimetre wave and infrared data. It is clear that theoretical treatments extended beyond the usual first order formulae must be used if we are to take full advantage of the extensive arrays of accurate line frequencies now assignable for many molecules. Thus the distortion effects in HNCO, HNCS<sup>52</sup> and HN<sub>3</sub><sup>51</sup> do not fit the simple expressions. Work on sulphur dioxide, extended to 142 Gc/s<sup>83</sup>, also indicates the need for higher order adjustments, the situation resembling that for OF<sub>2</sub><sup>84</sup>.

Dreizler and Dendl<sup>85</sup> have applied a computer programme to optimize the evaluation of rotational and distortion constants, by least squares, for various types of molecule and different ways of treating the data. They re-emphasize that certain distortion constants can only be very roughly determined. This group of workers have analysed statistically long series of lines, some involving  $J$ -values of 20 or more, for dimethyl sulphoxide<sup>85</sup> and dimethyl sulphide<sup>86</sup>. The optimized rotational constants are less closely determined than might be imagined from the accurate measurement of lines for very low  $J$ -values, and we must remember that distortion corrections for such frequencies may not be negligible. It is desirable and predictable that other molecules should be treated in similar ways. The general usefulness of such a computer programme in the rapid assignment of extensive asymmetric rotor spectra is also emphasized<sup>85</sup>.

Inversion in ammonia derivatives continues to be studied in a variety of ways. In ethylene imine<sup>87</sup>, the inversion level splitting is less than 25 kc/s, and the barrier to inversion is shown to be much higher than that in ammonia as expected on stereochemical grounds. In nitramide<sup>88</sup> the first excited level, while possibly less than 10 cm<sup>-1</sup> above the ground level in NH<sub>2</sub>NO<sub>2</sub>, differs from the latter in its rotational constants sufficiently to produce an entirely distinct spectrum. The barrier to inversion is estimated to be considerably larger than the 1050 cal/mole found for formamide<sup>89</sup>, in fact

about 2800 cal/mole. From a consideration of frequency displacements due to rotation-inversion interactions in the spectra of  $\text{NH}_2\text{CN}$ ,  $\text{NHDCN}$  and  $\text{ND}_2\text{CN}$ , Tyler and Costain have estimated the barrier in cyanamide to be about 2030 cal/mole<sup>90</sup>.

### Internal rotation studies

These are conveniently treated separately, though they are, of course, fundamentally inseparable from other numerous studies of force fields.

There is little recently published work on the simplest ethane-like structures, although there are many of these still to be studied. It is known that data on germyl silane<sup>91</sup> have been obtained and, as data accumulate, it may be possible to build more extensive empirical knowledge of the barriers. The behaviour of substituents in methyl silane, where fluorination of the  $\text{SiH}_3$  group lowers the barrier and shortens the C—Si bond<sup>92</sup> while insertion of chlorine in the methyl group has the opposite effects<sup>93</sup>, shows that future study of these systems should be rewarding.

Some further attention has been given to the symmetric-top cases, such as  $\text{CH}_3\text{SiF}_3$ , and elaborate theoretical treatment of the interaction of torsion with other vibrations in these has been published by Kirtman<sup>94</sup>. He proposes assignments of lines measured for  $\text{CH}_3\text{SiF}_3$  and  $\text{CD}_3\text{SiF}_3$  in my laboratory and the measurements were certainly easier than the interpretation. It is gratifying that progress has been possible with these complex

Table 1. Internal rotation barriers,  $V_3$

Molecule	$V_3$ (cal/mole)	Reference
$\text{CH}_3\text{—OCl}$	$3060 \pm 150$	95
$\text{CH}_3\text{—SCN}$	1570	96
$\text{CH}_3\text{—CCl=CH}_2$	$2671 \pm 20$	20
<i>cis</i> - $\text{CH}_3\text{—CH=CHCl}$	$620 \pm 10$	97
$\text{CH}_3\text{—CO—CCH}$	$1084 \pm 30$	98
$\text{CH}_3\text{—N=CH}_2$	$1970 \pm 25$	99
$\text{CH}_3\text{—NSO}$	$335 \pm 15$	100
$\text{CH}_3\text{—NCO}$	$49 \pm 3$	101

satellite spectra. Laurie<sup>94</sup> has shown that *l*-type Coriolis interactions in such molecules can allow direct observation of effects of internal rotation.

Most recent papers on torsional effects concern cases where methyl groups are attached to planar residues. Table 1 summarizes a selection.

In some cases, equilibrium configurations were deduced from isotopic substitution in the methyl group, the hydrogens in methyl hypochlorite<sup>95</sup> being staggered with respect to the chlorine, and a methyl proton in  $\text{CH}_3\text{N=CH}_2$ <sup>99</sup> eclipsing the double bond. In addition, accurate C—O and C—Cl substitution distances were obtained for methyl hypochlorite, and are both shorter than in methanol or oxygen chloride respectively. The barrier in this molecule is nearly three times that in methanol and the highest yet found for a methoxy derivative.

The data for chloropropenes extend work on related systems in which influences of substituents on the barrier were elegantly demonstrated. The results, summarized by Beaudet<sup>97</sup>, show that the lowering of the barrier by bulky *cis*-substituents is most marked in *cis*-1-chloropropene. The



isomeric 2-chloropropene<sup>20</sup>, as anticipated, has a much higher barrier. Other studies of changes in barriers with substituents in a common framework will no doubt be made. Barriers in  $\text{CH}_3\text{NSO}^{100}$  and, especially, in  $\text{CH}_3\text{NCO}^{101}$ , are very small and their assignment gives hope that molecules with similar discouragingly complex spectra will be successfully treated. Careful checking of intensities, and perhaps double radiation effects, should be worthwhile in such work.

Spectra of the "mixed dimer" of acetic acid and trifluoroacetic acid<sup>102</sup> show evidence of virtually free rotation of the  $\text{CX}_3$  groups, such as would result from easy tunnelling of the hydrogen-bonding nuclei and consequent disappearance of the three-fold term in the barrier potential.

Theoretical treatment has been given by Quade and Lin<sup>103</sup> of torsional splittings in molecules with partially deuterated methyl groups. They conclude that this could be extended to more general asymmetric cases and that the splittings are rather sensitive to details such as the tilting of methyl group axes, in  $\text{CH}_3\text{X}$ , out of the C—X bond direction.

Purely theoretical calculations of barriers are reviewed by Scott and Scheraga<sup>104</sup>, who propose new procedures with a certain amount of qualitative success.

Among molecules with two bonds about which rotation can occur, propionaldehyde<sup>37</sup> and 3-fluoropropene<sup>38</sup> have recently been especially fully studied. In each, the *cis*-rotamer is stabler than the *gauche*, in the aldehyde by the particularly large energy of  $900 \pm 100$  cal/mole, as compared with  $166 \pm 67$  cal/mole for 3-fluoropropene. *Cis*-propionaldehyde shows easier methyl group rotation than most ethane-type molecules, possibly on account of interaction of the oxygen atom with the methyl group. It is significant that substitution structures were obtained for both rotamers of 3-fluoropropene, but the uncertainties were rather too large to allow profitable bond-by-bond comparisons between them. An important feature of this work was that splittings due to tunnelling through the *trans*-barrier were observed despite the fact that torsion involves movement of a fluorine atom. From this effect and intensity measurements of excited torsional satellite lines, the *trans*-barrier was estimated to be  $2010 \pm 230$  cal/mole relative to the minima at the *gauche* configurations. The measurement by microwave methods of barriers in molecules where such heavy asymmetric groups are joined must be one of the next main objectives in this field.

The work at Louvain on ethyl alcohol<sup>105</sup> has also yielded much information about the rotamers, and details are to be given at this meeting. We are also to hear about two double-top molecules, dimethyl keten<sup>106</sup> and dimethyl sulphoxide<sup>107</sup> from the Freiburg group, who have contributed much to the study of such systems including a recent refinement of the study of acetone<sup>108</sup>, and further generalization of the theoretical treatment<sup>109</sup>.

### Hyperfine structures

Nuclear quadrupole hyperfine structure has been resolved and analysed in the spectra of many of the molecules already mentioned. Recent cases include some very precise determinations on diatomic molecules. Bromine and iodine couplings were very accurately determined for LiBr and LiI<sup>60</sup>

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and also the variations of coupling with vibrational quantum number. Nuclear coupling constants of  $^{27}\text{Al}$  were measured in  $\text{AlF}$  and  $\text{AlCl}^{59}$ ; that in  $\text{AlF}$  is almost identical with that for the free aluminium atom, and that in  $\text{AlCl}$  is only slightly less. When however, the very small coupling of the chlorine in  $\text{AlCl}$ , determined by solving the double coupling case for spins of  $5/2$  and  $3/2$ , is considered, the evidence favours highly ionic structures for these halides, with considerable hybridization of the aluminium orbitals $^{58}$ .

Since we are now usually dealing with asymmetric rotors, the question of the symmetry of the coupling tensor and the orientation of its principal axes with respect to the bond directions frequently arises. For cyclopropyl chloride $^{55}$ , 2-chloropropane $^{54}$ , ethyl chloride $^{110}$  methyl hypochlorite $^{95}$  and fluorobromomethane $^{111}$  the data were analysed with the usual assumption that the bond to the halogen lies in a principal axis of the coupling tensor. In the first three cases the coupling constants so derived are nearly symmetric about the bond direction; for  $\text{CH}_2\text{FBr}$  there is greater asymmetry in the sense that would be expected if the form  $\text{F}-\text{CH}_2=\text{Br}^+$  contributed. Alternatively, we may assume that the charge distribution at the nucleus concerned is cylindrical and for the chlorine couplings mentioned this gives couplings in the axial direction which are close to those obtained in the bond direction with the first assumption. Similar data for 2-chloropropene $^{20}$  have been extended by Good and Bauder $^{47}$ .

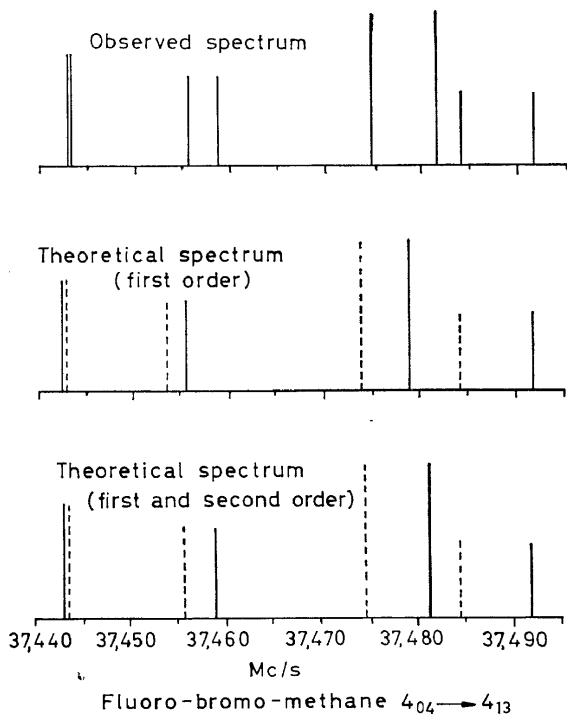


Figure 1. Second order quadrupole effects in  $\text{CH}_2\text{FBr}$  (-----  $^{81}\text{Br}$ , ———  $^{79}\text{Br}$ )

In ethyl chloride<sup>110</sup> the non-zero off-diagonal element in the tensor in the  $a, b, c$ -axis system was evaluated from the couplings in the two species  $\text{CH}_3\text{CH}_2^{35}\text{Cl}$  and  $\text{CH}_3\text{CD}_2^{35}\text{Cl}$ , and this confirmed that the potential near the chlorine nucleus is approximately cylindrically symmetrical about the C—Cl line, although a slight asymmetry, or slight bending of bonds, could not be excluded, or distinguished, with the available precision. In ethyl bromide<sup>112</sup> the off-diagonal term was found from second order quadrupole effects for various species, and the evidence against appreciable bond bending is even stronger. Second order effects in propargyl bromide<sup>113</sup> showed earlier that the  $z$ -axis of the coupling tensor coincided, within error, with the C—Br bond direction. In  $\text{CH}_2\text{FBr}$ <sup>111,114</sup> the off-diagonal term from the second order treatment again shows that the  $z$ -axis is very close to the C—Br bond direction, and hence the asymmetry of the field about the CBr bond in this molecule is real.

Many more second order quadrupole effects will have to be analysed in the future. Apart from the evidence, just illustrated, which may follow regarding electron distributions, the analysis may be necessary for the accurate assignment of rotational constants. *Figures 1 and 2* show second order effects in the spectra of  $\text{CH}_2\text{FBr}$ <sup>111,114</sup> and  $\text{CH}_2\text{FI}$ <sup>114</sup> which Curnuck has measured in my laboratory. Assignment of unperturbed frequencies, and, for  $\text{CH}_2\text{FBr}$ , the allocation of the two quartets of lines to respective bromine

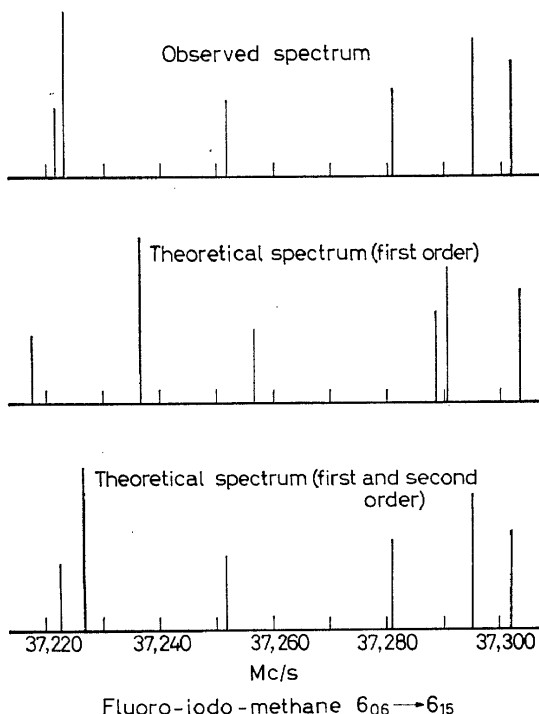


Figure 2. Second order quadrupole effects in  $\text{CH}_2\text{FI}$

isotopes, require second order treatment. Schwendeman<sup>115</sup> has recently published tables of functions useful in second order quadrupole calculations in asymmetric tops, and Curnuck and Stiefvater<sup>114,116</sup> in my laboratory, have developed the treatment by somewhat different methods which may be worth publishing in summary. Benz and Bauder<sup>117</sup> at this meeting have met the problem of second order effects in bromine couplings and have programmed a computer to deal with it. Schwendeman, Dougher and Tobiason<sup>118</sup> have also reported a computer programme for second order coupling.

The double chlorine coupling in dichlorofluoromethane has been analysed by McLay<sup>119</sup> and that in 1,1-dichloroethane by Flygare<sup>120</sup>. If cylindrical charge distribution about the C—Cl bonds is assumed, the component of the coupling tensor associated with the bond direction is in each case somewhat greater than found in similar ways for ethyl chloride. For 1,1-dichloroethane<sup>120</sup>  $\chi_a$ ,  $\chi_b$  and  $\chi_c$  were obtained with high accuracy by means of a source-stabilized spectrometer, and similar stabilization was used by Guarnieri and Favero<sup>121</sup> in their studies of couplings in NOCl and NOBr to be presented at this meeting.

Source stabilization is most useful when small couplings have to be measured, and was further used in the case of ethylene imine<sup>87</sup>, where nitrogen couplings were measured with the exceptional accuracy of better than 1 per cent. The small quadrupole coupling constants of deuterium have been accurately established in HDO, HDS, CHDO<sup>122</sup> and NH<sub>2</sub>D<sup>123</sup> by beam-maser methods, and accurate field gradients were estimated. Source-stabilized spectroscopy was also used to determine the deuterium couplings in CD<sub>2</sub>O and CHDO<sup>8</sup>, and the oxygen-17 coupling in CH<sub>2</sub><sup>17</sup>O<sup>124</sup>. The principal axis of the field gradient at the deuterium nucleus lies within 3 degrees of the C—D line. A description of the electronic structure of formaldehyde in terms of hybrid orbitals can satisfactorily reproduce the hyperfine data for this substance<sup>125</sup>. A similar study of keten<sup>126</sup> shows that the field gradient at the deuteron is considerably less than that in formaldehyde. Calculations by Kern and Karplus<sup>127</sup> of several deuteron and nitrogen quadrupole coupling constants, by various orbital methods, confirm the view that the experimental data offer critical tests of wave-functions.

### Other hyperfine effects

Many spin-rotation splittings have been analysed in the high-resolution work mentioned. Such hyperfine structure in the OF<sub>2</sub> spectrum<sup>128</sup>, resolved in a conventional spectrometer, has been more closely studied in a source-stabilized instrument<sup>129</sup>. Theoretical treatment of spin-rotation interaction has been extended<sup>130</sup> with a view to using such measurements to test molecular wave-functions.

A very full account of fine structure and magnetic coupling in the spectrum of NO<sub>2</sub> has appeared<sup>131</sup>, giving a consistent assignment of parameters. This paper is the successful outcome of long and difficult investigations, and contains a discussion of the results in terms of the electronic structure of this unique molecule.

## Stark and Zeeman effects

A large proportion of the molecules already mentioned were also subjected to electric dipole moment studies by means of Stark effect measurements. The moments of alkali halides<sup>23,60</sup> have been studied with extreme accuracy and their dependence on vibrational quantum number determined. The value from molecular beam methods for LiBr does not agree with earlier data from waveguide Stark effects. The relatively low moment of AlF<sup>59</sup>,  $1.53 \pm 0.1D$ , does not disagree with a largely ionic structure when the lone-pair moment is considered.

The moment of SO is measured as  $1.55 \pm 0.02D$ <sup>22</sup> and that of OH has been more accurately established as  $1.660 \pm 0.01D$ <sup>132,21</sup>. Cyclobutene<sup>40</sup> ( $\mu = 0.132D$ ) and HCP<sup>50</sup> ( $\mu = 0.390D$ ) have lower moments than might have been anticipated from those of related molecules, including cyclopentene, for which  $\mu_b$  is revised to  $0.190 \pm 0.006D$ <sup>71</sup> ( $\mu_c$  is thought to be at least  $0.05D$ ). The moment of 1,3-cyclohexadiene is  $0.437D$ <sup>40</sup>. Two determinations of the electric dipole moment of NO<sub>2</sub>, one using the normal form<sup>133</sup> and the other the same transition of <sup>15</sup>NO<sub>2</sub><sup>134</sup>, give  $0.316 \pm 0.01D$  and  $0.294 \pm 0.015D$  respectively. Larger dipoles established are those of nitramide<sup>88</sup> and 1,2,5-oxadiazole<sup>58</sup> and the *a*-components in methyl isocyanate<sup>101</sup> and methyl thiocyanate<sup>96</sup>.

Molecules for which more than one component of the dipole has been measured include nitric acid<sup>64</sup>, SSF<sub>2</sub><sup>52</sup>, 1,3,5-cycloheptatriene<sup>41</sup>, 1,1-difluorobutadiene<sup>35</sup>, isoprene<sup>34</sup>, vinyl formate<sup>36</sup>, CH<sub>3</sub>NSO<sup>100</sup>, CH<sub>3</sub>N=CH<sub>2</sub><sup>99</sup>, *cis*-1-chloropropene<sup>97</sup>, acetyl acetylene<sup>98</sup>, and 3-fluoropropene<sup>39</sup>. The *gauche*-form of the last is one of the very few cases where dipole components in all three inertial axes have been measured. There are still few cases where the line of action of the dipole has been uniquely determined by the effects of isotopic replacement on the squared axial components, but Dreizler and Dendl<sup>135</sup> have done this for dimethyl sulphoxide, from thorough measurements and careful consideration of errors in the evaluation. There is scope for much more work to establish axes of dipole moments, but it will be necessary to be sure of the best possible precision. The new studies by Laurie and Muentzer<sup>24</sup> are therefore of timely interest. It is noteworthy that Peter and Dreizler<sup>108</sup>, in their work on acetone, have warned that the moment determined by the more exact procedure of diagonalizing the energy matrix can differ significantly from that from second order perturbation treatment.

Lindfors and Cornwell<sup>136</sup> measure dipole moments to accuracies of several percent by a rate-of-growth technique at weak modulation fields; this could be important in the many cases where complexity of spectra or weak Stark effects have prevented the usual type of study.

There have been few recent studies of Zeeman effects. These have been measured for SO and accounted for in terms of the <sup>3</sup>Σ ground state by Winnewisser *et al.*<sup>22d</sup>. Molecular *g*-values for formaldehyde have been measured<sup>137</sup> with a source-stabilized instrument and used to deduce the anisotropy of the paramagnetic susceptibility along the O—C bond. We still await extensions of work<sup>138</sup> on *g*-factors for arrays of isotopic species leading to information on sign orientation of molecular dipoles. No doubt

this will be very difficult, but the results could be of great chemical interest in certain cases.

## CONCLUSION

The selection of work mentioned here shows clearly the great variety of the contributions of microwave spectroscopy to our knowledge of molecular structure. We know that many new studies are in progress on almost all aspects and it is certain that there will be no diminution of the flow of results along these lines. I have indicated some directions in which scope for the future is particularly clear, and indeed the past record of refinements in microwave electronic methods can only encourage an optimistic outlook. It is moreover, striking that what are really very complex problems in interpretation do not deter microwave spectroscopists from persistent attack, and are ultimately solved.

There will, of course, be an increase in investigations which refine and extend existing microwave work, and in the number of overlapping studies. But this is altogether to the good when we are examining very complex details of molecules, even by as excellent a method as microwave spectroscopy.

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