MICROWAVE SPECTROSCOPY

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INTRODUCTION

This paper is intended as a short survey of some special topics related to the progress in microwave spectroscopy during the years 1959 and 1960.

EXPERIMENTAL TECHNIQUE

Up to the present, the Stark modulation spectrometer is still the most widely used microwave spectrometer. There have been remarkable improvements in this type of spectrometer in recent years, and other types of microwave spectrometers have been developed and tested. Before discussing the developments in experimental technique, it may be useful to give some of the requirements which must be met by a microwave spectrometer that is to be used for investigations in molecular physics.

Firstly, it should be noticed that there are two requirements which are incompatible in that both cannot be met to the full simultaneously: these are maximum sensitivity and maximum resolution. Fortunately, the Stark modulation spectrometer is an instrument which can realize both requirements—though not at the same time. The instrument can be operated either at high power level and high gas pressures to detect extremely weak lines with restricted resolution, or at low pressures and low power level, *i.e.* with reduced sensitivity but with very high resolution. For extreme cases, however, the use of a special purpose spectrometer may be necessary.

The three properties which characterize the performance of a microwave spectrometer are:
(a) its sensitivity;
(b) its resolution;
(c) the accuracy of the line frequency determinations.
Let us consider each of these three characteristic qualities.

Sensitivity of a microwave spectrometer

The sensitivity of a spectrometer is of interest if one has to look for and measure very weak lines. In this case, one applies a gas pressure high enough to give the maximum value of the peak absorption coefficient for the transition to be studied. It is well-known that this maximum value is reached when collision-broadening represents the overwhelming part of line-broadening. This holds for gas pressures of about 30 μ of mercury and more. It is, of course, useless to increase the pressure much beyond this critical value, because the result is only a greater line-width without any improvement in peak intensity. With gas pressures between about 20 and 100 μ of mercury,

the line-widths, $\Delta\nu$ (half-width at half intensity), have values of several Mc/sec and the peak absorption is given according to the Van Vleck–Weißkopf theory by:

$$\alpha_{\text{peak}} = \frac{8\pi^2\nu_0^2 f}{3ckT}\mid \mu_{ij}\mid^2 \frac{N}{\Delta\nu}[\text{cm}^{-1}] \tag{1}$$

where $\nu_0 =$ frequency of the line centre, $\mu_{ij} =$ dipole matrix element of the transition, $N =$ total number of molecules per cm³, and $f =$ fraction of molecules in the lower state of the transition.

In the pressure region specified above, $N/\Delta\nu$ is independent of pressure, but a function of the substance and the temperature. The sensitivity of a spectrometer (more exactly, the limit sensitivity) is usually defined by α_{min}, viz. that value of α_{peak} which gives a signal equal to the noise level of the spectrometer. In practice, one determines experimentally the signal-to-noise ratio for a very weak line near the limit of detectability, and calculates α_{peak} for this line according to equation (1). This value α_{peak} depends on the temperature to a marked degree, and this dependence is the source of some confusion in the literature. In order to obtain the true value of the minimum detectable absorption coefficient, α_{peak} should be calculated for that temperature at which the signal-to-noise ratio has been measured. It has become the custom, however, always to calculate α_{peak} for $T = 300\,°\text{K}$, even though the signal-to-noise ratio may have been measured at a different temperature. This somewhat confusing situation may be clarified in the following manner. If one wishes to characterize the purely electrical performance of the spectrometer, the true value of α_{peak} must be given. If, however, the performance of the whole apparatus (including the effectiveness of the cooling system, etc.) is of interest, the calculated value at 300 °K may be used for comparison. In any case, the temperatures at which α_{peak} has been observed and at which it has been calculated should be clearly stated.

As regards the power level of the microwave radiation transmitted through the absorption cell for the detection of weak lines, powers of about 1 mW are used. Up to this value the signal caused by a given α_{peak} is proportional to the power level. Powers in excess of 1 mW would not improve the spectrometer sensitivity; this has been shown by investigations of the crystal detector properties. Radiation power of magnitude 1 mW in absorption cells of X-band or K-band dimensions would, it is true, cause considerable saturation broadening, and would, therefore, diminish α_{peak} if the line-width lay below about 0·2 Mc/sec. With line-widths of several Mc/sec, as are necessarily used for the detection of extremely weak lines, the saturation has no detectable effect.

Finally, it should be mentioned that lengthening of the absorption cell enhances the sensitivity of the spectrometer for extremely weak lines. Of course, there is a limit: the wall losses of the absorption cell reduce the power level transmitted by the cell. As soon as the power level at the end of the cell falls considerably below the value entering the cell, a further increase in the length of the cell leads to no advantage.

For the frequency region 10–40 kMc/sec, one can say that a microwave spectrometer of good performance has a sensitivitiy of $\alpha_{\text{min}} = 10^{-9}$–$10^{-10}$ cm⁻¹, the better value holding for the lower frequencies.

Resolution of a microwave spectrometer

The resolution of a microwave spectrometer should, of course, be defined in the same manner as in optical spectroscopy, *i.e.* by $A = \nu_0/2\Delta\nu$; two lines ν_1 and ν_2 ($\nu_0 = (\nu_1 + \nu_2)/2$) of about equal intensities can just be resolved and measured separately when their frequencies differ by $(\nu_1 - \nu_2) = 2\Delta\nu$. Microwave spectroscopists, however, prefer to consider the line-width, $\Delta\nu$, itself as a measure of resolution instead of the quantity A. With conventional spectrometers (except maser spectrometers and some of special design), there is an inevitable line-broadening effect, the Doppler broadening, which produces line-widths given by:

$$\Delta\nu_{\text{Doppler}} = 3 \cdot 58 \times 10^{-7} \times \sqrt{\frac{T}{M}} \nu_0 \qquad (2)$$

where M = molecular weight. In the frequency region near 20 kMc/sec, for example, the Doppler widths, $\Delta\nu$, lie between about 15 and 30 kc/sec. In high resolution work, the aim is to reduce the observed line-widths to this limit. The gas pressure is, therefore, lowered to a value (less than about 3×10^{-3} mm of mercury for the 20 kMc/sec region) at which collision-broadening may be neglected. Of course, this is incompatible with the requirement for optimum intensity, since the peak absorption coefficient diminishes with decreasing pressure as soon as collision-broadening becomes comparable with, or smaller than, the Doppler width (at pressures below about 20 μ of mercury). In general, lowering of the gas pressure alone will not suffice for the Doppler limit to be reached; other line-broadening effects must also be avoided. These are:

Line-broadening by wall collisions—By using X-band absorption cells in the 20 kMc/sec region and K-band cells in the 40 kMc/sec region, this broadening effect is made smaller than the Doppler broadening.

Saturation broadening—Power levels in the absorption cell of the order 1 mW, such as are used for the detection of extremely weak lines at high gas pressure, would cause strong saturation broadening at the low pressure necessary for high resolution work, and produce line-widths larger than the Doppler width. For this reason, the power entering the absorption cell must now be reduced to a few μW.

Frequency fluctuations of the radiation source—These should be eliminated by frequency stabilization by means of a quartz controlled oscillator. This is considered to be indispensable for high resolution work.

Modulation broadening—As is well-known, modulation of the radiation is used in order to attain high sensitivity. The modulation produces a line-broadening, the magnitude of which depends on the modulation frequency. With the frequently-used Stark effect modulation of 100 kc/sec, for example, it is impossible to reduce the line-widths, $\Delta\nu$, to below 100–200 kc/sec; that means that, in the 20 kMc/sec region, the Doppler limit cannot be reached with this modulation frequency. A 10 kc/sec modulation, on the other hand, gives no detectable line-broadening compared with the Doppler width for the above frequency region. Of course, the simplest way to avoid modulation broadening is to use no modulation at all; in order to get a sufficiently high sensitivity in this case, superheterodyne reception should be used.

Accuracy of frequency determinations

As regards the accuracy of frequency determinations, one can say that the absorption line frequencies can be measured with an accuracy of about one-tenth of their line-width; that means an accuracy better than $\pm$ 10 kc/sec for well resolved and narrow lines. In order to realize this high accuracy (which means measuring the frequency to 1 part in 3×10^6 for a line at 30 kMc/sec), the source must be frequency-stabilized and the stabilizing quartz oscillator must be continuously controlled, by comparison with frequency standards of an accuracy better than 1 part in 10^8. The limit of 3×10^{-7} given above is then determined by the accuracy of the interpolation oscillator or receiver, which is a part of any frequency measuring or AFC system, and interpolates the absorption line frequency between the discontinuous harmonics of the quartz frequency.

General progress since 1959

After these general remarks concerning the three principal properties of a microwave spectrometer, let us now consider the progress in experimental technique as described in the papers published since 1959.

Stark modulation spectrometer

The standard type of high-performance Stark modulation spectrometer now covers the frequency range from about 8 kMc/sec to about 40 kMc/sec with quartz-stabilized klystrons or backward-wave oscillators as radiation sources. Backward-wave oscillators offer the advantage of wide-range single-control tuning: Rudolph[236] has described a spectrometer using three backward-wave tubes (carcinotrons) which can be interchanged within a few minutes and which cover the frequency range 8–37·5 kMc/sec continuously without a gap. In addition, the tubes permit very convenient operation: tuning of these oscillators is effected by simply varying the voltage of the delay line contained in the tube, no mechanical tuning being necessary. Normally, the Stark modulation frequencies (square wave) lie between 10 and 120 kc/sec. Modulation near 100 kc/sec is preferably used in order to attain the highest possible sensitivity. However, it seems that, with a modulation frequency of about 30 kc/sec, the loss in sensitivity is only small whilst the improvement in resolution compared with that at 100 kc/sec modulation is remarkable. This is because, with this modulation frequency, the additional broadening by modulation is only a small fraction of the Doppler broadening for lines in the 20–30 kMc/sec region. The above spectrometer[236] employs 30 kc/sec modulation and detects an OCS-line of $\alpha_{\text{min, } 300°K} = 1 \cdot 1 \times 10^{-9}$ cm^{-1} at $-80°$ with a signal-to-noise ratio of about 5. This sensitivity seems to be characteristic of a good Stark modulation spectrometer. Line-widths of $\Delta\nu = 40$ kc/sec have been obtained with the spectrometer[236] at $-80°$, and with gas pressures near 3 μ of mercury for lines having an absorption coefficient $\alpha_{\text{peak, } 300°K} \geqslant 10^{-7}$ cm^{-1}.

In order to achieve such a high resolution, frequency stabilization of the radiation sources and cooling of the absorption cell are indispensable. On account of the vapour pressures necessary for detecting the lines, the low temperature limit customarily used lies at about $-80°$. As regards frequency stabilization, progress has been made in stabilizing the source with

respect to a reference cavity by introducing modulation into the microwave discriminator circuit. Such systems have been described by Dymanus[28] and by Bruin and Van Ladesteyn[10]. While the short-time stability (decisive for the elimination of line-broadening due to fluctuations in the frequency of the source) of such circuits is excellent, the long-time stability is that of the reference cavity, *i.e.* not so good. For this reason, a different AFC-system is frequently preferred: the microwave source is then locked with the harmonics of a quartz-controlled secondary standard, *cf.*, for instance, the papers of Zimmerer[123] and Rudolph[236].

As regards the detector which receives the radiation transmitted through the absorption cell, the well-known crystal diode is still in use. Its noise figure is, practically, that of the spectrometer, and sets the limit of sensitivity. In order to obtain the highest possible sensitivity, the most efficient practice is still to select the best crystal from as large a batch of crystal diodes as possible. Ohl *et al.*[93] describe a special treatment of the crystals which markedly improves their efficiency as mixers and generators of harmonics. Their usefulness for the improvement of sensitivity is not so clearly pronounced.

The properties which characterize the crystal diode as an electrical device are its noise figure and its conversion gain (often designated as conversion loss). The values for these two quantities which are to be found in the literature differ considerably, and are sometimes ambiguous. Credit is therefore, especially due to Long[180] and to Dymanus and Bouwknegt[141], who have clarified certain points in their papers. The first of these[180] compares the data of commercially-available crystal diodes, and shows how the specifications of the manufacturers should be used for calculating the electrical effect of the diode as part of a microwave spectrometer. The paper of Dymanus and Bouwknegt[141] relates exclusively to the well-known 1 N 26 crystal rectifier. The authors have made noise figure and gain measurements for this diode down to power levels as low as 1 μW, *i.e.* under conditions found when operating a microwave spectrometer at high resolution.

Other microwave spectrometers

The above survey indicates the present status of experimental technique in microwave spectroscopy as regards the most widely used spectrometer in this field, the Stark modulation transmission spectrometer. Other types of microwave spectrometers may be mentioned only very briefly as follows:

Video transmission spectrometer—The simple video transmission spectrometer has remained the preferred spectrometer for spectroscopy in the frequency range above 100 kMc/sec. Stark modulation has also been applied[144] for frequencies up to 170 kMc/sec; however, it was not used as a means of improving the sensitivity of the spectrometer, but only to study the Stark patterns of the lines in order to identify the transitions.

Cavity spectrometer—There has been renewed interest in the cavity spectrometer, partly in connection with the problems of intensity measurements [23,27,28,142], partly in connection with the beam maser spectrometer[5,223]. It seems that the two types of microwave spectrometers, the transmission spectrometer and the resonance (cavity) spectrometer, are equivalent as regards sensitivity, resolution and accuracy. The sensitivity of both types can be

markedly improved by employing Stark modulation, and still higher sensitivity can be attained by using superheterodyne reception instead of crystal rectification of the microwave power. The Stark modulation cavity spectrometer described by Dymanus[28] has, it is true, a more homogeneous Stark field, and, therefore, distinctly sharper Stark satellite lines, than a Stark modulation transmission spectrometer of conventional design. However, with Stark cells of the parallel-plate type, the same homogeneity can also be achieved with the transmission spectrometer. As far as can be seen, the cavity spectrometer is to be preferred only for special purposes. For standard spectroscopic work, *i.e.* looking for and measuring lines in a frequency range as wide as possible, it has the decisive disadvantage that several cavities are necessary to cover a frequency range of, for example, 10–40 kMc/sec, and that not only the oscillator but also the cavity has to be tuned. This makes the operation of the spectrometer distinctly more cumbersome.

Maser spectrometers—Finally, we have to mention the maser spectrometers, several types of which have been employed for spectroscopic work in recent years. Perhaps it will be useful to distinguish between two methods of operating a maser spectrometer.

In the first instance, there are the spectrometers which use an absorption cell of conventional design and take advantage of the possibilities given by "pumping" a second transition which has one level common with the transition to be studied. It is possible, in this way, to enlarge considerably the difference in population, and thus to enhance the line intensity. This method can be used successfully for the very weak lines below ~ 100 Mc/sec by pumping in the cm wave region[108]. Another way is to pump the (weak) transition to be studied and to observe another, much stronger, transition which has one level common with the first[220]. The authors call their procedure the "three-level technique". All the spectrometers which use pumping of a second transition in the above or a similar manner may, perhaps, be described most simply as "*double-resonance spectrometers*".

The other type of maser spectrometer is the "*molecular-beam maser spectrometer*". It is an apparatus quite different from the conventional microwave transmission spectrometer, and uses a parallel beam of molecules and a high-Q cavity[148]. It may be operated essentially as a sort of cavity spectrometer whose chief advantage is only the extremely low line-width ($\Delta\nu \sim$ 5 kc/sec for lines near ~ 20 kMc/sec). The sensitivity of such a beam maser spectrometer at frequencies above ~ 10 kMc/sec is distinctly lower than that of a conventional transmission spectrometer[223]. Therefore, in this region of the spectrum, this type of spectrometer is of interest only for special studies requiring extremely high resolution, such as, for example, in the investigation of extremely small hyperfine splittings (*e.g.* purely magnetic hyperfine interactions between nuclear spin and molecular rotation) of strong lines[113,114,210,238]. It seems that a great improvement in sensitivity could be attained without loss of resolution if the apparatus were operated as a maser oscillator or as a nearly-oscillating maser amplifier[214].

The future development of maser spectrometers will be of great interest to microwave spectroscopists. However, there seems no doubt that the maser spectrometer will remain a special purpose instrument which will be extremely valuable for work requiring the highest resolution, but that it will never serve
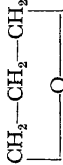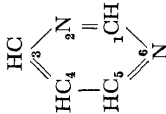
Table 1. Structure parameters

Substance	No. of isotopic species investigated	Structure parameters* (Å)	Reference
N_2O NH_2CN	$8(^{14}N, ^{15}N, ^{16}O, ^{18}O)$ $3(^1H, ^2D, ^{12}C, ^{14}N)$	$r(N-N)=1\cdot126\pm0\cdot002$; $r(N-O)=1\cdot186\pm0\cdot002$ $[\angle HNH]$: $r(N-H)$, $r(N-C)$; $r(C-N)$, for 3 different $[\angle HNH]$	97 117
HNO_3	$3(^1H, ^2D, ^{14}N, ^{15}N, ^{16}O)$	$r(O-H)=[0\cdot96]$; $r(N-OH)=1\cdot405\pm0\cdot005$; $r(N-O)=$ $=1\cdot206\pm0\cdot005$; $\angle NO_CH=102^\circ\pm30'$; $\angle O_ANO_B=$ $=130^\circ\pm20'$; $\angle O_ANO_C=114^\circ\pm20'$; $\angle O_BNO_C=116^\circ\pm20'$	184
S_2O $HDSe$	$2(^{16}O, ^{32}S, ^{34}S)$ $5(^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, ^{82}Se)$	$r(S-O)=1\cdot465\pm0\cdot01$; $r(S-S)=1\cdot884\pm0\cdot01$; $\angle=118^\circ0'\pm30'$ 1st Method: $r(Se-H)=1\cdot4521\pm0\cdot0005$; $r(Se-D)=1\cdot4456\pm$ $\pm0\cdot0005$; $\angle HSeD=90^\circ17'\pm50'$; 2nd Method: $r(Se-H)=1\cdot4519\pm0\cdot0005$; $r(Se-D)=1\cdot4458\pm$ $0\cdot0005$; $\angle HSeD=90^\circ10'\pm50'$	88 119
NO_2Cl CH_3SH	$2(^{14}N, ^{16}O, ^{35}Cl, ^{37}Cl)$ $3(^1H, ^2D, ^{12}C, ^{32}S, \beta_v\text{-value})$	$r(Cl-N)=1\cdot83$; $r(N-O)=1\cdot21$; $\angle ONO=129^\circ30'$ $r(S-H)=1\cdot335\pm0\cdot010$; $r(C-S)=1\cdot819\pm0\cdot005$; $r(C-H)=$ $=1\cdot092\pm0\cdot010$; $\angle CSH=96^\circ30'\pm30'$; $\angle HCH=$ $=109^\circ45'\pm30'$	16 166
$CH_2(CN)_2$	$5(^1H, ^2D, ^{12}C, ^{13}C, ^{14}N, ^{15}N)$	$r(C-C)=1\cdot468\pm0\cdot034$; $r(C\equiv N)=1\cdot167\pm0\cdot026$; $r(C-H)=$ $=1\cdot088\pm0\cdot010$; $\angle CCC=109^\circ22'\pm2^\circ54'$; $\angle HCH=$ $=108^\circ42'\pm1^\circ22'$; $\angle CCN=180^\circ-(3^\circ40'\pm2^\circ54')$	153, 154
$HCHO$	$5(^1H, ^2D, ^{12}C, ^{13}C, ^{16}O, ^{18}O)$	1st Method: $r(C=O)=1\cdot2063$; $r(C-H)=1\cdot117_4$; $\angle HCO=122^\circ5'$; (r_z); 2nd Method: $r(C=O)=1\cdot2051$; $r(C-H)=1\cdot110_9$; $\angle HCO=121^\circ56$; (r_0); 3rd Method: $r(C=O)=1\cdot2042$; $r(C-H)=1\cdot101_9$; $\angle HCO=121^\circ40'$; (r_s)	192
$HCOF$	$2(^1H, ^2D, ^{12}C, ^{16}O)$	$r(C-H)=1\cdot087\pm0\cdot01$; $r(C-O)=1\cdot182\pm0\cdot003$; $r(C-F)=$ $=1\cdot341\pm0\cdot003$; $\angle FCO=123\cdot04^\circ\pm0\cdot02^\circ$, $\angle FCH=114^\circ$; $\angle OCH=123^\circ$	145
$HCONH_2$	$10(^1H, ^2D, ^{12}C, ^{14}N, ^{15}N)$	For $HCO^{14}NH_2$: $r(N-H)'=1\cdot014$; $r(N-H'')=1\cdot002$; $r(N-C)=1\cdot375$; $r(C-O)=1\cdot194$; $r(C-H'')=1\cdot102$; $\angle H'NH''=118^\circ43$; $\angle H'NC=120^\circ35'$, $\angle H'NC=$ $117^\circ10'$; $\angle NCO=123^\circ48'$; $\angle OCH=113^\circ27'$, $\angle OCH=$ $=122^\circ45'$; $\angle DH'N-C_1H=12^\circ52'$	135

contd.

Table 1

Substance	No. of isotopic species investigated	Structure parameters* (Å)	Reference
$HCONH_2$	10(^1H, ^2D, ^{12}C, ^{14}N, ^{15}N, ^{16}O)	*For* HCO $^{15}NH_2$: $r(N—C) = 1·014$; $r(N—H') = 1·001$; $r(N—C) = 1·376$; $r(C=O) = 1·192$; $r(C—H'') = 1·103$; ∡ $H'NH'' = 119°3'$; ∡ $H''NC = 120°38'$; ∡ $H'NC = 117°9'$; ∡ $NCO = 123°48'$; ∡ $NCH = 113°1'$; ∡ $OCH = 123°11'$; ∡ $DH''N—CO = 6°43'$; ∡ $DH''N—CH = 11°18'$ (H' lies *trans* to aldehyde-H; H'' lies *cis* to aldehyde-H)	185
$HCOOH$	3(^1H, ^2D, ^{12}C, ^{16}O)	$r(C—H) = 1·092 \pm 0·01$; $r(C=O) = 1·237 \pm 0·002$; $r(C—O) = = 1·312 \pm 0·002$; $r(O—H) = 0·961 \pm 0·01$; ∡ $OCO = 12°57' \pm 15'$; ∡ $HCO = 120°58' \pm 15'$; ∡ $COH = 107°50' \pm 10'$	21
$HCOOCH_3$	9(^1H, ^2D, ^{12}C, ^{13}C, ^{16}O, ^{18}O)	$r(C=O) = 1·200 \pm 0·01$; $r(C—O)_{carboxyl} = 1·334 \pm 0·01$; $r(C—H)_{carboxyl} = 1·101 \pm 0·01$; $r(C—O)_{methoxyl} = 1·437 \pm 0·01$; $r(C—H)_{methyl} = 1·086 \pm 0·015$; ∡ $OCO = 125°52' \pm 1°$; ∡ $HCO_{carboxyl} = 109°18' \pm 1°$; ∡ $COC = 114°47' \pm 1°$; ∡ $HCH = 110°40' \pm 1°30'$	124
$CH_3—CH_2F$	12(^1H, ^2D, ^{12}C, ^{13}C)	$r(C—C) = 1·533$; $r(C—F) = 1·379$; $r(C_{(1)}—H) = 1·094$; $r(C_{(2)}—H_{(3)}) = 1·092$; $r(C_{(2)}—H_{(5)}) = 1·098$; ∡ $CCF = = 109°27'$; ∡ $C_{(2)}C_{(1)}H = 111°17'$; ∡ $C_{(1)}C_{(2)}H_{(3)} = 110°6'$; ∡ $C_{(1)}C_{(2)}H_{(6)} = 110°10'$	177
$CH_3—CH_2—CH_3$	6(^1H, ^2D, ^{12}C, ^{13}C)	$r(C—C) = 1·526 \pm 0·002$; ∡ $CCC = 112°24' \pm 12'$; CH_2-group: $r(C—H) = 1·096 \pm 0·002$; ∡ $HCH = 106°6' \pm 12'$; CH_3-groups: $r(C—H_{(6)}) = 1·089 \pm 0·009$; $r(C—H_{(a)}) = 1·094$; $r(C—H)_{av.} = 1·091 \pm 0·01$; ∡ $H_{(a)}CH_{(a)} = 107°18'$; ∡ $H_{(a)}CH_{(s)} = 108°6'$; ∡ $HCH_{av.} = 107°42' \pm 1°$; ∡ $CCH_{(s)} = 111°48' \pm 1°$; ∡ $CCH_{(a)} = 110°42'$	
$CH_3—COF$	8(^1H, ^2D, ^{12}C, ^{13}C, ^{16}O, ^{18}O)	*Assuming symmetrical* CH_3-*group*: $r(C—C) = 1·503 \pm 0·003$; $r(C—F) = 1·348 \pm 0·015$; $r(C=O) = 1·181 \pm 0·01$; ∡ $CCF = = 110°18' \pm 1°$; ∡ $CCO = 128°21' \pm 1°$; $r(C—H) = 1·084 \pm 0·003$; ∡ $CCH = 109°30' \pm 1°$ *Assuming asymmetrical* CH_3-*group*: $r(C—C) = 1·502$; $r(C—F) = = 1·343$; $r(C=O) = 1·185$; ∡ $CCF = 110°44'$; ∡ $CCO = = 127°54'$; $r(C—H)_{in-plane} = 1·082$; $r(C—H)_{out-of-plane} = 1·096$ ∡ $CCH_{in-plane} = 110°24'$; ∡ $CCH_{out-of-plane} = 108°48'$; ∡ $HCH_{in-plane} = 110°51'$ ∡ $HCH_{out-of-plane} = 107°16'$	99

Molecule	Isotopic species	Structural parameters	Ref.
CH₃·COCl		$= 1\cdot192\pm0\cdot01$; $r(C-Cl) = 1\cdot789\pm0\cdot005$; $\angle$ CCH $= 110°21'\pm10'$; $\angle$ CCO $= 127°5'\pm10'$; $\angle$ CCCl $= 112°39'\pm30'$	
CH₃—COCN	8(¹H, ²D, ¹²C, ¹³C, ¹⁴N, ¹⁶O, ¹⁸O)	$\pm0\cdot005$; $r(C≡N) = 1\cdot164\pm0\cdot005$; $r(C_{methyl}-C_{carbonyl}) = 1\cdot490\pm0\cdot01$; $r(C_{carbonyl}-C_{cyanide}) = 1\cdot466\pm0\cdot01$; $\angle$ HCH $= 108°44'\pm30'$; $\angle$ C_{methyl}CO $= 124°3'\pm1°$; $\angle$ CCN $= 114°50'\pm1°$	68
CH₃—SiH₂F	6(¹H, ²D, ¹²C, ²⁸Si, ²⁹Si, ³⁰Si)	$r(Si-C) = 1\cdot849\pm0\cdot005$; $r(Si-F) = 1\cdot597\pm0\cdot005$; $r(Si-H) = 1\cdot477\pm0\cdot005$; $r(C-H) = 1\cdot099\pm0\cdot005$; $\angle$ HSiH $= 110°0'\pm30'$; $\angle$ CSiH $= 112°28'\pm1°30'$; $\angle$ HCH $= 108°29'\pm30'$; $\angle$ CSiF $= 108°53'\pm30'$	171
CH₃—SiHF₂	4(¹H, ²D, ²⁸Si, ²⁹Si, ³⁰Si)	$r(Si-C) = 1\cdot840\pm0\cdot01$; $r(Si-F) = 1\cdot580\pm0\cdot008$; $r(Si-H) = 1\cdot471\pm0\cdot01$; $r(C-H) = 1\cdot094\pm0\cdot005$; $\angle$ FSiF $= 107°6'\pm30'$; $\angle$ CSiH $= 115°32'\pm1°$; $\angle$ CSiF $= 109°22'\pm30'$; $\angle$ HCH $= 108°32'\pm30'$	171
CH₂=CH—SiH₃	11	$r(C-C) = 1\cdot347$; $r(Si-C) = 1\cdot852)$; $r(Si-H) = 1\cdot475$; $r(C-H)_{trans} = 1\cdot097$; $r(C-H)_{cis} = 1\cdot097$; $r(C-H) = 1\cdot094$; $\angle$ SiCC $= 122°53'$; $\angle$ HSiH $= 108°42'$; $\angle$ CCH$_{trans} = 120°38'$; $\angle$ CCH$_{cis} = 120°18'$; $\angle$ CCH $= 117°59'$	194
CH₂=CHF	3(¹H, ¹²C, ¹³C)	$\angle$ HCH $= [120°]$; $\angle$ CCH $= [120°]$; $r(C_{(1)}-H) = 1\cdot075\pm0\cdot005$; $r(C=C) = 1\cdot337\pm0\cdot002$; $r(C_{(2)}-H) = 1\cdot080\pm0\cdot005$; $r(C-F) = 1\cdot344\pm0\cdot002$; $\angle$ CCF $= 121°\pm12'$	90
CH₂=CHCl	9(¹H, ²D, ¹²C, ¹³C, ³⁵Cl, ³⁷Cl)	$r(C_{(1)}-H) = 1\cdot07_9$; $r(C_{(2)}-H_{(2)}) = 1\cdot07_8$; $r(C_{(2)}-H_{(3)}) = 1\cdot09_0$ $r(C-C) = 1\cdot33_2$; $r(C-Cl) = 1\cdot72_6$; $\angle$ CCH$_{(2)} = 119°32'$; $\angle$ CCH$_{(3)} = 121°1'$; $\angle$ HCH $= 119°27'$; $\angle$ CCCl $= 122°18'$; $\angle$ CCH$_{(1)} = 123°49'$; $\angle$ HCCl $= 113°53'$	164
CH₂=CHCN	6(¹H, ²D, ¹²C, ¹³C, ¹⁴N, ¹⁵N)	$r(C≡N) = 1\cdot163_7$; $r(C-C) = 1\cdot42_5$; $r(C=C) = 1\cdot338_9$; $r(C_{(1)}-H) = 1\cdot086_3$; $\angle$ CCC $= 122°37'$; $\angle$ HCC $= 121°44'$	19
CF₂=CHCl	2(¹H, ¹²C, ³⁵Cl, ³⁷Cl)	$[r(C=C)] = r(C-F)$, $r(C-Cl)$, for 2 different $[r(C=C)]$	59
CH≡C—CHO	15(¹H, ²D, ¹²C, ¹³C, ¹⁶O, ¹⁸O)	$r(C-H_{methynyl}) = 1\cdot055_3\pm0\cdot001$; $r(C-H)_{aldehyde} = 1\cdot1\cdot64_6\pm0\cdot001$; $r(C≡C) = 1\cdot208_9\pm0\cdot001$; $r(C-C) = 1\cdot444_6\pm0\cdot001$; $r(C=O) = 1\cdot215_0\pm0\cdot001$; $\angle$ CCO $= 123°47'\pm10'$; $\angle$ CCC $= 178°24'\pm10'$; $\angle$ CCH$_{aldehyde} = 113°54'\pm10'$; $\angle$ CCH$_{methynyl} = 180°0'$	18
CH₂=C=O	5(¹H, ²D, ¹²C, ¹³C, ¹⁶O, ¹⁸O)	$r(C-H) = r(C-D) = 1\cdot083$; $\angle$ HCH $= \angle$ DCD $= 122°35'$; $r(C-C) = 1\cdot314\pm0\cdot01$; $r(C-O) = 1\cdot161\pm0\cdot01$	20
CH₃—O—CH₃	2(¹H, ²D, ¹²C, ¹⁶O)	*Assuming 3-fold symmetry for CH₃-groups:* $r(C-O) = 1\cdot417$; $r(C-H) = 1\cdot093$; $\angle$ COC $= 111°37'$; $\angle$ HCH $= 109°51'$	60

contd.

Table 1

Substance	No. of isotopic species investigated	Structure parameters* (Å)	Reference
CH_3—S—CH_3	4	r(C—S) = 1·800±0·002; r(C—H) = 1·098±0·004; $\angle$ CSC = 98°54'±12'; $\angle$ HCH = 109°8'±20'	152
CH_3—CO—CH_3	2(^{1}H, ^{2}D, ^{12}C, ^{16}O)	r(C=O) = [1·215±0·005]; r(C—C) = 1·515±0·005; r(C—H) = 1·086±0·01; $\angle$ HCC = 110°16'; $\angle$ CCC = 116°7'	111
CH_2—CH_2—CH_2 |_____| O	4(^{1}H, ^{2}D, ^{12}C, ^{16}O, ^{18}O)	r(C—C) = 1·549±0·003; r(C—O) = 1·449±0·002; r(C(α)—H) = 1·091±0·002; r(C(β)—H) = 1·100±0·003; $\angle$ CCC = 84°33'±1'; $\angle$ COC = 91°59'±7'; $\angle$ CCO = 91°44'±3'; $\angle$ HC(α)H = 110°18'±10'; $\angle$ HC(β)H = 110°44'±3'	224
HC=CH \ CH_2	4(^{1}H, ^{2}D, ^{12}C)	r(C—C) = 1·515; r(C=C) = 1·300; r(C—H)$_{methylene}$ = 1·087±0·004; r(C—H)$_{vinyl}$ = 1·070; $\angle$ HCH = 114°42'±10'; $\angle$ $C_{vinyl}C_{vinyl}$H = 149°55'	61
HC^3 HC$_4$ $_2$N HC$_5$ $_1$CH N^6	2(^{1}H, ^{2}D, ^{12}C, ^{14}N)	*Assuming planar ring:* r(C$_{(1)}$—N$_{(2)}$) = 1·34; r(N$_{(2)}$—C$_{(3)}$) = 1·34; r(C$_{(3)}$—C$_{(4)}$) = 1·39; r(C$_{(1)}$—H) = 1·09; r(C$_{(3)}$—H) = 1·085; r(C$_{(4)}$—H) = 1·08; $\angle$ NCN = 120°; $\angle$ CNC = 121°; $\angle$ N$_{(2)}$C$_{(3)}$H = 120°24'; $\angle$ NCC = 119°36'; $\angle$ CCC = 116°48'	206
CH_3—GeH_3	25(^{1}H, ^{2}D, ^{12}C, ^{13}C, ^{70}Ge, ^{72}Ge, ^{74}Ge, ^{76}Ge)	*1st Method:* r (C—H) = 1·089±0·005; r(Ge—H) = 1·534±0·005; r(C—Ge) = 1·9453±0·005; $\angle$ HCH = 108°14'±30'; $\angle$ HGeH = 108°38'±30' *2nd Method:* r(C—H) = 1·083±0·005; r(Ge—H) = 1·529±0·005; r(C—Ge) = 1·9453±0·005; $\angle$ HCH = 108°25'±30'; $\angle$ HGeH = 109°15'±30'	71
$(CH_3)_3$CH	6(^{1}H, ^{2}D, ^{12}C, ^{13}C)	*Assuming H atoms of CH_3-groups are equidistant:* r(C—C) = 1·525±0·001; $\angle$ CCC = 111°9'±6'; r(C$_{tertiary}$—H) = 1·108±0·001; r(C$_{methyl}$—H$_{(s)}$) = 1·100±0·003; $\angle$ CCH$_{(s)}$ = 109°24'±18'; r(C$_{methyl}$—H$_{(a)}$) = 1·092; $\angle$ H$_{(a)}$CH$_{(a)}$ = 108°30'; $\angle$ H$_{(a)}$CH$_{(s)}$ = 107°54'	178
$(CH_3)_3$SiH	11(^{1}H, ^{2}D, ^{12}C, ^{13}C, ^{28}Si, ^{29}Si, ^{30}Si)	r(C—Si) = 1·868±0·002; r(Si—H) = 1·489±0·001; r(C—H) = 1·095±0·002; $\angle$ CSiC = 110°10'±12'; $\angle$ HCH = 107°56'±14'	196

*Assumed values are given in square brackets.

166
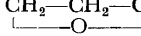
as a wide range spectrometer of the type necessary for structural determinations, *etc.*, in molecular physics.

RESULTS CONCERNING MOLECULAR STRUCTURES

In the years 1959 and 1960, the structure parameters of about forty molecules have been determined. *Table 1* contains the results for those cases where the rotational constants of a sufficient number of isotopic species have been available for the structure parameters to be determined. In addition, some other molecules have been included, for which only one parameter

Table 2. Potential barriers

Substance	V_0 (cal/Mol)	V_0 (cm^{-1})	Reference
One group with 3-fold axis of symmetry			
CH_3—COF	$1,041 \pm 6$	364 ± 2	99
CH_3—COCl	$1,296 \pm 30$	453 ± 10	237
CH_3—COBr	$1,305 \pm 30$	456 ± 10	170
CH_3—COCN	$1,210 \pm 30$	444 ± 10	68
CH_3—GeH$_3$	$1,239 \pm 25$	433 ± 8	71
HCOOCH$_3$	$1,190 \pm 40$	416 ± 13	21
CH_3—CH$_2$—CH$_3$ $\left\{\begin{array}{l}\\\\\end{array}\right.$	$> 3,000$ $> 2,700$	$> 1,049$ > 944	74 177
CH_3—CH$_2$CN	$3,050$	$1,067$	72
CH_3—CH=CHCN (*trans*)	$> 2,100$	> 734	175
CH_3—CH=CHF (*cis*) .	$1,030$	360	128
SiH$_3$—CH=CH$_2$	$1,500 \pm 30$	523 ± 10	194
CH_3—O—NO$_2$ (ground state)	$2,300$	804	$\left.\begin{array}{l}\\\\\end{array}\right\}$ 24
CH_3—O—NO$_2$ (first excited state of NO$_2$-torsional vibration)	$1,800$	630	
Two groups with 3-fold axis of symmetry			
CH_3—O—CH$_3$	$2,720 \pm 150$	950 ± 50	60
CH_3—S—CH$_3$ $\left\{\begin{array}{l}\\\end{array}\right.$	$2,090 \pm 100$ $2,130 \pm 30$	730 ± 30 745 ± 10	204 152
$(CH_3)_2SiH_2$ $\left\{\begin{array}{l}\\\end{array}\right.$	$1,665 \pm 10$ $1,647 \pm 120$	582 ± 3 576 ± 40	98 234
$(CH_3)_2C$=CH$_2$	$2,300$	804	70
Three groups with 3-fold axis of symmetry			
$(CH_3)_3As$	$1,500$–$2,500$	525–874	75
$(CH_3)_3SiH$	$1,830 \pm 400$	640 ± 140	196
2-Fold potential			
F$_2$N—N$_2$F	$> 3,000$	$> 1,049$	78
⬡—OH	$3,150 \pm 300$	$1,100 \pm 100$	165
"Inversion"			
CH$_2$—CH$_2$—CH$_2$ $\underline{\quad}$O$\underline{\quad}$	100 ± 15	35 ± 5	134

value had to be assumed in order to calculate the others from the available rotational constants.

Besides the determination of very accurate values for molecular structure parameters, the determination of low potential barriers for internal rotation has become one of the most important and useful contributions of microwave spectroscopy to the investigation of molecular properties. *Table 2* contains the results in this field which have been published since the beginning of 1959.

Table 3. Equilibrium configurations of rotational isomers
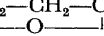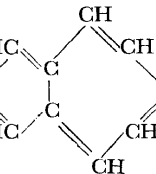
Substance	Equilibrium configuration	Reference
CH_3—CH_2F	Staggered	124
CH_3—COF	O eclipsed with one methyl-H	99
CH_3—COCl	O eclipsed with one methyl-H	237
CH_3—COCN	O eclipsed with one methyl-H	68
CH_3—CH_2—CH_3	Both methyl groups staggered with respect to methylene group	177
$(CH_3)_3CH$	Each methyl group staggered with respect to methine group	178
$(CH_3)_3SiH$	Each methyl group staggered with respect to siline group	194
CH_3—$SiHF_2$	Staggered	171
CH_2=CH—SiH_3	Silyl group staggered with respect to methine group	194
$HCOOCH_3$	Methyl group staggered with respect to formyl group	21
⬡—OH	Planar	165

Table 4(a). Dipole moments of molecules which are linear or symmetric tops

Substance	μ (D)	Reference
Linear molecules		
DCl	$1 \cdot 12 \pm 0 \cdot 04$	12
DBr	$0 \cdot 83 \pm 0 \cdot 02$	12
DI	$0 \cdot 445 \pm 0 \cdot 02$	12
OH radical $\left\{\begin{array}{c}\\\\\end{array}\right.$	$1 \cdot 65 \pm 0 \cdot 25$	232
	$2 \cdot 1 \pm 0 \cdot 4$	225
HCN	$2 \cdot 986 \pm 0 \cdot 002$	47
FCN	$1 \cdot 68 \pm 0 \cdot 05$	209
HC≡CF	$0 \cdot 75 \pm 0 \cdot 01$	217
Symmetric tops		
ReO_3F	$0 \cdot 85 \pm 0 \cdot 05$	84
CH_3—GeH_3	$0 \cdot 635 \pm 0 \cdot 006$	71
$(CH_3)_3CD$	$0 \cdot 132 \pm 0 \cdot 001$	178
$(CH_3)_3SiH$	$0 \cdot 525$	196
$(CH_3)_3As$	$0 \cdot 86 \pm 0 \cdot 02$	75
$(CH_3)_3NBF_3$	~ 5	198
CF_3Cl	$0 \cdot 499 \pm 0 \cdot 002$	229

Table 4(b). Dipole moments of molecules which are symmetric tops

Substance	$\overset{*}{\mu}_a$ (D)	$\overset{*}{\mu}_b$ (D)	μ_{total} (D)	*Ref.*
F_2N—NF_2			0·26	78
NH_2CN			4·3	117
NOCl	1·86			6
NOBr	1·80			31
NO_2Cl			0·53	16
HNO_3	1·99	0·83	2·16±0·02	184
S_2O	0·875±0·01	1·18±0·02	1·47±0·02	88
SF_4			0·64	227
CH_3—O—NO_2	3·06	0·2	3·07	24
$CH_2(CN)_2$			3·735±0·017	153
$CHClF_2$	0·12±0·02	$\overset{*}{\mu}_c = 1·45±0·02$	1·46±0·02	129
HCOF	0·595±0·006	1·93₄±0·02	2·02±0·02	176
	0·58±0·02	1·91±0·03	1·99±0·03	144
DCHO	0·61±0·03	1·96±0·03	2·05±0·03	144
	0·21	2·30	2·31	220
$HCOOCH_3$	1·63	0·68	1·77±0·03	21
CH_3—CH_2I	1·75±0·05	0·25±0·1	1·77±0·1	160
CH_3—CH_2CN	3·78±0·03	1·38±0·04	4·02±0·04	72
CH_3—CH_2OH	1·18	1·37	1·81	104
CH_3—CHF_2	2·01±0·01	1·12±0·03	2·30±0·03	173
CH_3—COF	2·83	0·88	2·96±0·03	} 99
CH_3—$C^{18}OF$	2·92	0·30	2·94±0·06	
CH_3—COCN	2·42	2·46	3·45±0·06	68
CH_3—CH_2—CH_3			0·083±0·001	177
CH_2=CHCl	1·42±0·02	0 or < 1		164
CHF=CHF			2·43±0·03	231
CH_3—CF=CH_2	0·92±0·01	1·31±0·01	1·60±0·02	100
CH_3—CO—CH_3			2·90	111
$(CH_3)_2SiH_2$			0·75±0·01	234
CH_3—CH_2—SiH_3	0·72	0·36	0·81	195
CH_2=CH—SiH_3	0·648	0·133	0·662	194
CH_2—CH_2—CH_2 └──O──┘			1·93±0·01	134
H_2C—CO │ │ H_2C—CH_2	3·02			239
H_2C——CH_2 │ H_3C CH_2 CO	3·30±0·01	0	3·30±0·01	66
HC=CH \/ CH_2	0·455±0·01	0	0·455±0·01	61
CH HC C CH HC CH HC C CH CH			1±0·5	239
⬡—F			1·66±0·03	67

Substance	$\mu_∥$† (D)	$\mu_⊥$† (D)		
CH_3SH (ground state)	1·33±0·03	0·73±1·03		166
CH_3SH (excited state of torsional oscillation)	1·36	0·76		

* a, b and c refer to the axes of the smallest, medium and greatest moments of inertia respectively.
† ∥ and ⊥ respectively refer to the directions parallel and perpendicular to the axis of internal rotation.

In measuring the potential barrier to internal rotation, it is often possible to determine from the microwave spectrum the exact molecular configuration for the equilibrium positions of the movable group. There are several different methods, and the results are assembled in *Table 3*.

Yet another field of molecular physics for which microwave spectroscopy gives information not attainable by other methods is the determination of dipole moments by means of the Stark effect of the rotational spectra. There are two advantages of the microwave spectroscopic method compared with the usual dielectric method. Firstly, the Stark effect gives the components of the dipole moment related to the axes of inertia of the molecule. That means that, in molecules of low symmetry, for which the orientation of the dipole moment within the molecule is not given by the symmetry, this orientation can be deduced from the values of the dipole components. Secondly, very small dipole moments can be measured reliably and accurately by this means. *Table 4* contains the results of microwave spectroscopic dipole moment determinations which have been published since the beginning of 1959, and gives numerous examples of the advantages claimed for this method.

Abstracts are indicated by the letter **A.**

1959

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