

# MODERN ASPECTS of MICROWAVE SPECTROSCOPY

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## 4. Modern Submillimetre Microwave Scanning Spectrometry

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### 1. INTRODUCTION

For a very long period of time, the sensitivity of the techniques available to the submillimetre spectroscopist were so significantly behind those available in the neighbouring microwave and infrared regions that the constant reference to the "submillimetre spectroscopic gap" was fully justified. Initially the submillimetre region was explored by extending the capabilities of the familiar infrared spectrometers to longer wavelengths. These spectrometers are equipped with a thermal (i.e. hot black-body) source and they therefore have the advantage that a wide spectral range can be readily scanned. One can get therefore a broad continuous picture of the region to be investigated and this can give a wealth of information and be of

considerable heuristic significance. The disadvantages all stem from the low power per unit frequency interval of black body sources. This means that the resolving power will always be low and the sensitivity poor.

The first penetration into the submillimetre range from the microwave side was made in the forties and fifties using microwave spectrometers having a classical layout appropriate for the centimetre-band scheme of operation but using a harmonic generator as the source of the coherent radiation [1]. This first microwave approach to the submillimetre range made possible substantial increases in the resolving power, the accuracy of measurement of the line frequency and (with the further development of the technique) the sensitivity of these spectroscopic methods when compared with the infrared-type incoherent ones. However, in comparison with the microwave spectrometers in the centimetre region which had quickly achieved sensitivity and resolving power values close to the theoretically predicted limits for this type of spectrometer [2], these submillimetre microwave spectrometers, of the first generation, had some orders of magnitude poorer sensitivity and they were not able to scan a broad range of frequencies. These disadvantages were mainly due to the low efficiency of harmonic multiplication which meant that there was little power in the harmonics and also to the complexity of the radiation spectrum produced by the harmonic generators. However, there were other difficulties such as the problem of broad-band tuning, the increasing problem of mode interference in the oversized guides, the worsening of receiver characteristic with increasing frequency as well as the inefficiency of the conventional methods of signal recovery. Nevertheless the great skill of the experimenters working in this field made it possible to obtain submillimetre spectroscopic data on a large number of molecules; but the inefficiency and complexity of these methods prevent their being suitable for the extensive spectroscopic exploration of the submillimetre region of the spectrum (for example the development of commercial spectrometers, spectral catalogues, etc.). A systematic presentation of the state-of-the-art of these techniques has been given in some recent books [3, 4, 5].

The appearance of broad-band primary sources of coherent submillimetre radiation with considerably larger power—the backward-wave oscillators (BWOs) [6]—has stimulated new efforts in the development of scanning submillimetre spectrometers. In this connection, the pioneering work of A. M. Prokhorov and his co-workers should be especially mentioned [14]. However, to make the most effective use of such radiation sources in a microwave gas spectrometer, it was necessary to develop adequate broad-band and frequency-independent receivers, to devise effective means of recovering useful spectral line signal and to have available methods of control and measurement of the output frequency of these

coherent sources over a requirements it first proved design in which changes in s for example) are monitored one detects changes in the r To realize this concept for t it is convenient to use the detection† [8].

The scanning spectrom submillimetre backward-wa RAD [7, 9] (from the initia acoustic detection"). The increase of the available sig up to some millions. With t precise digital control of tl been possible to increase t region to one part in  $10^8$  or microwave spectroscopy 1 magnitude up to frequencie secured with an experimen for commercial exploitation

The availability of scan metre region opened a n development the sensitivit measurement of the alterna chapter). The new spectrom coherent spectrometers in regions. Thus they had t scanning microwave spec frequency precision of c example the spin-flip Rama loss of sensitivity. Figure 1 coherent scanning system spectroscopic method will frequency measurement and suppose that the main inte

† This method is particularly su liquid samples one might use th variations of capacity for register the sample ( $\Delta\epsilon/\epsilon \sim 10^{-11}$ ) under proposition is to use the coherent the radiation from the source.

tages all stem from the low  $\gamma$  sources. This means that sensitivity poor.

range from the microwave microwave spectrometers centimetre-band scheme of the source of the coherent to the submillimetre range ing power, the accuracy of further development of the methods when compared er, in comparison with the region which had quickly s close to the theoretically r [2], these submillimetre tion, had some orders of able to scan a broad range due to the low efficiency of ere was little power in the idiation spectrum produced ere other difficulties such as creasing problem of mode ing of receiver characteristic ciciency of the conventional eat skill of the experimenters submillimetre spectroscopic efficiency and complexity of the extensive spectroscopic spectrum (for example the pectral catalogues, etc.). A of these techniques has been

ources of coherent submilli-power—the backward-wave efforts in the development of ; connection, the pioneering workers should be especially effective use of such radiation t was necessary to develop endent receivers, to devise e signal and to have available e output frequency of these

coherent sources over a broad continuous range. To satisfy these requirements it first proved very useful to adopt the concept of spectrometer design in which changes in some parameter of the specimen (its temperature for example) are monitored rather than to follow the older practice in which one detects changes in the radiation after it has traversed the specimen [7]. To realize this concept for the particular case of a microwave spectrometer it is convenient to use the well known and proven method of acoustic detection† [8].

The scanning spectrometer developed on the basis of broad-band submillimetre backward-wave oscillators and acoustic detection was called RAD [7, 9] (from the initial letters of the phrase "radio-spectroscope with acoustic detection"). The development of this spectrometer led to an increase of the available signal-to-noise ratio from values of typically 1–10 up to some millions. With the addition in very recent years of the system of precise digital control of the submillimetre BWO output frequency it has been possible to increase the accuracy of frequency measurements in this region to one part in  $10^8$  or even one part in  $10^9$ , and the range of scanning microwave spectroscopy has been extended more than an order of magnitude up to frequencies greater than 1 THz. These advances have been secured with an experimental system so simple that it is readily adaptable for commercial exploitation.

The availability of scanning microwave spectrometers in the submillimetre region opened a new field of spectroscopy, since prior to this development the sensitivity, resolution limits and accuracy of frequency measurement of the alternative methods were all much lower (see the next chapter). The new spectrometers, moreover, compared very favourably with coherent spectrometers in either of the adjoining microwave or infrared regions. Thus they had broader spectral coverage than the centimetre scanning microwave spectrometers and they could readily better the frequency precision of coherent scanning infrared spectrometers (for example the spin-flip Raman laser). These advantages were secured without loss of sensitivity. Figure 1 shows the spectral regions covered by the three coherent scanning systems. The "information yielding power" of a spectroscopic method will be defined by its sensitivity, its precision of frequency measurement and its bandwidth and there is thus every reason to suppose that the main interest in microwave spectroscopy will continue to

† This method is particularly suitable but one can readily think of others. Thus for solid and liquid samples one might use the circuit given later for determining small ( $\Delta C/C \sim 10^{-11}$ ) variations of capacity for registering the corresponding variations of the dielectric constant of the sample ( $\Delta\epsilon/\epsilon \sim 10^{-11}$ ) under the action of radiation. For gaseous specimens, an attractive proposition is to use the coherent spontaneous radiation from molecules previously excited by the radiation from the source.

be (see Chapter 1) at its high-frequency limit and this at present lies in the submillimetre range.

The spectroscopic potential of the submillimetre region is enhanced by the lucky coincidence that the maxima of intensity of the rotational spectra of a large number of molecules of interest lie in this range. Submillimetre spectroscopy has its own "distinguished class of spectra". This is illustrated in Fig. 1 where is shown the envelope of the room-temperature rotational spectrum of OCS. The potential of the high sensitivity of the method

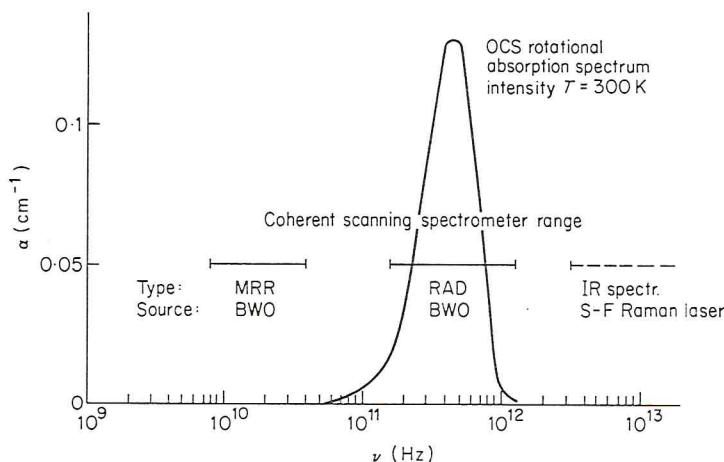


FIG. 1. The region covered by coherent submillimetre scanning RAD spectrometers and the region of maximum intensity of OCS rotational lines (at 300 K). For comparison are shown the neighbouring regions which are covered by coherent scanning spectrometers: microwave MRR [24] and infrared with spin-flip Raman lasers [31]. The existing upper end of precise microwave methods of scanning the frequency lies at approximately 1100 GHz. For lower frequencies the typical accuracy of scanning of the frequency reaches  $\sim 10^{-8}$ - $10^{-9}$  but for higher frequencies only  $\sim 10^{-5}$  [23, 24, 27, 31].

coupled with the maximum of intensity, for detecting the rotational spectra of molecules present at low concentration (free radicals for example) is obvious. The present stage of development of submillimetre scanning spectrometry provides a solution to the practical needs of those exploring the submillimetre region at very high resolution. Earlier steps in the ongoing programme of development are described in a review [9]. This chapter describes further developments of new methods of submillimetre microwave scanning spectrometry and also analyses some related consequences of these methods.

## 2. NOV THEOR' A COHI

It was mentioned above that in spectroscopy it is rather difficult to obtain from spectral lines is now being investigated, under the active practice, based on this method. RAD, has been developed significantly broader and higher sensitivity limits of micro techniques and methods for present chapter. The main earlier, are the possibility with RRCS (Table 1), the and the absence of false signals.

The RSCS sensitivity is due to the elimination of the large errors and the centimetre range. The scanning spectrometer records scanning the radiation source.

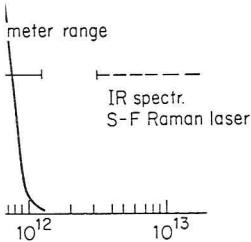
The elimination in RSCS is valuable for the realization of the possibility of recording the sensitivity.

TABLE 1. General classification of methods

I	Registering Radial Changes Spectrometer
IIA	Registering Sample Changes Spectrometer
IIB	

and this at present lies in the centimetre region is enhanced by sensitivity of the rotational spectra in this range. Submillimetre f spectra". This is illustrated by room-temperature rotational sensitivity of the method

OCS rotational absorption spectrum intensity  $T = 300\text{ K}$



scanning RAD spectrometers and the  $300\text{ K}$ ). For comparison are shown scanning spectrometers; microwave . The existing upper end of precise approximately 1100 GHz. For lower frequency reaches  $\sim 10^{-8}\text{--}10^{-9}$  but for

detecting the rotational spectra (free radicals for example) is of submillimetre scanning needs of those exploring . Earlier steps in the described in a review [9]. This w methods of submillimetre analyses some related con-

## 2. NOVEL DEVELOPMENTS IN THE THEORY OF SPECTROMETRY WITH A COHERENT RADIATION SOURCE

It was mentioned above that for the development of scanning submillimetre spectroscopy it is rather useful to employ spectrometers in which the signal from spectral lines is registered as a change, in a sample parameter investigated, under the action of radiation (RSCS, see Table 1) [7, 9]. In practice, based on this conception, a submillimetre scanning spectrometer, RAD, has been developed; but the RSCS conception proved to be significantly broader and leads, in particular, to a re-estimation of the sensitivity limits of microwave spectrometers and to some new suggestions for techniques and methods of spectrometry. These will be given in the present chapter. The main consequences of RSCS application, mentioned earlier, are the possibility of considerable sensitivity increase in comparison with RRCS (Table 1), the independence of the sensitivity on the frequency and the absence of false signals [7, 9].

The RSCS sensitivity independence of the frequency makes possible the elimination of the large difference in sensitivity between the submillimetre and the centimetre ranges and is rather valuable for the realization of the scanning spectrometer regime which can be achieved in RSCS merely by scanning the radiation source frequency.

The elimination in RSCS of the majority of the false signal sources is also valuable for the realization of the scanning regime since it gives the possibility of recording large parts of the spectrum at the maximum sensitivity.

TABLE 1. General classification of spectrometers according to the method of signal formation from spectral lines

I	Registering Radiation Changes Spectrometers	RRCs with radiation receivers
IIA	Registering Sample Changes Spectrometers	RSCS with microscopic parameters receivers ("particles-in-the-level-counter" type)
IIB		RSCS with macroscopic parameter receivers ("acoustic detector" type)

Especially noted should be the possibility of increasing microwave spectrometer sensitivity associated with the use of RSCS. In references [7] and [9] there are given some estimations; they show that even spectrometers of the RAD type (registering the change of macroscopic gas parameters) may have better sensitivity in comparison with the conventional microwave Stark spectrometers. But the use of RSCS with a receiver of the type of "particles-in-the-level counter" will give essentially higher spectrometer sensitivity. Still more promising may be devices with receivers depending on the coherent parameters of molecular ensembles, the theory of which is now being developed. The creation of such spectrometers would be in our opinion the next important step in the development of microwave spectrometry.

New theoretical consequences of the use of RSCS, considered here, are rather general principles of the spectral line-shape and width control [10] and the possibility of obtaining additional information under conditions of spectral line saturation.

## 2.1. A New Method for Obtaining Sub-Doppler Resolution in Gas Spectrometers

At present there are two main directions for eliminating the Doppler line-broadening in gas spectrometers. Firstly one may select a group of molecules with a narrow spread of velocities about a mean (usually zero) or secondly one may use a means for compensating (i.e. subtracting) the Doppler shift. The selection method, of which the archetype is molecular beam spectroscopy, requires the physical separation of the molecules with the desired velocities from all the others. The group when separated will have a highly non-thermal velocity distribution. This is an illustration of the general principle that to obtain sub-Doppler resolution it is necessary to disturb the thermodynamic equilibrium of the gas.

It is worth noting that the interaction of an intense coherent wave with a gaseous sample is a non-equilibrium interaction and one may invoke this non-equilibriumity to obtain sub-Doppler line-widths. In quantum terms the primary effect of the resonance radiation action on the gas is to change the population of the resonant levels of the set of molecules whose velocities correspond to the radiation frequency. In other words one "burns a hole" in the population distribution. To then separate a group of molecules with zero Doppler frequency shift it is necessary to set up for the molecules a system of coordinates *fixed relative to the radiation source*. This may be done in only two ways: firstly by the radiation field itself (by for example setting up a standing wave pattern when the radiation passes through the cell twice in opposite directions), or secondly by mechanical means, using

the cell walls, diaphragms non-linear method [11, al new linear method of obta only be realized in RSCS s

The realization of this n based on the two-stage na spectrometer. In the first s phase) interacts with th radiation. At the second directly by a counter of effect it has on the macrosc is created corresponding physically separate the re diaphragms and baffles is molecules delivering the e velocity component in the large Doppler shifts, i.e. direction of the normal to instead lose their excita diaphragms. The RSCS corresponding to the cent considerable line-narrowi beam methods and here t plays the same role as doe beam methods, but this me methods, such as the ne operation of line-width compared with the non-s RRCS spectrometer is ill narrowing it is necessary t the molecules  $l_f$ , the dime angle (radians) of the dia radiation  $\lambda$ . In fact one mu

The calculation of the technique is detailed in Ap

<sup>†</sup>The receiver of excited part ionization by metastable atoms, excited atoms or molecules or a sufficiently large (to ensure the Finally the coherently excited en coherent spontaneous emission o

of increasing microwave of RSCS. In references [7] ; they show that even change of macroscopic gas comparison with the con- the use of RSCS with a unter" will give essentially using may be devices with of molecular ensembles, the ation of such spectrometers step in the development of

RSCS, considered here, are ape and width control [10] mation under conditions of

#### Doppler Resolution in Gas

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intense coherent wave with a on and one may invoke this widths. In quantum terms the n on the gas is to change the of molecules whose velocities r words one "burns a hole" in a group of molecules with o set up for the molecules a radiation source. This may be on field itself (by for example radiation passes through the by mechanical means, using

the cell walls, diaphragms, etc. The first way corresponds to the Lamb dip non-linear method [11, also Chapter 3]. The second way corresponds to a new linear method of obtaining a sub-Doppler line-width, but one that may only be realized in RSCS spectrometry.

The realization of this new form of sub-Doppler spectroscopy in RSCS is based on the two-stage nature of the formation of the signal in this class of spectrometer. In the first stage a particle (for example a molecule in the gas phase) interacts with the radiation field and absorbs a quantum of radiation. At the second stage this excited particle is registered either directly by a counter of excited particles<sup>†</sup> or else indirectly through the effect it has on the macroscopic parameters of the gas. In either way a signal is created corresponding to the absorption line. Now clearly we may physically separate the regions of absorption and detection and if a set of diaphragms and baffles is set up inside the cell, we can ensure that the molecules delivering the excitation to the detector will have an almost zero velocity component in the direction of the beam. Excited molecules having large Doppler shifts, i.e. moving with significant components along the direction of the normal to the wave front will not reach the detector but will instead lose their excitation in collisions with the walls or with the diaphragms. The RSCS receiver will therefore only register signals corresponding to the central part of the Doppler line and there will be a considerable line-narrowing. The process is strongly akin to molecular beam methods and here the geometrical angle defined by the diaphragms plays the same role as does the angle of divergence of the molecular beam in beam methods, but this method is free from some of the drawbacks of beam methods, such as the necessity to have permanent pumping, etc. The operation of line-width reduction in RSCR, by velocity selection as compared with the non-selective full Doppler-broadened operation of an RRCS spectrometer is illustrated in Fig. 2. Of course for effective line-narrowing it is necessary to fulfill some conditions on the mean free path of the molecules  $l_f$ , the dimensions of the plane wave front  $R$ , the geometrical angle (radians) of the diaphragm aperture  $\theta$  and the wavelength of the radiation  $\lambda$ . In fact one must have

$$l_f \gtrsim R \gg \lambda; \quad \theta \ll 1. \quad (2.1)$$

The calculation of the shape of sub-Doppler lines obtained by this technique is detailed in Appendix 1 and is shown in Fig. 3.

<sup>†</sup>The receiver of excited particles may be for example a detector which relies on surface ionization by metastable atoms, or a photomultiplier which detects the fluorescence from the excited atoms or molecules or a thermal acoustic receiver. In the last case the receiver is a sufficiently large (to ensure thermalization of the gas) chamber fitted with a microphone. Finally the coherently excited ensemble of particles may be detected by the reception of their coherent spontaneous emission of radiation.

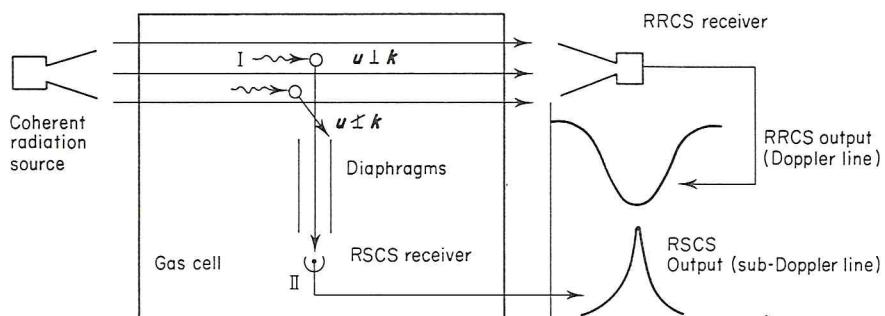


FIG. 2. A new method of obtaining sub-Doppler lines in gas spectrometers of RSCS type. Molecules are excited by the radiation from the coherent radiation source; diaphragms (partitions), before the receiver of excited molecules, select only Doppler-free molecules, the velocities of which are perpendicular to the direction of the radiation propagation ( $u \perp k$ ). Molecules for which  $u \parallel k$  strike the diaphragm. On the right are shown the forms of the output signals for the spectral lines obtained in the same gas cell with frequency scanning: sub-Doppler from RSCS detector (excited molecule detector) with molecule velocity selection and full Doppler from RRCS detector.

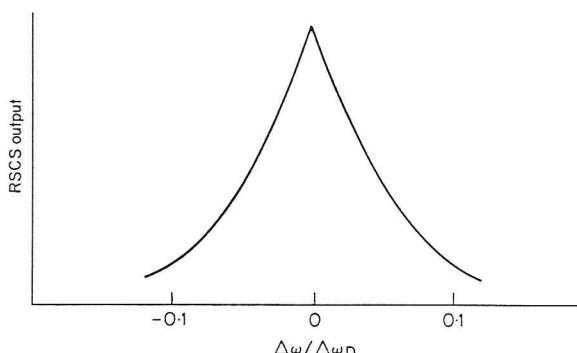


FIG. 3. Calculated shape of the sub-Doppler line for the RSCS cell of Fig. 12 (Appendix).  $\theta = 0.1$  and vanishingly small homogeneous line-width. In real conditions the peak is "rounded" by homogeneous (for example, time-of-flight) broadening. The scale along the frequency axis is in units of the Doppler line HWHM.

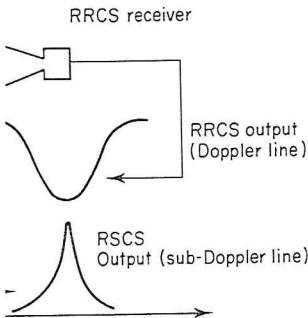
This new method completes, in principle, a certain class of methods for sub-Doppler operation based on velocity selection. What remains to be done is to determine the possible range of application of the method. This will depend on its inherent peculiarities namely that it is linear, it involves only a single passage of the beam through the cell and the line is properly recorded from a true zero level (not in the form of a dip as in the non-linear methods). It is possible that the optimum spectral region for the application of this method may be at shorter wavelengths, since there each molecule arriving at the detector will be bringing more energy and of course the

starting Doppler width is 1 spontaneous radiation als example it may be shown particular case of observat exceeds the sensitivity of th [12] especially in the case method may also be us spectrometer depending on by the molecules.

## 2.2. New Possibilities for Spectral Line Saturation

The regime of spectral line microwave spectroscopy. It may be used to provide a 1 It may also be used as Harrington [13] has illust type) where the saturation permits the determination i various species present in practical analytical problems. radiation power is different some new possibilities for s regime. RSCS also offers considerably larger radiati possible (in principle, any broader range of the experi

In contrast to Stark-modulation power increases, the signal and then tends to zero [1 centre of the line only is shape and of the amplitude Appendix 2. At large values of the amplitude (for RSCS) at the population of the lower level through the cell. The line-shape is proportional to the main root of the radiation power to determine the lower level separately unlike the case occur as a product [2, 13]



as spectrometers of RSCS type.  
t radiation source; diaphragms  
only Doppler-free molecules, the  
radiation propagation ( $u \perp k$ ).  
re shown the forms of the output  
l with frequency scanning: sub-  
h molecule velocity selection and

starting Doppler width is that much greater. Additionally, the intensity of spontaneous radiation also increases with increasing frequency. As an example it may be shown that the sensitivity of the new method in the particular case of observation of the excited particles by their fluorescence exceeds the sensitivity of the non-linear fluorescence method considered in [12] especially in the case of small intensity of the radiation field. This method may also be used to realize a "space-resolved" microwave spectrometer depending on the coherent spontaneous emission of radiation by the molecules.

## 2.2. New Possibilities for Spectroscopic Measurements under Conditions of Spectral Line Saturation

The regime of spectral line saturation is used for various purposes in microwave spectroscopy. Thus we have already seen in Chapter 1 how it may be used to provide a means of modulating a microwave spectrometer. It may also be used as an aid to quantitative measurement. Thus Harrington [13] has illustrated this for Stark spectrometers (i.e. the RRCS type) where the saturation effect is used for a specific calibration which permits the determination in quantatative terms of the concentrations of the various species present in the mixture and that is of course the whole practical analytical problem. Since the variation of signal with incident radiation power is different in RRCS and RSCS the use of the latter opens some new possibilities for spectroscopic measurements under the saturation regime. RSCS also offers the advantage that, since it is possible to use considerably larger radiation powers than are convenient in RRCS, it is possible (in principle, anyway) to achieve the saturation regime over a broader range of the experimental conditions.

In contrast to Stark-modulated spectrometers where, as the radiation power increases, the signal from the lines first passes through a maximum and then tends to zero [13], in RSCS the amplitude of the signal at the centre of the line only is saturated. The details of the calculation of the shape and of the amplitude of the spectral line signal observed are given in Appendix 2. At large values of the saturation parameter, the signal amplitude (for RSCS) at the centre of the line is proportional to the population of the lower level and does not depend on the power passing through the cell. The line-width, on the other hand, under these conditions is proportional to the matrix element of the transition and to the square root of the radiation power. It therefore follows that in RSCS it is possible to determine the lower level population and the transition matrix element separately unlike the case for RRCS where these two quantities always occur as a product [2, 13]. Following on from this, the possibility arises of

RSCS cell of Fig. 12 (Appendix).  
conditions the peak is "rounded"  
e scale along the frequency axis is

certain class of methods for  
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that it is linear, it involves  
ell and the line is properly  
of a dip as in the non-linear  
l region for the application  
since there each molecule  
energy and of course the

using RSCS measurements under the saturation regime as an aid to making assignments especially for broad-band sweeps. One looks for lines with the same signal amplitude and assumes these to have also the same or closely lying lower levels. It should be noted here that the line-shapes expected are close to the Lorentzian form (see Appendix 2). A final point is that it is possible to achieve an absolute calibration of the sensitivity (i.e. to determine line-intensities absolutely) in RSCS spectrometers by registration of the maximal signal value from the lines together with some additional measurements. These would include a measurement of the gas pressure in the cell and just a few frequency measurements to define the statistical sum, i.e. the structure of the molecular levels and the widths and the frequencies of the spectral lines.

### 3. MODERN CONSTRUCTION OF RAD SPECTROMETERS

A submillimetre RAD spectrometer consists of a scanned source of coherent submillimetre radiation (a BWO) with devices for radiation frequency control and frequency measurement together with an absorption cell (or cells) fitted with a microphone. The microphone is followed by the usual microphone circuits, amplifiers, synchronous detectors, etc., and the chain ends in a two-channel recorder. The devices considered in this section are those which correspond to the two principal modes of operation of the RAD spectrometer namely broad-band survey sweeps with a non-stabilized BWO and precise relatively narrow-band scans with the BWO stabilized against an accurately known reference signal.

#### 3.1. Scanning Sources of Submillimetre Coherent Radiation

The development of submillimetre scanning microwave spectrometers became a practical possibility only when backward wave oscillators covering this region became available. These sources have a monochromatic output, a "one-handle" frequency control and broad-band tuning capabilities. The main characteristics of the submillimetre BWOs which have been developed in the U.S.S.R. are shown in Table 2 [6]. Methods of frequency control and frequency measurement to be used with them are described below.

##### 3.1.1. Fast Broad-band Scanning of the BWO Output Frequency

Scanning of the BWO output frequency without stabilization is used to obtain the general picture of the spectrum over a broad frequency range. A frequency scale is set up on the record by simultaneously recording a

known reference spectrum. In this regime of work it is given by sufficiently stable driving of oscillation<sup>†</sup>. Its oscillations in the stabilized regime the BW sub-Doppler lines as narrow as possible. However, in this frequency range is rather unsatisfactory due to the dependence of the oscillation

TABLE 2. Main

Operating frequency range (GHz)	Magnetic field (Gauss)
175–270	
250–375	
370–535	
530–715	
710–940	
925–1250	
1200–1500	

Notes: (a) BWO current no milliwatts in the low-frequency range.

most important of which is the band spectrum with RAI. The response of the thermistor detector has to be a compromise between the frequency drift does not exceed the scale on the chart recorder. It can be easily taken into account in practice there is little problem enough to record most spectra and achieve resolution better than 100 MHz.

<sup>†</sup> The BWO may sometimes (either simultaneously or else from a spectroscopic point of view) be stabilized using a diffraction grating spectrometer using a known spectrum recorded and properly adjusted relative to the reference spectrum.

time as an aid to making  
looks for lines with the  
also the same or close-  
line-shapes expected are  
final point is that it is  
the sensitivity (i.e. to  
trometers by registration  
er with some additional  
nt of the gas pressure in  
define the statistical sum,  
widths and the frequencies

## SPECTROMETERS

canned source of coherent  
for radiation frequency  
than an absorption cell (or  
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ectors, etc., and the chain  
sidered in this section are  
modes of operation of the  
veeps with a non-stabilized  
with the BWO stabilized

## Radiation

microwave spectrometers  
backward wave oscillators  
rces have a monochromatic  
broad-band tuning capa-  
limetre BWOs which have  
Table 2 [6]. Methods of  
to be used with them are

## Input Frequency

out stabilization is used to  
a broad frequency range. A  
simultaneously recording a

known reference spectrum. A block diagram of the RAD device intended for this regime of work is given in Fig. 4. When the BWO is supplied from a sufficiently stable driving unit and it is operating in a single-frequency mode of oscillation† its oscillation is quite monochromatic: even in the non-stabilized regime the BWO radiation spectrum was sufficiently pure that sub-Doppler lines as narrow as 20 kHz [15] could be observed in a fast sweep. However, in this regime the long-time stability of the BWO frequency is rather unsatisfactory (hundreds of MHz) due to the strong dependence of the oscillation frequency on a number of parameters, the

TABLE 2. Main characteristics of submillimetre BWOs [6]

Operating frequency range (GHz)	Magnetic field strength (kOe)	Magnetic pole-to-pole distance (mm)	Maximum applied voltage (kV)
175–270	6	22	4
250–375	7	22, 30	4
370–535	9	30	4
530–715	10–12	40	6–6.5
710–940			
925–1250			
1200–1500			

Notes: (a) BWO current no more than 50 mA. (b) Output power varies from tens of milliwatts in the low-frequency region to 100 microwatts near 1500 GHz [6].

most important of which is the high voltage supply. In recording a broad-band spectrum with RAD and an unstabilized BWO, the mode of operation has to be a compromise between going slow enough to match the slow response of the thermal detector and going fast enough that BWO frequency drift does not seriously distort line profiles. The "local" frequency scale on the chart record will then be, of course, not constant but this can be easily taken into account by consideration of the reference spectrum. In practice there is little problem and the range of allowed scan rates is large enough to record most spectra. Difficulties only arise when one is trying to achieve resolution better than  $10^{-4}$  or  $5 \times 10^{-5}$  at a time constant of 1 s.

† The BWO may sometimes oscillate on two neighbouring modes of the slow-wave structure (either simultaneously or else jumping from one to the other). This phenomenon is, from a spectroscopic point of view, similar to that of "ghosts" which appear in the operation of diffraction grating spectrometers. The control of the BWO into a one-frequency regime is made using a known spectrum record: the principal experimental point is to ensure that the BWO is properly adjusted relative to the focusing magnetic field.

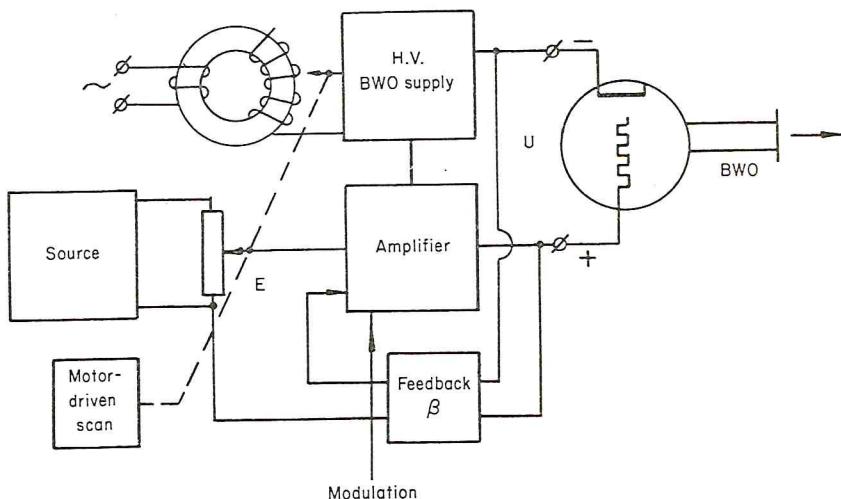
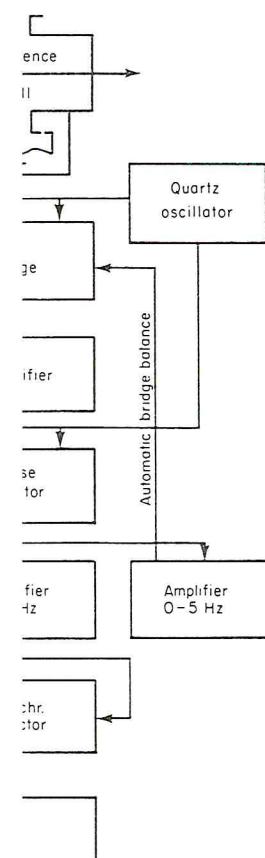


FIG. 5. Block-diagram of scanning stable supply source for the BWO used for the recording of survey spectra with the RAD spectrometer.

characteristics of  $10^{-5}/^{\circ}\text{C}$  and as the divider a precise multiturn potentiometer driven by a synchronous motor with variable gearing.

Deviation of the output voltage  $U$  from the desired value  $\beta^{-1}E$  may be due to an insufficient amplification coefficient  $K_e$  or else to drift of the D.C. amplifier. To provide the required quality of stabilization, the value  $\beta K_e$  of the stable source in this system amounts to  $5 \times 10^6$  and the drift is reduced to  $\sim 0.1 \text{ mV}/^{\circ}\text{C}$  by employing an amplifier built on the "modulator-amplifier-demodulator" principle in which the main amplification takes place at a high carrier frequency. The amplitude/frequency characteristic of the amplifier must satisfy the twin requirements of reproducing the square-wave modulation envelope without serious distortion and also of providing stable amplification. The modulation waveform has an amplitude up to 50 V with a frequency of 180 Hz and the stability requirement is that the amplitude/frequency characteristic should have a slope of less than 20 dB/decade except for the region where  $|\beta K_e| < 1$ . The design compromise chosen is to have an amplifier bandwidth of nearly 0.5 MHz and to choose an amplitude/frequency characteristic of the form

$$|\beta K_e| = (5 \times 10^5)/\nu \quad (3.1.1)$$

for frequencies greater than 0.1 Hz. This is achieved by the use of correcting filters.

The system described provides a power supply and a modulation for the BWO in the range 500-5000 V (currents up to 50 mA) with residual pulsations no more than 2 mV, drift no more than 50 mV (at the maximum

of the spectrum with moderate from a reference spectrum. As the cell) and the reference spectrum on of scanning in one experiment

17] for a scanning BWO. Fig. 5. It is basically a servomechanism at a much higher power level. The reference voltage is supplied by it. The source of the voltage is obtained by dividing the linear scanning voltage by a step value of nearly  $10^{-5}$ . The reference voltage of a stabililator with stability