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MICROWAVE SPECTRAL STUDIES OF INTERSTELLAR MOLECULES

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Abstract - Although the study of the rotational spectra of molecules considerably predates the discovery of interstellar molecules, the radioastronomical applications make three special demands. The first of these is that large radiotelescopes often have been designed for work at lower frequencies than the frequency ranges popularly studied by microwave spectroscopists. A second problem is that some potentially interesting interstellar species are short-lived and rapidly destroyed under normal laboratory conditions. A third problem is that other interesting substances especially those of biological importance are not volatile under normal laboratory conditions. Much of the activity of the Monash University Microwave Group has been directed towards tackling these problems. For the first problem a large L-band cell suitable for Stark modulation has been built. Its performance is illustrated by some recent results on a low frequency line of deuteromethanol.
For the second problem several special purpose spectrometers have been constructed at Monash. Among other successful studies of unstable species we have recently detected HNC and its various isotopic variants. This molecule was simultaneously detected by two other groups using rather different experimental procedures. The Monash work alone led to a determination of the dipole moment of HNC.
To overcome the problem of molecules of low volatility other special spectrometers have been constructed. With these the spectrum of urea was analysed then, more recently, a number of lines in the spectrum of the simplest amino acid - glycine - have been detected. A partial analysis of the spectrum has already been achieved and the complete assignment is expected shortly.

The first interstellar molecules discovered-CH, CH^+ and CN - were identified in the 1930's from the presence of certain lines in the optical spectra of some distant hot stars such as ζ Oph (1). They remained something of an astronomical curiosity until, with the use of radioastronomy, first OH (2) and then, from 1969 on, a pharmacopoeia of chemical compounds were identified. A current list of known interstellar molecules is given in Table 1.

TABLE 1. Interstellar Molecules

Interstellar Molecules			
H_2		NH_3	$HC\equiv C-CN$
CH		H_2O	$CH_3-C\equiv CH$
CH^+		H_2CO	CH_3CN
CN		H_2CS	$HCONH_2$
CO		OCS	CH_3OH
CS		HCN	CH_3CHO
SiO		HNCO	CH_3OCH_3
SiS		H_2S	C_2H_5OH
SO		SO_2	$CH_2=CH-CN$
NS		HNC	HCO_2CH_3
OH		C_2H	NH_2CN
	HCO^+	HNO	$CH\equiv C-C\equiv C-CN$
	N_2H^+	HCO_2H	$CH_3-C\equiv C-CN$
	HCO	CH_2NH	$H-C\equiv C-C\equiv C-C\equiv C-CN$
			C_2H_5-CN
		CH_2-CH_2 \O/	$CH_2=C=O$

The molecules have been found, in the main, in dark nebulae-massive clouds of dust and gas that occur in various places in the Milky Way Galaxy and other galaxies. The discoveries have attracted great interest, not only because they provide valuable spectroscopic "tools" that enable astronomers and astrophysicists to elucidate the physical nature and composition of these, the coldest objects in the universe, but because dark nebulae are considered to be the sites of formation of new stars and new planetary systems. The chemical evolution of dark nebulae may be a significant first step along the tortuous path of evolution of life on suitable planets.

Microwave spectroscopy has played a crucial role in the discovery of interstellar molecules because it is the rotational transitions occurring in the microwave region that have been detected by radiotelescopes trained on dark nebulae. It was in a sense fortunate that this branch of molecular spectroscopy had been extensively developed in advance of the radioastronomical studies. In nearly all cases the interstellar molecular lines are so weak that there is no chance of scanning through a wide frequency range in the hope of detecting a molecular line. The telescope is used in multichannel mode in which a very tiny frequency range, usually just encompassing a single line, is observed over a very long integration time. Long integrations are usually needed in order to achieve acceptable signal/noise ratios. For example Fig. 1 illustrates the multiplet that was first detected by us on the Parkes radiotelescope and identified with the laboratory multiplet of the $1_{10} \rightarrow 1_{11}$ transition of methanimine ($CH_2 = NH$). It required integration over four days to achieve the modest S/N ratio exhibited in Fig. 1.

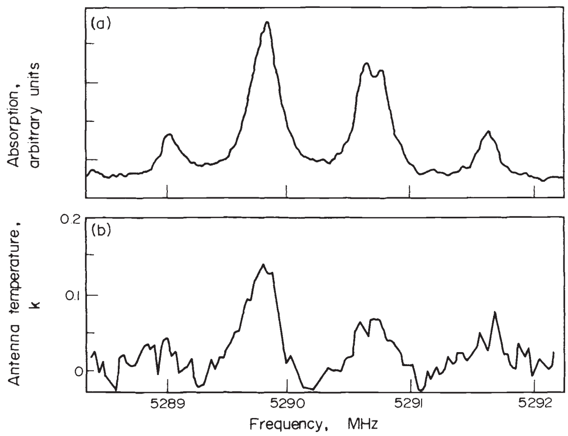

Fig. 1. The $1_{10} \leftarrow 1_{11}$ interstellar line of methanimine in Sgr. B2 (from P. D. Godfrey and R. D. Brown et. al., Astrop. Letters 13, 119-121 (1973)).
(a) laboratory spectrum
(b) telescope signal

From the spectroscopist's point of view there are several kinds of challenges associated with the study of interstellar molecules. Firstly some of the interesting molecular transitions involving the lowest rotational energy states fall at frequencies below those normally studied by microwave spectroscopists (i.e. below 8 GHz). At Monash University we have risen to the challenge by building a very large (L - band 15 cm × 71/2 cm cross-section) waveguide cell suitable for Stark modulation (Fig. 2) which, with suitable BWO sources, enables us to scan the frequency range down to 1 GHz.

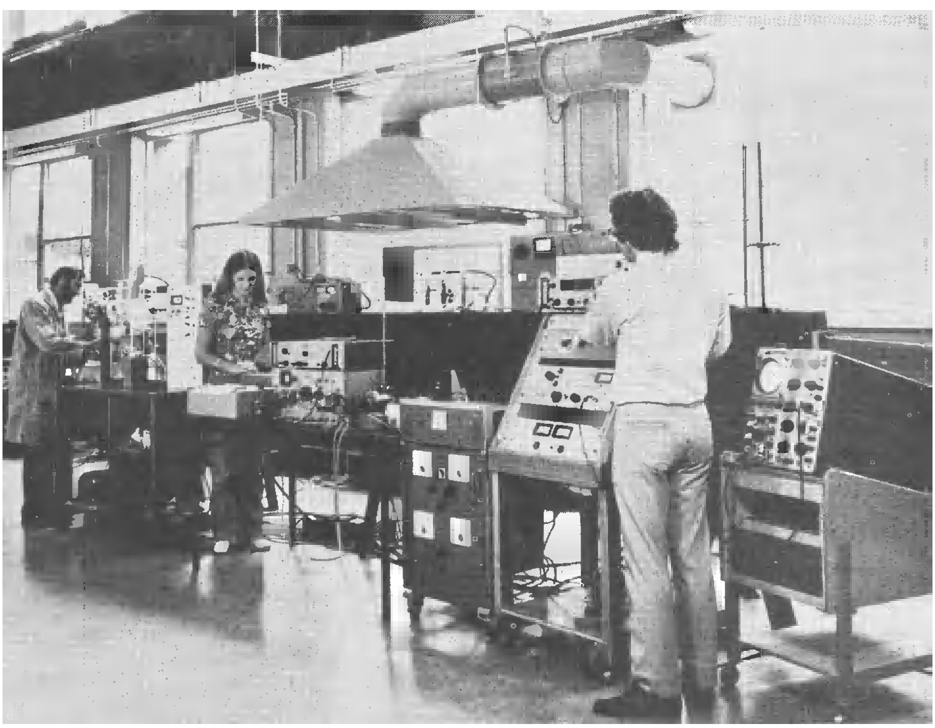

Fig. 2. Microwave spectrometer for measuring molecular absorptions in the microwave region down to frequencies of 1 GHz.

At these low frequencies the strengths of absorption lines are very low and so repetitive scanning with computer controlled sampling and processing of data is often essential if adequate signals are to be obtained.

Fig. 3 shows a block diagram of the spectrometer/computer combination and Fig. 4 shows the $1_{10} \leftarrow 1_{11}$ transition of CH_3OD at 1.3603 GHz that we recently observed before starting a search on the 140' radiotelescope at Greenbank, W. Virginia. Incidentally, the quadrupole hyperfine structure arising from the deuterium is reasonably well resolved, this being feasible with such low-frequency lines in the L-band spectrometer.

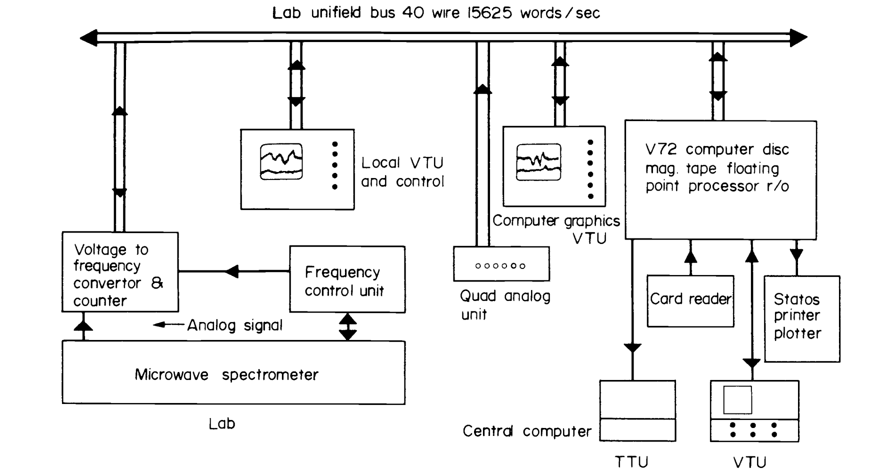

Fig. 3. Block diagram of spectrometer/computer combination used at Monash University.

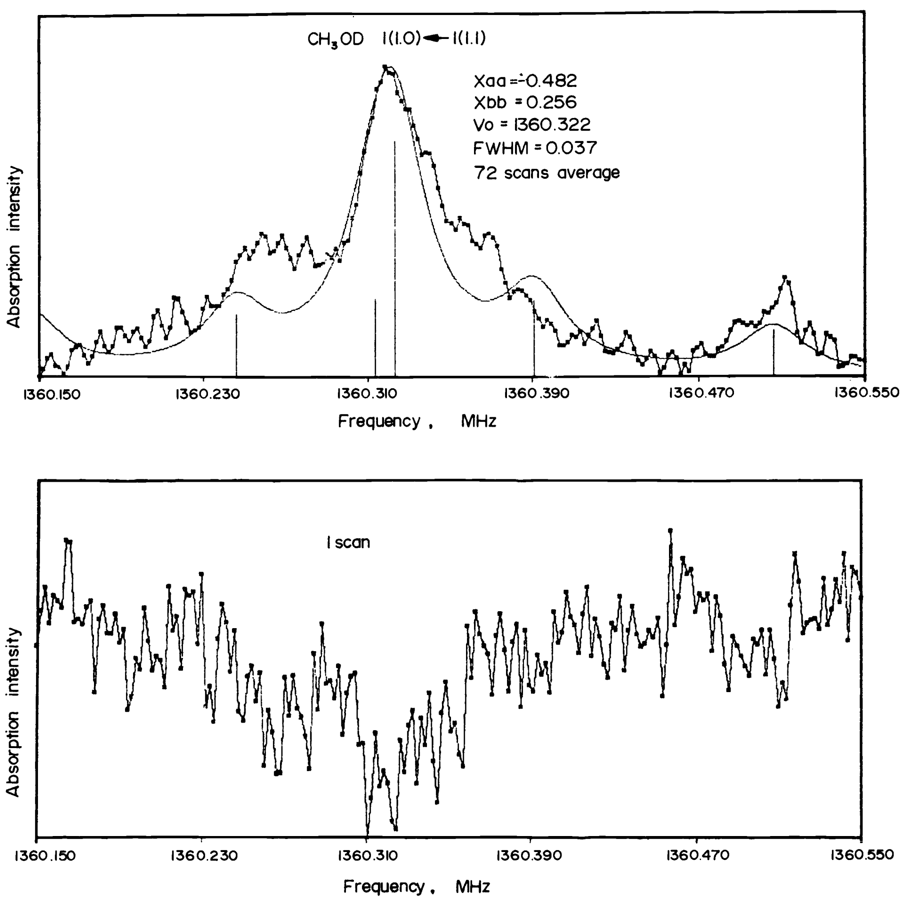

Fig. 4. Deuteromethanol line at 1.3603 GHz observed in L-band microwave spectrometer: (lower) single scan, (upper) computer averaged 72 scans and computer-filted multiplet superimposed.

A second problem is that some potentially interesting interstellar species are short-lived radicals or other highly reactive molecules that are rapidly destroyed under normal laboratory conditions. This was the case for the first molecular species detected by radioastronomy - the OH radical. Its detection depended on a pioneering study in the laboratory by C. H. Townes and co-workers using a free-space glass cell and a discharge in a side arm to produce the OH which was steadily pumped through te cell. We have used a similar cell at Monash University to study other radicals like NO_2 and NF_2 (Fig. 5).

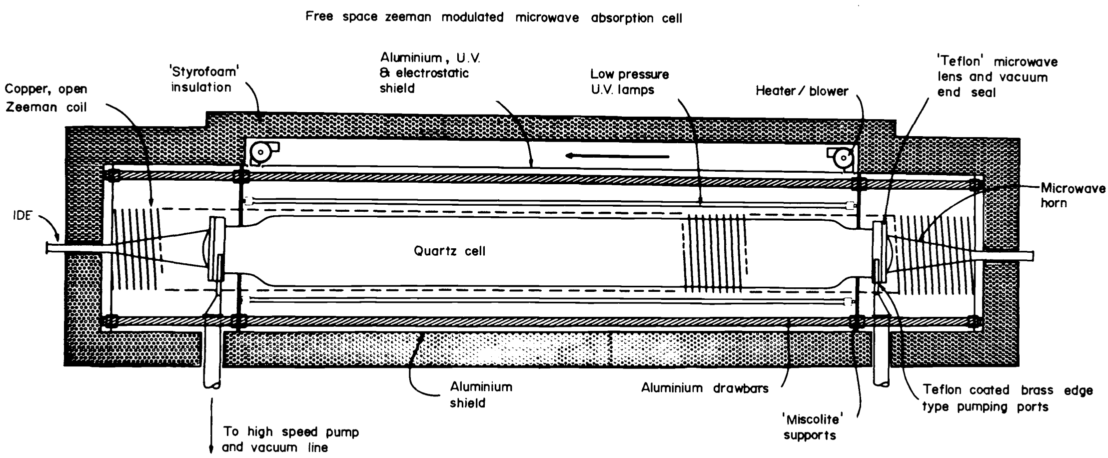

Fig. 5. Free space Zeeman-modulated quartz cell used for study of radicals.

A number of other short-lived species of astronomical interest have been studied by the expedient of generating them in the side-arm of a spectrometer cell, a microwave discharge or pyrolysis being used to disrupt a suitable precursor molecule and the species so generated being pumped through the spectrometer cell. Here in Japan Dr. Saito has been particularly successful with this technique. Table 2 summarises the species so far studied. Special mention must be made of the success of R. Claude Woods and his colleagues in observing for the first time the rotational spectra of the ions CO^+ (3) HCO^+ (4) and N_2H^+ (5). The novel technique of generating these ions in a plasma tube and detecting microwave absorptions through the plasma was used.

TABLE 2. SHORT-LIVED SPECIES

SHORT-LIVED SPECIES			
OH	Sanders, Schawlow, Dousmanis, Townes	1953	free space cell, Zeeman mod., discharge in H_2O vap.
CS	Mockler & Bird	1955	X-band cell, Stark mod., 60Hz discharge in CS_2.
SO	Powell & Lide	1964	split wave guide cell, RF discharge: O + OCS.
SiS	Hoeft	1965	high temperature cell, FeS + Si at 1050° - 1300°.
SiO	Törring	1968	high temperature cell, Si + SiO_2 at 1800°.
NS	Amano, Saito, Hirota	1969	parallel plate cell, Stark mod., RF discharge N_2 + SCl_2
HCO	Saito	1972	parallel plate cell, Stark mod., H_2CO + product of discharge on CF_4.
H_2CNH	Johnson & Lovas	1972	parallel plate, Stark mod., pyrolysis of CH_3NH_2.
HNO	Saito, Takagi	1973	parallel plate, Stark mod., H atom +NO.
HCO^+	Woods, Dixon, Saykally, Szanto	1975	plasma cell, video det., CO + H_2.
HNC	Blackman, Brown, Godfrey, Gunn	1976	parallel plate, Stark mod., pyrolysis of HCN.
	Saykally, Szanto, Anderson, Woods		plasma cell, source mod.
	Creswell, Pearson, Winnewisser, Winnewisser		free space cell, video det., active N + CH_3Br.
N_2H^+	Saykally, Dixon, Anderson, Szanto, Woods	1976	plasma cell, source mod., N_2 + H_2.

Another species first detected by the accidental discovery of its $J = 1 \rightarrow 0$ transition among radiotelescope signals and for which we had searched for some years at Monash is HNC. We tried to produce this molecule in a variety of ways, including seeking it in equilibrium with its more stable isomer HCN. We finally succeeded by using a sufficiently high temperature, rapidly expanding HCN through a row of tiny holes in a long stainless steel tube heated to about 1000°C. The issuing gas streams passed between parallel plates of a microwave spectrometer cell. By this means we succeeded (6)(7) in observing the $J = 1 \leftarrow 0$ absorptions of HNC, DNC, $HN^{13}C$ and $H^{15}NC$ (Table 2). The technique that we used enabled us to determine the dipole moment of HNC as 3.05D from the Stark effect. It is symptomatic of the way in which science evolves that simultaneously and independently R. Claude Woods and colleagues (8) and Creswell et. al. in Germany (9) succeeded in detecting HNC but generated it by means of a plasma discharge through a suitable mixture of precursor gases.

The third kind of challenge that is associated with the study of interstellar molecules is that one would like to search the dark nebulae for molecules of particular biological interest, such as urea or simple aminoacids. Such compounds are normally encountered in the laboratory as involatile solids that decompose chemically on heating. However by using carefully designed heated cells it has proved possible to observe and analyse the microwave spectrum of urea (10). In this case the optimun conditions within the cell were determined by continuous direct monitoring of the cell contents with a mass spectrometer while the spectrum was being scanned (Fig. 6).

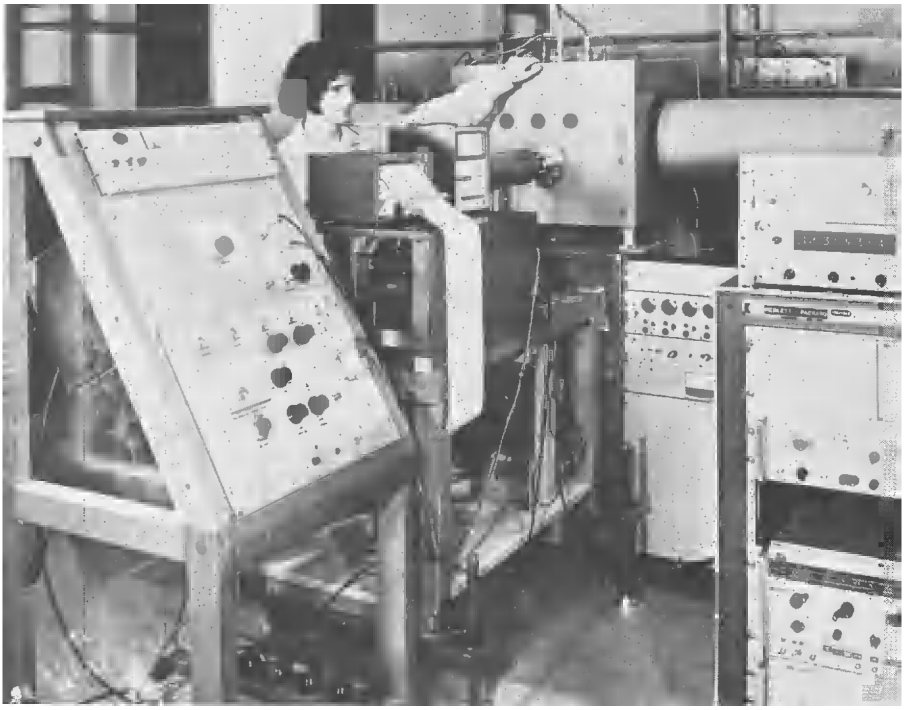

Fig. 6. Combination of heated waveguide cell and quadrupole mass spectrometer for optimising conditions for observing microwave spectra of species of low volatility.

More recently we have detected a number of lines in the microwave spectrum of glycine using a still more elaborate heated cell (Fig. 7). The lines are so weak that the analysis has taken some time and is not yet complete but it seems clear that, if sufficient time and effort are devoted to it, it will be possible to study many of the smaller biologically significant molecules by this technique.

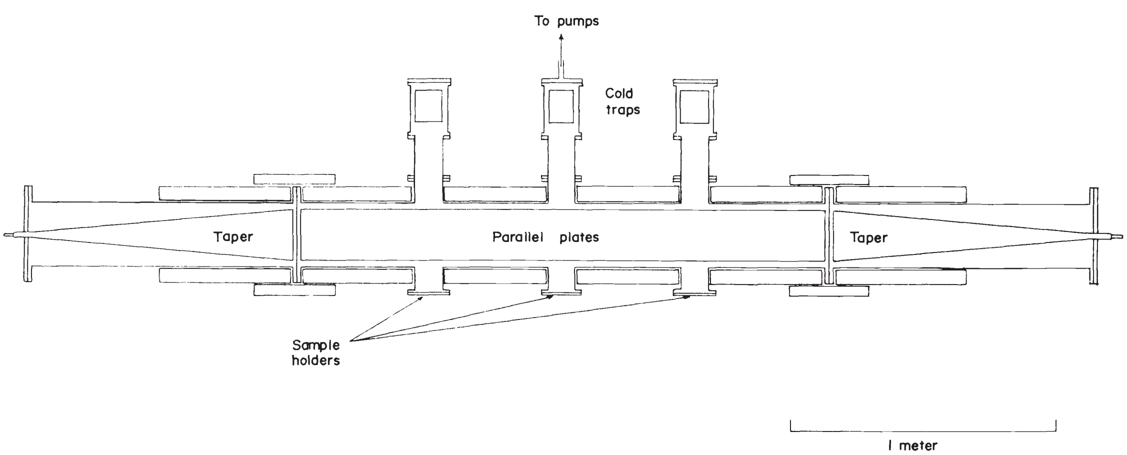

Fig. 7 (a). Heated parallel-plate cell used for studying the microwave spectrum of glycine.

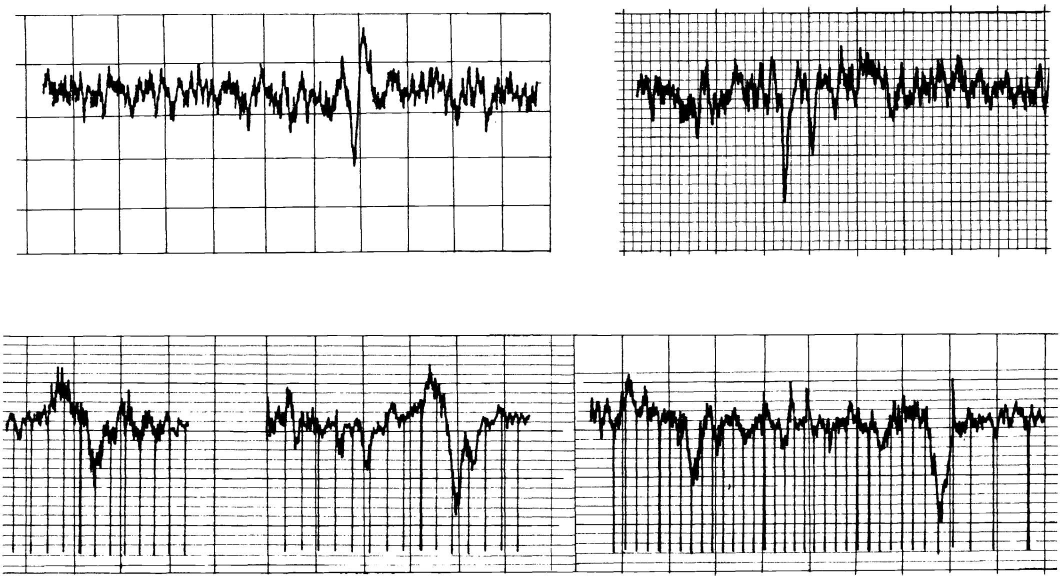

Fig. 7 (b). Some lines of glycine detected in the heated cell.

In the next few years we can expect to see a steady stream of accomplishments in microwave spectroscopy for small transient species of shorter and shorter lifetimes while the study of molecular ions, now in its infancy, will surely rapidly blossom. This will not only provide astronomers and astrophysicists with more extensive data for elucidating the chemistry and physics of dark nebulae but will of course greatly enrich our knowledge of the structural chemistry of hitherto elusive species.

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LEGEND TO FIGURES.

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