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TECHNICAL REPORT

RESEARCH IN MICROWAVE SPECTROSCOPY

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Abstract

Details are summarized of refinements in methods of generation and detection of microwave harmonics which have led to improved consistency and efficient reproducibility of spectroscopic procedures at wavelengths down to the 1 – 2 mm region. Preferred methods are given for selection, shaping, mounting and adjustment of the point-contact diodes used, and desirable extensions of the work are indicated. Other refinements of instrumentation are described which have allowed the measurement of spectra of unstable and involatile molecules with the ability to resolve important hyperfine structures.

New microwave spectroscopic measurements made in connexion with these developments are listed in detail, and their contribution to new knowledge is indicated. This includes evaluation of precise interatomic distances in fluorine cyanide and chloroacetylene, of electron-distribution properties of cyanamide and diazomethane from nuclear quadrupole effects, and the first precise structural information regarding nitramide in the gas phase. Several other substances have been studied, and refined values of centrifugal distortion constants have been obtained for several molecules, in some of which even the sign of certain distortion constants has been in doubt.

1. General

The work performed under this contract is of two main types, the study of millimetre-wave techniques and the measurement of microwave spectra leading to new information on molecular structure. Spectroscopic techniques have been studied with the principal object of obtaining efficient and reproducible operation over a wide range of frequencies through harmonic generation. This has necessarily followed established lines, but we have been able to make considerable progress, through refinements of published procedures, in our control of harmonic generation and detection, to the extent that we can now generate and detect, with relative ease and consistency, spectroscopically useful powers of radiation at frequencies up to the region of 200 kMc/s (wavelengths between 1 and 2 mm). The refinements which we have found worthwhile are given in sufficient detail here. We have also tested various semi-conducting materials for operation in these diodes, and various methods of fabrication and assembly.

The experimental measurements of spectra made during the contract period have been selected partly in order to test the progress of the techniques, but in this we have been able to extend our structural studies in significant ways. We have also regarded as of special importance molecules which, through instability or lack of easy volatility, are difficult to investigate structurally in the gas phase, and we have been able to add to our success in studying three such molecules through attention to absorption-cell construction, and spectroscopic sensitivity and resolution, at the more conventional microwave wavelengths. We have also made exploratory surveys of the microwave spectra of further substances, which, while successful analysis of the data has not yet been completed, are certainly due for intensive study. A summary of the scientific significance of the measurements made is given here; full accounts of how these results are integrated into other work performed over a longer period in this laboratory are being prepared as Technical Notes for later circulation.

2. Microwave Spectroscopic Techniques

2.1 Harmonic generation and detection

Attention has been concentrated on the method employing waveguide point-contact diodes, the effectiveness of which has been well established, but in which many refinements and variations in parameters remained untried. The harmonic generators used have all been of the crossed waveguide type, and, as may be seen from Fig. 1, approximate closely in general design to the published versions^{1,2}. We have chiefly tested the detailed design and construction of the insulated probe and cat-whisker which carry the fundamental power out of the larger waveguide, and of the very small semi-conductor wafer with which the critically adjusted contact is made within the small harmonic waveguide. Six such harmonic generators have been assembled which may be driven by radiation in either the 20 - 30 kMc/s or 30 - 40 kMc/s ranges, and with harmonic output guides small enough to select harmonics at wavelengths down to the 1 mm region. Very similar critically adjusted detector diodes have likewise been used. The following is a summary of operational experience which seems worth recording in connexion with these diodes.

2.1.1 Crystal preparation

Most of the work has been done with silicon crystals, to which the following account applies. As can be seen from the scale of Fig. 1 and Fig. 2, the semi-conductor is reduced in surface diameter to 0.01 - 0.02 inches. Dicing techniques have been found to be much more successful if the silicon is initially prepared in an optically polished sheet only about 0.005 inches thick. To secure the necessary good ohmic contact between the metal stub and the back of the wafer, this surface of the silicon is plated, usually with nickel; some of the wafers we have tested have had an additional plating of gold. In a typical nickel plating

Fig. 1 Section of harmonic generator with differential-screw adjustment of semi-conductor wafer.
Linear scale = twice actual.

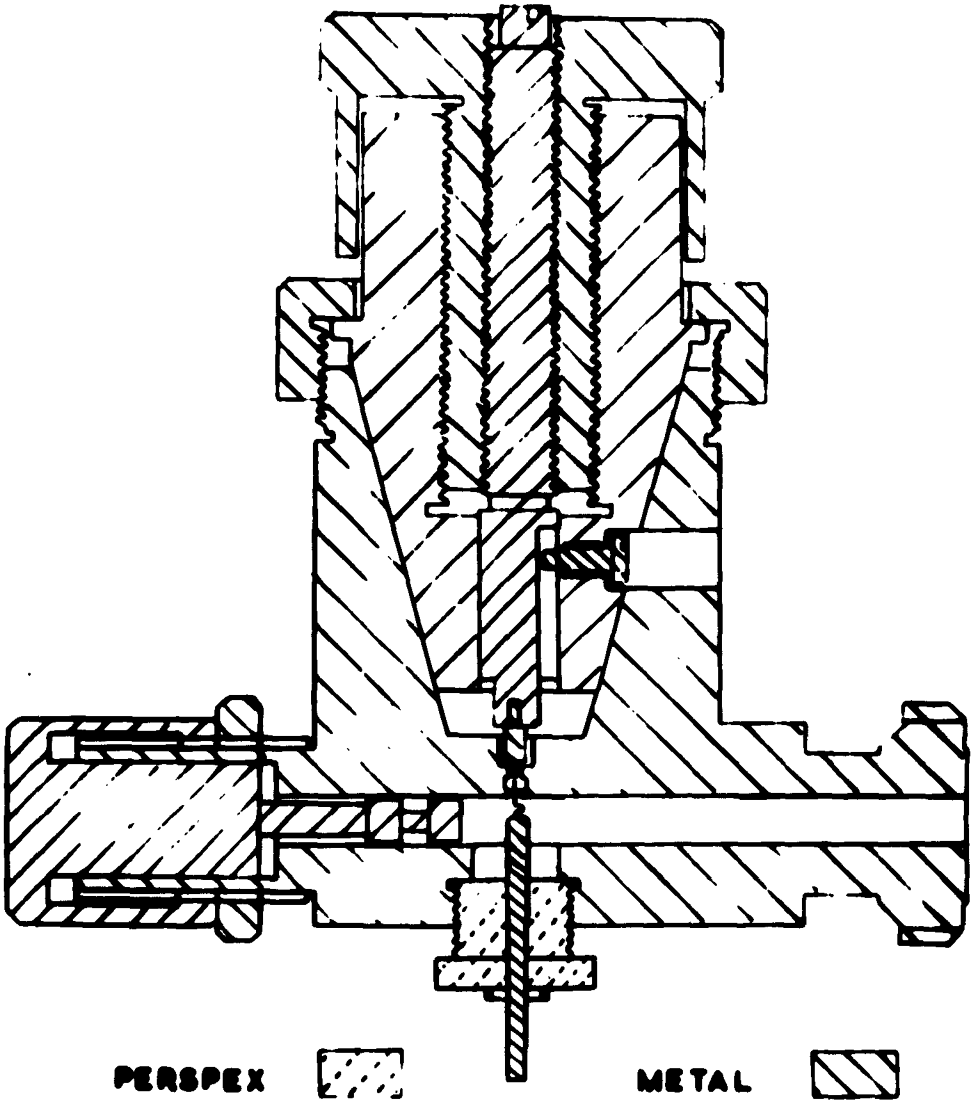
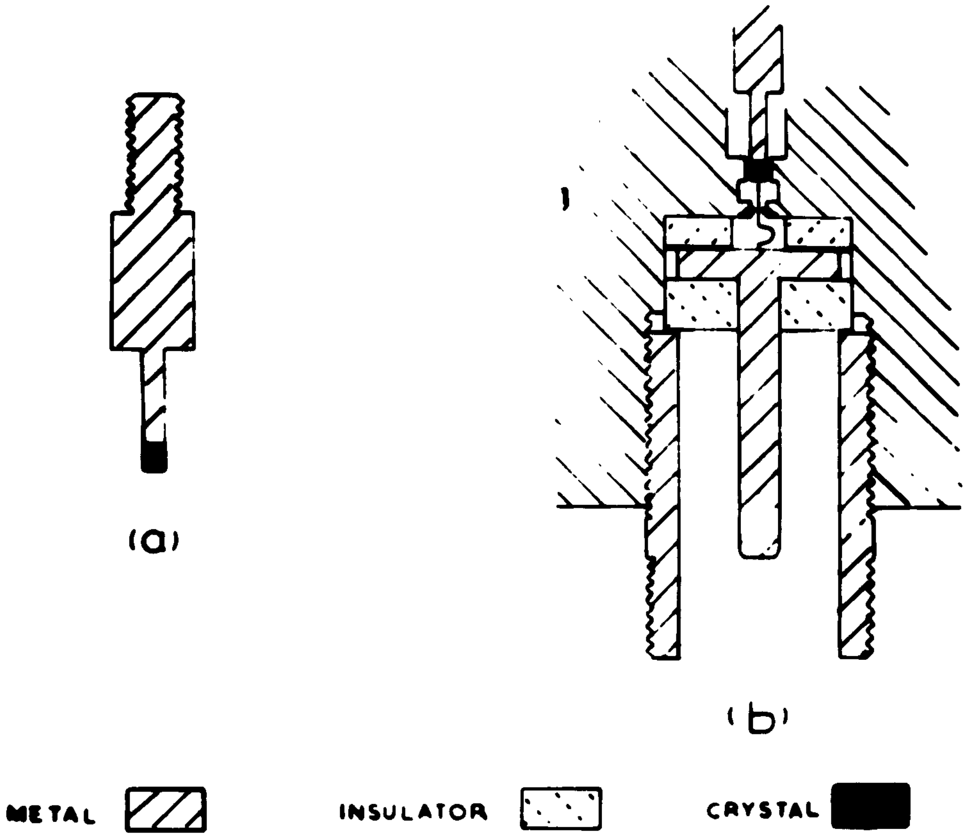

PERSPEX
METAL

Fig. 2 (a) Detail of brass stub carrying semi-conductor wafer. Linear scale = ten times actual

(b) Detail of semi-conductor and whisker in detector mounting. Linear scale = five times actual. The cat-whisker passes through a watch jewel above the crimped section.


(a)
(b)
METAL
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procedure, the silicon wafer is first immersed in dilute hydrofluoric acid for one minute, and plated for 2 minutes at 85°C in a solution composed of ammonium hydrogen citrate (65 g), ammonium chloride (50 g), nickel chloride (30 g) and sodium hypophosphite (10 g) in one litre of water, to which strong ammonia has been added until the colour changes from green to blue. The plating is then sintered at 650°C for half an hour in an oven in an inert atmosphere. Finally the wafer is re-treated with hydrofluoric acid and plated for a further four minutes. This plating is stronger mechanically than the silicon itself.

The high polish applied to all semi-conductors used in this work has been obtained by standard metallurgical techniques adapted for use in a spectroscopy laboratory. The speciment, about one inch in diameter and 0.01 inches thick, is mounted in black wax on an accurately ground metal support, and taken down to a dull shine by graded carborumdum paper. The final finish is obtained with the finest diamond lapping compound, of quarter micron particle size, suspended on the finest micro-cloth, and the surface then shows no flaws at x 150 magnification.

Controlled shaping of the mounted semi conductor is a vital stage in a successful routine, and the following is an outline of a carborundum grinding method which we have found to give good yields of suitable assemblies. A slab of silicon, 0.003 - 0.005 inches thick, is split with a razor blade into pieces 0.02 - 0.03 inches across. The tip of the small brass stub (Fig. 1 and 2) which carries the semi-conductor is just covered with a blob of "Cryolux" solder-paint. A chip of silicon is picked up by its plated side by adherence to the solder-paint. The stub is held vertical, and heated at its base with a small iron, when the wafer adjusts its position on the molten solder. This procedure will consistently give bonding which is good both mechanically and electrically. The stub is next spun in a lathe, and the wafer and its supporting brass abraded to a diameter of about 0.015 inches, care being taken to avoid abrasion of the polished surface.

One of our aims has been the study of point-contacts to semi-conductors which are as free as possible from surface damage. We believe we have achieved this by the following chemical etching technique, in which there is no recourse to abrasives. The chemical etchant used is a mixture of concentrated nitric acid (100 ml) glacial acetic acid (60 ml) and 48% hydrofluoric acid (60 ml), and removes silicon surfaces to depths of about 0.001 inches per minute. The wafer is first chemically polished by waxing it to glass by its plated side and etching until its thickness is 0.002 - 0.003 inches; a high mirror finish is so created. After removal from the glass and cleaning with trichlorethylene, the wafer is re-waxed down, this time plating uppermost, and its surface covered with a series of small blobs of black wax of diameter about 0.02 inches, slightly larger than the size of dice ultimately desired. The uncovered plating and silicon are then etched away, and the dice washed and finally soldered to stubs as already described. Crystals which do not overhang the stub-head can be obtained directly in this way, and stub-diameters as low as 0.010 inches are usable. One etching procedure may yield as many as 50 suitable dice, and wastage is therefore much less than by the mechanical method. The surface condition, moreover, is better controlled.

We have also tested the method of ultrasonic drilling for dicing semi-conductors for this work, through the courtesy of the Services Electronics Research Laboratory, Baldock. The ultrasonic drill-piece is a copper tube of internal diameter 0.015 inches. Many suitable dice can be obtained from a wafer about 0.003 inches thick. This method will be advantageous with materials less suited to the other methods; for example, gallium arsenide dice have been made in this way.

In later work, a heat treatment stage was added to the crystal preparation. While primarily viewed as a cleaning operation, this is also believed to have a useful "healing" effect on surface sites, through a little-understood mechanism. A silicon wafer, lapped on one side and optically polished on the other, is heated to 1100°C in an aseptically clean furnace in a current of steam for 15 minutes. The unpolished side is plated, the wafer diced mechanically and the dice mounted as before. Before use, the blue protectively oxidised surface is etched to the silicon by brief immersion in hydrofluoric acid.

2.1.2 Cat-whisker preparation

Tungsten is almost certainly the best general material for point-contacts to silicon for the present purposes, and nearly all our tests have been made with this material. The tungsten wire, of diameter 0.002 inches, is first degreased, then electrolytically cleaned by briefly applying a few volts alternating potential between it and a large copper electrode in 14% potassium hydroxide solution. The tip of the wire is plated with copper in a solution of copper sulphate (200 g), potassium alum (12 g) and sulphuric acid (55 g) in one litre of water. The anode is a very clean copper strip, and a very small current is passed for about 10 seconds from a 2 volt source. The tungsten must be removed from the bath while current is still flowing, to prevent formation of a poor electrodeless deposit. After the plated end of the wire has been soldered to the mounting, the wire is crimped to shape with surgical tweezers; the most convenient shape, mechanically, has been used, namely a U-crimp which does not overhang the backing-stub. The whisker is then electrolytically etched to the required length, and made coaxial with its support by spinning on a watchmaker's lathe. After further electrolytic polishing, it is again checked, and minor adjustments made if necessary, before the final pointing, which is carried out by the established electrolytic method, the whisker being touched to the surface of 14% potassium hydroxide and a few volts alternating potential applied until continuity of the circuit is broken at the liquid surface.

2.1.3 Watch-jewel insulation between whisker and waveguide

We have found it advantageous, with a view to continuous stable functioning of millimetre-wave harmonic generators and detectors, to employ watch-jewels as insulators in the waveguide wall of these devices where the cat-whisker passes through the small hole at a point just beyond its crimp. This idea, which was introduced in millimetre-wave detectors by Tolberg, Henderson and Jache (Rev. Sci. Instrum., 1958, 29, 660), has been successfully adopted here also for harmonic generators working in the 1 - 2 mm region. The location of the jewels may best be seen from Figs 3 and 4, where they are shown in somewhat larger waveguide systems suitable for lower harmonics. The normal shape of the perforation in the jewel is favourable to passage of the cat-whisker without blunting. These jewels are installed by enlarging part of the original whisker-hole, with a specially made cutter, to the extent that the jewel may be pressed firmly into place flush with the waveguide surface.

2.1.4 Assembly of units, and routine for millimetre-wave spectroscopy

The mounting of the stub carrying the semi-conductor wafer on the differential-screw mechanism, and the positioning of the wafer just outside the harmonic guide is a straightforward routine. When a satisfactory whisker-point has been made, the point is cleaned hydrofluorice acid for 10 minutes, a process making for more uniform performance at highest frequencies. The washed and dried whisker is screwed into its accurately made perspex plug until its point is protected, when the plug is installed in position. The whisker is then advanced to the far side of the harmonic waveguide, via the watch jewel. A slightly different alignment procedure is adopted in advancing the whisker in detector mountings, where an insulating bush is used to ensure that the whisker is accurately aligned as it approaches the jewel.

The spectroscopic arrangement in which the devices have been tested, and the routine followed, are very similar to those described by King and Gordy[2]. A conventional video spectrometer, with 50 c/s sweeping and oscilloscope presentation through a wide-band amplifier was used. The highest frequencies were used with an absorption cell 3 ft. long,

Fig. 3 Detail of harmonic generator for maximized performance at lower harmonics.

Inset = detail of waveguide wall, with watch jewel insulator.

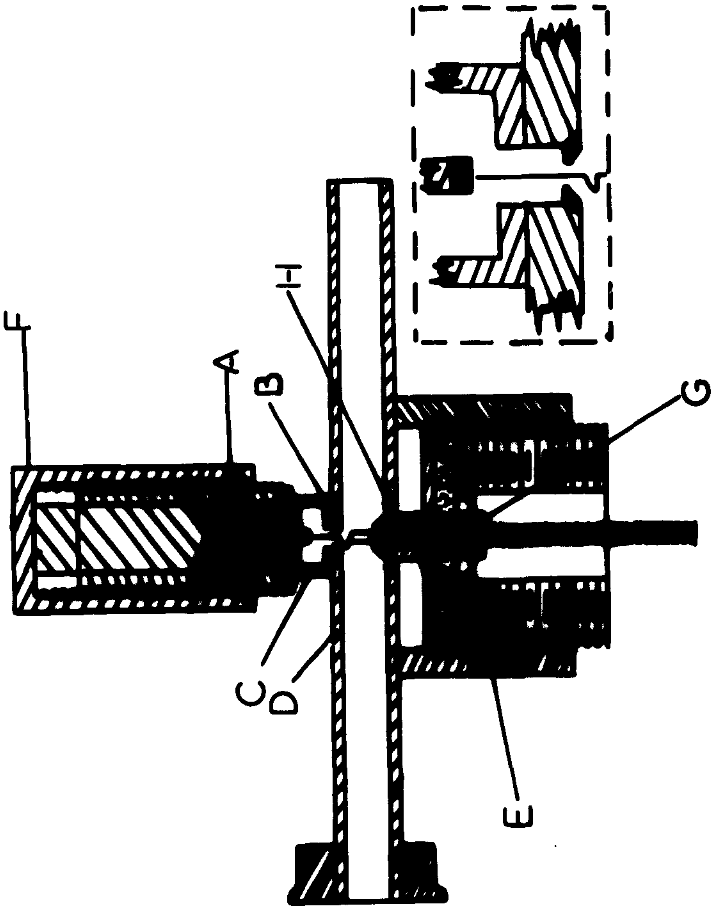
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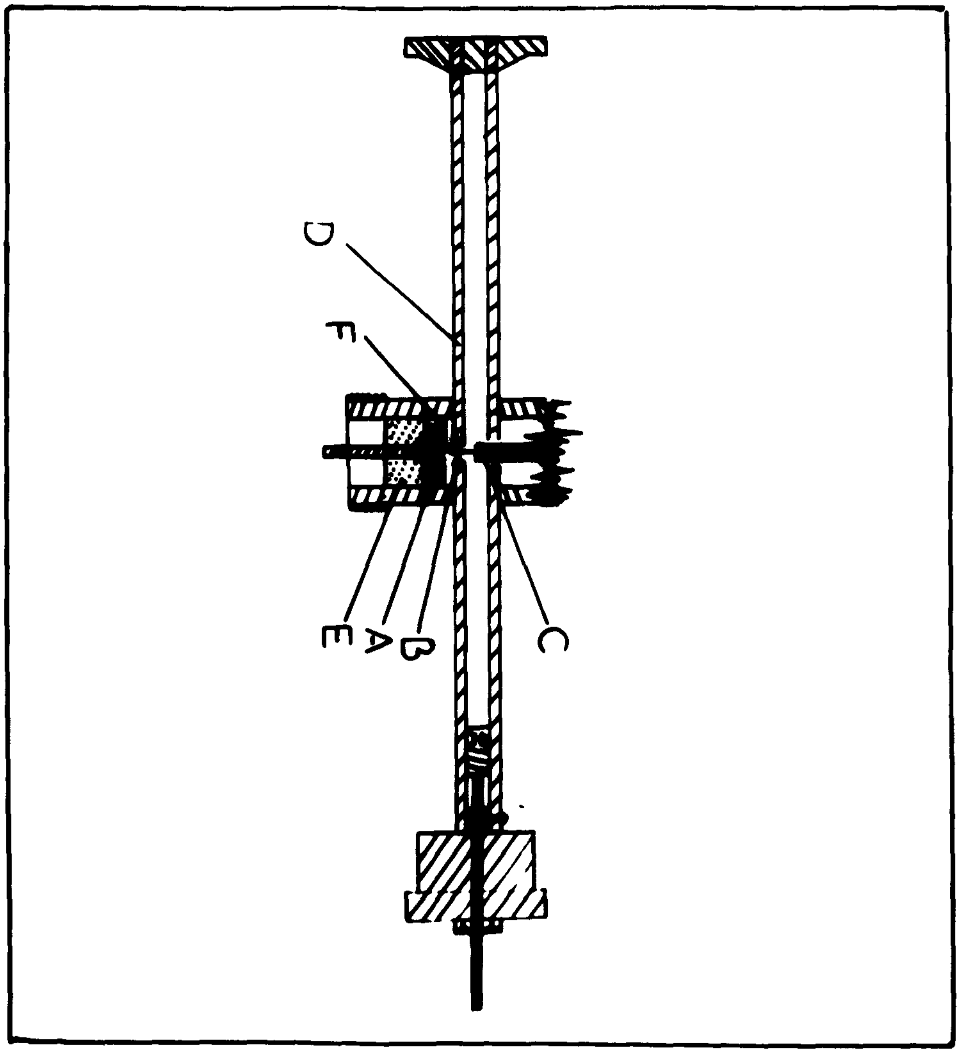
Fig. 4 Detail of detector for maximized performance in 40 - 100 kMc/s range.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of waveguide of inner dimensions 0.188" x 0.094". At somewhat lower frequencies, a six-foot cell of guide of inner dimensions 0.280" x 0.140" was preferred, while at wavelengths near 3 mm or more it was possible to use a 28 ft. cell of K-band waveguide. All these cells were straight and aligned as carefully as possible.

Adjustment of the point-contacts and the maximizing of the tuning of the fundamental and harmonic waveguide circuits have been made in ways essentially similar to those described by King and Gordy (loc. cit.). We have confirmed that the first contacts at both generator and detector are usually the best, although it is often possible to make fine adjustments of a contact to improve the signal-to-noise ratio at later stages in its use. The detector contact is usually lighter at optimum performance that that in the generator, and is therefore more susceptible to mechanical disturbance. A well-shaped crimp is important in this connexion. Harmonic generator contacts may remain good for periods of weeks.

We have found little obvious correlation between forward- and reverse-resistance ratio in these contacts and their performance; a resistance ratio as low as 8 may still be associated with good high frequency generation.

In common with earlier workers, we have found that biasing of the diodes is not a critical matter in deciding ultimate performance (although it will be when other semi-conductors, such as bombarded silicon, are used). Automatic biasing by placing resistance of up to 500 ohms between the cat-whisker and earth has often improved the generation of harmonics up to the fourth, but for the higher harmonics, which are normally sought, it is often necessary to disconnect this biasing circuit.

The assignment of the harmonics absorbed has normally been made through the use of "tuning molecules" of linear or symmetric-top structure, as described by King and Gordy (loc. cit.), in conjunction with the known cut-off characteristics of the waveguides used. The frequencies of lines were measured in the usual way by abstraction of a small portion of the fundamental radiation.

2.1.5 Comparison of semi-conductor materials

Although quantitative comparisons are difficult in such work, and would involve statistical analysis of many more tests than we have been able to carry out, we have made some systematic tests of types of silicon and more exploratory tests of some other materials. Single crystal, boron doped, p-type silicon with resistivities ranging from 0.1 to 0.001 ohm cm. was systematically studied. For the fundamental powers of the order of 100 mw which we have used, a resistivity of 0.01 - 0.02 ohm cm.

proved about the optimum for harmonic generation, and was also a good detector material. This corresponds to about 40 parts of boron per million. The ultimate performance obtained for a given material was not strongly dependent on whether mechanical shaping or chemical etching was used. Polycrystalline silicon proved generally less effective than single crystals.

For detection, it was thought advisable to test germanium and gallium arsenide as semi-conductors, and some preliminary work on these has been carried out. Evaluation is tentative, because parallel work will be necessary using various whisker materials for these softer semi-conductors. The results to date, however, suggest that germanium is not very suitable for detection at the low power levels available at the highest frequencies, although we have found that the recently developed commercial germanium crystals can be excellent for detection at higher power levels in the 1 cm region. Gallium arsenide has shown little success in our tests, probably on account of its softness.

2.1.6 Efficient generation of harmonics in the 40 - 100 kMc/s range

Figs. 3 and 4 show generators and detectors which we have found spectroscopically useful in this frequency range. Details need not be given, since they employ similar principles to those already discussed, and the easier tolerances of construction have allowed a simple screw control for the semi-conductor. The need for maximum possible efficiency in generating and detecting low harmonics in this range arises partly because the primary sources, such as the klystrons in this range which are available in Europe, are very costly and short lived, and partly also because the use of primary radiation above 40 kMc/s demands more elaborate frequency measuring equipment than is commonly available. It is especially desirable to be able to use enough power in this range, from harmonics, to operate Stark modulated spectrometers and so perform spectroscopy of very high sensitivity. We have achieved some success in this direction with the devices shown, as exemplified by Fig. 5, which shows the 1→2 transition of diazomethane at 44 kMc/s, studied in a 16 ft. Stark modulation cell, with harmonic generation from 22 kMc/s. Although diazomethane decomposes completely in the spectrometer in a few minutes, it is still possible to detect easily the weak satellites of the line due to the molecular ground state, which arise from molecules with respectively one quantum of each of three lowest vibrational modes. The weakest of these has an intensity only a few percent of that of the strongest line, and it would therefore be feasible by these methods to measure spectra such as those of stable molecules containing carbon-13 in its natural concentration of 1%, in the 40 - 100 kMc/s range.

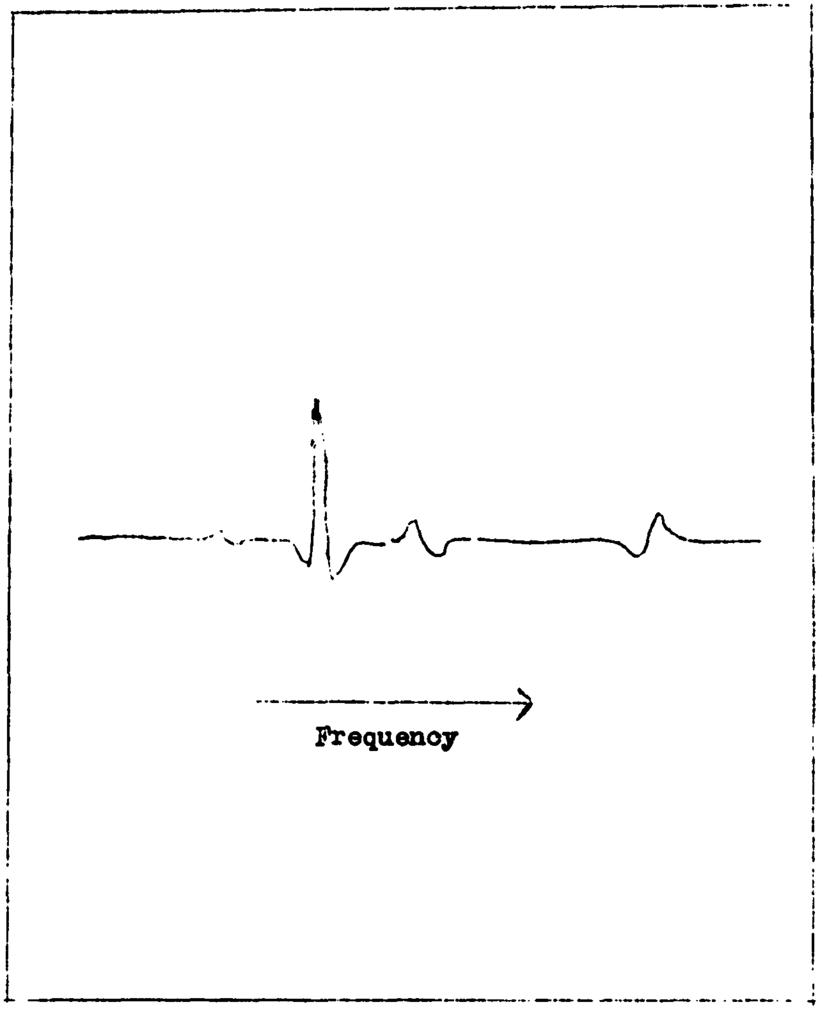

Fig. 5 Recorder tracing of $1_{0,1} \longrightarrow 2_{0,2}$ lines of diazomethane made with 16 ft. Stark-modulated spectrometer and harmonic generator source. Satellite lines are due to molecules with one quantum of 3 different vibrational modes of the molecule.

2.2 Other developments of instrumentation

Some attention has been given to refinements of cell construction and detection methods in connexion with problems in the spectroscopy of involatile substances. Most of our work with these, such as with cyanamide, has been done in an essentially conventional Stark spectrometer, with 100 kc/s modulation, the cell for which (6 ft. long, in K band guide) can be heated to temperatures up to 200°C. The substances under investigation are swept through the cell under carefully adjusted conditions of pumping and of sample- and cell-temperature. The resolution of such an instrument is limited to about 0.5 Mc/s by modulation broadening and by a certain amount of collision broadening of lines which is present at the gas-pressures used to obtain high sensitivity. In particular, the instrument was unable to resolve important closely spaced hyperfine structures, such as those due to quadrupole effects of nitrogen-14 nuclei in cyanamide. Sufficient resolution was attainable in simple video spectrometers, but no analysis of the effects could be made because only the strongest members of each hyperfine multiplet could be detected.

To retain the resolution of the video method, while maintaining high sensitivity, a spectrometer employing 100 kc/s source modulation was constructed, the absorption-cell being carefully made from a straight 28 ft. length of K-band waveguide. The electronic components employed circuits of essentially established designs. With careful choice of modulation amplitude, it was possible to achieve a considerable increase in sensitivity over that of the simple video system, even with oscilloscope presentation and rapid sweeping, without loss of the high resolution (lines about 0.2 Mc/s apart could be resolved). Accurate measurements of frequencies and frequency-separations could be made by means of relatively simple modifications of the usual system. This instrument made possible the solution of the outstanding problem of the nuclear quadrupole effects in cyanamide.

Exploratory tests were made of all-glass cells for involatile and reactive substances. A cylindrical Pyrex glass cell, some 3 inches in diameter and 3 ft. long, with the ends, also of Pyrex glass, flattened while hot in a very simple manner, was tested in the video spectrometer. In spite of the crudeness of the cell construction, and of the fact that the horns feeding radiation to the cell and receiving it at the detector were not of optimum design for the purpose, the performance was good enough to suggest that the cell would be effective for involatile substances of some molecular stability and large dipole moment. Tests of such a system for nitramide were postponed, however, since the undesirable catalytic decomposition of this substance in metal cells ultimately proved less serious than was thought, and the spectra were analysed successfully with the conventional spectrometer.

3. Spectroscopic measurements and derived information

3.1. Millimetre-wave spectra of simple molecules

The linear molecules fluorine cyanide and cyano acetylene, the latter in two isotopic forms, were studied for the first time in the mm-wave region as part of the programme of evaluation of techniques. Similar studies were made of methyl fluoroform and methyl trifluorosilane, where the very small splittings due to centrifugal distortion effects for different values of the quantum number K were resolved for the first time. The measured frequencies for these substances are listed in Tables 1 to 5. In Table 6 the spectroscopic constants for these molecules are given. The frequencies calculated from these constants agree very closely with those measured, the difference between observed and calculated frequencies being often less than 0.05 Mc/s; the usual plots of the centrifugal distortion effects in terms of quantum numbers showed a high degree of internal consistency, and left no doubt of the correctness of the assignments and the precision of the constants.

The distortion constants D_J listed are all determined for the first time; their magnitudes are close to those anticipated from results for similar molecules and from the expected force constants of the bonds mainly involved in centrifugal stretching. In the case of the constants D_{JK}, here determined for the first time for methyl fluoroform and methyl trifluorosilane, some doubt existed previously regarding the sign of these coefficients. They were known to be of very small magnitude, from failure to resolve K-splitting at transitions as high as $J = 3 \rightarrow 4$, but it was not possible to predict whether they would be positive, as in other A_3BC molecules, or negative as in fluoroform and trifluorosilane themselves. The present work establishes them as positive, and derives accurate values for these very small constants. No marked effect ascribable to internal rotation about the central bond could be detected in the K-splittings for these substances, the displacements of the lines in terms of K following the usual symmetric-top pattern.

Lines due to cyanoacetylene in excited bending vibrational states were measured at certain high transitions. The usual ℓ-type doubling constants were confirmed with improved accuracy for DCCCN. A feature of the spectrum for which $v_7 = 2$, $\ell = 0$ was its splitting into a triplet at the $9 \rightarrow 10$ transition of HCCCN; similar triplets were also observed, though not measured, for the $v_7 = 2$ state of DCCCN at the $10 \rightarrow 11$ and $9 \rightarrow 10$ transitions. Splitting of over four megacycles could not possibly arise from nitrogen quadrupole effects at these J-values, and the difference between the spectra and the single lines predicted by the simple theory of such spectra must arise from neglect of small factors in the theory. A more exhaustive study will be made later.

TABLE 1

Measured transitions of fluorine cyanide, FCN

Transition	Frequency (Mc/s) (Corrected for nuclear quadrupole effects)
J = 0 → 1	21,108.37
1 → 2	42,216.60
2 → 3	63,324.61
3 → 4	84,432.28
4 → 5	105,539.45

TABLE 2

Transitions of cyanoacetylene, HCCCN

Transition	Frequency (Mc/s) (Corrected for nuclear quadrupole effects)	
J = 2 → 3	27,294.29	
3 → 4	36,392.34	
7 → 8	72,783.79	
9 → 10	90,979.00	
14 → 15	136,464.36	
19 → 20	181,944.40	
9 → 10	91,554.64 91,556.24 91,558.72	Vibrationally excited state, $v = 2$, $\ell = 0$

TABLE 3

Transitions of cyanoacetylene-d, DCCCN

Transition	Frequency (Mc/s)
J = 3 → 4	33,772.56
9 → 10	84,429.88
10 → 11	92,872.80
21 → 22	185,730.88

10 → 11	92,936.80	v_5 = 1 state
	92,995.96	
	93,010.32	v_6 = 1 state
	93,079.56	
	93,092.40	v_7 = 1 state
	93,222.04	
21 → 22	186,169.04	v_7 = 1 state

TABLE 4

Transitions for methyl fluoroform, $CH_3 \cdot CF_3$

Transition		Frequency (Mc/s)
J = 1 → 2		20,740.53
J = 2 → 3		31,110.67
J = 3 → 4		41,480.72
J = 8 → 9,	K = 0	93,328.68
	K = 3	93,328.32
	K = 4	93,328.08
	K = 5	93,327.76
	K = 6	93,327.40
	K = 7	93,326.96
	K = 8	93,326.44

TABLE 4 (Continued)

Transition	Frequency (Mc/s)
J = 10→11, K = 0	114,066.16
K = 3	114,065.69
K = 4	114,065.40
K = 5	114,065.06
K = 6	114,064.65
K = 7	114,064.09
K = 8	114,063.46
K = 9	114,062.72
K = 10	114,061.90

TABLE 5

Transition for methyl trifluorsilane, CH_3SiF_3

Transition	Frequency (Mc/s)
J = 2→3	22,293.87
J = 3→4	29,724.99
J = 4→5	37,156.07
	37,155.84
J = 14→15, K = 0	111,458.35
K = 3	111,457.38
K = 4	111,456.92
K = 5	111,456.32
K = 6	111,455.52
K = 7	111,454.61
K = 8	111,453,46
K = 9	111,452.30
K = 10	111,450.80
K = 11	111,449.36
K = 12	111,447.63
K = 13	111,445.74

TABLE 6

Spectroscopic Constants

Molecule	B_0 (Mc/s)	D_J (kc/s)	ℓ-type doubling constant, q. (Mc/s)
FCN	10,554.191	4.91	-
HCCCN	4,549.060	0.560	-
DCCCN	4,221.588	0.445	$q_5 = 2.69 \pm 0.01$ $q_6 = 3.15 \pm 0.01$ $q_7 = 5.89 \pm 0.01$

Molecule	B_0 (Mc/s)	D_J (kc/s)	D_{JK} (kc/s)
CH_3CF_3	5,185.137	1.292	1.90_4
CH_3SiF_3	3,715.67	1.41	2.21

3.2 Study of rare isotopic forms of linear molecules

We have measured for the first time the spectra of the isotopic forms of fluorine cyanide, chlorine cyanide, iodine cyanide and chloro-acetylene which are recorded in Tables 7 and 8. These new data enabled us to make the first full determinations of structure parameters for these molecules by the method of isotopic displacements. The resulting values for the bond distances are summarized in Table 9. It is notable that the CN bond has the same length, within the errors of one part in several hundred, in all the halogen cyanides: the lengthening of this bond as the electronegativity of the halogen is increased, which has commonly been presumed, is not substantiated. In chloro-acetylene, the carbon-carbon bond is somewhat shorter than calculated from previous data, and the new value falls well into line with bond distances in related acetylenes. A full discussion of these results must take into account a wide range of measurements made in this laboratory at other periods,[3] and a paper giving this discussion has been prepared for later submission.

Efforts were made to measure microwave spectra of iodo-acetylene, a molecule for which there was no acceptable record of any previous preparation. We found that, while some of the earlier reported methods certainly did not yield the substance, small yields of it could be made by the passage of acetylene through alkaline iodine solutions, and the first authentic samples of ICCH and ICCD were prepared. Their mass spectra and infra-red spectra left no doubt as to their identity and essential purity. We have been unable to detect microwave spectra of this substance, presumably on account of the smallness of its dipole moment. The Stark effects, which must be of second order, would be small and perhaps unresolvable for the values of J which would be involved in accessible transitions, and with electric fields limited to less than about 2,000 volts/cm. Stark modulation of the lines might then not be achievable without special high-field cells. The dipole moment of iodoacetylene is expected to be small, but would not be expected to be as low as that reported for bromoacetylene of 0.00 ± 0.01 D.

An analysis of the infra-red data on ICCH and ICCD has been made, and details will be given as a separate technical communication.

TABLE 7

Measured lines for rare isotopic forms of linear molecules

Molecule	Transition	Frequency (Mc/s)
$F^{13}CN$	$J = 0 \rightarrow 1$	21,095.71
	$F = 1 \rightarrow 2$	
$FC^{15}N$	$J = 0 \rightarrow 1$	20,372.82
$^{35}ClC^{15}N$	$J = 2 \rightarrow 3$	
	$F = \frac{1}{2} \rightarrow 3/2,\ 3/2 \rightarrow 5/2$	34,484.32
	$F = 5/2 \rightarrow 7/2,\ 7/2 \rightarrow 9/2$	34,489.21
$^{37}ClC^{15}N$	$J = 2 \rightarrow 3$	
	$F = \frac{1}{2} \rightarrow 3/2,\ 3/2 \rightarrow 5/2$	33,755.32
	$F = 5/2 \rightarrow 7/2,\ 7/2 \rightarrow 9/2$	33,759.18
$IC^{15}N$	$J = 4 \rightarrow 5$	
	$F = 9/2 \rightarrow 11/2$	30,819.59
	$F = 13/2 \rightarrow 15/2$	30,839.63
	$F = 11/2 \rightarrow 13/2$	30,849.90
$^{35}ClC^{13}CH$	$J = 2 \rightarrow 3$	
	$F = 5/2 \rightarrow 7/2,\ 7/2 \rightarrow 9/2$	32,819.35
$^{35}Cl^{13}CCH$	$J = 2 \rightarrow 3$	
	$F = 5/2 \rightarrow 7/2,\ 7/2 \rightarrow 9/2$	33,934.10

TABLE 8

Spectroscopic constants for linear molecules (Mc/s)

Molecule	B_o
$F^{13}CN$	10,547.80
$FC^{15}N$	10,186.42
$^{35}ClC^{15}N$	5,748.061
$^{37}ClC^{15}N$	5,626.425
$IC^{15}N$	3,082.661
$^{35}Cl^{13}CCH$	5,655.57
$^{35}ClC^{13}CH$	5,469.78

TABLE 9

Internuclear distances (Å)

F ——— 1.262 ——— C ——— 1.159 ——— N

Cl ——— 1.631 ——— C ——— 1.159 ——— N

I ——— 1.994 ——— C ——— 1.159 ——— N

Cl ——— 1.637 ——— C ——— 1.204 ——— C ——— 1.055 ——— H

3.3 Nuclear quadrupole coupling constants in diazomethane and cyanamide

3.3.1 Diazomethane, H_2CNN

Diazomethane is very unstable, and it is probable that the microwave method is the only means of studying its structure which is not seriously impeded by this property. The lifetime of the substance in the spectrometer cells cooled to -70°C, except in the region of the cell-windows, is a few minutes. In our high resolution spectrometers it has been possible to resolve many lines of diazomethane into nuclear quadrupole multiplets due to coupling of nitrogen-14 nuclei. In the normal form of the molecule, the simultaneous coupling of two of these nuclei leads to patterns which can not easily be analysed accurately, since it is clear that the coupling constants for both nitrogen positions are appreciable, and in certain axial directions are of comparable magnitude. We have adopted the most satisfactory way of obtaining individual coupling constants, that of replacing each nitrogen in turn by the non-quadrupole nitrogen-15 nucleus, and measuring the remaining splittings due to the single nitrogen-14. The data reported here refer to the form $H_2C^{15}N^{14}N$, which was synthesised in 90% isotopic purity by straightforward chemical means, and the splittings of the lines are due to the interaction of the terminal nitrogen atom with the electron field.

The measured frequencies and their assignment are listed in Table 10; Table 11 gives the derived rotational and quadrupole coupling constants in the three inertial axes of the molecule. The relative intensities of all the lines measured agreed with the assignments made.

TABLE 10

Spectrum of $H_2C^{15}N^{14}N$

Transition	Frequency (Mc/s)
$0_{0,0} \longrightarrow 1_{0,1}$	
F = 1 → 1	22,148.19
1 → 2	22,148.69
1 → 0	22,149.43
$1_{0,1} \longrightarrow 2_{0,2}$	
F = 0 → 1, 2 → 2	44,296.00
F = 1 → 2, 2 → 3	44,296.52
F = 1 → 1	44,297.34

TABLE 10 (Continued)

Transition	Frequency (Mc/s)
$1_{1,1} \longrightarrow 2_{1,2}$	
F = 1→1	43,833.26
1→2	43,835.00
2→3	43,835.42
2→2	43,836.52
0→1	43,837.18
$1_{1,0} \longrightarrow 2_{1.1}$	
F = 2→2	44,754.16
F = 0→1, 1→2	44,755.24
F = 2→3	44,755.82
F = 1→1	44,757.76
$9_{1,9} \longrightarrow 9_{1,8}$	
F = 9→9	20,699.80
10→10	20,702.82
8→8	20,703.19
$10_{1,10} \longrightarrow 10_{1.9}$	
F = 10→10	25,299.09
11→11	25,302.16
9→9	25,302.49

TABLE 11

Spectroscopic constants for $H_2C^{15}N^{14}N$ (Mc/s)

		nitrogen-14 coupling constants		
$B_o + C_o$	$B_o - C_o$	$(eqQ)_a$	$(eqQ)_b$	$(eqQ)_c$
22,148.57	460.15	-1.73	+5.15	-3.42

The asymmetry of the nuclear coupling constants is very marked, and shows clearly that the electronic structure $H_2\overset{+}{C} = \overset{-}{N} = N$ is important; the appreciable value of $(eqQ)_a$, however, shows also that the state $H_2\overset{-}{C}-\overset{+}{N}\equiv N$ has a large contribution to the structure. These conclusions agree with those based on internuclear distances determined from a very full study of a series of isotopic forms of diazomethane made in this laboratory at other periods.[4] A full account in which all the data for this molecule are considered together is in preparation for later submission.

3.3.2 Cyanamide

Earlier work by this group[3,5] had previously established rotational constants for various forms of cyamide, H_2NCN. As in the isomeric substance, diazomethane, two simultaneously coupled nitrogen-14 nuclei are present in the normal form of the molecule, and there was little doubt that the coupling constants would be of comparable magnitude for each location of nitrogen in the molecule. Very incomplete resolution of the hyperfine splittings of lines was attained for the $H_2{}^{14}NC^{14}N$ form, and it was decided to determine the coupling constants individually in this case also by replacing each nitrogen in turn by nitrogen-15. The species $H_2{}^{15}NC^{14}N$ and $H_2{}^{14}NC^{15}N$ are in tautomeric equilibrium, and cannot therefore be obtained in more than 50% concentration in each case; in practice a 90% enrichment of nitrogen-15 was used, giving about 45% of each form in the mixture. By use of the source-modulation spectrometer already described, the quadrupole splittings if the spectra of each form were resolved and analysed. The frequency-differences measured are given in Tables 12 and 13; the patterns found and the relative intensities of lines agreed satisfactorily with these assignments.

TABLE 12

Nuclear quadrupole splittings in $H_2{}^{14}NC^{15}N$ (in ground state, except where stated)

(Frequencies of lines in each group increase in the order given)

Transition	Frequency differences (Mc/s)
$1 \longrightarrow 2$ 0,1 0,2	
F = 1→1	Line seen; no accurate measurement
F = 2→3, 1→2	0.84
F = 0→1, 2→2	

TABLE 12 (Continued)

Transition	Frequency differences (Mc/s)
$1_{1,0} \longrightarrow 2_{1,1}$	
F = 0→1	1.14
F = 2→2	0.70
F = 2→3	0.91
F = 1→2	0.94
F = 1→1	
$1_{1,1} \longrightarrow 2_{1,2}$	
F = 1→1	1.44
F = 2→3, 0→1	1.05
F = 1→2	0.4
F = 2→2	
$1_{0,1} \longrightarrow 2_{0,2}$ (first excited vibrational state)	
F = 1→1	1.43
F = 2→3, 1→2	0.92
F = 0→1, 2→2	

TABLE 13

Nuclear quadrupole splittings in $H_2{}^{15}NC^{14}N$ (in ground state, except where stated)

(Frequencies of lines in each group increase in the order given)

Transition	Frequency difference (Mc/s)
$1_{0,1} \longrightarrow 2_{0,2}$	
F = 0→1, 2→2	0.87
F = 2→3, 1→2	
F = 1→1	Line seen, no accurate measurement

TABLE 13 (Continued)

Transition	Frequency difference (Mc/s)
$1_{1,0} \longrightarrow 2_{1,1}$	
$F = 1 \rightarrow 2,\quad 2 \rightarrow 2$	) 1.00
$F = 2 \rightarrow 3$	
$F = 0 \rightarrow 1,\quad 1 \rightarrow 1$	broad, weak line seen; not measured
$1_{1,1} \longrightarrow 2_{1,2}$	
$F = 1 \rightarrow 1,\quad 1 \rightarrow 2$	)0.96
$F = 2 \rightarrow 3,\quad 2 \rightarrow 2$	)1.42
$F = 0 \rightarrow 1$	
$1_{0,1} \longrightarrow 2_{0,2}$	
(first excited vibrational state)	
$F = 0 \rightarrow 1,\ 2 \rightarrow 2$	)1.01
$F = 2 \rightarrow 3,\ 1 \rightarrow 2$	)1.57
$F = 1 \rightarrow 1$	

It is immediately apparent from the patterns of the $K_{-1} = 0$ lines, that the coupling constant $(eqQ)_a$ is positive for the amino nitrogen and negative, with almost the same absolute magnitude, for the cyanide nitrogen. In the first excited vibrational state, for which the lines with $K_{-1} = 0$ are stronger than for the ground state, the coupling patterns were more easily measurable. These stronger multiplets confirm the signs of the couplings as indicated above, and show that the coupling constants are not greatly affected by the vibration, though both may possibly be slightly increased by it.

The $K_{-1} = 0$ lines are completely different in pattern for the two isotopic forms, showing that the asymmetry of the couplings at the two positions is different. Table 14 shows the coupling constants which are derived from these data, averaged for overall consistency.

TABLE 14

Nitrogen coupling constants in cyanamide (Mc/s)

Location of Nitrogen-14	$(eqQ)_a$	$(eqQ)_b$	$(eqQ)_c$
Amino	+2.96	+1.96	−4.92
Cyano	−3.03	+3.12	−0.09

The considerable negative value of $(eqQ)_a$ for the cyanide nitrogen shows that the state $H_2N-C\equiv N$ has a large importance. The asymmetry of this coupling, however, is what would be expected if $H_2\overset{+}{N}-C=\overset{-}{N}$ also made a considerable contribution, though its effect is not so great as that of the corresponding state in diazomethane. The coupling of the amino nitrogen appears in reasonable qualitative agreement with the contributions of the two states mentioned.

More detailed discussion of these results will form part of a later paper in which the couplings will be correlated with information on the molecular geometry of cyanamide.

3.4 Microwave spectrum of nitramide, H_2NNO_2

Work on this molecule was begun partly because of its expected resemblence to cyanamide, particularly in the probability of low-lying vibrational levels associated with the easy inversion of an amino group adjacent to a strong electron-attracting group. Nitramide is also very unstable, being decomposed with ease into water and nitrous oxide, and has a low volatility, so that it falls into the category of substances for which the microwave method is more potentially powerful than any other for structural investigation.

Early experiments did not yield spectra of this substance, although lines due to decomposition products were seen. At this stage it was believed that the known catalysis of nitramide decomposition by metallic surfaces and metal compounds might prevent the successful study in a metal waveguide, and plans were made to study the substance in glass cells (section 2.2) or in lined waveguide cells in the millimetre range. A second search, however, in a simple Stark modulated spectrometer, showed that many lines undoubtedly due to nitramide could be measured, the substance being pumped through the cell at room temperature from the solid sample.

Table 15 lists the frequencies of the chief lines for which observations of Stark effects were made in the most important frequency regions. Assignments of eighteen of the lines are given which are in agreement with Stark effect classifications and which yield very consistent values of the spectroscopic constant (A-C) for a value of the asymmetry parameter, kappa, of +0.764. We may conclude, therefore, at this stage that (A-C) is 6492 Mc/s, and that the value of kappa given is a good first estimate. Progress was also made (see Table 15) on assignment of lines which would determine independently the values of the constants (B+C) and B-C). Conclusions were delayed by the apparent absence of the $0_{0,0}\rightarrow 1_{0,1}$

line for the ground state of the molecule, but it appeared possible that this was due to the presence of the very low vibrational level mentioned previously, which, with the expected nuclear statistical weight factors, and at the particular frequency concerned (18,056 Mc/s), could have made the predicted line difficult to observe.

On the information obtained within the contract period, it may be asserted that the molecule of nitramide certainly yields its gas-phase spectrum under the conditions chosen. The spectroscopic constants are consistent with the molecular state H_2NNO_2, and the assignments made are for a dipole component in the A-axis, such as would be the main component in this molecule, but it would not be impossible for a tautomeric form to have similar constants and a finite A-component of dipole. The form H_2NNO_2, however, is probable on general grounds and fits the spectra well. Should the phenomena tentatively attributed to the presence of low vibrational level, and associated nuclear spin statistical effects, be confirmed*, this would be strong evidence for the form H_2NNO_2, with a plane of symmetry.

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* Work since carried out by Dr.J.K.Tyler, at the National Research Council, Ottawa, has now provided this confirmation (private communication).

TABLE 15

Lines and assignments for nitramide

Frequency (Mc/s)	Intensity	Assignment	(A-C)/2 for kappa = +0.764
17,470.12	w		
17,524.50	w	$10_{8,3} \rightarrow 10_{8,2}$	3246.8
18,034.78	s		
18,244.00	m		
18,423.56	s		
18,544.06	s		
20,460.18	s	$9_{7,3} \rightarrow 9_{7,2}$	3247.1
23,162	mw	$8_{6,3} \rightarrow 8_{6,2}$	
25,504.66	ms	$7_{5,3} \rightarrow 7_{5,2}$	3245.6
26,328	w		
26,609	w		
27,268	w		
27,423	s	$6_{4,3} \rightarrow 6_{4,2}$	3246.7

TABLE 15 (Continued)

Frequency (Mc/s)	Intensity	Assignment	(A-C)/2 for kappa = +0.764
27,550	m		
27,769	w		
27,872	s		
28,031	w		
28,707	m		
28,833	s	$5_{3,3} \longrightarrow 5_{3,2}$	3246.9
29,132	s		
29,678	s		
29,745	w	$4_{2,3} \longrightarrow 4_{2,2}$	3246.9
29,856	s		
29,999	m		
30,132	w		
30,238	m	$3_{1,3} \longrightarrow 3_{1,2}$	3246.6
30,259	w		
30,384.57	s	$1_{1,1} \longrightarrow 2_{1,2}$	
30,566.55	s		
30,600	w	$3_{0,3} \longrightarrow 3_{2,2}$	3246.8
30,605	s		
30,811.08	s	$4_{1,3} \longrightarrow 4_{3,2}$	3246.6
31,004	m		
31,067.62	s	$1_{0,1} \longrightarrow 2_{0,2}$	
31,205.39	s		
31,260.87	s	$5_{2,3} \longrightarrow 5_{4,2}$	3246.3
31,438	w		
31,668	w		
31,806	m		
31,950.91	s	$12_{9,4} \longrightarrow 12_{9,3}$	3245.8
32,002	w		
32,094.38	s	$6_{3,3} \longrightarrow 6_{5,2}$	3246.0

TABLE 15 (Continued)

Frequency (Mc/s)	Intensity	Assignment	(A-C)/2 for kappa = +0.764
32,131	w		
32,233	m		
32,299	w		
32,534	w		
32,654	w		
33,114 doublet	m		
33,249 doublet	s		
33,324	w		
33,426	m		
33,459	m		
33,497.22	m	$7_{4,3} \rightarrow 7_{6,2}$	3245.5
33,503	m		
33,548 doublet	s		
33,606.11	s		
34,118	m		
34,618	m		
35,488	w		
35,678	s	$8_{5,3} \rightarrow 8_{7,2}$	3244.0
36,848	m		
37,560	m	$10_{7,4} \rightarrow 10_{7,3}$	3246.2

3.5 Other spectroscopic work

Several other spectroscopic topics received attention during the period. Fairly extensive preliminary work was carried out on trifluoromethane thiol, CF_3SH, for which the molecular geometry and internal mechanics, particularly the rotation about the CS bond, were of interest. Earlier studies made in this laboratory had encountered difficulty in the satisfactory chemical preparation of sufficiently pure samples. With the publication[6] of an improved means of preparation, we were able to obtain good samples and to detect many strong lines in their spectra. The spectra proved complicated, and analysis has not yet been possible. Table 16 lists certain lines which have been accurately measured, in the hope of identifying, from frequencies and observations of Stark effects, R-branch groups not strongly affected by the internal rotation of the SH group. The complications caused by this internal degree of freedom, however, are sufficient to prevent assignments at the stage reached. Many other lines besides those in Table 16 were observed throughout the region.

Mass-spectra of samples of CF_3SH showed variable CF_2S peaks, and it appears probable that they contained some of the latter substance as a decomposition product. Accordingly, some of the observed lines might be due to CF_2S. Further work on CF_3SH, CF_3SD and CF_2S is projected.

TABLE 16

Measured lines of CF_3SH samples

Frequency (Mc/s) (wavemeter measurement unless given to less than 1 Mc/s)

9,214
9,236
9,336
18,400
18,450
18,426
19,301
19,325
19,354.1
19,358.4
19,423.5
19,450.1
19,472.3
19,483.4
19,511.2
19,549.5
19,664
19,775
19,942
20,191
24,667
24,758
25,065
25,369
25,485
25,497
25,527
25,595
25,865
25,876
25,884
25,920
25,932
25,975.14
25,990
26,016.63
26,070.88
26,105
26,128
26,162
26,190
26,242
26,309
26,388
26,622.30
26,632.41
26,651.68
26,666.81
26,698.2
26,724.8
26,747.8
26,994
32,473
32,530
32,860
38,510
38,540
39,036

Chemical work was carried out on trifluorsilyl isocyanate, SiF_3NCO, and spectroscopic searches were made, in the expectation that the substance would be a symmetric-top molecule. Although a very strong absorption was found near 36,000 Mc/s, no satisfactory assignments could be made.

Computational work was carried out on precise measurements[4] on spectra of keten and diazomethane in order to obtain accurate values of the rotational constant, A, which is only poorly established from much of the spectrum. It may be derived from the Q-branch series, $J_{2,(J-1)} \rightarrow J_{2,(J-2)}$ provided allowance can be made for centrifugal distortion effects. At this stage reached in the period, it is believed that the uncertainties in allowing for these effects still limit accuracy of A to about 1%, but that some additional information will be obtainable from R-branch spectra in the millimetre range.

4. Implications for possible future work

In the work reported on millimetre wave generation and detection we have made no special effort to maximise the sensitivity of the conventional units of the spectrometer, or the power used at the fundamental frequency, since comparative studies of the procedures listed can be more rapidly and economically made in the ways described. Enough knowledge is already to hand,[1,2] however, to show that considerable enhancement of the performance can be achieved where appropriate by (a) use of source modulation of the klystrons coupled with phase-sensitive detection and recording of the spectra, and (b) overdriving the klystron sources at increased cathode potentials and cathode currents, in conjunction with water-cooling of these oscillators. With the existing arrangement, we should expect the addition to these two established procedures to make possible measurements at wavelengths of 1 mm.

Other developments in these techniques which are indicated depend to some degree on availability of semi-conductors and means of surface treatment. Aluminium doped silicon should be tested as detector material, and more extensive tests should be made on such semi-conductors as gallium arsenide and various whisker materials. We believe that some improvement would result from use of aluminium doped silicon, but other tests are of a more exploratory nature at this stage.

An important development[1] has been the use of bombarded silicon in harmonic generators. Facilities for securing the necessary ion-beams at sufficient energies proved difficult to obtain, and in the contract period it was only possible to undertake preliminary design work on the necessary electrodes and to arrange sources of the necessary high voltages. Attention was also given to the possibility of securing worthwhile improvement in semi-conductor performance by bombardment performed in more readily available instruments, such as sputter-coating units. It may be expected that the continuance of this phase of the work will also give a distinct improvement in both the performance and durability of the harmonic generators.

A considerable number of spectroscopic measurements can be profitably made in the presently accessible region, and these include measurements of distortion effects in an array of simple molecules similar to those already discussed. A variety of simple asymmetric-top molecules will repay investigation in the mm-wave range, both for the establishment of certain distortion effects and also for the refinement of certain rotational constants for structural studies. This group includes keten, diazomethane and formaldehyde, and numerous other near-prolate asymmetric rotor molecules. Progress in the study of symmetric rotors through mm-wave studies of the isotopically asymmetric forms, such as CH_2DF and SiH_2DF, is also due at this stage.

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Glossary of Symbols

J $J_{K_{-1},K_{+1}}$ K	Rotational quantum number involved in spectral transitions, in standard notation.
$(eqQ)_x$	Nuclear quadrupole coupling constant with respect to the direction x.
A B C	Rotational inertial constants of a molecule, in standard notation

List of Illustrations

Scientific papers published on the contract

Several of these are in preparation, as indicated in the text of the Report.

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J.SHERIDAN, A.P.COX, J.K.TYLER. Jan. 1962

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