FIG. 2. Oscilloscope display of part of the ^{127}I quadrupole structure of the $J = 1 \rightarrow 2$ transition of D^{127}I at 390 GHz [14].

tic decrease of available microwave power and an increase of molecular absorption with decreasing wavelength. As a result source modulation is ordinarily used at millimeter and submillimeter wavelengths rather than the Stark modulation which is commonly used in the centimeter region. Other techniques which make use of small dedicated computers both for signal-to-noise enhancement and spectral frequency measurements have been used with success [82].

In addition to the harmonic generation techniques discussed above, various other techniques are being developed and have been used in this region. They include far-infrared molecular lasers, spin–flip Raman lasers with difference mixing, direct electronic oscillators, Fourier transform spectroscopy, laser–microwave double resonance, etc. Some of these techniques are essentially microwave in character; others are of essentially infrared character, and many are hybrid techniques. Several excellent volumes are available which discuss them. *Spectroscopic Techniques for the Far-Infra-red, Submillimeter, and Millimeter Waves*, edited by D. H. Martin [63] contains several interesting contributions including articles by P. L. Richards who discusses Fourier transform spectroscopy and by P. N. Robson who discusses millimeter and submillimeter electronic oscillators. *Submillimeter Spectroscopy*, by G. W. Chantry [5] contains excellent discussions of far-infrared lasers and other " infrared " techniques for this region. *Submillimeter Waves*, edited by J. Fox [21], contains numerous contributions of interest to the millimeter

and submillimeter spectroscopist. Included in this commemorative volume is an article by A. F. Krupnov and A. V. Burenin which describes their excellent spectroscopic work with millimeter and submillimeter BWO's. These techniques, combined with those of harmonic generation, represent a formidable arsenal for the attack on the many and diverse problems of physical interest in the millimeter and submillimeter region.

III. Absorption Spectroscopy of Stable Molecules in the Ground State

The vast majority of experiments in microwave spectroscopy have been studies of the absorption spectra of molecules. These molecules are ordinarily in $^1\Sigma$ ground electronic states as well as in ground vibrational states. These studies have resulted in extensive knowledge of the fundamental nature and properties of molecules. In addition, their spectra are important to the understanding of a wide variety of physical phenomena from the nature of the interstellar medium to the constituents of atmospheric pollution.

Comprehensive bibliographies of microwave work by Guarnieri and Favero [28] and by Starck and Kettemann [70] should be called to the attention of the reader. Volume 6 of the New Series Landolt–Bornstein is an extensive compilation of molecular constants with bibliography [30]. In addition, a new series is being prepared by the National Bureau of Standards to replace the NBS Monograph 70 Series. The first part of this series, "Microwave Spectral Tables I. Diatomic Molecules," is now available [57]. These compilations should provide the interested reader with a comprehensive understanding of previous work in microwave spectroscopy.

Since small molecules, particularly those containing hydrogen and other light elements, have small moments of inertia and correspondingly large rotational constants, there is a strong correlation between the study of these species and millimeter and submillimeter spectroscopy. These species are of particular importance. Their simplicity allows the theorist to aspire to understand their properties on the basis of fundamental physical laws and, in addition, makes them excellent prototypes for testing spectroscopic models. They also occur commonly in nature and therefore are of importance to a wide variety of workers in other fields.

A. DIATOMIC AND LINEAR MOLECULES

Diatomic and linear molecules are the simplest molecules, have the simplest spectra, and have been long studied by microwave spectroscopists. In the ground vibrational state their transition frequencies are given by [27]

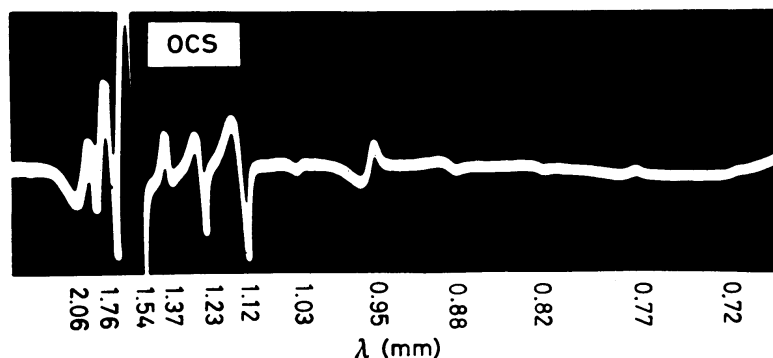$$\nu_{J \to J+1} = 2B_0(J + 1) - 4D_J(J + 1)^3, \tag{1}$$

FIG. 3. Oscilloscope display of absorptions in the 6th through 17th harmonics of a 24 GHz klystron [11].

where v is the microwave frequency, J is the rotational quantum number, B_0 is the rotational constant, and D_J is the first order distortion constant. Even for relatively heavy molecules, these transitions fall into the millimeter region at low J and millimeter and submillimeter transitions are required for accurate calculation of D_J. These molecules are particularly well suited for study by means of harmonic generation techniques in that "harmonic series" occur. If the fundamental klystron is tuned to 2 B_0 (or some multiple), the successive transitions at higher J cause an absorption to occur in every klystron harmonic. Because of the centrifugal distortion term D_J, the harmonic relation is not exact, and the series of closely spaced lines as shown in Fig. 3 results. This technique not only allows the measurement of several lines at once, but is also a convenient and simple means for the evaluation of spectrometer performance.

Of diatomic molecules, the hydrogen halides as a group represent perhaps the greatest challenge experimentally to the microwave spectroscopist because their large rotational constants result in numerous transitions well into the submillimeter region. For example, the lowest frequency rotational transition of HCl, shown in Fig. 4, falls at 625 GHz. This rotational transition is split into a closely spaced triplet by the interaction of the nuclear quadrupole moment of the chlorine nucleus and the gradient of the molecular electric field at the nuclear site. In addition, each of these lines is slightly displaced by the interaction between the magnetic dipole moment of the nucleus and the magnetic field generated by molecular rotation. This is an excellent example of the resolving power of these techniques. The components of this transition at 20 cm^{-1} are separated by only 5×10^{-4} cm^{-1} and this separation can be measured to an accuracy of 3×10^{-6} cm^{-1}. Significantly higher resolutions are attainable by use of the techniques of Section VI.

Of all the hydrogen halides, only HF for which the $J = 0 \to 1$ transition falls at about 1200 GHz is at present beyond the range of the techniques of harmonic generation. Table I shows the data obtained for the hydrogen
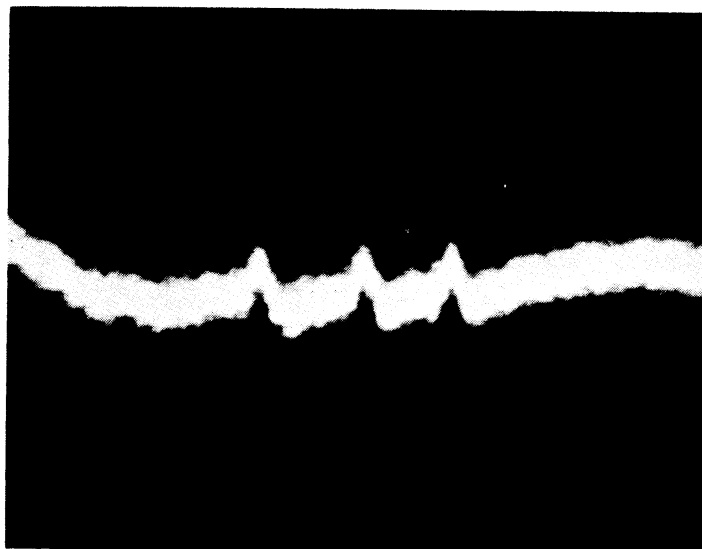
FIG. 4. Oscilloscope display of the ^{35}Cl fine structure of the $J = 0 \to 1$ rotational transition of H^{35}Cl at 625 GHz [14].

halides [14]. The spectra of all other stable diatomic and linear molecules lie at lower and more accessible frequencies. As a result, present day experimental activity is aimed at extending the short wavelength limit of the technique to below 0.3 mm so that HF and some of the higher J transitions of the lightest species can be observed. Vigorous work is also in progress to detect and measure the spectra of unstable diatomic species as well as molecules in excited states (see Sections IV and V). It should be pointed out that the

TABLE I

Spectral Constants of the Hydrogen Halides

	B_0 (MHz)	D_0 (MHz)	$(eQq)_{hal}$ (MHz)	$(C)_{hal}$ (MHz)
D^{19}F	325 584.98 $\pm$ 0.300	17.64^a	—	—
H^{35}Cl	312 989.297 $\pm$ 0.020	15.836^a	-67.800 ± 0.095	0.068 $\pm$ 0.010
H^{37}Cl	312 519.121 $\pm$ 0.020	15.788^a	-53.436 ± 0.095	0.056 $\pm$ 0.010
D^{35}Cl	161 656.238 $\pm$ 0.014	4.196 $\pm$ 0.003	-67.417 ± 0.098	0.026 $\pm$ 0.011
D^{37}Cl	161 183.122 $\pm$ 0.016	4.162 $\pm$ 0.003	-53.073 ± 0.113	0.024 $\pm$ 0.013
H^{79}Br	250 358.51 $\pm$ 0.15	10.44 $\pm$ 0.06^a	535.4 $\pm$ 1.4	0.29 $\pm$ 0.20
H^{81}Br	250 280.58 $\pm$ 0.15	10.44 $\pm$ 0.06^a	447.9 $\pm$ 1.4	0.31 $\pm$ 0.20
D^{79}Br	127 357.639 $\pm$ 0.012	2.6529 $\pm$ 0.0014	530.648 $\pm$ 0.074	0.148 $\pm$ 0.009
D^{81}Br	127 279.757 $\pm$ 0.017	2.6479 $\pm$ 0.0020	443.363 $\pm$ 0.105	0.158 $\pm$ 0.012
H^{127}I	192 657.577 $\pm$ 0.019	6.203 $\pm$ 0.003	-1828.418 ± 0.200	0.349 $\pm$ 0.010
D^{127}I	97 537.092 $\pm$ 0.009	1.578 $\pm$ 0.001	-1823.374 ± 0.105	0.165 $\pm$ 0.006

^{a} Calculated from infrared data.
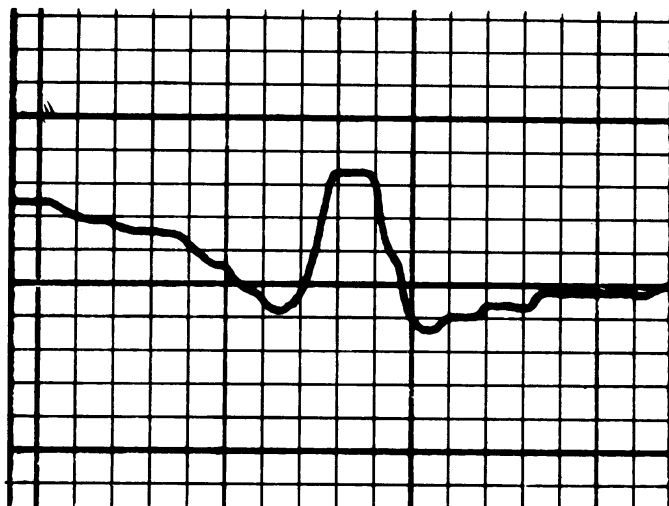
FIG. 5. Chart recorder tracing of the $J = 6 \rightarrow 7$ rotational transition of $^{12}C^{16}O$ at 806 GHz [31].

absorptions of diatomic and linear molecules in the millimeter and submillimeter wavelength region are extremely strong. For example, the $J = 6 \rightarrow 7$ transition of CO at 806 GHz, shown in Fig. 5, will absorb virtually all of the incident microwave radiation in only a 10 cm long cell, even though its dipole moment is only 0.1 D. As a result, isotopic species whose abundances are substantially less than 1% are commonly observed in natural abundance and with good signal-to-noise ratios.

B. SYMMETRIC TOP MOLECULES

The spectra of symmetric top molecules are similar to those of linear molecules, except for the so-called K-splitting of the rotational transitions. The frequencies of the rotational transitions are given by [27]

$$v = 2B_0(J + 1) - 4D_J(J + 1)^3 - 2D_{JK}(J + 1)K^2, \tag{2}$$

where v is the microwave frequency, J and K are rotational quantum numbers, B_0 is the rotational constant, and D_J and D_{JK} are distortion constants. An example of this K-structure is shown in Fig. 6. Again, as for linear molecules, these transitions fall into the millimeter region for relatively low J and millimeter and submillimeter transitions are needed for evaluation of D_J and D_{JK}.

The rotational spectra of the lightest symmetric top rotors are easily within the range of harmonic generation techniques. Table II shows the rotational constants derived for these species. The extension of these
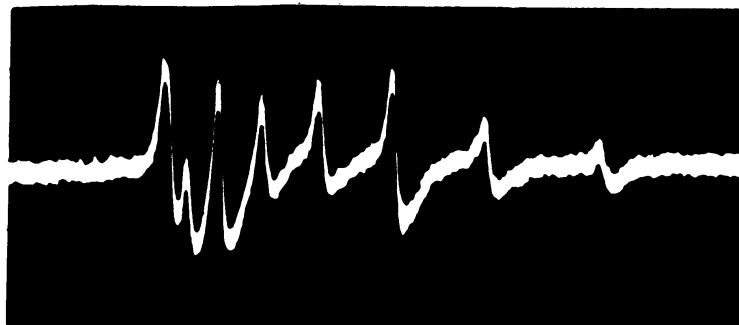
FIG. 6. Oscilloscope display of the eight K lines of the $J = 8 \rightarrow 9$ transition of CF_3H at 190 GHz [3].

techniques to higher frequencies would allow the measurement of the $J = 1 \rightarrow 2$ transition of NH_3 and the calculation of the values of D_J and D_{JK} directly from the microwave data. Otherwise the spectroscopy of the ground states of symmetric top molecules is well within the present state of the art although an extension of the technique to still shorter wavelength would allow D_J and D_{JK} to be more accurately calculated.

C. ASYMMETRIC ROTORS

Although heavy, many-atom asymmetric rotors have long been studied in the centimeter region of the spectrum, the characterization and interpretation of the spectra of light asymmetric rotors have been one of the most elusive and challenging problems for the microwave spectroscopist. Included in this class of molecules are species of the form $H_2 X$, HDX, $D_2 X$, XH_2D, and XD_2H where X represents any chemically appropriate atom. These molecules are not only sufficiently simple to serve as prototypes for

TABLE II

Rotational Constants of the Group V Hydrides

	B_0 (MHz)	D_J (MHz)	D_{JK} (MHz)	References
$^{14}NH_3$	298 115.37	24.31[a]	−45.27[a]	[33]
$^{14}ND_3$	154 173.38 ± 0.05	5.91 ± 0.01	−10.49 ± 0.02	[33]
$^{14}NT_3$	105 565.37 ± 0.03	2.598 ± 0.002	−4.472 ± 0.006	[36]
$^{31}PH_3$	133 480.15 ± 0.10	3.95 ± 0.01	−5.18 ± 0.02	[32a]
$^{31}PD_3$	69 471.09 ± 0.05	1.02 ± 0.005	−1.31 ± 0.01	[32a]
$^{75}AsH_3$	112 470.59 ± 0.03	2.925 ± 0.003	−3.718 ± 0.004	[32]
$^{75}AsD_3$	57 477.60 ± 0.02	0.741 ± 0.002	−0.928 ± 0.003	[32]
$^{121}SbH_3$	88 038.99 ± 0.03	1.884 ± 0.004	−2.394 ± 0.015	[32]
$^{121}SbD_3$	44 694.92 ± 0.03	0.473 ± 0.004	−0.598 ± 0.009	[32]

[a] From infrared data.

the testing of molecular theory, but are also important in their own right because of their natural abundance. Early microwave spectroscopists recognized this importance and observed and assigned several lines in many of the species, but were generally unable to characterize their spectra [40, 73].

The principal problem from the point of view of the microwave spectroscopists is that at most only a few lines of each species fall in the centimeter or longer millimeter wavelength regions of the spectrum. Table III shows the distribution in frequency of the transitions that have now been observed by microwave techniques. Since present theoretical techniques require on the order of 20 parameters to characterize the rotational spectrum of this class of molecule, this table clearly demonstrates the necessity for a large number of measurements in the millimeter and submillimeter wavelength region.

The lack of an accurate theoretical model for the extreme centrifugal distortion exhibited by these light asymmetric species has compounded the problem. Recently, however, Watson [75-77] has proposed a reduced centrifugal distortion Hamiltonian which in large part provides a solution to this problem; it is given by

$$\mathscr{H} = \mathscr{H}_r + \mathscr{H}_d^4 + \mathscr{H}_d^6 + \cdots$$

$$\mathscr{H}_r = \tfrac{1}{2}(\mathscr{B} + \mathscr{C})P^2 + [\mathscr{A} - \tfrac{1}{2}(\mathscr{B} + \mathscr{C})](P_z^2 - b_p P_-^2),$$

$$\mathscr{H}_d^{(4)} = -\Delta_J P^4 - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 - 2\delta_J P^2 P_-^2 - \delta_K(P_z^2 P_-^2 + P_-^2 P_z^2),$$

$$\mathscr{H}_d^{(6)} = H_J P^6 + H_{JK} P^4 P_z^2 + H_{KJ} P^2 P_z^4 + H_K P_z^6 + 2h_J P^4 P_-^2$$
$$+ h_{JK} P^2(P_z^2 P_-^2 + P_-^2 P_z^2) + h_K(P_z^4 P_-^2 + P_-^2 P_z^4), \tag{3}$$

TABLE III

Frequency Distribution of Observed Transitions of the Lightest Asymmetric Rotors.

Molecule	Frequency (GHz)				Total observed	Hamiltonian terms	References
	< 80	80–300	300–600	600 >			
ND_2H	12	17	14	0	43	14	[18]
NH_2D	6	10	12	0	28	15	[18]
D_2S	0	13	46	7	66	22	[9]
HDS	12	10	22	1	45	14	[34]
H_2S	1	9	17	12	39	24	[35]
D_2O	8	19	8	1	36	22	[2]
HDO	19	19	14	1	53	22	[15]
H_2O	1	1	11	2	15	21	[16]
T_2O	5	25	19	2	51	22	[17]
DTO	5	22	14	3	44	21	[37]
HTO	11	22	13	2	48	22	[37]

where $\mathscr{A}$, $\mathscr{B}$, and $\mathscr{C}$ are the rotational constants, Δ_J, H_J, etc. are the centrifugal distortion parameters; $b_p = (\mathscr{C} - \mathscr{B})/(2\mathscr{A} - \mathscr{B} - \mathscr{C})$ is Wang's asymmetry parameter; and $P_-^2 = (P_x^2 - P_y^2)$. The extension of this Hamiltonian to include the higher order terms necessary for the light asymmetric rotors is straightforward.

This Hamiltonian has been shown to be capable of fitting all observed data to within the experimental uncertainty, of producing meaningful spectral constants and energy levels, and of accurately predicting the frequencies of unobserved transitions [15, 35]. On the other hand, too many distortion constants are required for it to be philosophically satisfying; prediction with high accuracy of transitions far removed in J_τ from the observed transitions is sometimes difficult; and, because of the transformation required for removal of the fitting indeterminacy present in previous Hamiltonians, the relation between the Watson rotation–distortion parameters which result from these analyses and the molecular parameters is not well defined. This latter objection is circumvented to some extent by a Hamiltonian developed by Kneizys, Freedman, and Clough [51].

Table III is more or less inclusive of light asymmetric rotors that have been analyzed on the basis of microwave data. Only in the case of H_2O has it been necessary to supplement the microwave data with infrared data. Probably the most stringent test of the theoretical model is HTO which has large rotational constants and for which a large body of high accuracy data has been recently acquired. For this species the microwave spectrum can be fitted to within expected experimental uncertainty ($\lesssim 0.1$ MHz) and unmeasured lines can be predicted with high accuracy.

One alternative to the power series expansion of Eq. (3) is an approach based upon the particular geometry of the asymmetric species (e.g., bent XYZ [44] or pyramidal XY_2Z [12]). The economy of coordinates which results should be useful in both reducing the number of distortion parameters required and in improving the convergence of the system. Hoy and Bunker [45] have applied this technique to the infrared data of several isotopic species of water with some success. It would be extremely interesting to see the results of a similar analysis based upon the high precision H_2O, HDO, D_2O, HTO, and T_2O microwave data contained in the references of Table III.

Slightly asymmetric species with large $\mathscr{A}$ rotational constants form another interesting class, particularly from a theoretical point of view. In general transitions which characterize $\mathscr{B}$, $\mathscr{C}$ and related distortion constants (Δ_J, etc.) fall in the longer millimeter or centimeter region and have been observed by conventional microwave techniques for many years. On the other hand transitions which make possible the accurate calculation of $\mathscr{A}$ and its related higher order constants (Δ_K, etc.) as well as more definitive checks of centrifugal distortion theory fall in the shorter millimeter and

submillimeter region. For the slightly asymmetric CH_2DF data adequate for the accurate calculation of $\mathscr{A}$, $\mathscr{B}$, $\mathscr{C}$ and the P^4 distortion constants of Eq. (3) has been acquired in the millimeter and submillimeter region [7]. For the even more symmetric HNCS the constants are less well-established because the extremely large value of $\mathscr{A}$ makes the measurement of the required lines difficult [74]. Molecules, such as HCNO, are more properly characterized as "quasi-linear" and form an interesting transition between those molecules which are truly linear and slightly asymmetric species such as HNCS. The theoretical aspects of this transition are discussed in an excellent article by Yamada et al. [86].

D. EXTERNAL FIELDS

The previous sections of this article have been concerned with the spectroscopy of molecules in the absence of external electric or magnetic fields. Studies of molecules in external fields can provide information about a wide range of molecular properties including electric dipole moments, electric polarizability anisotropies, molecular g factors, magnetic susceptibility anisotropies, and molecular quadrupole moments. Since many of these effects are second-order, strong electric and magnetic fields, high resolution, and precise frequency measurements are required to obtain meaningful results. The flexibility of quasi-optical techniques and the strong molecular absorptions in the millimeter and submillimeter region make possible a number of interesting experiments. Gustafson and Gordy [29] have made use of a phase-locked millimeter wave spectrometer with closely spaced parallel-plate Stark cell to produce a sufficiently strong electric field to observe a microwave Stark effect in the nonpolar oxygen molecule. Figure 7 shows the results of this experiment. For high field Zeeman studies, a small Fabry–Perot cavity placed between the pole pieces of a large electromagnet results in a spectrometer of long effective path length, low loss, and high magnetic
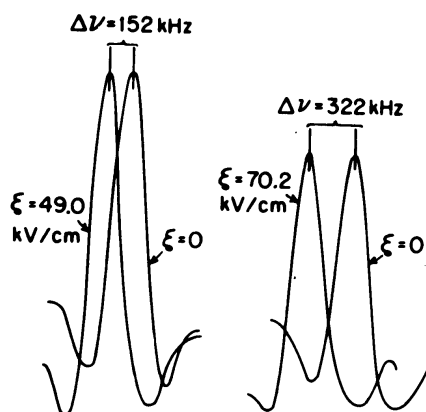

FIG. 7. The Stark shift of the 118 GHz line of oxygen [29].

field strength. In the future more spectroscopists will take advantage of this combination of strong absorptions, flexibility of mode propagation, and precise frequency control to study topics including induced dipole moments (including "forbidden" transitions), higher order Stark and Zeeman effects, unstable paramagnetic species, and the effects of centrifugal distortion on the electric dipole moments of molecules.

IV. Excited State Spectroscopy

Most microwave absorption spectroscopy has been performed on molecules in ground vibrational and electronic states that are well removed in energy from any excited state. In these cases the rotational part of the wavefunction is essentially separable from the vibrational and electronic wavefunctions, which in turn have little effect upon the observed ground state spectra. However, several interesting experiments have been performed for which this is not the case.

Certainly the first example of this class of molecules is ammonia, the inversion spectrum of which provided the basis for the first detection of a microwave absorption by Cleeton and Williams [8]. This inversion has also been observed in the millimeter and submillimeter region as splittings of the rotational transitions of NH_3 and ND_3 [33, 53], of NT_3 [37], and of NH_2D and ND_2H [18]. In addition, ND_2H shows an interesting rotation–vibration interaction which significantly perturbs the energy of a number of rotational energy levels. This interaction is a direct result of the small energy difference between the O^+ and O^- vibrational levels of ammonia.

Internal rotation also results in low-lying excited vibrational states which fundamentally alter the character of the observed spectra. Included among the species for which millimeter and submillimeter techniques have provided valuable information are methyl alcohol [54], hydrogen peroxide [65], and hydrogen disulfide [78]. Although the study of internal rotation is in many senses still in its infancy, it is inevitable that the techniques of millimeter and submillimeter spectroscopy will make major contributions to the understanding of these complex interactions by providing the investigator with a significantly larger amount of information than is obtainable in the centimeter region alone.

In more "well-behaved" molecules, microwave spectroscopy has been primarily the study of the ground vibrational state simply because at room temperature the vast majority of molecules are in the ground state because of the large ratio of the vibrational energy to kT. However, this has not been the case for one very interesting and profitable class of experiments, the so called "hot-cell" experiments. The original motivation for these experiments was the desire to study the properties of molecules that have significant

vapor pressures at elevated temperatures. A byproduct of this elevated temperature (approximately 1000°C) is a significant population in the excited vibrational states. For diatomic molecules, Dunham [20] has produced a theory which makes possible an accurate calculation of the equilibrium parameters of the molecule from the measurement of lines in varying v (vibrational) and J (rotational) states. Ordinarily the enhancement of the vibrational population produced by the elevated temperatures and the sensitivity of millimeter and submillimeter techniques allow the measurement of these lines. For example, AlI transitions as high as $J = 38 \rightarrow 39$ and $v = 14$ have been observed and the parameters of this molecule calculated [85]. Recently several experiments have been reported on unstable chemical species that are produced by high temperature chemical reactions. Among these are the aluminum monohalides (Lide [56]; Wyse and Gordy [84, 85]; Hoeft et al. [42]) and the copper monohalides (Hoeft et al. [43]; Manson et al. [59–61]). These experiments are particularly interesting because they result in transient species which are often examples of unusual bonding states. Research in this area is now centered on the extension of these techniques to shorter lived chemical species and to species that require higher temperature for vaporization.

Linear and symmetric top molecules often have bending vibrational modes of sufficiently small energy that for spectroscopic studies in the millimeter and submillimeter region they are adequately populated at room temperature. Although the spectra of these states are somewhat more complex, the same general experimental requirements remain with a somewhat increased sensitivity required. In many cases, the absorptions of molecules in the millimeter and submillimeter region are so strong that the higher energy and thinly populated stretching modes can also be studied. In such cases the equilibrium spectral constants and, if an adequate number of isotopic species are studied, the equilibrium structure can be calculated. An interesting example of this work is the study of Hirota and Morino of PF_3 [41]. Several such studies are discussed in a recent monograph by Gordy and Cook [27].

The excited vibrational states of the asymmetric rotor SO_2 have been extensively studied by Steenbeckeliers and Bellet [71] in the millimeter wave region. These studies have made possible accurate characterizations of the rotational energy level structure in a number of vibrational states, investigations of rotation–vibration interactions in the excited states, and the calculation of equilibrium rotational constants and structural parameters.

The light, hydrogen containing species have been more difficult, however. Because their vibrational energies are substantially larger as a result of their small reduced mass, the populations in the excited states are very small. Also, because of their small moments of inertia, their transition frequencies in general fall at the more inaccessible shorter millimeter and submillimeter
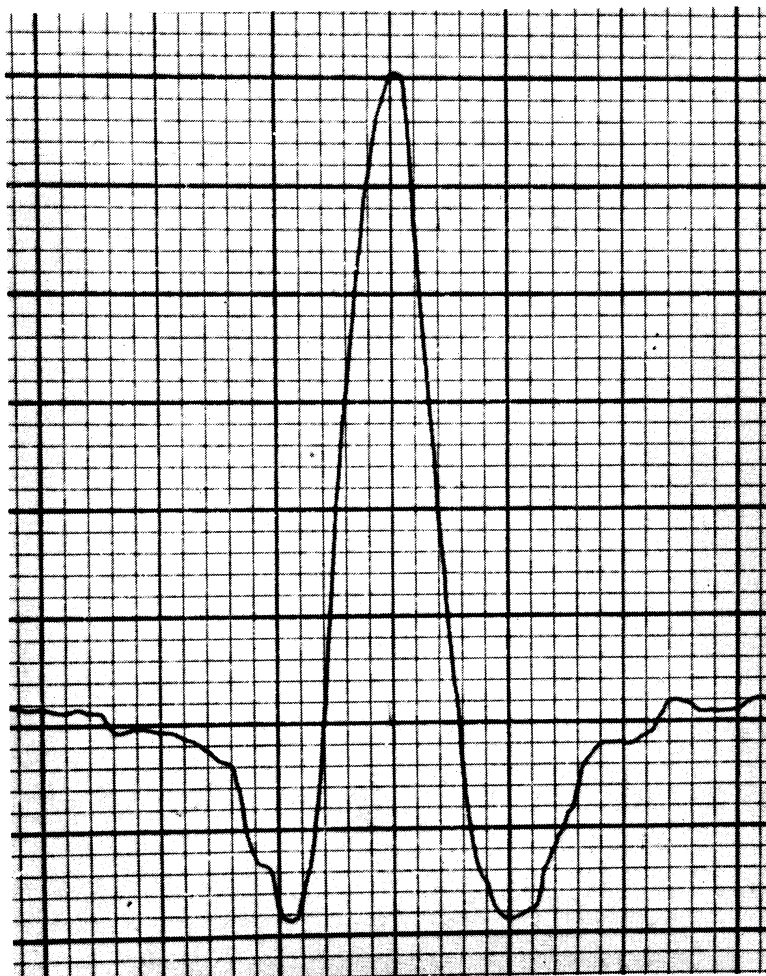
FIG. 8. The $J = 5 \rightarrow 6$ transition of SO at 256 GHz in the $^1\Delta$ excited electronic state [6].

wavelengths. The measurement of significant numbers of excited state vibrational transitions in many of the light hydrogen containing species represents a significant challenge. However, calculations indicate that the experimental techniques discussed in this article should make possible the observation of enough transitions for formulation of mixed infrared and microwave analyses based upon the Hamiltonian of Eq. (3). This should result in substantially improved knowledge of excited state energy levels.

In addition to the need for these excited state studies to allow calculation of the equilibrium properties of molecules, there are several other pressing needs of a more applied nature. The molecular lasers that operate in the submillimeter region are active on excited vibrational states. Most of these lasers have been discovered empirically with little or no knowledge of their molecular mechanisms or of the energy levels involved (and in some cases even without knowledge of the lasing species). Progress in the understanding of these mechanisms requires more detailed knowledge of the excited state

energy levels than exists at present for most of these species. This understanding is important both for the improvement of known molecular lasers and for the development of new ones. A detailed knowledge of the energy levels of the excited state is also of significant importance to our understanding of the atmospheric absorption of electromagnetic radiation.

Because of the extremely short lifetimes of excited electronic states, pure microwave studies of molecules in these states are substantially less common than those of molecules in excited vibrational states. Nevertheless, the $J = 2 \to 3$ transition at 127 GHz [69] as well as the $J = 3 \to 4$, $4 \to 5$, and $5 \to 6$ transitions [6] of SO have been measured in the $^1\Delta$ excited electronic state. In these experiments the molecular population in the $^1\Delta$ electronic state is the product of the reaction of atomic oxygen with a sulfur containing compound, such as H_2S. Fig. 8 shows the $J = 5 \to 6$ transition at 256 GHz.

V. Unstable Species

The original motivation for the study of free radicals and other unstable molecular species came from their postulated importance as intermediaries in chemical reactions. While this importance remains, their abundance in interstellar gas/dust complexes and their subsequent microwave detection has given further impetus to their spectroscopic study. Although large numbers of these species have been observed for many years by optical techniques [38, 39], relatively few have been observed by high resolution microwave techniques. These microwave techniques can be divided into two general categories: EPR experiments (see Carrington [4] for an extensive review of the vigorous experimental activity in this field) and microwave absorption spectroscopy. Although optical and EPR spectroscopy have resulted in a wealth of information, direct microwave measurements are necessary for a complete characterization of the rotational spectrum, especially if this characterization is to be useful for astrophysical purposes.

The first microwave measurements were reported by Dousmanis, Sanders, and Townes [19] of the Λ-type doubling spectrum of OH in the 7–37 GHz region. In a study of SO, microwave measurements were extended well into the millimeter region by Kewley et al. [47] by means of the system shown in Fig. 9. Although several different experimental configurations have been used in the longer millimeter region, a system of this type is an excellent prototype for future work in the shorter millimeter and submillimeter region. In such a system, millimeter and submillimeter waves are focused by quasi-optical techniques through a free space absorption cell with typical dimensions of 1 m in length by 10 cm in diameter. The free radicals are produced by such methods as rf (microwave) induced decomposition of a parent species or by direct reaction of a parent molecule with rf (microwave)
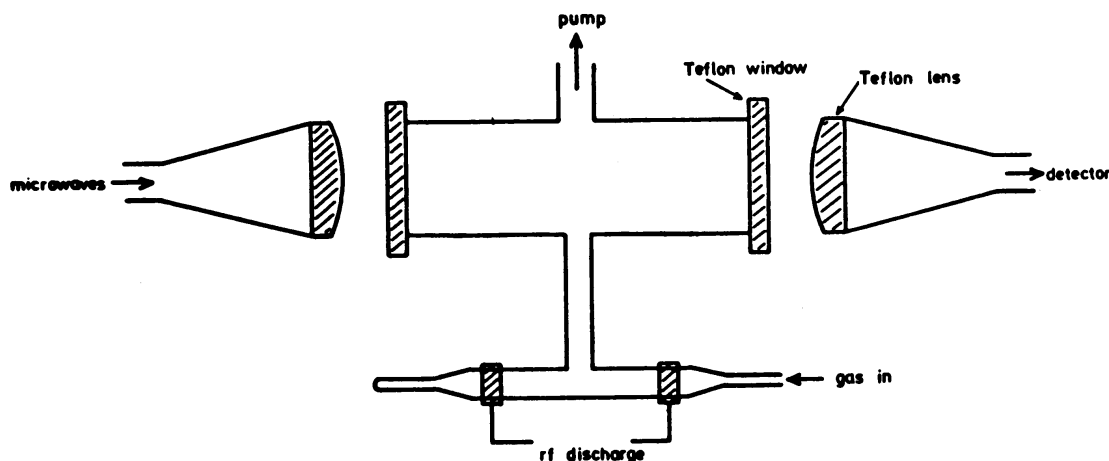
FIG. 9. Free space cell for the study of unstable species (after Kewley *et al.* [47]).

produced free atoms. The rest of the spectrometer remains unchanged from that shown in Fig. 1.

The significant advantages of the described techniques should make possible rapid advances in the microwave study of unstable species. The quasi-optical techniques result in large volume to surface ratios and large interaction regions thereby minimizing decay processes induced by both wall interactions and the frequent intermolecular collisions in the higher pressure gases commonly encountered in smaller cells. Although the wall deposits that inevitably result from either the molecular production or decay processes are in many cases serious problems in other types of spectrometers, the large dimensions associated with the quasi-optical geometry ordinarily reduce this problem to a minor annoyance. This geometry also makes possible the construction of high temperature spectrometers and the study of species which can either only be formed at high temperatures or which would condense after formation at 300°K. In addition, the systematic increase in absorption that accompanies an increase in frequency allows the detection of very small fractional concentrations of the unstable species. Of more fundamental importance is the fact that many of the interactions associated with unstable species with unfilled electronic shells represent energies substantially greater than the energies which correspond to centimeter-wave frequencies. As a result, these interactions often have little or no effect on the centimeter-wave transitions and can only be studied by means of millimeter and submillimeter measurements. In many cases, these interactions with the electronic structure of the molecule are among the most interesting and informative properties of free radicals.

VI. Specialized Techniques

In earlier sections of this article, experiments have been described which involve the use of millimeter and submillimeter waves to probe bulk samples of gas phase molecules in absorption cells. In this section will be described experimental techniques in which the molecular systems and the electromagnetic radiation interact under more controlled conditions.

One of the fundamental limitations of millimeter and submillimeter absorption spectroscopy is the Doppler broadening that often obscures hyperfine structure or reduces the accuracy with which rotational frequencies can be measured. One means of circumventing the Doppler broadening is by the use of saturation (Lamb-dip) spectroscopy. This technique requires that the propagating beam of microwave energy interact twice with the molecules, once in each direction. If sufficient power is available to saturate the molecules, only those molecules at the center of the Doppler profile (those moving perpendicularly to the direction of propagation of the microwaves) interact with both microwave beams simultaneously, and at this point an excess of saturation occurs. This effect has been observed in the longer millimeter-wave region by Costain [10]. In the shorter millimeter region, a convenient means of achieving both adequate power to saturate the transition and propagation of microwave energy in both directions is by use of a Fabry-Perot cavity. Winton and Gordy [83] have used this technique to make high precision measurements of the rotational frequencies of OCS and CH_3F. Figure 10 shows an example of this saturation dip. In an experiment on HCNO, Winnewisser [81] has used the technique of simple reflection of the signal back through a free space cell.
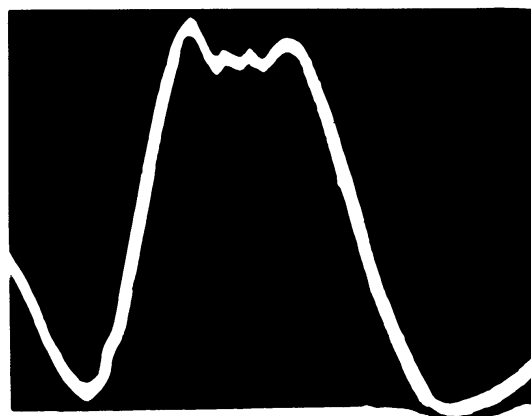

FIG. 10. The $J = 15 \rightarrow 16$ transition of $^{35}ClCN$ showing the closely spaced Lamb dips of the hyperfine components with separation of 50 kHz [83].

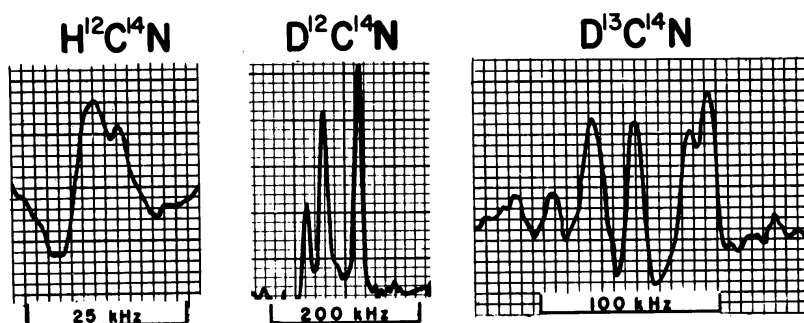$$H^{12}C^{14}N \qquad D^{12}C^{14}N \qquad D^{13}C^{14}N$$

FIG. 11. The effects of isotopic substitution on the hyperfine structure of the $J = 1 \rightarrow 0$ transition of hydrogen cyanide [22].

Several experiments have now been performed at millimeter and submillimeter wavelengths that involve the use of molecular beams. Huiszoon and Dymanus [46] have made use of a high resolution molecular beam absorption spectrometer to study the hyperfine structures of H_2S, HI, and HBr in the millimeter and submillimeter region. Marcuse [62] and Krupnov and Skvortsov [52] reported the successful operation of molecular beam masers in the 4 mm region. De Lucia and Gordy [13] reported the extension of these techniques to wavelengths as short as 1.7 mm and their use as spectroscopic devices in the millimeter region. These spectroscopic techniques have now been extended into the submillimeter region by Garvey and De Lucia [23].

The resolution of beam experiments is intrinsically high because Doppler and pressure broadening are essentially eliminated. The linewidth is then primarily determined by the time of flight of the molecule across the microwave region ($\Delta v \simeq 1/t$) and the spectral purity of the microwave source. All of the experiments discussed in this section are based on harmonic generation techniques in which the low frequency klystron source is referenced to WWVB or some other stable standard as shown in Fig. 1. In actual practice it is possible to achieve linewidths that are comparable with those determined by the molecular time of flight in the microwave field.

Figure 11 shows the beam maser spectrum of the structure within one of the ^{14}N quadrupole components of the $J = 1 \rightarrow 0$ rotational transition of hydrogen cyanide [22]. The $H^{12}C^{14}N$ was recorded under conditions of maximum resolution in order to resolve the 4.6 kHz splitting which results from the magnetic dipole interaction of the hydrogen nucleus. Isotopically enriched samples were used to observe the $D^{12}C^{14}N$ and $D^{13}C^{14}N$ spectra shown in this figure, although the $D^{13}C^{14}N$ can be observed in the natural abundance of ^{13}C by use of a supersonic nozzle source. Figure 12 shows the beam absorption spectrum of the hyperfine structure of the $1_{10}-1_{01}$ transition of $H_2{}^{32}S$ near 2 mm wavelength [46]. This technique is also adequately sensitive to allow the observation of $H_2{}^{34}S$ in natural abundance. For these and other beam experiments in the millimeter region, the cryogenic detector
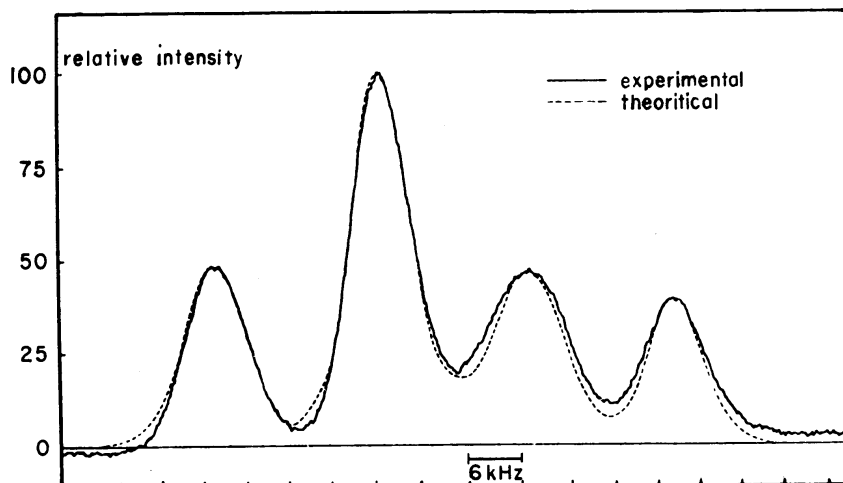
FIG. 12. Beam absorption spectrum of the $1_{10}-1_{01}$ transition of $H_2{}^{32}S$ at 168 GHz [46].

shown in Fig. 1 is often replaced by superheterodyne detection techniques. Although the details of frequency stabilization and measurement vary somewhat from experiment to experiment, the rest of the spectrometer is similar to that shown in Fig. 1 and discussed in Section II with the exchange of the quasi-free-space absorption cell for either the beam maser or beam absorption spectrometer.

Figure 13 shows the hyperfine structure of the $1_{10}-1_{01}$ transition of D_2O

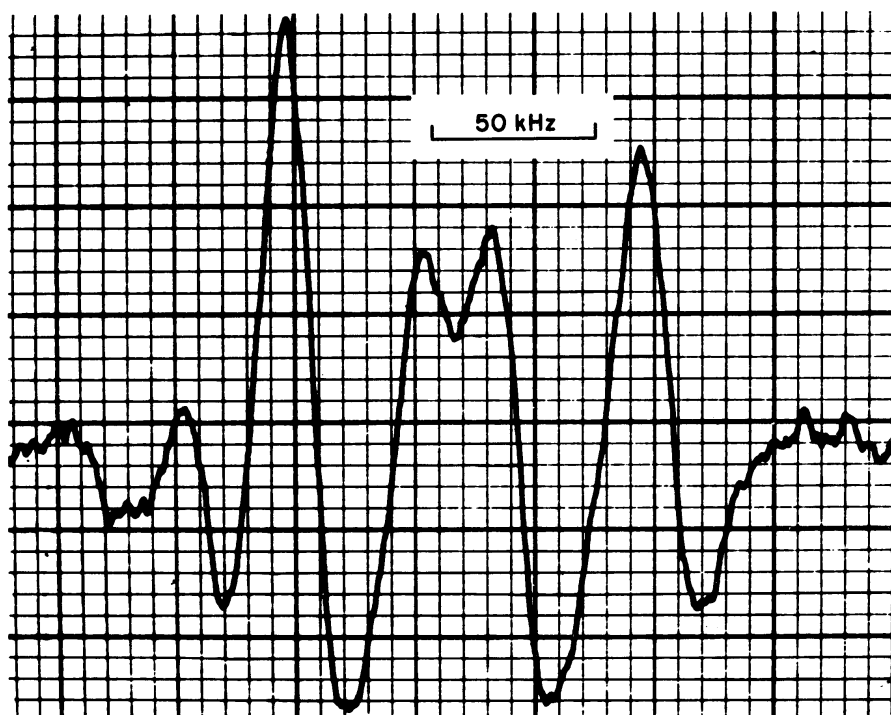FIG. 13. Beam maser spectrum of the $1_{10}-1_{01}$ transition of $D_2{}^{16}O$ at 317 GHz [23].

at 317 GHz [23]. The hyperfine structure of the $J = 1 \rightarrow 0$ transition of ND_3 at 309 GHz has also been observed. For both of these experiments the observed linewidths are comparable to those calculated from the time of flight relation above, and the contributions from collisions, Doppler, and saturation broadening are small. In addition, the strength of the signals which resulted from these experiments was such that the convenient, broad-banded liquid helium temperature detector of Fig. 1 was used rather than the more complex superheterodyne systems that have been used for similar experiments in the millimeter and centimeter wave regions.

All of these beam experiments result in linewidths that are 50–100 times narrower than the usual Doppler broadened line. As illustrated in Figs. 11–13 a wealth of hyperfine structure, previously obscured by Doppler broadening, emerges. This hyperfine structure is often associated with the very small splitting produced by the deuterium quadrupole and hydrogen spin–rotation interactions. The study of these interactions provides a powerful probe of the internal electric and magnetic fields of the molecule and an excellent test of theoretical calculations. In addition, since harmonic generation techniques result in microwave energy which is easily referenced to WWVB, high accuracy absolute frequency measurements can be made. One example of the usefulness of these measurements are the precise rotational frequencies of $H^{12}C^{14}N$ that can be predicted from the measurements of De Lucia and Gordy [13].

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