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Abstract

Apparatus and experimental techniques for Zeeman-effect measurements on microwave spectra are described. The method uses a waveguide-type absorption cell and provides for either π - or σ - type observations. Molecular rotational and nuclear gyromagnetic ratios are found to be measurable to about 1 percent accuracy.

A method is presented for sign determination of these gyromagnetic ratios using circularly polarized microwaves. The microwave components used in setting up the circularly polarized waves are described.



ZEEMAN-EFFECT MEASUREMENTS ON MICROWAVE SPECTRA

I. Introduction

Magnetic moments due to molecular rotation and in some cases nuclear magnetic moments can be determined from Zeeman-effect measurements on microwave absorption spectra. In order of magnitude the largest rotational gyromagnetic ratios are a few tenths of a nuclear unit and the Zeeman splittings encountered turn out to be uncomfortably small in relation to microwave absorption line widths for practical magnetic field strengths. The determination of such moments, therefore, presents quite a different experimental problem from that in the special cases of the microwave Zeeman spectrum of molecular oxygen and nitric oxide, where magnetic moments of the order of a Bohr magneton are involved and where small stray fields may even become troublesome. The present paper describes the experimental technique and apparatus used by us for measurements of rotational and nuclear magnetic moments (1, 2).

In the past, others have used both cavity and waveguide-type absorption cells for microwave Zeeman experiments. Coles and Good (3) were the first to observe the Zeeman effect on microwave spectra. Jen (4) has used a high-Q cavity method in which the absorption lines appear within the cavity resonance curve on an oscilloscopic display. Jen's measurements have been made on σ -type Zeeman components ($\Delta M = \pm 1$). Gordy and Gilliam (5) have used a waveguide, coiled up between the pole pieces of a magnet, to observe π -type components ($\Delta M = 0$). The apparatus described below employs a waveguide absorption cell in such a way that the setup may easily be changed between the σ and π arrangements. Also described is apparatus for observing σ -type components with circularly polarized microwave radiation, thus providing for the determination of the sign of the molecular and nuclear gyromagnetic ratios by microwave spectroscopy. The possibility of conveniently observing both π and σ transitions is important since, in general, several quantities of interest may appear in the theoretical expression for the splitting factor of a given Zeeman component. These quantities include the elements of the molecular gyromagnetic tensor (1), i. e. the gyromagnetic ratios along different molecular fixed axes and the nuclear gyromagnetic ratios that may be involved. In order to obtain sufficient data to determine these quantities separately, both π and σ measurements must usually be made (see particularly ref. 2).

In our experiments all numerical data were taken, using linearly polarized microwave radiation propagating in the familiar dominant mode of a rectangular waveguide (TE_{01}). Since the absorption cell was a straight section of waveguide and the faces of the magnet-pole pieces were long and narrow, the magnetic field was transverse to the waveguide axis, and the cell could easily be turned 90° about its longitudinal axis for either π or σ observations. The circular polarization apparatus was used solely for gyromagnetic ratio sign determination. In using this apparatus, we were interested only in the direction of the splitting of the Zeeman components, i. e. to higher or lower microwave frequency (energy) than the zero-field absorption, and thus a solenoidal

magnetic field of rather poor homogeneity sufficed.

Although the following discussion of Zeeman apparatus and method may be adapted to various types of microwave spectrographs, a few words might be said about the spectrograph used in our measurements. The detection scheme was that of Stark modulation (6) now in general use and, in particular, was similar to that reported in reference 7. One may wonder at the advisability of trying to cope with the analysis of a simultaneous Stark-Zeeman effect, but actually we were not faced with that problem directly. On recalling that the Stark modulation method gives both the Stark components and the undeviated absorption line (each modulated at the Stark-field frequency and 180° out of phase with each other), it will be recognized that the additional application of a steady magnetic field will split the Stark components into Stark-Zeeman components and the original absorption line into its pure Zeeman components. It is the latter with which we work. With proper choice of the Stark-field strength, the unwanted Stark-Zeeman components could usually be removed from the frequency region of interest for the pure Zeeman effect. Further, the Stark-Zeeman components could easily be identified as such, since the recorder on the detector output was arranged to read in opposite directions for Stark and non-Stark components by taking advantage of the 180° phase difference. Another scheme which worked satisfactorily was the use of a trapezoidal waveshape for the Stark field in place of the usual on-off (square-wave) field. This had the effect of "smearing out" the Stark components so that they consisted of a negligibly small signal spread over several Mc/sec, instead of the usual relatively narrow absorption line.

It is desirable to have a spectrograph of good sensitivity for Zeeman work, since it is apparently a whim of nature that absorption lines whose Zeeman effects are most susceptible to analysis are of low intensity. Further, due to the small splitting factors inherent with rotational and nuclear magnetic moments, and the accuracy required when working with small frequency differences, good resolution is essential. However, the need for ease in searching over a wide frequency range, which is desirable in other work, is not important here, since the absorption may be initially located on a search-type spectrograph. The Stark-detection method in conjunction with a special scheme for controlling the klystron oscillator provided a good answer to these requirements. The spectrograph embodied the following features. The tuned amplifier in the receiver was a very stable, narrow-band device, so that fluctuations due to noise and other effects were reduced as much as possible. Time constants of from one second to several minutes were used. With these long time constants it was necessary to provide means for relatively slow tuning rates and good frequency stabilization of the klystron. The details of the method will be described in a paper now in preparation (8).

II. Linear Polarization

The amount of first-order frequency splitting ($\Delta\nu$) of a Zeeman component may be written simply as

$$\Delta\nu = \frac{\mu_0}{h} gH \quad (1)$$

where μ_0 is the nuclear magneton ($\mu_0/h = 0.7623$ Mc/sec per kilogauss); H is the magnetic field (measured, for example, in kilogauss); and g is a splitting factor for the particular Zeeman component in question and is a dimensionless quantity. The theoretical expressions for the splitting factors contain the molecular rotational and nuclear spin quantum numbers and rotational and nuclear gyromagnetic ratios (1), which are the quantities of ultimate interest. However, it is the experimental determination of the splitting factor g which concerns us here. (Note that g , as defined here, includes the magnetic quantum numbers M_J (molecular rotation) and M_I (nuclear spin) or M_F (total angular momentum)).

From Eq. 1 it is clear that two quantities must be measured to determine g , namely $\Delta\nu$ and H . The factors affecting the accuracy of measurement of these quantities will be discussed following a brief description of the magnet and absorption cell, but, in general, each of these quantities was separately and conveniently measurable to about 1 percent by the methods used. This meant that there was little incentive to improve greatly the accuracy of measurement of one of these quantities unless the other could be correspondingly improved, since the accuracy of g is essentially the poorer of the two.

A cross-sectional view of the magnet used with linearly polarized microwaves is shown in Fig. 1. Figure 2 shows the waveguide orientations in this magnet for σ and π observations when the dominant mode is used. The pole pieces of the magnet are 36 inches long and 1 inch in width, and the maximum gap is 1 inch so that X-band

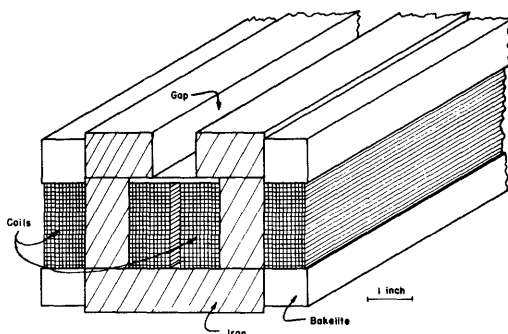


Fig. 1

Magnet cross-sectional view.

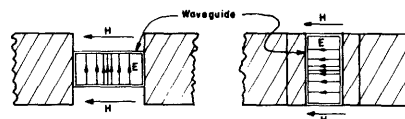


Fig. 2

Waveguide orientation in magnet.

waveguide (or smaller) can be accommodated. The gap can be reduced by iron inserts, when permitted by waveguide dimensions, for obtaining greater field strengths. For a one-half inch gap (X-band guide in π orientation or K-band guide in σ orientation) the maximum obtainable field was about 10,000 gauss, the limiting factor being the heat dissipation in the coils of the magnets. For the highest fields, dry-ice cooling was used.

Relative magnetic field measurements were made by oscilloscopic comparison of the voltage signal from a motor-driven search coil placed in the field with a standard signal. The standard signal was compared after rectification with the potential of a standard cell. The absolute calibration of the search-coil apparatus was accomplished by taking advantage of the unusual magnet configuration. That is, a straight wire, 82-cm long, was suspended in the magnet gap from one arm of a chemical balance and a current was passed through it. Measurement of the current and the force on the wire provided a measurement of the magnetic field from Ampere's Law. The signal from the search coil was found to have only a very small deviation from linearity over the available range of magnetic field strengths. A small correction was applied to account for the forces of stray fields on the lead-in wires outside of the magnet gap. The probable errors in these measurements were analyzed and resulted in a probable error of 0.2 percent in the search-coil constant (voltage output per unit field strength). In using the field-measuring apparatus it was found that a given measurement could be repeated to about 0.5 percent.

The uniformity of the magnetic field along the long axis of the gap was investigated with the search-coil apparatus. With a nominal gap width of one-half inch, the largest deviations from the average field along this axis were 0.6 percent, and the variations correlated in the expected way with gap-width variations. That is, at a place where the gap width was, for example, 0.001 inch less than the average, the field was about 0.2 percent greater than the average (for a one-half inch gap). This variation in field along the absorption cell would be expected to produce a correction to the line shape of a Zeeman component where the correction is proportional to the field strength, that is, proportional to the Zeeman splitting. However, with the field strengths and line widths occurring in the experiments such corrections were unobservable, since the average deviation from the mean-field strength over the cell length was about 0.05 percent. Variations of the magnetic field across the cross section of the cell are to be expected in view of the comparable size of the cell and gap. However, the transitions occur in proportion to the microwave energy density which is greatly concentrated in the central part of the gap.

The order of magnitude of the Zeeman splittings encountered may be estimated from Eq. 1. The magnitudes of the splitting factors g range from near unity, which are exceptional, on down to zero (1). Thus, for practical field strengths, typical splittings are of the order of 1 Mc/sec though one is often forced to work with less. With an X-band waveguide as a cell and the usual detection schemes, a typical minimum attainable

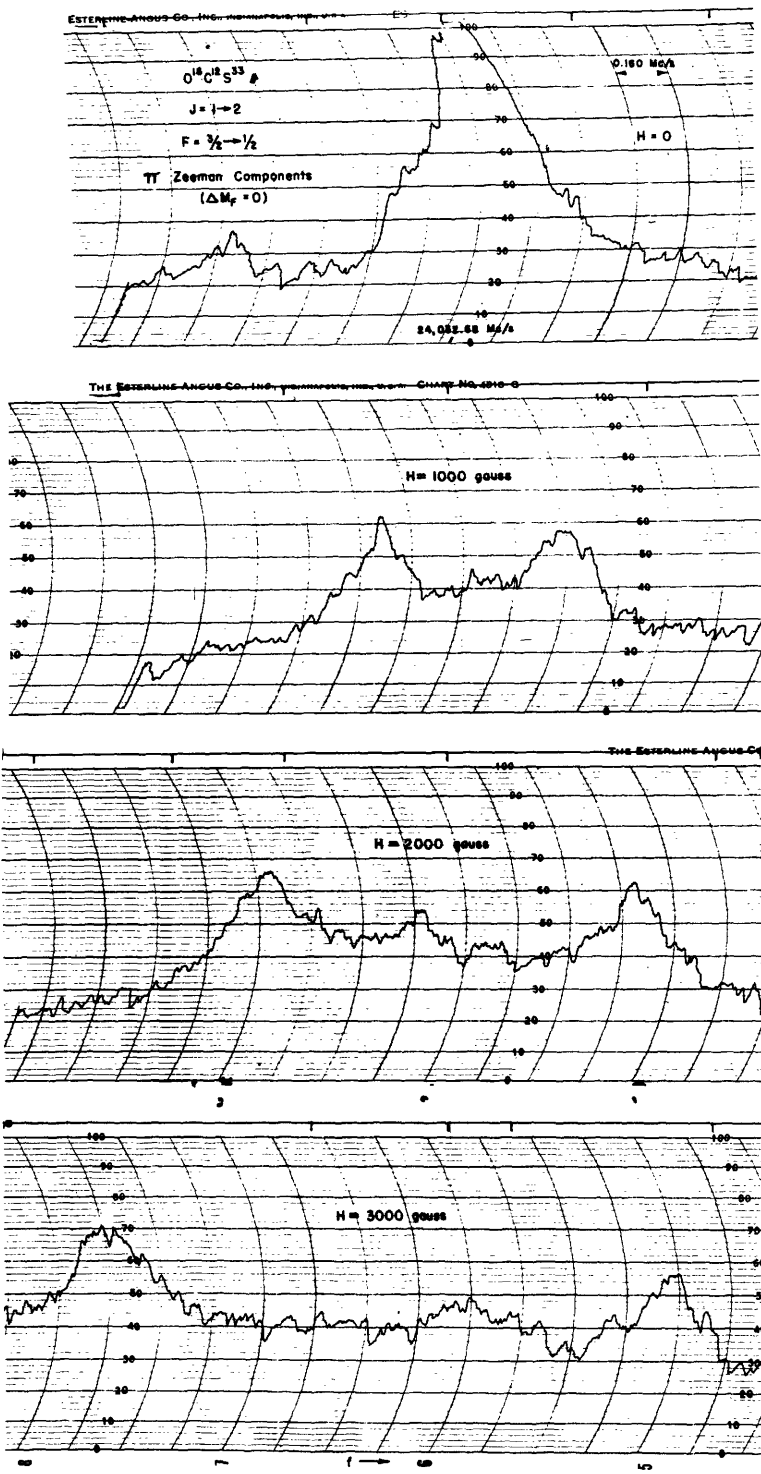


Fig. 3
Typical Zeeman spectrogram.

full line width at half-intensity is 0.120 Mc/sec (8); and with reasonable signal-to-noise ratio, the peak position of the absorption component can be ascertained to within 0.010 Mc/sec. Thus, 1-percent accuracy is reasonable in measuring $\Delta\nu$. Note that absolute frequency measurements are not necessary, and thus frequency-difference measuring schemes may be used. Our frequency measurements, however, were made with the secondary frequency standard in the laboratory (9), since the inaccuracy in the difference between the measured values of two nearby frequencies due to the standard itself was less than the other factors mentioned above.

It was previously noted that an increase in field strengths and correspondingly larger Zeeman splittings could be obtained by going to smaller magnet gaps and waveguide cells of smaller cross sections. Unfortunately the apparent advantages are not realized in practice. This is because the absorption line widths are ultimately determined by the mean time between molecular collisions with the cell walls (8). Thus, in going from cells of X-band to K-band waveguide, the line width was found to double and, in effect, canceled the gain in field strength as far as accuracy of measurement was concerned. It was found convenient to use X-band cells, even at K-band frequencies, though always in the dominant mode.

Results of measurements with the above apparatus have been given elsewhere (1, 2); spectrograms of a typical Zeeman splitting are shown in Fig. 3. The line shown is a rather weak absorption and thus the noise level is higher than is desirable, but the splitting as a function of the field is clear. The four spectrograms are lined up with respect to the zero-field position and a second-order shift is noticeable in the shift of the center of gravity of the two components.

III. Circular Polarization

In order to determine the signs of the gyromagnetic ratios involved in a given Zeeman spectrum, one must ascertain which of the σ -Zeeman components correspond to $\Delta M = +1$ and which to $\Delta M = -1$ transitions. This can be done by using circularly polarized microwave radiation and an applied magnetic field directed along the propagation direction. With this arrangement either the $\Delta M = +1$ or $\Delta M = -1$ transitions are observed, depending on the relative direction of rotation of the microwave electric vector to the magnetic field direction, but not on the propagation direction. The $\Delta M = +1$ transitions occur if, when one looks down the waveguide in the direction of the applied magnetic field, the electric vector of the microwave field at a fixed point is rotating in a clockwise direction. The $\Delta M = -1$ transitions occur if either the field or the direction of the electric vector rotation are reversed. The two cases are shown in Fig. 4.

The sign determination can be understood rather nicely if one considers the conservation of angular momentum between the microwave field and the absorbing molecule. The direction of the magnetic field establishes a reference direction for angular momenta. Thus, a microwave field has positive angular momentum, if the electric vector at a fixed point is rotating like a right-handed screw whose axis is in the direction

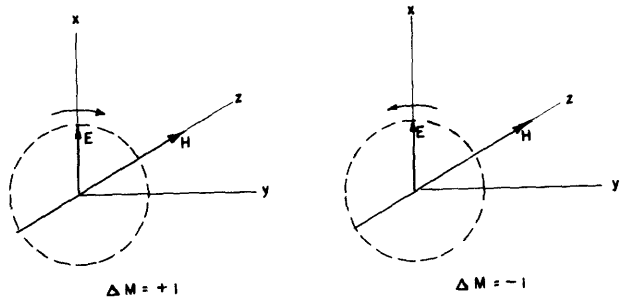


Fig. 4
Geometry defining allowed transitions.

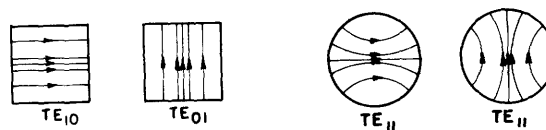


Fig. 5
Degenerate waveguide modes.

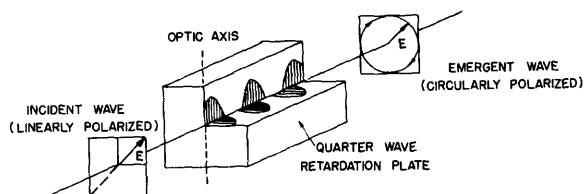


Fig. 6
Circular polarizer using birefringent quarterwave plate.

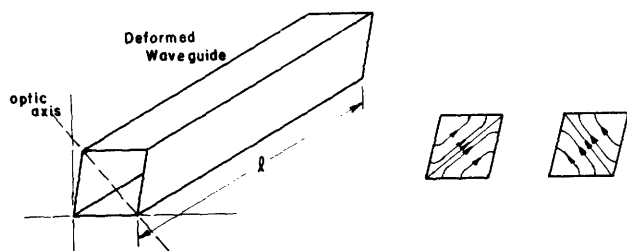


Fig. 7
Waveguide circular polarizer.

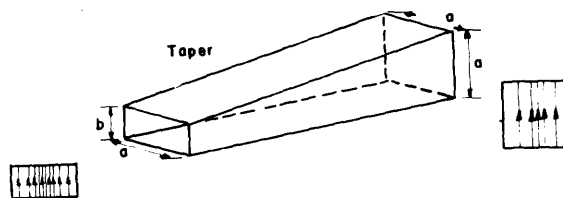


Fig. 8
Taper section.

of the magnetic field. If a quantum is absorbed from such a field, the Z component of angular momentum of the absorbing molecule increases ($\Delta M = +1$). The other case also follows.

If linearly polarized microwaves are used as in Fig. 2 for σ transitions, both $\Delta M = +1$ and $\Delta M = -1$ transitions will be observed. The measured frequency splittings and intensities will be independent of the sign of the net gyromagnetic ratio of the molecular system, even when second and higher order terms in the Zeeman expression are taken into account. Thus, it is impossible from such measurements to determine which observed components correspond to $\Delta M = +1$ and which to $\Delta M = -1$. With circular polarization the experimental arrangement determines which type of transition will occur, as described above. Thus, the observed direction of splitting of a given component with increasing applied magnetic field reveals the required sign.

A circularly polarized plane wave propagating in free space may be visualized as the resultant of two linearly polarized plane waves. Each will have the same frequency and intensity. They will be superimposed with their polarization directions at 90° to each other, with one delayed in time with respect to the other by a quarter of their period. An observer at a fixed point would then measure an electric vector of constant strength and rotating at a uniform rate.

The transmission of a "circularly polarized wave" in a waveguide needs some explanation. Clearly a waveguide mode cannot be circularly polarized throughout its entire cross section, for at the guide walls in particular, boundary conditions require that the electric vector be always normal to the wall (assuming perfectly conducting material). However, for the present application it is important to remember that an absorbing molecule feels only the local field and is unaware of the over-all waveguide mode. Thus, if over the guide cross section a mode can be established which is predominantly either right or left circularly-polarized when considered point by point, either $\Delta M = +1$ or $\Delta M = -1$ transitions will predominate; and a corresponding alteration of the component intensities will be observed.

Such a situation can be established in any waveguide possessing a doubly degenerate mode arising from geometrical symmetry. (Two modes with equal guide wavelengths are degenerate.) Particular practical examples are square and circular waveguides, although any cross section which is unchanged by a 90° rotation would satisfy this condition. Figure 5 shows the electric field configuration of the two degenerate modes. The electric field is totally transverse in these cases. As in any problem with degenerate characteristic values, any linear combination of the degenerate normal modes is also a normal mode with the same guide wavelength. The optimum combination for the problem at hand is a superposition of the TE_{01} and TE_{10} modes (for the square-guide case) with equal intensity and 90° out of phase in time. This will result in perfect circular polarization at points along the guide axis; but as one moves toward a wall, the polarization becomes elliptic and finally linear at the wall. In the case of a square guide, calculation shows that about 90 percent of the absorbing molecules will make transitions

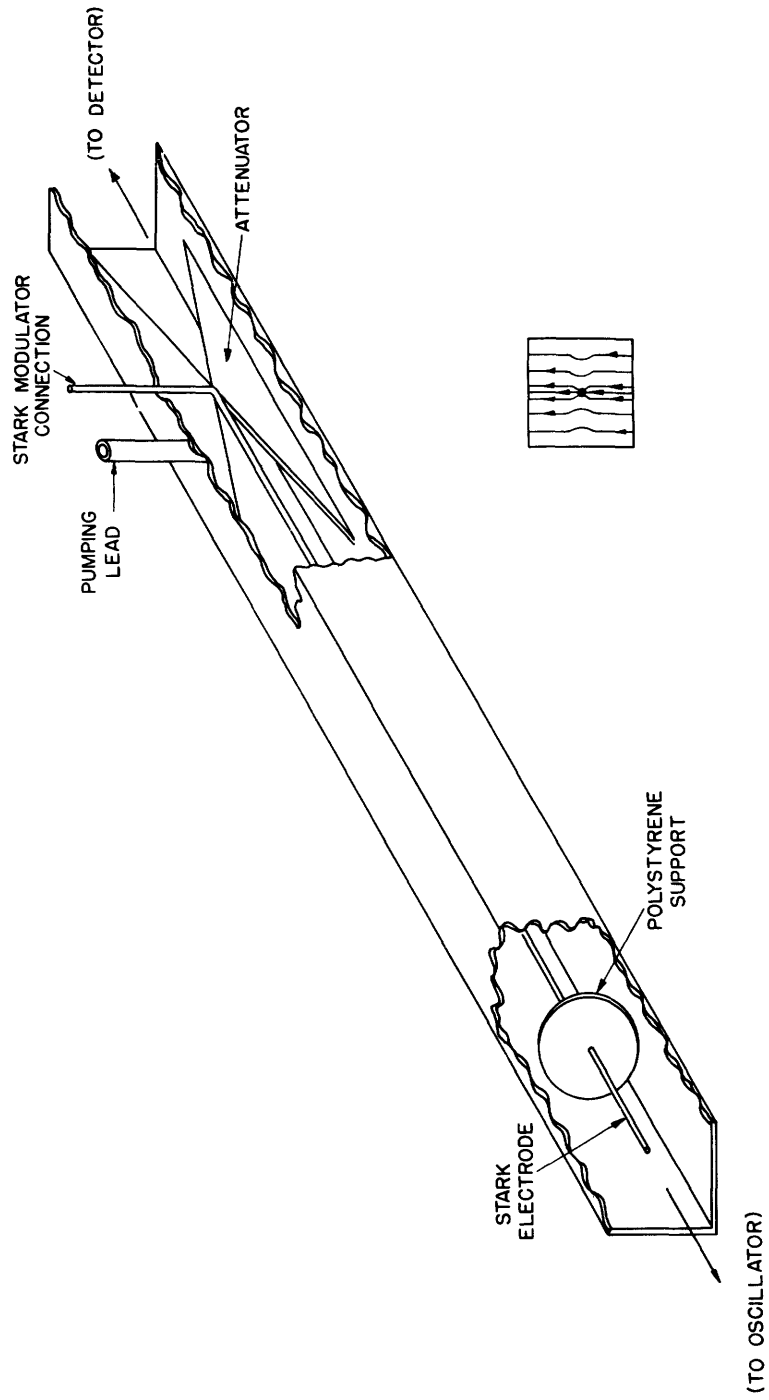


Fig. 9
Circular polarization absorption cell.

of one type, for example, $\Delta M = +1$ and 10 percent of the other type, $\Delta M = -1$.

The device used for setting up the circularly polarized wave in the square waveguide absorption cell was a microwave equivalent of a quarter-wave retardation plate as used in optics to convert linearly polarized light into circularly polarized light. The operation is shown schematically in Fig. 6. The microwave counterpart of the birefringent material is the slightly deformed square waveguide of Fig. 7. Since the degeneracy of the mode is removed by the perturbation, the choice of normal modes is no longer arbitrary. The correct normal modes become, by symmetry, those shown in Fig. 7. These modes now have slightly different guide wavelengths; the mode on the left in the figure has the larger. Thus, the length of the deformed guide and the amount of deformation can be adjusted for quarter-wave retardation between the two modes.

In using this device, the incident wave must be linearly polarized at 45° to the optic axis, as shown in Fig. 6. Since the optic axis is now a diagonal of the waveguide, the correct incident wave may be obtained simply from the dominant mode of a rectangular waveguide by means of a suitable tapered section, as shown in Fig. 8.

An expression for the change of guide wavelength for the square waveguide under this perturbation may be derived using a method similar to that used for perturbed resonant cavities (10). The result is

$$\frac{d\lambda_g}{dD} = -\frac{9\sqrt{2}}{\pi^2} \left[\frac{\lambda_g}{\lambda_c} \right]^3 \quad (2)$$

where λ_g is the guide wavelength, defined by

$$\frac{1}{\lambda_o} = \frac{1}{\lambda_g} + \frac{1}{\lambda_c}$$

λ_o is the free space wavelength

λ_c is the cutoff wavelength ($\lambda_c = 2a$ for the modes under consideration, see Fig. 8)

D is the length of the diagonal of the waveguide cross section which is perpendicular to the electric field of the mode considered.

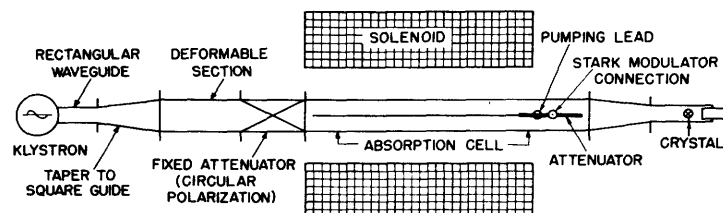


Fig. 10

Circularly polarized, microwave-absorption apparatus.

In the design of a waveguide-absorption cell for use with the circularly polarized waves, two difficulties were encountered. Since it was desired to use the Stark modulation detection method, an insulated electrode which would not disturb the circular polarization had to be provided in the cell. This was made in the form of a thin rod along the axis of the guide, supported by two thin polystyrene discs, as shown in Fig. 9. Although the mode configuration is slightly disturbed near the guide axis as shown in this figure, the wave is still essentially circularly polarized. The region of perfect circular polarization is no longer on the guide axis, however.

The Stark electric field in such a guide will, of course, be quite nonuniform but, as explained earlier, the broadened Stark components resulting from this actually helped in the identification of the pure Zeeman components.

The second difficulty came from reflections of the microwave radiation at the lead-in to the Stark electrode and at the hole for the vacuum-pump connection. Such reflections could not be tolerated, since they would disturb the polarization of the wave in the absorption region. The difficulty was resolved by placing a tapered, attenuating sheet in the plane formed by the Stark lead-in and the guide axis in the region of these discontinuities and by putting this lead-in and pumping lead at the opposite end of the absorption cell from the microwave oscillator. This attenuator served two purposes. One was to prevent reflections, as intended, and the other was to provide an analyzer for the circularly polarized wave. That is, the attenuator absorbed one linear component of the circular wave; the other linear component was allowed to pass and was introduced into a rectangular guide through a taper and then detected by a crystal as usual.

The magnetic field for these experiments should be parallel to the guide axis, so the guide was placed in a solenoid. The magnetic field of a long solenoid is fairly uniform near the center but falls off at the ends to approximately one half of the value at the center. This nonuniformity tends to broaden the Zeeman components but, since all that was desired was to determine the direction of splitting of the component, it was not serious.

The complete experimental arrangement is shown in Fig. 10.

Sign determinations of molecular and nuclear gyromagnetic ratios with this apparatus have been previously reported (1, 2).

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