Submitted to the Review of Scientific Instruments

The Measurement of Absolute Absorption Intensities with a Stark-Modulated Microwave Spectrograph*

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Abstract

The method developed by Baird and Bird for the measurement of relative absorption intensities with the Stark-modulated microwave spectrograph has been extended to the measurement of absolute absorption intensities. The determination of absolute intensity is based on the measurement of the ratio of modulation-frequency component to direct component of crystal current at several microwave power levels and the extrapolation of the ratio to zero power.

This method has been tested on the line CH_3Cl^{35} $J = 0 \rightarrow 1$, $F = 3/2 \rightarrow 5/2$, with measured intensities 1% less than the calculated intensity being obtained over a range of 250% in microwave power. Measurements at very low powers are prevented by the presence of a small amount of pickup in the crystal circuits from the square wave generator.

Since other sources of error are present (notably multiple reflections in the absorption cell) the uncertainty of this method cannot be evaluated as well as would be desirable. It is certainly not greater than 25% for medium intensity lines, and this is adequate for the identification of asymmetric rotor lines.

* This research was supported in part by the Office of Naval Research under Contract N5ori 76, Task Order V.

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The Stark-modulated spectrograph is a sensitive and versatile instrument used widely by microwave spectroscopists.[1] A method has been developed by Baird and Bird[2] for making measurements of relative absorption intensities with this instrument. This paper will deal with the extension of Baird's method to the measurement of absolute absorption intensities.

Baird's method is based upon the theoretical relationship between the direct and modulation-frequency components of crystal current when square wave modulation is used and certain other conditions are satisfied.[2] This relationship is:

$$\frac{i_\rho}{i_{d.c.}} = -\frac{\alpha \ell_e}{\pi} \sin \rho t \left[\frac{\sum_{n=1}^{\infty} n C_n E^n}{\sum_{n=1}^{\infty} C_n E^n} \right] \qquad (1)$$

i_ρ = modulation frequency component of crystal current

$i_{d.c.}$ = direct crystal current

α = gaseous absorption coefficient

ℓ_e = effective length of the absorption cell

ρ = modulation angular frequency

C_n = the nth coefficient of a polynomial representing direct crystal current as a function of unmodulated peak microwave electric field at the crystal ($i_{d.c.} = C_1 E + C_2 E^2 + C_3 E^3 + \ldots$)

E^n = the nth power of the peak microwave electric field at the crystal

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[1] a R. H. Hughes and E. B. Wilson, Jr., Phys. Rev. 71, 562 (1947).

b K. B. McAfee, Jr., R. H. Hughes, and E. B. Wilson, Jr., Rev. Sci. Inst. 20, 821 (1949).

c W. Gordy, Rev. Mod. Phys. 20, 668 (1948).

[2] D. H. Baird and G. R. Bird, Rev. Sci. Inst.

The difficulty involved in making absolute absorption measurements is that, in general, microwave rectifying crystals have complex response laws, and it is not easy to determine the coefficients C_n of the polynomial relating crystal response to microwave power. For an n law detector (one whose response is $i_{d.c.} = C_n E^n$) the expression just given takes a very simple form:

$$\frac{i_\rho}{i_{d.c.}} = -\frac{\alpha \ell_e n}{\pi} \sin \rho t \qquad (2)$$

Thus if a detector were available with a known, simple response law, it would be possible to make a direct determination of the absorption coefficient of the gaseous sample by measuring the ratio of components of crystal current. The effective length ℓ_e of the absorption cell is readily determined from the geometry of the waveguide and a knowledge of the mode of propagation excited if no serious reflections occur.[3]

[3] Marcuvitz, Waveguide Handbook, McGraw-Hill, New York (1951).

Though the response laws of rectifying crystals are generally complex, it is known that for very low microwave power levels (one microwatt or less) crystals respond as square-law detectors. This property of crystals is frequently utilized in the routine measurement of standing waves or attenuation.[4] Unfortunately, one microwatt is well below the power levels

[4] C. G. Montgomery, Technique of Microwave Measurements, McGraw-Hill, New York (1947).

commonly used in the Stark-modulated spectroscope. A possible approach to this problem is the measurement of the ratio of components of crystal

current over a wide range of microwave power, with extrapolation of the measured ratio to zero power. If the extrapolation can be performed, it should give the ratio of crystal current components corresponding to a square law detector.

Several additional experimental conditions must be satisfied if such measurements are to be made. The direct and modulation frequency components of crystal current are separated, as in Baird's method, by a choke and condenser having very high and very low reactance, respectively, at the modulation frequency.[2] The resistance of the choke and direct current meter must be increased by the addition of a series resistor to match the resistance of the modulation-frequency circuit -- the condenser, receiver and resistance. This has the effect of loading the crystal with a single resistance and a negligibly small reactance. The circuit constants of the comparison signal attenuator must be determined accurately to establish the relationship between the partially attenuated comparison signal voltage and the modulation-frequency component of crystal current with which it is matched. Finally, pickup in the crystal and comparison signal circuits becomes particularly critical, since the extrapolation procedure will tend to emphasize the presence of stray signals from the square wave generator. The best procedure for minimizing pickup is to use the receiver and output meter as a measuring device and try various shielding and grounding arrangements until the stray signal level is minimized.

As a test of this method, the intensity of the line CH_3Cl^{35} $J = 0 \longrightarrow 1$, $F = 3/2 \longrightarrow 5/2$ at 26,589.49 mc. was measured over a range of crystal currents from 40 to 2 microamperes. The intensity of this line has been calculated

as $6.6 \cdot 10^{-6} cm^{-1}$ for an assumed line breadth constant of 25 mc/mm Hg.[5] The

[5] P. Kisliuk and C. H. Townes, J. Res. Natl. Bur. Standards, 44, 611 (1950).

line breadth constant was measured by Baird's method for relative intensities and found to be 20.9 ± 1.0 mc/mm Hg. This makes the calculated intensity $7.9 \pm .4 \cdot 10^{-6} cm.^{-1}$

The intensity of the line was slightly reduced by saturation, but this was measured and a correction introduced. "Padding" attenuation was inserted between the crystal and the absorption cell to prevent multiple reflections between the crystal and the ends of the absorption cell.

The results of this experiment are shown in graphical form with the intensity obtained, assuming square law detection plotted against crystal current. A crystal current of 20 microamperes corresponds roughly to 135 microwatts of microwave power. The remarkable feature of the data is that the measured intensity is greater than 75% of the calculated intensity for currents ranging from 40 to 5 microamperes. The closest correspondence is obtained for currents ranging from 20 to 8 microamperes with a measured intensity equal to 85% of the calculated value. At very low crystal currents, the measured intensity drops rapidly; this is probably due to a very small amount of pickup from the square wave generator out of phase with the modulation-frequency component of crystal current.

From this data it may be concluded that the method may be used to estimate the intensity of medium-strength absorption lines to within about 25%. For some purposes, such as the identification of asymmetric rotor lines, this accuracy will be sufficient. The question of whether the method can be refined

to yield accuracies of 5% to 1% can only be answered by a detailed analysis of errors. The ability of the experimenter to eliminate pickup will determine the limitations of the method when weak lines are measured.

The systematic error resulting from reflections at the ends of the Stark electrode has been discussed qualitatively by Baird et al[2] and assigned as the principal source of error in their work. Detailed attenuation and standing wave measurements have been made on the waveguide used in this research,[6] and these show that the waveguide may be represented as having equal reflections at the ends. The measured reflection coefficients for the electric vector were r = 0.31 (corresponding to a 10% reflection of power from a single window) and the attenuation of the electric vector was 0.50 for one transit of the guide between windows at 26,600 mc. Calculations indicate that the maximum error introduced into a single intensity measurement by the presence of these reflections is 5% (10% for a relative measurement of two intensities).[7] However, the mechanical mounting of the waveguide was such that the gaps between the Stark electrode ends and the transformer horns could be varied by vibration or thermal expansion with a resulting variation in both phase and magnitude of the reflections. Other observations on this waveguide indicated that such variations did occur, and that errors as large as 10% occurred in measurements of the intensity of a single line. This uncontrollable variation prevents any

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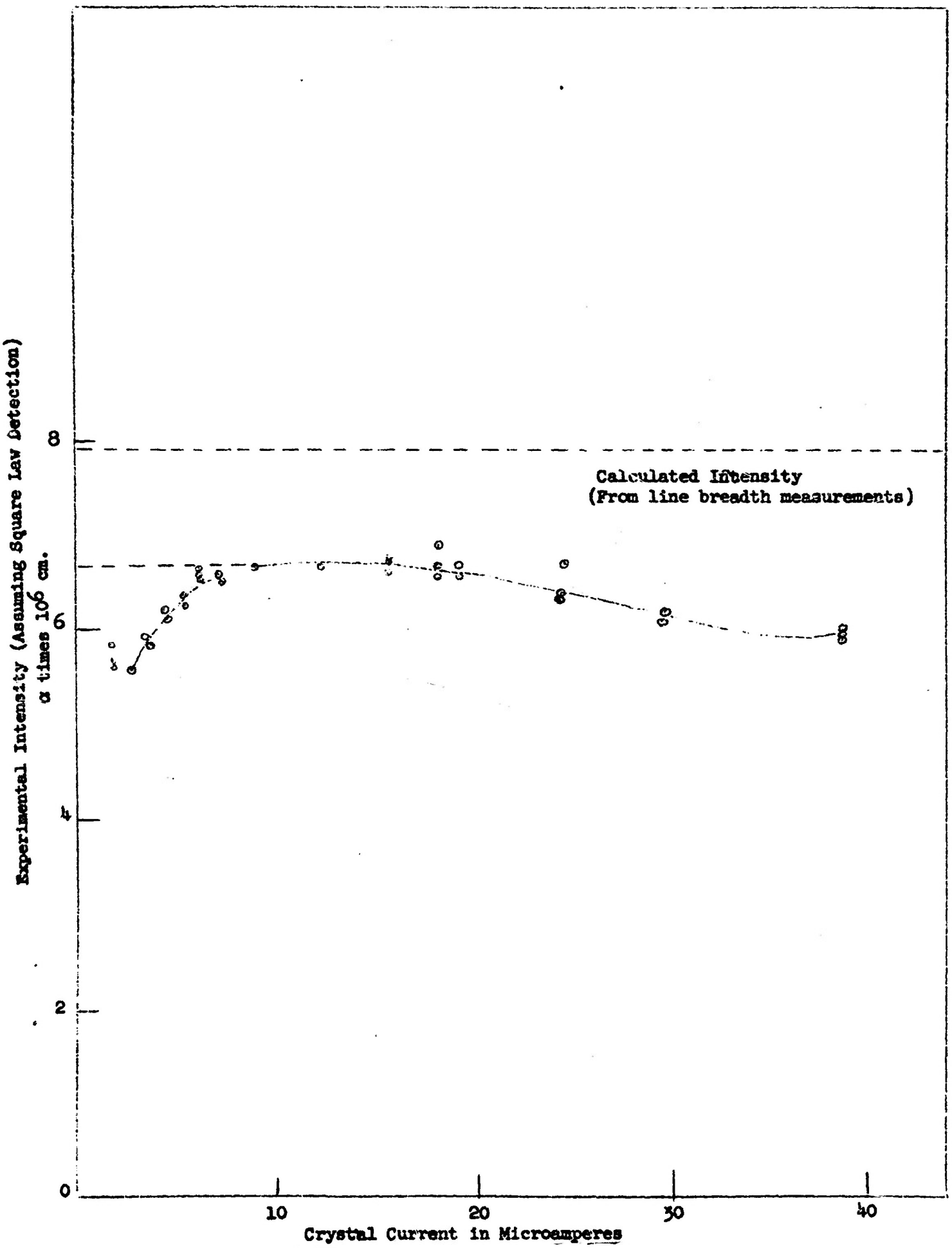
[6] N. Muller, The Spectrum of Chlorofluoromethane, Doctoral Thesis, Harvard University, 1952.

[7] G. R. Bird, Properties of Spectral Absorption Lines, Doctoral Thesis, Harvard University, 1952.

detailed analysis of the potentialities of this method, since the error caused by reflections might be responsible for most of the difference between measured and calculated intensities in this experiment, or might partially compensate for a larger error in the method. However, it does seem reasonable to set a maximum uncertainty of 25% on the method of extrapolating the ratios of components of crystal current to obtain absolute intensities. Incidentally, the measurement of line-breadth used to calculate the intensity of the absorption line is free from the large uncertainty caused by multiple reflections, since the actual breadth of the line was much smaller than the frequency separation of successive maxima and minima of the periodic systematic error.

The possible refinement of this method is by no means a trivial question. Microwave intensity measurements commonly have uncertainties of 10% or more, with a few measurements made under favorable conditions having 5% uncertainty. Such measurements have been few in number because of the laborious techniques involved. Much useful information could undoubtedly be obtained if a rapid and accurate method for making absolute intensity measurements existed. The recognized potentialities of microwave spectroscopy as a method for chemical analysis of gaseous mixtures have not yet been realized as a result of this same lack. Unfortunately, the next step in the investigation of this method would involve the design and construction of a more satisfactory Stark-effect waveguide absorption cell, and time to carry out such a program was not available to the author.

The author gratefully acknowledges the help and encouragement of Professor E. Bright Wilson, Jr.


Experimental Intensity (Assuming Square Law Detection)
α times 10⁶ cm.
8
6
4
2
0
Calculated Intensity
(From line breadth measurements)
10
20
30
40
Crystal Current in Microamperes

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