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New Technique for High-Resolution Microwave Spectroscopy*

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An experiment is described in which microwave resonance lines have been obtained having widths substantially less than the normal Doppler width. The line shape obtained depends on the properties of a radiating gas when contained in a cavity in the form of a pillbox, of diameter large compared to height. Collisions of molecules with the walls take place in such a manner that the collisions narrow the line instead of broadening it. The 1.25-cm inversion transition in ammonia was observed, and lines one quarter the normal Doppler width of 73 kc/sec obtained; further narrowing appears feasible. The line shapes and widths are in good agreement with the calculations.

By employing a gas cell of special shape and gas at low pressure, it is possible to produce microwave spectral lines having widths substantially less than Doppler breadth. The essential feature of the gas cell is that it should consist of two flat parallel walls, separated by approximately $\lambda/2$, where λ is the free-space wavelength of the radiation, operating in a mode for which the electromagnetic wave bounces back and forth between the two walls. One suitable form of such a gas cell is a pillbox shaped cavity having a diameter large compared to a wavelength, operating in the TE_{111} mode.

Although these narrow spectral lines should be obtainable using standard microwave absorption detection equipment, some improvement in average signal power is expected from a detection system based on pulse induced coherent spontaneous radiation,[1] and it was this technique which was used in our experiments.

It is somewhat paradoxical that the effect of wall collisions which strongly disturb the internal state of the molecule should be such as to lead to a spectral line more narrow than that obtained in the absence of wall collisions. It was shown by Johnson and Strandberg[2] that the previous simple considerations of the effect of wall collisions on a gas were basically incorrect. These simple considerations had assumed a Lorentz line shape with a line width proportional to the characteristic molecular speed, $v_0=(2kT/m)^{\frac{1}{2}}$, divided by a length characteristic of the gas cell, this length being given by the shortest dimension of the cell in case the cell had one of its dimensions much smaller than the others. In particular, Johnson and Strandberg took as a model of a long wave-guide cell, one of whose cross-sectional dimensions L was considerably shorter than the other, a cell composed of two infinite parallel plates separated by a distance L. They showed that the line shape to be expected from wall collisions alone in such a cell was not a Lorentz line of full width $\Delta\nu\cong 0.2v_0/L$, as had been previously assumed, but was actually far from a Lorentz line, having a logarithmic singularity at the line center. They pointed out that this singularity would be masked by any finite Doppler broadening, resulting from motion of molecules along the wave guide, yielding an effective contribution to the line width arising from wall collisions of approximately $\Delta\nu \cong 0.8v_0/L$. Danos and Geschwind[3] subsequently pointed out that for the power levels commonly employed in microwave spectrometers, the simple theory, although fundamentally incorrect, did in fact give results which were fairly accurate. The non-Lorentz shaped lines predicted were shown to be realizable only for rather unusual operating conditions of extremely low incident power levels. They showed that even if not masked by the Doppler effect, the singularity in the line shape would be removed by power saturation effects, and the effective contribution to the line shape from wall collision effects could be well represented by the simple theory, giving approximately a Lorentz shape.

In the gas cell to be described, the Doppler effect is missing, and by maintaining the proper operating conditions, a line breadth may be realized, arising solely from wall collision effects, which is substantially less than the value $\Delta\nu=v_0/L$, where L is the smallest dimension of the cell. The obtainable line shape is in fact determined primarily not by the smallest cell dimension, but by the other dimensions of the cell. To understand the beneficial effect of the wall collisions in producing a narrow spectral line by avoiding Doppler broadening, it is necessary first to understand that for an absorption spectrometer as well as for the pulse induced emission spectrometer[4] the source of the signal power is an electromagnetic wave radiated by the gas. For an absorption spectrometer, the radiated wave might be called an "absorption wave" in that it is the destructive interference with this wave that reduces the intensity of the incident microwave when absorption by the gas is occurring. The gaseous origin of this signal energy is easily demonstrated experimentally. If the incident wave is suddenly turned off, the gas continues to radiate for perhaps 10 microseconds. From this point

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[1] R. H. Dicke, Phys. Rev. **93**, 99 (1954).
[2] H. R. Johnson and M. W. P. Strandberg, Phys. Rev. **86**, 811 (1952).
[3] M. Danos and S. Geschwind, Phys. Rev. **91**, 1159 (1953).
[4] The details of a pulse induced emission spectrometer are given in an article to be published in *The Review of Scientific Instruments*.

of view the only effect of the incident electromagnetic wave is to excite the gas into a state in which the individual molecules possess oscillating electric dipole moment expectation values. This results in an oscillating polarization of the gas, the radiation from which can be treated classically. In the pulse induced emission technique, molecules are excited by a microwave frequency pulse into superposition energy states in which each molecule possesses an oscillating electric dipole moment. A given molecule continues to radiate until it hits another molecule or a wall of the container. For the pillbox cavity of height $\lambda/2$ with low gas pressure, the collisions occur primarily at the two large parallel flat surfaces. To understand the beneficial significance of the collision, it need only be noted that if the pillbox height were greater than $\lambda/2$, say λ, with the cavity operating in the TE_{112} mode, then a given molecule, instead of colliding with the wall would continue to move across a nodal plane in the cavity into a region where the electric field is reversed in direction. It here radiates (classically) with the opposite phase with respect to the standing wave in the cavity, and its wave interferes destructively with the waves radiated by molecules which have not crossed a nodal plane. To state it another way, the collisions with the walls are damaging in that molecules are removed from the radiating system. However, collisions are not as serious as the absence of collisions, in which case the molecular motion mixes the oscillating molecules of different phases, resulting in destructive interference between the contributions from individual molecules.

It is now easy to comprehend the origin of the narrow spectral line. For the pillbox cavity, the number of radiating atoms, and hence the amplitude of the radiated wave, since the molecules radiate in phase, falls off after a short time as the reciprocal of the elapsed time after the exciting pulse. (See Fig. 1.) This $1/t$ dependence lasts for a time which is greater the larger the diameter of the pillbox. After about 15 microseconds in the case of ammonia, most of the molecules which have not yet collided with a wall are moving nearly parallel to the flat surfaces. After a sufficiently long period, the effect of the side walls must be included.

For a cylindrical cavity of the same diameter as the pillbox but many wavelengths long, the interference effects, arising from motion of the molecules into regions where the electric field has various phases, as previously discussed, cause the radiated amplitude to fall off as a Gauss error function of the time. The line shape is given by the Fourier transform of this envelope function. This is the usual Gaussian shaped line characteristic of Doppler broadening. On the other hand, for an amplitude variation proportional to the reciprocal of the time, characteristic of the pillbox, the Fourier transform gives a narrow line more sharply peaked than a Lorentz profile. Were it not for the side walls and other practical difficulties, the line shape would have a logarithmic singularity at its center.[2]

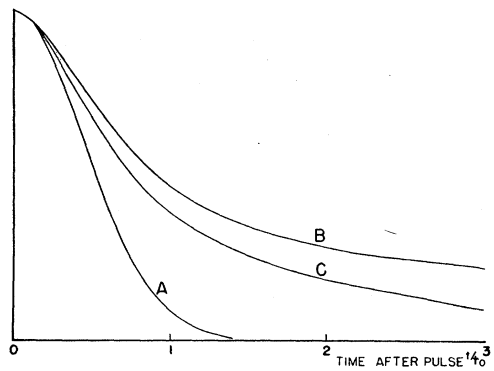

FIG. 1. Calculated envelopes of radiation from ammonia at low pressure and room temperature. Curve A: Large gas cell: normal Gaussian Doppler decay. Curve B: Infinite diameter pillbox cavity, uniform field assumed: asymptotically proportional to $1/t$. Curve C: Finite diameter pillbox, considering field distribution effects. Diameter to height ratio of cavity 9.2. $t_0=\lambda/2v_0=11.5$ microseconds.

In the case of an absorption apparatus, although the details differ, the main conclusion remains the same. In the absence of wall collisions, a destructive interference effect remains which leads to the normal Doppler broadened line, but when a gas cell in the form of a pillbox cavity of height $\lambda/2$ is operated at low gas pressures and low incident power, the molecules with long free paths are strongly favored. They are excited for a long time, giving rise to a large oscillating electric moment, and they radiate for a long period. Because of the long uninterrupted radiation period, these molecules contribute principally to the spectral line intensity at its center, which, because of the strongly oscillating character of these molecules and their long radiation time, becomes strongly peaked.

Consider now in more detail the line shape expected when an infinite diameter pillbox cavity is used. The cavity is formed by two parallel plates of infinite extent, separated by $\lambda/2$. A wave guide couples to the normal mode of the cavity which is a standing plane wave of uniform amplitude over the extent of the plates. A short intense radio-frequency pulse excites the gas. Since the cavity is only of height $\lambda/2$, it is a fair approximation to say that the exciting field is in phase and of equal amplitude throughout the cavity. (If the cavity were, for example, λ in height, then this approximation could not be made, since the exciting field would have opposite phases in different regions of the cavity.) To this approximation, all the molecular dipoles are oscillating with equal amplitude, and in phase with each other. Thus the radiated amplitude is proportional to N, the number of contributing molecules, N being at most equal to the thermal equilibrium difference in population of the two states. Because the electric field actually has a sinusoidal distribution over the gap between the plates, the molecules are actually excited by various amounts dependent upon their location. Also, the radiated amplitude from a molecule

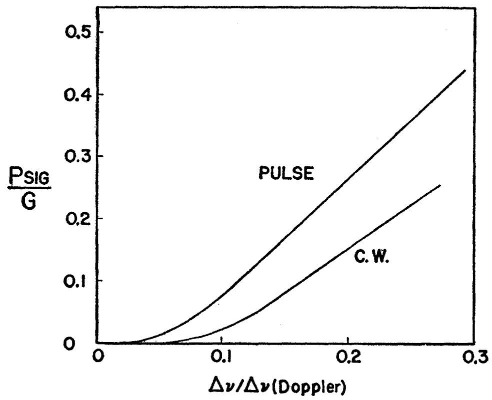

FIG. 2. Calculated available signal power (in units of G), as a function of line width (in units of the normal Doppler width), for pulsed excitation and continuous absorption experiments in infinite diameter pillbox cell. Line width in the two cases is that due to finite interval between pulses in the pulsed experiment, and that due to saturation broadening in the c.w. experiment. $G=Q_0\omega_0^3\mu_0^2n^2\hbar^2/8v(kT)^2$, where Q_0=unloaded Q of cavity; v=volume of cavity; n=total number of molecules in the two energy states; μ_0=absolute value of electric dipole matrix element. $\Delta\nu$ (Doppler)$=(\ln 2)^{\frac{1}{2}}v_0\omega_0/\pi c$ where $v_0=(2kT/m)^{\frac{1}{2}}$.

will depend on its location at the time it is radiating. However, in a relatively short time after the pulse, because of the molecular motion the oscillating dipole moment density of the gas will become uniform, after which time the lack in uniformity of the field strength has no effect. Thus, the assumption of uniformity of the oscillating electric field affects only the initial part of the time dependence of the radiation intensity. This part contributes only slightly to the shape of the line in the vicinity of the line center. In addition to the simplification which results from the assumption of uniformity of the field, there is the additional advantage that a direct comparison can be made with the earlier absorption calculations.[2,3]

If a molecule undergoes a collision, it is restored to a state of thermal equilibrium, or at least the phase of its oscillating moment is disturbed, so that after the collision it is just as likely to be out of phase as in phase with the undisturbed molecules. Molecules which have suffered a collision may be considered to have been removed from the radiating system, since, on the average, they contribute nothing to the macroscopic polarization. Then $N=N(t)$, where t is the elapsed time since the exciting pulse was turned off, and where $N(t)/N(0)$ is the fraction of molecules which have not had a collision since $t=0$. Ignoring radiation damping,[5] and also assuming a pressure low enough so that collisions between gas molecules can be ignored,

$$N(t)/N(0)=\frac{2}{v_0\lambda\pi^{\frac{1}{2}}}\int_0^{\lambda/2}dz\int_{-z/t}^{(\lambda/2-z)/t}\exp(-v^2/v_0^2)dv. \quad (1)$$

The radiated amplitude is proportional to $N(t)$, and thus the real part of the Fourier transform of $N(t)$ gives the line shape

$$\text{Real part } g(\omega)=\frac{\sqrt{2}}{v_0\lambda\pi}\int_0^\infty \cos(\omega-\omega_0)tdt$$
$$\times\int_0^{\lambda/2}d\int_{-z/t}^{(\lambda/2-z)/t}\exp(-v^2/v_0^2)dv. \quad (2)$$

For large t,

$$\lim_{t\to\infty}N(t)/N(0)=\lambda/(2\pi^{\frac{1}{2}}v_0t). \quad (3)$$

The Fourier transform of a function which is proportional to $1/t$ as t becomes infinite has a logarithmic singularity at $\omega=\omega_0$, and thus, in principle, lines as narrow as desired can be obtained by this method.

By a series expansion and partial integration, the line shape [Eq. (2)] can be transformed into

$$\text{Real part } g(\omega)=\frac{1}{(2\pi)^{\frac{1}{2}}(\omega-\omega_0)}$$
$$\times\int_0^\infty[1-\exp(-1/x^2)]\sin\left[\frac{(\omega-\omega_0)\lambda x}{2v_0}\right]dx. \quad (4)$$

A line shape of identical form has been calculated by Johnson and Strandberg[2] and later by Danos and Geschwind[3] for a c.w. (continuous wave) absorption experiment in a similar cell, with a vanishingly small amount of incident power. As Danos and Geschwind point out, any nonzero amount of power incident on the gas, which is necessary to produce an observable signal, introduces saturation effects which remove the singularity in the line shape. Similarly, in the pulse experiments considered here, in order to obtain a usable signal, there must be a finite interval between successive exciting pulses. Under these conditions, molecules with velocities parallel to the faces of the cell are not allowed to continue radiating for infinitely long times, and for this reason in addition to others, the singularity in the line shape is removed, by cutting off the $1/t$ decay at a finite time. As the repetition interval is decreased, the signal power and the line width increase, just as in the c.w. experiment, the signal power and line width increase as the incident power is raised. The calculated signal power at the center of the line is given as a function of calculated line width for the two idealized cases in Fig. 2. The line width in the c.w. case is calculated from Danos and Geschwind's results. The line width in the pulsed excitation case is calculated from the transform of $N(t)$, Eq. (1), cut off at the repetition interval T:

$$\text{Real part } g(\omega)=\frac{1}{(2\pi)^{\frac{1}{2}}}\int_0^T N(t)\cos(\omega-\omega_0)tdt. \quad (5)$$

[5] In a coherent spontaneous emission process, the line width caused by radiation damping may be as high as $n\hbar\omega\gamma/4kT$, where n is the total number of radiating molecules and γ is the natural line width for one isolated excited molecule. (See reference 1.) This damping cannot be neglected in all cases.

The line width is given in units of the normal Doppler width,

$$\Delta\nu(\text{Doppler}) = (\ln 2)^{\frac{1}{2}} v_0 \omega_0 / \pi c.$$

In the experiment performed, the gas was excited by a sequence of rf pulses, the phase of the rf oscillation being preserved from one pulse to the next. After each exciting pulse, the gas radiated a wave of decaying amplitude, whose phase was determined by the phase of the exciting rf. The frequency spectrum of the radiation from the gas then consisted of a component at the center frequency of the exciting pulse, plus side bands above and below this frequency, spaced by the pulse repetition frequency. The detection system selected the frequency component of this radiation at the center frequency of the exciting pulses, and it is the available signal power in this component and not the total radiated power which is plotted in Fig. 2.

Unfortunately, a severe loss is taken in signal to noise ratio in order to achieve narrow spectral lines by using a cavity of this special pillbox shape. First, a low pressure must be used to obtain the required long mean free path, which must be at least comparable to the diameter of the pillbox cavity. Second, only a small fraction of the molecules have the long trajectories that avoid the top and bottom faces of the cavity. The net result is that as the line width is decreased by increasing the cavity diameter, the signal power varies directly with the square of the line width.

The data[6] which Danos and Geschwind used as a check on their wall broadening theory and also the data used by Johnson and Strandberg[2] to check their earlier calculation of the same effect, were based on experiments in an ordinary long microwave absorption cell. In such experiments, the molecules can move many wavelengths in the direction of propagation of radiation, and the full Doppler width is observed, as discussed earlier. Under conditions of low pressure and low incident rf intensity, the major source of broadening in such a cell is the Doppler effect, and wall collision effects are present only as a correction to the Doppler width. The expected width is calculated by adding this correction term in a rather arbitrary manner to the large Doppler width.

In the experiments considered here, however, the exciting field, instead of being propagated parallel to the surfaces of the plates, is approximately a plane wave bouncing back and forth between the plates. In such an experiment, as has been mentioned, it is a fairly good approximation to regard the electric field as being in phase and of uniform amplitude throughout the cell, so that the wall collision effects are the only source of line width. Such an experiment allows a direct comparison of observed and calculated wall collision widths.

[6] Gunther-Mohr, White, Schawlow, Good, and Coles, Phys. Rev. **94**, 1187 (1954).

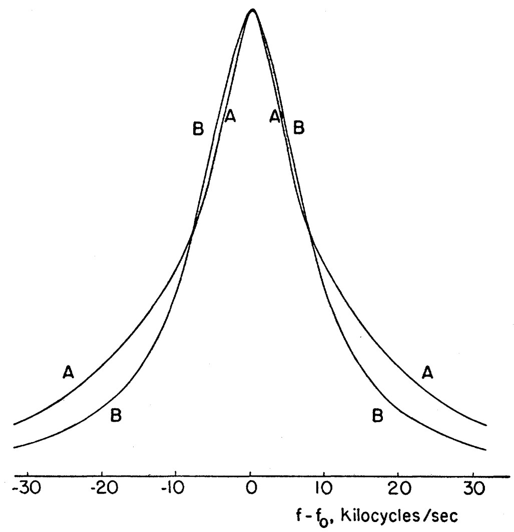

FIG. 3. Curve A: Calculated line shape, 5.75 cm diameter pillbox (diameter to height ratio 9.2). Curve B: Lorentz line shape chosen to have same height and width at half-maximum amplitude as curve A.

In the experiments performed here, the $J=K=3$ inversion transition in ammonia at 24 000 Mc/sec was observed. The gas, at low pressure and at room temperature, was contained in a cylindrical copper cavity of height approximately $\lambda/2=0.62$ cm, diameter 5.75 cm, operating in the TE_{111} mode. The line width was determined by the finite size of the cavity. The addition of side walls at a moderately small radius makes the amplitude decay faster than $1/t$ when molecules begin to suffer collisions with these walls. (See Fig. 1.) For sufficiently low pressures and long pulse repetition intervals, the line width is determined by the diameter of the cavity. A numerical calculation of the line shape to be expected from such a cavity, taking into account the field distribution in the cavity, which was ignored in the previous discussion where the radiated amplitude was taken as strictly proportional to the number of radiating molecules, predicts a line 16.2 kc/sec wide (full width at half-maximum amplitude), of nearly Lorentz shape but slightly sharper at the peak than a Lorentz line of the same width. (The field distribution in the cavity does not have a drastic effect on the line shape. The line computed without taking the field distribution into consideration is of the same general shape, with a width of about 14.5 kc/sec.) The normal Doppler width is 73 kc/sec. Observed lines are about 18 kc/sec wide, with shapes and widths in good agreement with the calculation. The calculated line shape and a Lorentz line of the same width as the calculated line are plotted in Fig. 3. Note that the Lorentz line, chosen to have the same width at half-maximum amplitude, has a somewhat broader peak than does the calculated line. A Lorentz line chosen to have the same curvature at the line center as the calculated line would have a

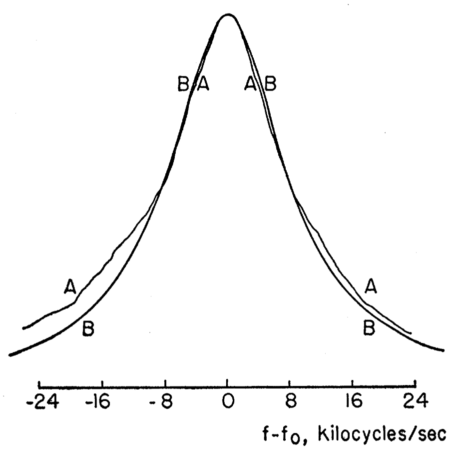

FIG. 4. Curve A: An observed line shape, 5.75-cm diameter pillbox with slight asymmetry arising from phase errors in detection system, 17.9 kc/sec wide at half-maximum amplitude. Curve B: Calculated Lorentz line, of approximately same width as curve A at half-maximum amplitude.

width slightly smaller than that of the calculated line. In Fig. 4 is plotted an observed line, whose width is 17.9 kc/sec. The slight asymmetry of the line may be attributed to slight phase errors in the detection system. Also plotted in Fig. 4 is a Lorentz line chosen to have approximately the same width at half-maximum amplitude as the observed curve. Note that the observed line is slightly sharper at the peak than the Lorentz line of the same width, bearing out qualitatively the predictions of the calculation (Fig. 3). The signal was 35 db above noise in the above measurements for an information bandwidth of 0.5 cycles/sec. The calculated signal to noise ratio, assuming a crystal conversion gain of $\frac{1}{4}$, a crystal noise temperature of 2, and an i-f (intermediate-frequency) amplifier noise figure of 4 (an over-all receiver noise figure of 20, or 13 db), is

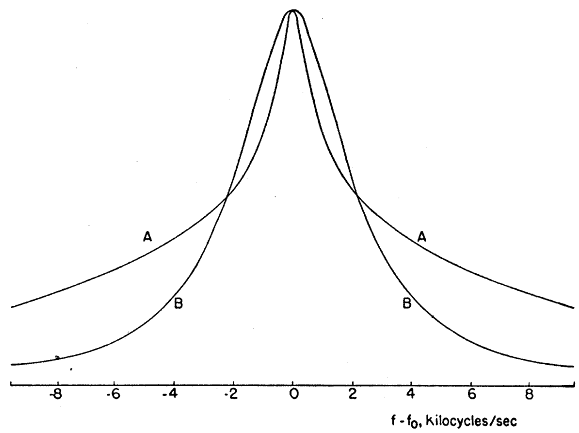

FIG. 5. Curve A: Calculated line shape, 62.5-cm diameter pillbox (diameter to height ratio 100). Curve B: Lorentz line shape chosen to have same width at half maximum amplitude as curve A.

approximately 42 db for operation at the required low-pressure and low-pulse repetition rate.

By increasing the cavity diameter, it seems feasible to decrease the line width by about another factor of four, but beyond this point, technical problems appear to make further narrowing considerably more difficult.

The calculated line shape for a cavity of diameter 62.5 cm, a diameter to height ratio of 100 to 1, is plotted in Fig. 5, together with a Lorentz line of equal width at half-maximum amplitude. The departure of the calculated line from the Lorentz shape is evident. Note that although the calculated width at half-maximum amplitude is approximately 4 kc/sec, a Lorentz curve with the same degree of sharpness at the line center as the calculated line would have a width of about 1.5 kc/sec. Thus, greater resolution is possible than that implied merely by the value of the width at half-maximum amplitude.