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Pressure, Light, and Temperature Shifts in Optical Detection of 0-0 Hyperfine Resonance of Alkali Metals

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Precision measurements of the hyperfine splitting of Cs^{133} or Rb^{87}, in a cell with buffer gases and using optical pumping, show a frequency shift when the intensity of the exciting resonance light is varied. Use of high buffer gas pressures will reduce considerably the light intensity shift. Also, in some cases, the magnitude and sign of the light intensity shift can be changed appreciably by varying slightly the frequency of the hyperfine components of the exciting light. Tentative explanations of the light shift are discussed. Frequency shift variations with light intensity, buffer gas pressure, and temperature of the cell, show the existence of an invariant point whose frequency, when reduced to zero pressure and zero field, is very close to the value obtained by the atomic beam resonance method. This invariant point is the basis for a definition of the pressure shift and temperature shift coefficients. Experimental determination of these coefficients is given for Cs^{133} and Rb^{87}.

INTRODUCTION

THE atomic beam technique has been used to measure accurately the hyperfine splitting of numerous paramagnetic atoms. In some cases, the accuracy of the measurements is sufficiently large to form the basis for the definition of a frequency standard. For example, by definition, in the *A*-1 time scale the Cs^{133} frequency is $\Delta\nu = 9\,192\,631\,770$ Mc/sec. More recently, the accurate measurement of the hyperfine splitting in a simple gas cell containing the alkali metal vapor has also been made possible by the development of several techniques such as the use of nonmagnetic buffer gases to reduce the Doppler width of the line, and the use of optical pumping and optical detection to increase considerably the signal-to-noise ratio of the detection of the microwave transition. However, these techniques, under certain conditions, can produce large frequency shifts and this paper reports precision measurements of such effects under varying conditions of buffer gas pressure, resonance light intensity, and temperature of the cell. Most detailed measurements have been made with Cs^{133}, but a few results are given also for Rb^{87}.

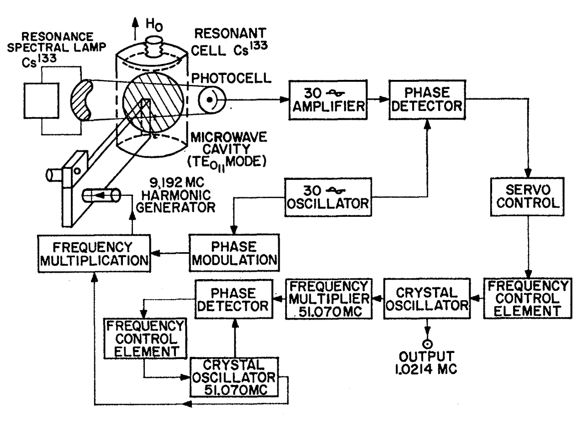

FIG. 1. Experimental arrangement.

EXPERIMENTAL ARRANGEMENTS

The principles of the double resonance method used for the detection of the microwave transition $\Delta F=1$, $m_f=0$ to $m_f=0$, in the ground state of alkali metal vapors, using optical pumping and optical detection have been previously described.[1] The apparatus used is illustrated in Fig. 1. A sealed-off gas cell contains the alkali vapor metal mixed with buffer gas to reduce Doppler broadening of the microwave transition.[2] A beam of resonance radiation from a resonance lamp is passed through the gas cell and is focused on a photocell. A homogeneous magnetic field of a few tenths of an oersted is produced in the region of the cell. The gas cell is placed in a microwave cavity which is excited by microwave at a frequency corresponding to the energy separation of the hyperfine levels of the ground state. This produces a saturation of these levels and the amount of resonance radiation transmitted through the gas cell is changed. By modulating, at low rate, the frequency of the microwave radiation, the output current of the photocell is modulated at the same rate and, by using this signal in a synchronous phase detector, a null is obtained when the frequency of the microwave radiation is exactly the frequency of the hyperfine resonance. If the output of the phase detector is fed back, in proper phase, to an element controlling the frequency of the microwave radiation, one can obtain a microwave frequency which is locked to the

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[1] A. Kastler, J. Opt. Soc. Am. **47**, 460 (1957); J. Brossel and A. Kastler, Compt. rend. **229**, 1213 (1949); H. G. Dehmelt, Phys. Rev. **105**, 1487 (1957); W. E. Bell and A. L. Bloom, *ibid.* **109**, 219 (1958); M. Arditi and T. R. Carver, *ibid.* **109**, 1012 (1958), **112**, 449 (1958); P. L. Bender, E. C. Beaty and A. R. Chi, *ibid.* **112**, 450 (1958), Phys. Rev. Letters **1**, 311 (1958).

[2] R. H. Dicke, Phys. Rev. **89**, 472 (1953).

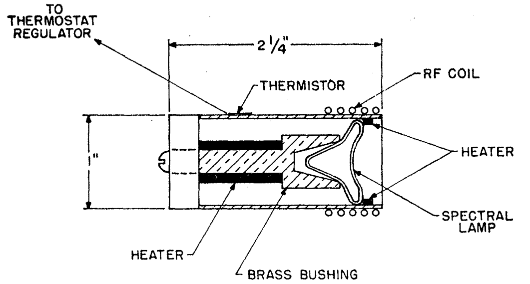

FIG. 2. Resonance lamp.

stable atomic resonance. This principle is used in so-called "gas cell atomic frequency standards."

The gas cell is made of low-loss 707 glass, and filled with pure alkali metal and spectroscopically pure buffer gases. The microwave cavity, excited in the TE_{011} mode, is carefully thermostated to produce a uniform temperature in the cell and the temperature is monitored with a thermocouple.

The light source of resonance radiation is an electrodless discharge produced in a small hemispherical bulb about 1 inch in diameter containing argon at a pressure of a few millimeters Hg and pure alkali metal. It is excited at 60 Mc/sec inside an rf coil and well-thermostated to avoid changes in light intensity due to the alkali metal migrating in the lamp[3] (Fig. 2). With this design the intensity of the light was very stable over a period of more than 3000 hr of continuous operation and because of this stability great accuracy and good reproducibility of the observations were possible.

The microwave frequency is obtained by multiplication from a stable crystal oscillator at 1.0214···Mc/sec which is the 9000th subharmonic of the cesium frequency. However, it is known that spurious side-bands in the microwave spectrum can produce systematic errors in the determination of the hyperfine frequency.[4] Since most of these spurious side-bands are produced in the low stages of frequency multiplication, they can be greatly minimized in the microwave spectrum by using, as a driver, a simple crystal oscillator at 51.0701 Mc/sec loosely phase-locked to the more stable oscillator at 1.0214···Mc/sec.

In determining the frequency corresponding to the maximum of the absorption curve, in most cases, the signal-to-noise ratio of the optical detection is good enough to observe the signal output of the narrow-band photocell amplifier directly on an oscilloscope, and to measure the frequency corresponding to a null with an accuracy of a few parts in 10^{10}. The use of the synchronous phase detector and servo is most convenient, however, in these cases where the signal-to-noise ratio of the detection does not permit such a direct measurement; however, when using the synchronous phase detector, special care must be taken in adjusting the servo because some relaxation effects taking place in the gas cell can give an out-of-phase component which can produce systematic errors in the position of the servo. Details of the adjustment procedure of the servo to minimize such errors can be found in reference 5. The frequency was measured with the setup shown in Fig. 3. Essentially the frequency of the oscillator driving the gas cell was compared against the frequency of an ultra-stable James Knight crystal oscillator type JKFS-1000 after a multiplication in frequency by a factor of 2500. The ultra-stable oscillator frequency was compared, for calibration, either directly with an Atomichron frequency, or with broadcast frequencies at 133.33 kc/sec from Station A5KA, Fort Monmouth, New Jersey, or at 18 kc/sec from Station NBA, Summit, Canal Zone, both stations being monitored by Atomichrons. An absolute accuracy of a few parts in 10^{10} could thus be obtained in the frequency measurements.

For the $\Delta F=1$, $m_f=0$ to $m_f=0$, magnetic dipole transition, the Breit-Rabi formula shows that the dependence of the frequency with the magnetic field is given by a quadratic term. The magnetic field at the gas cell could be varied by adjusting the current in a pair of Helmholtz coils at right angles around the gas cell. The magnetic field at the cell, inside the resonant cavity, was measured accurately by inducing simultaneously the low frequency Zeeman transitions $\Delta F=0$ $\Delta m_f=1$ with a small auxiliary coil placed near the cell inside the cavity. At resonance the intensity of the detected hyperfine signal is reduced because of a change in the population distribution of the $m_f=0$ levels. An accuracy of ±5 millioersteds can be obtained easily by this method. In the earth's magnetic field this corresponds to a maximum frequency error of ±2 parts in 10^{10} for Cs^{133} and ±3.5 parts in 10^{10} for Rb^{87}.

Since many factors can affect the optical pumping, it is necessary to define carefully the conditions under which the subsequent experimental results were

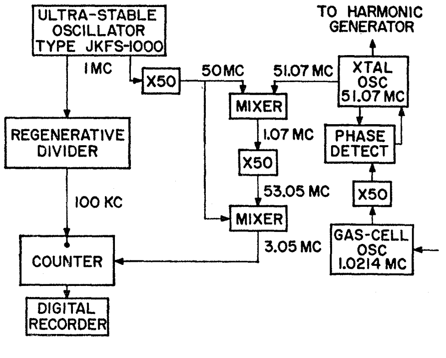

FIG. 3. Schematic of frequency measurement components.

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[3] This design is a modification of a model originally developed by P. L. Bender and E. C. Beaty of the National Bureau of Standards.

[4] J. A. Barnes and R. C. Mockler, IRE Trans. on Instrumentation 9, 149 (1960).

[5] M. Arditi, Proc. 15th Symp. Freq. Control 1961 (to be published).

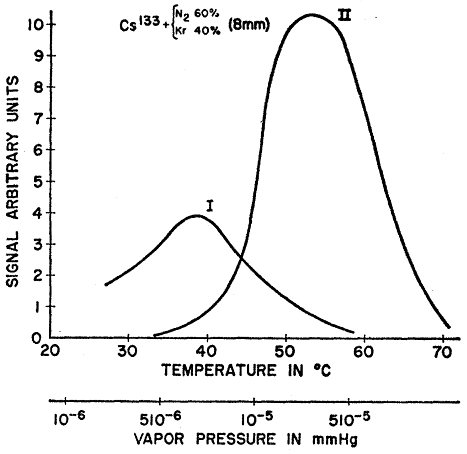

FIG. 4. Signal strength of optically detected 0-0 transition in cesium: I with resonance light filtered through a D_2 filter. II with no outside filtering, or D_1 filtering.

observed. When using unpolarized resonance radiation, it has been found that the optical detection of the 0-0 microwave transition is not only a function of the selective absorption of the hyperfine components of the exciting resonance radiation but also depends on the percentage of the D_1-D_2 components, in a certain range of temperature. This is illustrated in Fig. 4, which shows the detected signal in the case of Cs^{133} in a spherical bulb about 1½ inches in diameter filled with a mixture of nitrogen (60%) and krypton (40%) at a filling pressure of 8 mm Hg. (This mixture has a minimum of pressure shift.) Curve I refers to the signal obtained when using an interferometer filter which lets pass only the D_2 radiation (8521 A). For purpose of comparison in these curves, it should be noted that the D_2 filter absorbed about 80% of the total incident radiation. Curve II refers to the case where no outside filter is used; here, self-filtering of the resonance radiation takes place inside the cell since the D_2 radiation is strongly absorbed above a temperature of 45°C, and only the D_1 radiation is active above that temperature. In this latter case, operation is possible at much higher temperature than when using a D_2 filter. Since a high temperature of ambient operation is required in some applications, this mode of optical pumping has been more particularly studied here. Figure 5 shows the effect of varying the light intensity: It can be seen that in the temperature range between 30° and 45°C, the curves are overlapping due to the conflicting pumping effects of D_1 and D_2 radiations. The position of the maximum of the curves agrees qualitatively with previously published analysis.[6] Also, a shorter length of the cell in the path of the light shifts the maximum of the detected signal toward the higher temperatures.

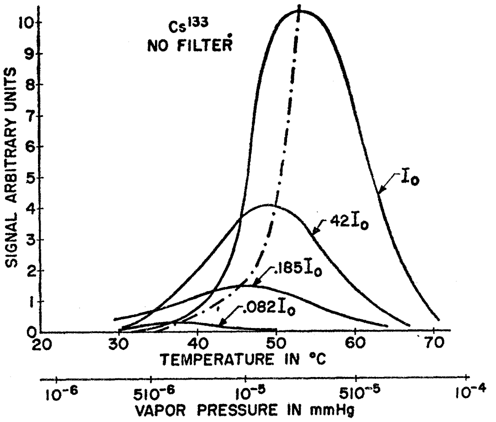

FIG. 5. Signal strength of optically detected 0-0 transition in Cs^{133} as a function of light intensity and cell temperature.

Somewhat similar effects have been observed in the optical detection of the 0-0 transition of Rb^{87} in a two-inch bulb filled with the natural isotopic mixture of Rb^{85} and Rb^{87} (Fig. 6). The exciting lamp in this case was filled with the same mixture as in the resonance cell. The D_2 filter passing the 7800-A radiation has an absorption coefficient of about 62%.

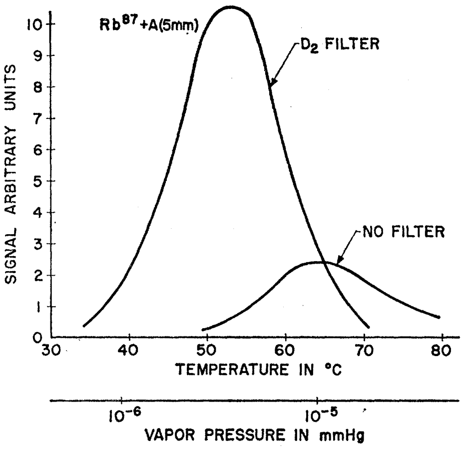

FIG. 6. Signal strength of optically detected 0-0 transition in Rb^{87}.

In all the following experiments, the results will be given for Cs^{133} for the condition where no outside filtering of the resonance radiation was used, except otherwise specified. Filtering with a D_2 filter has been used in the experiments with Rb^{87}. Otherwise the experimental arrangement is essentially the same for cesium and rubidium.

The factors producing a frequency shift in the hyperfine resonance frequency will now be studied under these conditions of optical pumping. In actual operation, since these factors are interacting, it is not always possible to separate them clearly, but since most of the effects are proportional to the density of alkali

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[6] W. E. Bell, A. Bloom and R. Williams, IRE Trans. on Microwave Theory and Techniques 7, 95 (1959); T. M. Andres, D. J. Farmer and G. T. Inouye, IRE Trans. on Military Electronics 3, 178 (1959).

atoms in the gas cell, it has been found convenient in this study to take the temperature as the variable parameter.

EXPERIMENTAL RESULTS

A. Effect of Buffer Gases

Buffer gases are used in the gas cell, both to obtain a reduction of the Doppler width and to increase the efficiency of optical pumping. However, it has been found previously that the presence of buffer gases produces an appreciable pressure shift. Pressure shifts have been measured in the particular cases of atomic hydrogen,[7,8] deuterium,[8] tritium,[8] sodium 23,[9] potassium 39,[10] rubidium 87,[11,12] and cesium 133.[13] The proportional shifts $\Delta\nu/\nu$ for the various alkalies and for a given buffer gas have the same sign and increase slowly in magnitude with increasing alkali atomic number. The pressure shift depends on the buffer gas.

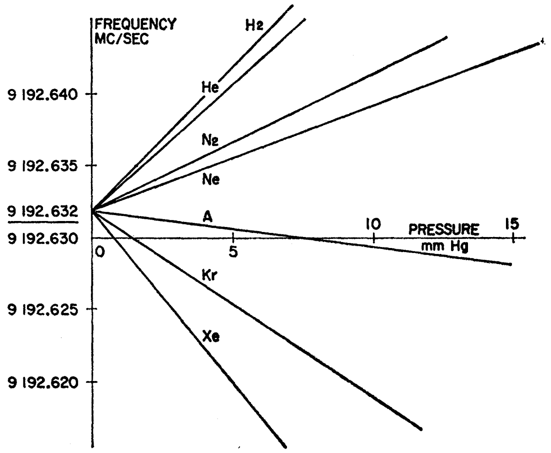

FIG. 7. Pressure-shift of zero-field hyperfine splitting of Cs^{133}.

Shifts to higher frequencies occur for light atoms such as hydrogen, helium, nitrogen or neon and shifts to lower frequencies occur for heavy atoms such as argon, krypton, or xenon (Fig. 7). Mixtures of gases giving low-pressure shifts can be obtained by the proper combination of buffer gases giving pressure shifts in opposite directions. However, there usually is a residual temperature-dependent shift which is a function of the nature of the buffer gases in the mixture. Details on this temperature-shift will be given in the next sections.

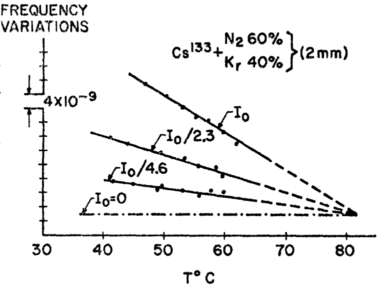

FIG. 8. Light-intensity frequency shifts as a function of light intensity and cell temperature. Low density of buffer gas.

B. Frequency Shifts with Light Intensity Variations

It has been found that, for low buffer gas pressure, varying the intensity of the light source shifts the resonant frequency by a substantial amount. The data may best be expressed in terms of the following plot in Fig. 8, which refers to a sealed-off cesium cell, $1\frac{1}{2}$ inches in diameter and filled with a mixture of nitrogen (60%) and krypton (40%). (This buffer gas mixture was prepared to obtain a minimum of pressure shift, taking into consideration the pressure shifts shown in Fig. 7.) The relative frequency variations have been plotted as a function of the temperature of the cell and for various values of the incident light intensity I_0. The light intensity was varied by means of the interposition of neutral density filters. The following remarks can be made: First, the frequency variations are linear, within the temperature range of the experimentation. (The measurements were stopped when the

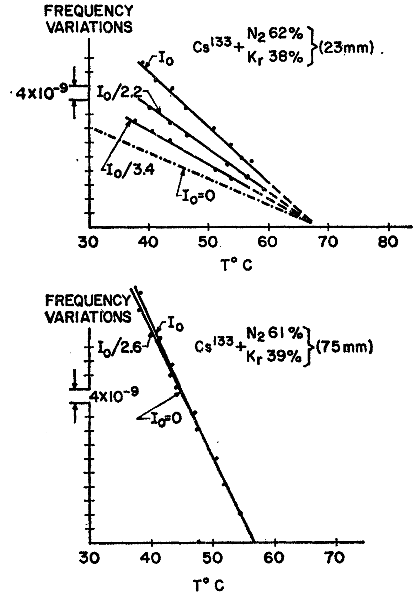

FIG. 9. Light-intensity frequency shifts as a function of light intensity and cell temperature, with increasing density of buffer gas.

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[7] J. P. Wittke and R. H. Dicke, Phys. Rev. **96**, 530 (1954).

[8] L. W. Anderson, F. M. Pipkin, and J. C. Baird, Phys. Rev. Letters **4**, 69 (1960). Phys. Rev. **120**, 1279 (1960).

[9] M. Arditi and T. R. Carver, Phys. Rev. **109**, 1012 (1958); M. Arditi, J. phys. radium **19**, 873 (1958).

[10] A. Bloom and J. B. Carr, Phys. Rev. **119**, 1946 (1960).

[11] R. H. Dicke, T. R. Carver, C. O. Alley, and N. S. VanderVen, Final report, U. S. Army Signal Corps Engineering Laboratories, 1957 (unpublished).

[12] E. C. Beaty, P. L. Bender, and A. R. Chi, Phys. Rev. Letters **1**, 311 (1958).

[13] M. Arditi and T. R. Carver, Phys. Rev. **112**, 449 (1958); E. C. Beaty, P. L. Bender, and A. R. Chi, *ibid.* **112**, 450 (1958).

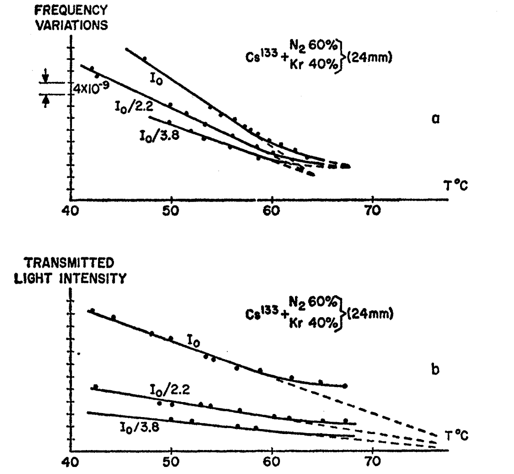

FIG. 10. Light-intensity frequency shifts and corresponding light absorption in a cesium cell.

signal-to-noise ratio of the detection did not permit a determination of the frequency with an accuracy better than ±1 part in 10^9); second, the frequency shifts are directly proportional to the incident light intensity (the broken line in the curves corresponds to the extrapolated limiting value at $I_0=0$); third, the straight lines converge toward a definite point, usually inaccessible to direct observation because of poor signal-to-noise ratio of the detection at this temperature; fourth, in this case, the frequency shifts are positive, i.e., the frequency of the hyperfine splitting is increased when the intensity of the exciting resonant light is increased.

It has been found also that the dispersion of the frequency shifts with light intensity variations is a function of the buffer gas density. As the filling pressure of the buffer gas is increased, the fantail array of the curves becomes narrower and for sufficiently high pressure, the curves merge into one curve, within experimental errors (Fig. 9). A corresponding increase in the light absorption in the gas cell is observed as the buffer gas density is increased. (See Fig. 10. At sufficiently high temperatures the absorption of light is no longer linear, with a corresponding tapering-off of the frequency shifts in this temperature range.) When the buffer gas density is increased, it should be noted that the temperature of the converging point of the linear extrapolations is shifted toward the lower values. This is related to the increased absorption of the resonant light. Also the slope of the extrapolated line corresponding to $I_0=0$ changes when the buffer gas density is changed. In describing the pressure shifts and temperature shifts in the following section the shifts are based on such an extrapolation to zero light intensity.

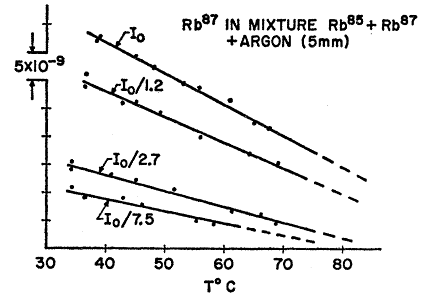

FIG. 11. Light-intensity frequency shifts in Rb^{87} and pure argon.

Somewhat similar results have been obtained in the case of Rb^{87} under the conditions of optical pumping previously defined (see Figs. 11 and 12).

C. Pressure-Shift and Temperature-Shift Coefficients

In Fig. 7, which represents the pressure shift of Cs^{133}, the hyperfine frequency was plotted against the filling pressure of the buffer gas, at room temperature, with the cell also at room temperature. Actually the term "pressure shift" is not very well chosen to define the effect. Since, in first approximation, the shift observed depends on the number of collisions between the alkali atoms and the buffer gas molecules, the term "density shift" would be more appropriate. The collision frequency is proportional to $n\sigma(2kT/m)^{\frac{1}{2}}$ and consequently the pressure shift or density shift should be proportional to $T^{\frac{1}{2}}$. In addition to the density shift there is an independent temperature shift. These temperature-shift coefficients as previously defined[14] were the observed shifts in frequency for a given change

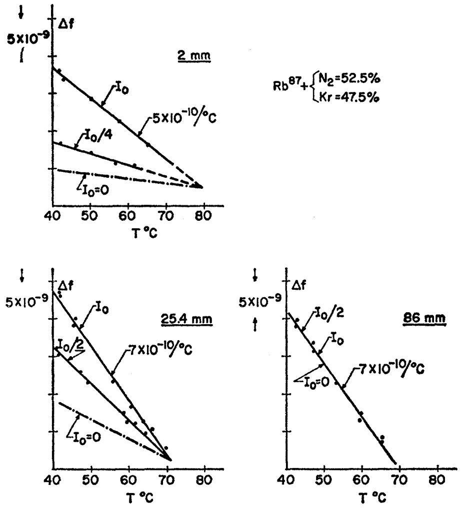

FIG. 12. Light-intensity frequency shifts as a function of light intensity and cell temperature, with Rb^{87} (isotopic mixture of Rb^{87} and Rb^{85}) with increasing density of buffer gas.

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[14] E. C. Beaty, P. L. Bender, and A. R. Chi, Phys. Rev. 112, 450 (1958); Phys. Rev. Letters 1, 311 (1958).

in temperature of the whole cell, and this was not measured at constant pressure. However, these simple approximations do not seem to check the experimental data over a large range of temperature. In the light of the experiments previously described, all the data of frequency shifts may be better expressed in terms of a semiempirical formula, as follows:

1. With buffer-gas mixtures having a minimum of pressure or density shift, and at low density for the buffer gas, the frequency of the converging point is very close to the frequency f_0, of the cesium or rubidium atoms as measured by the atomic beam method.

2. With buffer gases at high density, the frequency, $f_{T_{cp}}$, of the converging point is still related to the frequency, f_0, by the relation:

$$f_0=f_{T_{cp}}-\alpha p T_{cp}/303, \qquad (1)$$

where α is the pressure or density shift in cps per mm Hg, p is the filling pressure in mm Hg at 303°K, and T_{cp} is the temperature of the converging point.

3. The extrapolated line corresponding to $I_0=0$ can be considered as the resultant of two linear variations, one due to the density coefficient α, and equal to $\alpha p(T_{cp}-T)/303$, and the other due to the temperature coefficient δ, and equal to $\delta p(T_{cp}-T)$. (See Fig. 13.) The slope of this line is equal to $p\gamma$ in cps per degree, where $\gamma=\alpha/303+\delta$, and can be positive or negative depending on the relative signs of α and δ (Fig. 14). The frequency, f_T, of a point on the extrapolated line $I_0=0$, at a temperature T, can then be expressed by the formula:

$$f_T=f_0+(\alpha p/303)(2T_{cp}-T)+\delta p(T_{cp}-T), \qquad (2)$$

where $f_0=9\,192\,631\,770\pm10$ cps (A_1 time) with $313°\text{K}<T<333°\text{K}$ for Cs^{133}, and $f_0=6\,834\,682\,600\pm15$ cps (A_1 time) with $313°\text{K}<T<343°\text{K}$ for Rb^{87}, and where α and δ are given in Table I for Cs^{133} and in Table II for Rb^{87}.

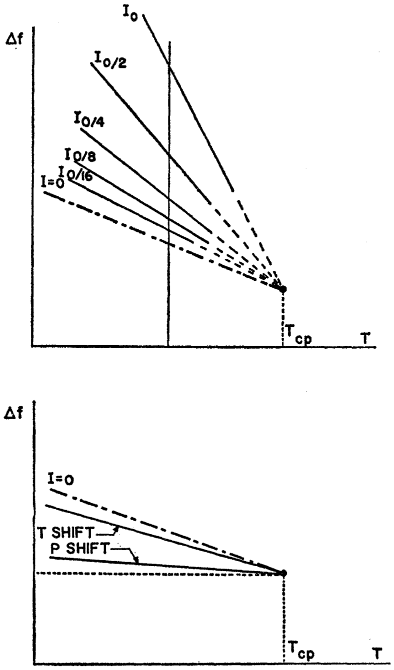

FIG. 13. Linear extrapolation of light intensity shifts versus cell temperature. The converging point T_{cp} is used for the definition of the temperature-shift coefficient, as well as reference point for the pressure-shift.

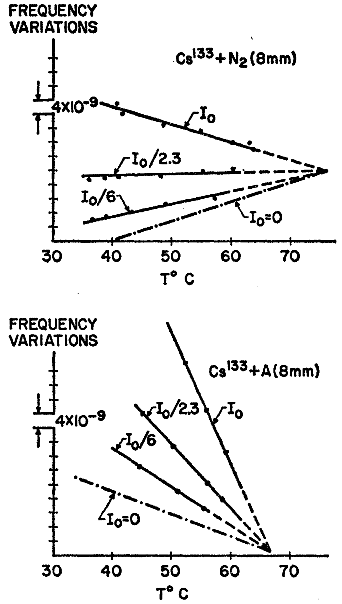

FIG. 14. Light-intensity frequency shifts in Cs^{133} mixed with pure nitrogen or pure argon, showing effect of using a positive pressure-shift or negative-pressure shift buffer gas.

The values of α and δ can be obtained by making measurements with pure buffer gases or with mixtures of gases. The accuracy is limited by the extrapolations and the uncertainties in the pressure and temperature of the cell, but the values indicated are in good agreement with the measurements of the hyperfine splitting made by atomic beam methods.[15] The values of δ^*, shown for purpose of comparison, correspond to previously published data[14] for a somewhat different definition of the temperature coefficient. In the derivation of the values of α and δ shown in Tables I and II, it has been implicitly assumed that the pressure-shift or temperature-shift coefficients of a gas mixture are the algebraic sum of the pressure or temperature-shift coefficients of the component gases of the mixture. The experimental evidence seems to bear this point of view.

Formula (2) gives a better agreement with the experimental data than formula (3) which is based on the assumption that the density shift varies as $(T)^{\frac{1}{2}}$, since the collision frequency is proportional to $(T)^{\frac{1}{2}}$.

$$f_T=f_0+\alpha p[2(T_{cp}/303)^{\frac{1}{2}}-(T/303)^{\frac{1}{2}}]+\delta p(T_{cp}-T). \qquad (3)$$

Using formula (3) as a definition for α and δ gives the values shown in Table III. Although formulas (2)

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[15] L. Essen, J. V. L. Parry, W. Markowitz, and R. G. Hall, Nature **181**, 1054 (1958). L. Essen, E. G. Hope, and D. Sutcliffe, *ibid.* **189**, 298 (1961).

TABLE I. Pressure and temperature shifts with buffer gases in Cs^{133} [formula (2)].

Gas	α (cps/mm)	$\alpha/303$	δ (cps/mm deg)	δ^*	Remarks
He	+1200	+3.96	−3.6	+1.5	Measured in {He 15%, Ar 85%}
N_2	+840	+2.77	−2.1		Measured directly and in {N_2 30%, Ar 70%}, {N_2 60%, Kr 40%}, {N_2 70%, Xe 30%}
Ar	−212	−0.70	−0.10	−0.7	Measured directly and in {N_2 30%, Ar 70%}
Kr	−1360	−4.33	+2.38		Measured in {N_2 61%, Kr 39%}
Xe	−2350	−7.59	+6.2±0.3		Measured in {N_2 70%, Xe 30%}
{N_2 30%, Ar 70%}	+104	+0.34	−0.64		
{He 18%, Ar 82%}	+45	+0.148	−0.72		
{N_2 70.8%, Xe 29.2%}	−78	−0.26	+0.5±0.1		
{N_2 62%, Kr 38%}	−0.33	−0.001	−0.39±0.1		

TABLE II. Pressure and temperature shifts with buffer gases in Rb^{87} [formula (2)].

Gas	α (cps/mm)	$\alpha/303$	δ (cps/mm deg)	δ^*	Remarks
Ar	−52	−0.171	−0.017	−0.30	Measured directly
{N_2 52.4%, Kr 47.6%}	−8.3	−0.027	−0.03±0.01		

and (3) give values of α which are very close to each other, the values of δ differ significantly. When cells filled with mixtures of various buffer gases are tested, the experimental results are more accurately represented by formula (2) than by formula (3) (see Table IV). This may be due to the fact that not only the number of collisions between alkali atoms and buffer gas molecules but the energy of the collisions is to be considered in a more detailed theory of the pressure shift.[16] The temperature T_{cp} of the converging point is related to the absorption of the resonance radiation in the cell, and consequently is a function of the geometry of the cell and of the density of the buffer gas filling the cell (Fig. 15). Similarly the temperature coefficients indicated in the Tables ought to be restricted to the particular size of the cells and the geometry of the light beam used in these experiments.

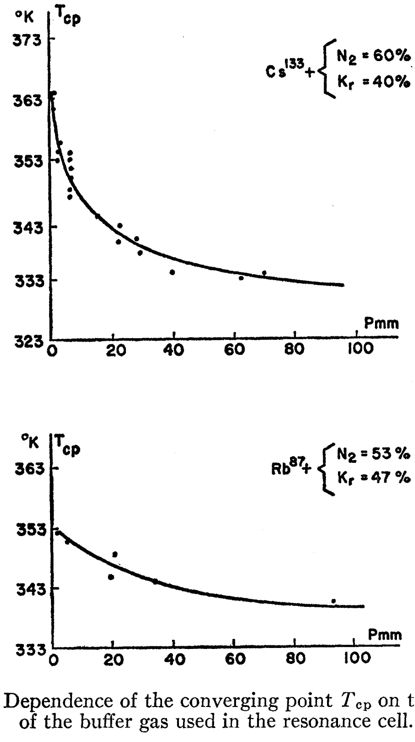

FIG. 15. Dependence of the converging point T_{cp} on the density of the buffer gas used in the resonance cell.

DISCUSSION OF EXPERIMENTAL RESULTS

The frequency shifts produced by variations of the exciting resonance light intensity are not due to an asymmetrical broadening of the microwave resonance. In the experiments the linewidth of the field insensitive 0-0 microwave transition is rather large, of the order of 600 to 800 cps, and much larger than an expected linewidth of 20 to 30 cps. However, the line shape is quite symmetrical as shown in Fig. 16, which represents the amplitude of the signal at the output of the photocell amplifier versus the microwave frequency.

If the exchange cross section for Cs-Cs or Rb-Rb collisions[11] is indeed about 3.5 to 7×10^{-14} cm^2 at high

TABLE III. Pressure and temperature shifts with buffer gases in Cs^{133} [formula (3)].

Gas	α (cps/mm)	δ (cps/mm deg)
He	+1200	−1.44
N_2	+820	−0.74
Ar	−212	−0.435
Kr	−1320	+0.29
Xe	−2350	+3.68

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[16] H. Margenau, P. Fontana, and L. Klein, Phys. Rev. **115**, 87 (1959); L. B. Robinson, *ibid.* **117**, 1275 (1960), E. M. Purcell (private communication) R. Bersohn (private communication).

Table IV. Pressure and temperature shifts with buffer gases in Cs^{133}.

	α (cps/mm)			δ (cps/mm deg)		
	Computed			Computed		
Gas	(3)	(2)	Measured	(3)	(2)	Measured
{N_2=62%, Kr=38%}	+7	−4	−0.3	−0.35	−0.40	−0.39
{N_2=65.5%, Kr=24.5%, Xe=10%}	−21	−18	−20	−0.045	−0.202	−0.206
{N_2=67%, Kr=20%, Xe=13%}	−20.4	−14	−10	+0.040	−0.17	−0.18

temperature like 60°C, the exchange collisions lead to a linewidth of this magnitude. However, reduction in rubidium pressure by an order of magnitude does not lead to narrower lines. Also the linewidth is not reduced more than about 20% when the intensity of the incident light is reduced within a ratio of 4 to 1, for example. (The maximum intensity I_0 of the exciting light falling directly on a 927 type photocell screened by a 6-mm Corning filter No. 5850 gives a photocell current of about 2.5 μamp.) This would indicate a very large amount of self-reversal in the emitted light in the lamp. Collisions of the alkali atoms with the walls of the cell contribute very little to the linewidth since cells coated with GE. SC-77 Dri-film, which is known to reduce disorienting effects,[17] give the same linewidth as noncoated cells as soon as a few mm of buffer gas are introduced in the cell. The broadening of the microwave transition may be due to the fact that here there is a great deal of light trapping and filtering in the cell itself while the atoms are simultaneously subjected to the microwave field. Since the filtering and trapping is not homogeneous in the cell along the beam path, it is possible that the resonance is apparently broadened by these inhomogeneities. Somewhat smaller linewidths have been obtained with larger cells when the microwave field was localized to the back of the cell with a microwave horn. Much narrower linewidths have been obtained, under different experimental conditions,[14] when the light filtering was produced essentially in a filter cell separate from the sample cell subjected to the microwave field.

The magnitude of the light-intensity shift observed is somewhat of a "volume effect" involving the whole of the cell, and will vary with the geometry or temperature of the cell and with the density of the buffer gas. As pointed out above, the light trapping and filtering is not homogeneous along the path of the light beam; raising the temperature of the cell will localize the trapping near the input window, where the exciting light beam enters and the effect of light intensity shift in the whole cell will be reduced. This will be true also if the buffer gas density is increased because collisions between alkali atoms and buffer gas molecules, without loss of orientation, will also permit a more efficient utilization of the incident photons and again will restrict the maximum absorption of light close to the input window. That such a geometrical effect exists can be demonstrated by the following experiment: a second source of resonance light is used at right angle to the main beam of light (Fig. 17). When this source lies in the plane XX' an additional frequency shift is produced; when the source lies in the plane YY' practically no additional effect is observed because in this region the light trapping is so intense that a saturation is produced.

The geometrical aspect of the light intensity shift is also in agreement with the almost linear variation of the frequency shift with incident light intensity and is closely related to the absorption of resonance radiation (Fig. 10).

Although the previous remarks tentatively explain the variations of the light intensity shifts with temperature of the cell or the density of the buffer gas, they do not provide an explanation for the origin of the shift itself. Several models appear to present themselves and will be briefly discussed here.

At first, one is tempted to ascribe the frequency shifts observed with the light intensity variations to a wall effect: collisions of the alkali atoms with the glass walls of the cell could produce a frequency shift from the true resonant frequency of the free alkali atoms.

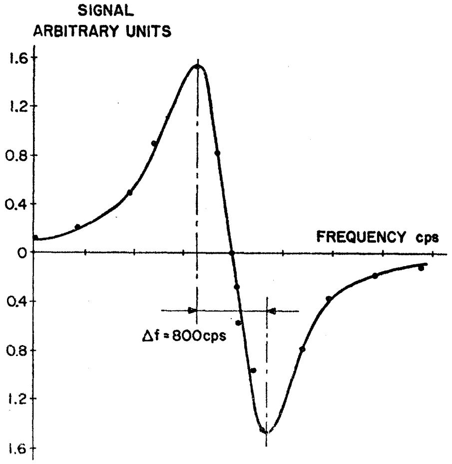

Fig. 16. Line shape of optically detected 0-0 transition in Cs^{133}.

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[17] Non-disorienting wall coatings were originally proposed by R. H. Dicke (see reference 7). Also H. G. Robinson, E .S. Ensberg, and H. G. Dehmelt, Bull. Am. Phys. Soc. 3, 9 (1958). The GE. SC-77 Dri-film coating, a mixture of dimethyldichlorosilicane and methyltrichlorosilicane, was suggested by R. A. Naumann and with it C. Alley obtained strong signals in the detection of the low-frequency Zeeman transitions in Rb^{87}.

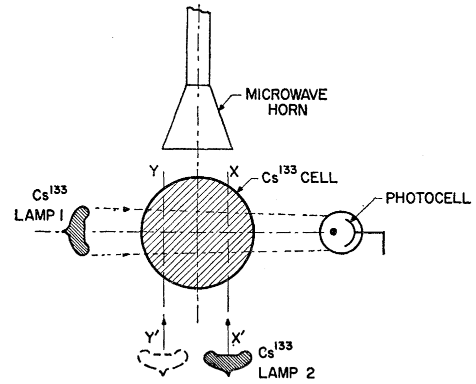

FIG. 17. Double light beam experimental arrangement for investigation of light intensity frequency shifts in a large resonance cell (XX' and YY' represent planes along which auxiliary resonance radiation from lamp 2 is focused).

By increasing the light intensity, atoms farther away from the walls are oriented and contribute more to the detected microwave signal. Since the number of wall collisions per second is reduced as the alkali atoms are farther away from the walls, a frequency shift could thus occur. Also as the density of the buffer gas is increased, the number of wall collisions per second is decreased and the effect of the light intensity should be less pronounced, as found experimentally. However, with this model, the sign of the frequency shift predicted is not in agreement with experimental results; also tests with Dri-film coated cells, filled with buffer gases, show that a light-intensity frequency shift of the same magnitude is obtained than when using uncoated cells filled with the same buffer gas. With a filling of a few mm of buffer gas in the cell, the wall coating effect is almost completely masked by the buffer gas action. Thus it is unlikely that wall collisions contribute significantly to the light intensity shift.

In another model, one could think of a coupling between the ground-state and the excited-state energy levels, through optical pumping, with the retention of a certain amount of coherence in the resonance fluorescent light.[18] The fact that the alkali atoms are submitted to the simultaneous processes of optical pumping and microwave transition could place them in superposition states with both hyperfine levels of the ground state slightly displaced upward, but with the upper level displaced a little more than the lower level, thus producing a positive frequency shift. The reduction of the light intensity shift at high densities of buffer gas could be due to the fact that at these densities the collisions of the alkali atoms in the excited states with buffer gas atoms tend to mix the hyperfine levels, leading to complete intensity pumping rather than to stochastic pumping.

Recently a more satisfactory model, leading to a semiquantitative explanation, has been suggested by C. Cohen-Tannoudji, with regard to his theoretical work, with J. P. Barrat, on the light shift of the Zeeman sublevels of the mercury isotopes.[19] Frequency shifts of magnetic resonances associated with virtual transitions produced by optical excitation has been observed experimentally.[20] The following explanation[21] has been proposed for the light intensity shift of the hyperfine transition:

"Let 1 and 2 represent the two hyperfine levels of the ground state and e one of the sublevels of the excited states (Fig. 18). The two hyperfine components of one of the doublet lines are represented by the wave numbers k_1 and k_2. Thus k_1 acting on the alkali atoms located in level 1 produces real transitions while producing virtual transitions when acting on atoms located in level 2, since the distance 1–2 is much larger than the Doppler breadth. According to the theory[19] k_1 gives a self-energy $\Delta E'$ to level 2 and the sign of $\Delta E'$ is the sign of $1/(k_1-k_2)$, which in this case is negative. Similarly k_2 gives a self-energy to level 1 with the sign of $1/(k_2-k_1)$, and this is positive. The energy gap between 1 and 2 is thus increased. With this interpretation the exciting resonant light produces simultaneously real and virtual transitions depending on the energy level considered, and a positive frequency shift is obtained when the light intensity increases. Every time an atom in level 1 absorbs a k_1 photon it decreases the number of photons available to produce virtual transitions for atoms located in level 2, and it is conceivable that the factors affecting the optical pumping could greatly influence the magnitude of the light intensity shift observed."

It may be that parts of the proposed models concord in the true explanation of the effect, but the ideas of Cohen-Tannoudji suggest several experiments to test his theory. In particular, a variation of the light-intensity frequency shift could be produced by shifting slightly the hyperfine components of the exciting light compared to the hyperfine components of the resonance cell itself. In one experiment this was verified by placing the light source in a magnetic field; by varying the magnetic field intensity the light shift could be reduced, annulled, or even slightly reversed (Fig. 19). In another experiment, a filter cell was used between the light

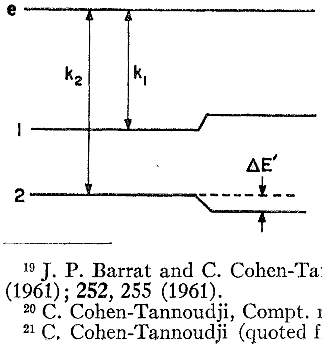

FIG. 18. Virtual transitions induced by radiation k_1 on atoms located on level 2.

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[18] J. N. Dodd, W. N. Fox, G. W. Series, and M. J. Taylor, Proc. Phys. Soc. **74**, 789 (1959).

[19] J. P. Barrat and C. Cohen-Tannoudji, Compt. rend. **252**, 93 (1961); **252**, 255 (1961).

[20] C. Cohen-Tannoudji, Compt. rend. **252**, 394 (1961).

[21] C. Cohen-Tannoudji (quoted from private communication).

source and the resonance cell. In this case a positive frequency shift of $+7.5\times10^{-9}$, corresponding to a 2 to 1 change in light intensity, was changed to a negative shift of -6.5×10^{-9} when a magnetic field of about 500 gauss was applied to the filter cell. (The isotopic mixture of Rb^{87} and $Rb^{85}+2$ mm argon was used in the light source. The same mixture +5 mm argon was used in the filter cell, while the resonance cell was filled with the rubidium isotopic mixture +4 mm of nitrogen 53%+krypton 47%.) It is interesting to note that the frequency displacement of the hyperfine components produced by a magnetic field of a few hundred gauss is of the order of magnitude of the Doppler breadth of the optical lines.

Other experiments, using various filtering schemes affecting the relative intensity of the hyperfine optical lines used for optical pumping, could be devised with more flexibility if one uses separate filter and sample cells as in the optical pumping of a rubidium 87 sample through a rubidium 85 filter cell.[14] Experiments in this direction have already been performed.[22]

These experiments, although in qualitative agreement with the theory of virtual transitions, are not easily subjected to quantitative treatment since the number of hyperfine components to be considered is rather large and their mutual interaction extremely complex. The authors have therefore felt it useful to publish, at this time, as much of the experimental results and tentative conclusions as possible, even though in somewhat empirical form.

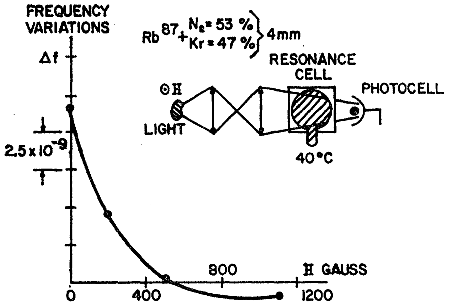

Fig. 19. Light-intensity frequency shifts as a function of magnetic field intensity at the light source: The magnetic field in displacing slightly the hyperfine components of the light source, as compared to the hyperfine components in the resonance cell, can change the magnitude or the sign of the light-intensity frequency shift.

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[22] P. Bender (private communication).