# Spin-Exchange Cross Section for $Rb^{85}$-$Rb^{87}$ Collisions*†

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(Received 28 June 1963)

The spin-exchange cross section for $Rb^{85}$-$Rb^{87}$ collisions has been measured to be $(1.70\pm0.21)\times10^{-14}$ cm² using the techniques of optical pumping and an interferometric method for measuring the Rb vapor density. The $Rb^{87}$ constituent in a vapor of natural Rb was polarized through absorption of circularly polarized resonance radiation, and the $Rb^{87}$ polarization was partially transferred to the $Rb^{85}$ constituent through spin-exchange collisions. A phenomenological theory of the optical pumping plus the exchange polarization process which neglects nuclear spin was used to relate the cross section to the ratio of the signal strengths for the $Rb^{87}$ and $Rb^{85}$ Zeeman resonances, the relaxation time, and the $Rb^{87}$ vapor density. The density was measured by comparing spectral profiles of the resonance radiation transmitted through the optical pumping cell at room temperature with the resonance radiation transmitted at the temperature at which the signal strengths were measured. These spectral profiles were obtained through use of a scanning Fabry–Perot interferometer.

## I. INTRODUCTION

THE first determination of an atomic spin-exchange cross section was accomplished by Wittke and Dicke[1] in their experiments on the hyperfine splitting in the ground state of atomic hydrogen using microwave absorption techniques. In subsequent experiments by others, optical pumping techniques[2] have been exploited to determine spin-exchange cross sections for several different systems. In this work, an alkali vapor contained in a Pyrex cell is polarized through absorption of circularly polarized resonance radiation, and this polarization is partially transferred to another atomic or subatomic specie in the cell through spin-exchange collisions. This phenomenon of exchange polarization was first used by Dehmelt[3] to polarize an electron gas through collisions with an optically pumped Na vapor. Shortly after, exchange polarization in Rb-Cs,[4] Na-K,[5] and Na-Rb [6] systems was demonstrated. Numerical estimates of spin-exchange cross sections for alkali-electron and alkali-alkali collisions were obtained from these experiments. These estimates had large uncertainties connected with them, and in effect the cross sections quoted in this early work were order of magnitude estimates. The main reason for the uncertainty in this early work was that in an optical pumping experiment, the quantity measured directly is the rate of polarization transfer from one vapor to another. This

rate depends upon the spin-exchange cross section, the relative velocities of the members of the collision, and the density of the two vapors. The difficulty lies in obtaining reliable estimates of the vapor densities.

In the present work,[7] we have measured the spin-exchange cross section for $Rb^{85}$-$Rb^{87}$ collisions through optically pumping $Rb^{87}$ and exchange polarizing $Rb^{85}$, and by measuring the vapor density in the optical pumping cell using an interferometric technique. This technique compares the spectral profile of the Rb $D_1$ line transmitted through the cell at room temperature with the spectral profile of the same line transmitted through the cell at the temperature at which the optical pumping is performed. These profiles were obtained through use of a scanning Fabry-Perot interferometer constructed for this purpose. The interferometric technique of vapor density measurement frees this experiment from the major uncertainty involved in experiments of this type. The experimental results for $Rb^{85}$-$Rb^{87}$ collisions yield a cross section of $(1.70\pm0.21)\times10^{-14}$ cm².

## II. DENSITY MEASUREMENT

Two pieces of information are generally available in an optical pumping experiment to yield density estimates. These are the temperature of the optical pumping cell and the fraction of the light transmitted through the cell at optical pumping temperatures. Neither of these two pieces of information can be used to obtain reliable density estimates. The observed behavior of alkali vapor pressure below 1 mm shows a very strong functional dependence upon the temperature.[8] A change in temperature of about 30°C is sufficient to change the pressure by an order of magnitude. Therefore, the temperature of the alkali vapor source must be known quite accurately for these data to be used. A more difficult problem in using vapor density data arises from the construction of optical pumping cells. Alkali

* This research was supported by the U. S. Atomic Energy Commission.

† Based on a thesis submitted to the Horace H. Rackham School of Graduate Studies of The University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[2] For a review of optical pumping techniques see A. Kastler, J. Opt. Soc. Am. 47, 460 (1957) and G. V. Skrotskii and T. G. Izyumova, Usp. Fiz. Nauk 73, 423 (1961) [translation: Soviet Phys.—Usp. 4, 177 (1961)].

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[8] S. Dushman, *Scientific Foundations of Vacuum Technique* (John Wiley & Sons, Inc., New York, 1949), Chap. II, pp. 740–745.

metal is distilled into a Pyrex cell, covering some fraction of the cell wall. The film of alkali metal acts as a source of the vapor, but the bare glass wall of the cell acts as a sink for the alkali vapor. Therefore, the alkali vapor density at a given cell temperature depends upon how the cell is prepared, that is, on the ratio of glass wall with alkali film to bare glass wall. Knowledge of the fraction of light absorbed in the cell[9] cannot give reliable density estimates under usual optical pumping conditions either. This information can only be used if the emission line of the lamp were identical to the absorption line of the vapor in the cell. This would be a highly unusual situation for the lamps and cells used in optical pumping experiments. The method of density measurement used in this work[10] is felt to be capable of yielding results of about 10% accuracy as opposed to the order of magnitude estimates from the methods previously mentioned. This method will now be discussed.

If a parallel beam of light of wave number $\nu$ passes through a cylindrical cell of length $L$, the incident intensity $I_\nu{}^0$ is related to the transmitted intensity $I_\nu$ through an exponential law of absorption,[11]

$$I_\nu = I_\nu{}^0 e^{-k_\nu L}. \tag{1}$$

This relation is a defining equation for the absorption coefficient $k_\nu$. The integral of the absorption coefficient over the absorption line is related to the density of the vapor $N$ through

$$\int k_\nu d\nu = (\lambda_0{}^2 g_2/8\pi c g_1 \tau)N, \tag{2}$$

where $\lambda_0$ is the wavelength of the center of the absorption line; $g_1$ and $g_2$, the statistical weights of the ground and excited states of the transition involved in the absorption; $\tau$, the lifetime of the excited state under spontaneous decay to the ground state; and $c$, the speed of light. This relation was used in conjunction with the high-frequency hyperfine component of the $D_1$ line of Rb[87], $\lambda_0 = 7948$ Å. The accuracy with which this relation may be applied is limited by the accuracy of the lifetime measurements. A recent determination by Stephenson[12] gives $\tau = (2.85 \pm 0.09) \times 10^{-8}$ sec. Using this value, $c = 3.00 \times 10^{10}$ cm/sec, $g_1 = g_2$ for the Rb[87] $D_1$ line, and recognizing that only $\frac{3}{8}$ of the absorption is in the high-frequency hyperfine component ($^2P_{1/2}$ to $^2S_{1/2}$, $F = 1$), the relation becomes

$$N = 9.07 \times 10^{12} \times \int k_\nu d\nu \text{ atoms/cm}^3 \tag{3}$$

with an uncertainty of about $\pm 3\%$.

[9] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, London, 1961) Chap. 3, p. 118–119.
[10] S. M. Jarrett and P. A. Franken (to be published).
[11] See Ref. 9, Chap. 3, pp. 92–97, 124–127.
[12] G. Stephenson, Proc. Phys. Soc. (London) **A64**, 458 (1951).

The integrated absorption coefficient was determined by comparison of spectral traces of the transmitted Rb[87] $D_1$ high-frequency hyperfine component at room temperature (negligible Rb[87] density) and at 90°C, the temperature at which the optical pumping experiment was performed.[13] The traces were obtained with a scanning Fabry-Perot interferometer. The light transmitted through the optical pumping cell entered a vacuum chamber containing an etalon of thickness 1.1 cm, with 95% reflecting silver coatings. The fringe system was focused on a metal plate by a 508-mm focal length achromat. A circular hole of diameter small compared to the fringe diameter was placed at the center of the center fringe and the light passing through was monitored by a photomultiplier. The vacuum chamber was pumped down to fore pump pressure, and air slowly leaked back into the chamber through a capillary tube. This provides a time variation in the index of refraction of the medium between the Fabry-Perot plates, and thus the spectral profile of the transmitted light intensity can be obtained. For more details of this method the reader is referred to Refs. 7 and 10.

## III. OPTICAL PUMPING SIGNALS

A phenomenological theory of the optical pumping plus exchange polarization process in Rb will be given in this section. A relation between the spin-exchange cross section for Rb[85]-Rb[87] collisions, the signal strengths encountered using the transmission monitoring technique, and the relaxation times will be derived. The spin-exchange cross section introduced in the theory will be determined through use of this relation and the measured signal strengths and relaxation times. In the present experiment, Rb[87] is optically pumped and Rb[85] exchange polarized. For a given magnetic field, the Zeeman resonances for the two isotopes appear at different frequencies due to their different nuclear spins. For Rb[87], $I = \frac{3}{2}$ and for Rb[85], $I = \frac{5}{2}$. If the field is sufficiently low, the individual Zeeman resonances for each isotope will be unresolved.

The theory developed is based upon a model which neglects the nuclear spin of both isotopes. That is, the optical pumping signals are assumed to depend only upon the spin polarization of the optical electrons of the Rb[87] atoms. Spin exchange results in a change of the Rb[87] electron polarization through Rb[85]-Rb[87] collisions. This model is expected to be a good approximation to the more complicated situation in which nuclear spin is considered, when the individual Zeeman resonances for each isotope are unresolved and thus detected simultaneously. Other assumptions used in this theory

[13] An absorption cell 1.4 cm long was used in the present experiment. No absorption of Rb[87] radiation was observed in this cell at room temperature. An absorption cell of sufficient length would of course yield measurable absorption at room temperature. A thin cell was chosen so that direct comparison of the room temperature and 90°C spectral traces could be made. The 70% absorption observed at 90°C represents a density in the cell which is about a factor of 100 higher than at room temperature.

are that the polarization achieved during the pumping process is low, in the range of a few percent, the ratio of the densities of the $Rb^{85}$ to $Rb^{87}$ vapors in the cell is given by the natural abundance in the metal, the relaxation rates in the ground state for both $Rb^{85}$ and $Rb^{87}$ are the same (this was shown to be the case experimentally), and that complete mixing in the excited state obtains due to the presence of a Ne buffer gas of 28 mm. The last assumption means that a $Rb^{87}$ atom in the excited state is randomly distributed amongst the excited state sublevels before decay to the ground state. The effect of pumping with $D_1$ light alone will be considered, which was the case experimentally.

Consider a cylindrical absorption cell of length $L$ containing a vapor of natural Rb irradiated with a parallel beam of right-hand circularly polarized $Rb^{87}$ $D_1$ radiation (only $Rb^{87}$ will absorb). A weak dc magnetic field is applied to the cell in the direction of the incident radiation. Neglecting nuclear spin, and in low field at a temperature of about 90°C, the $Rb^{87}$ atoms are essentially equally distributed between the $^2S_{1/2}$ $M_J = +\frac{1}{2}$ and $M_J = -\frac{1}{2}$ sublevels. Only the atoms in the $M_J = -\frac{1}{2}$ sublevel can absorb the circularly polarized $D_1$ radiation since a $\Delta M_J = +1$ transition must be made. The rate of change of the light intensity $I(x)$ as a function of distance through the cell $x$ is given by

$$[dI(x)/dx] = -N_- \sigma_0 I(x), \qquad (4)$$

where $\sigma_0$ is the cross section for optical absorption and $N_-$ is the number of atoms per cm³ in the $M_J = -\frac{1}{2}$ sublevel. Introducing the polarization of the $Rb^{87}$ vapor $P_1 = (N_+ - N_-)/N$, where $N_+$ is the number of atoms in the $M_J = +\frac{1}{2}$ state per cm³ and $N$ the total number of $Rb^{87}$ atoms per cm³, the above becomes

$$[dI(x)/dx] = -(N\sigma_0/2)(1 - P_1)I(x). \qquad (5)$$

This equation may be integrated over the length of the cell yielding

$$I = I_0 e^{-(N\sigma_0/2)L(1-\bar{P}_1)}, \qquad (6)$$

where $\bar{P}_1$ is the average value of the polarization over the length of the cell, and $I_0$ is the intensity of the incident pumping radiation. The signal $S$ is the difference in light intensity transmitted through the cell when an rf magnetic field at the $Rb^{87}$ Zeeman frequency is applied to the cell ($\bar{P}_1 = 0$) and when it is turned off. Under the assumption of low polarization ($\bar{P}_1 \leqslant 10^{-1}$), the signal is given by

$$S = -(N\sigma_0/2)LI_0 e^{-(N\sigma_0/2)L} \bar{P}_1. \qquad (7)$$

The exchange signal $S_x$ is the difference in the incident pumping radiation transmitted through the cell when an rf magnetic field at the $Rb^{85}$ Zeeman frequency is applied to the cell and when it is turned off. The average value of the $Rb^{87}$ polarization is different from $\bar{P}_1$ when this rf is applied. Let the new polarization be $\bar{G}_1$. $S_x$ is

given by

$$S_x = I_0 e^{-(N\sigma_0/2)L(1-\bar{G}_1)} - I_0 e^{-(N\sigma_0/2)L(1-\bar{P}_1)} \qquad (8)$$

or

$$S_x = -(N\sigma_0/2)LI_0 e^{-(N\sigma_0/2)L}(\bar{P}_1 - \bar{G}_1) \qquad (9)$$

under the assumption of low polarization. The ratio of the two signals is then

$$(S_x/S) = 1 - (\bar{G}_1/\bar{P}_1). \qquad (10)$$

The average values of the $Rb^{87}$ polarization will now be calculated. First, consider the situation in which there is no interaction between the $Rb^{87}$ and $Rb^{85}$ vapors. In the absence of circularly polarized pumping radiation, the sublevels of $Rb^{87}$ are essentially equally populated at optical pumping temperatures in a field of a few gauss. Therefore, the relaxation rate for an atom going from the $M_J = +\frac{1}{2}$ to the $M_J = -\frac{1}{2}$ sublevel is equal to the rate for the reverse process. The rate equation for $N_+$ at a position $x$ in the cell is given by

$$(dN_+/dt) = -N_+ R + N_- R + \tfrac{1}{2}N_- \sigma_0 I(x), \qquad (11)$$

where $R$ is the relaxation rate and the factor of $\frac{1}{2}$ in the last term comes from the assumption of complete mixing in the excited state. With the introduction of spin exchange, atoms of $Rb^{87}$ and $Rb^{85}$ can exchange their electronic spin orientations during collision. The cross section for the process $Q_x$ is the spin-exchange cross section to be experimentally determined. Only those collisions in which the $Rb^{85}$ and $Rb^{87}$ are initially in opposite spin states can give rise to changes in the populations of the $Rb^{85}$ and $Rb^{87}$ ground states' sublevels. The rate equations for $Rb^{87}$ and for $Rb^{85}$ with spin exchange are

$$(dN_+/dt) = -N_+ R + N_- R + \tfrac{1}{2}N_- \sigma_0 I(x)$$
$$\qquad\qquad + N_- n_+ v_r Q_x - N_+ n_- v_r Q_x, \qquad (12)$$

$$(dn_+/dt) = -n_+ R + n_- R + n_- N_+ v_r Q_x - n_+ N_- v_r Q_x, \qquad (13)$$

where $n_+$ and $n_-$ are the populations of the $M_J = +\frac{1}{2}$ and $M_J = -\frac{1}{2}$ ground-state sublevels of $Rb^{85}$ and $v_r$ is the relative velocity of $Rb^{85}$ and $Rb^{87}$ atoms. The terms involving spin exchange in the rate equations neglect the velocity distribution (and thus relative energy distribution) of the members of the collision. The simplification is made because of the unknown energy dependence of $Q_x$. The $v_r$ used will be the root mean square relative velocity.[14] All atoms of $Rb^{85}$ will be taken to have the same velocity, i.e., that velocity which will give the correct total energy of the $Rb^{85}$ vapor at a temperature $T$ and likewise for the $Rb^{87}$ atoms. Let the $Rb^{85}$ polarization be defined by $P_2 = (n_+ - n_-)/n$ where $n$ is the $Rb^{85}$ density. Substituting $P_1$, $P_2$, and $a = n/N$, the ratio of $Rb^{85}$ to $Rb^{87}$ vapor densities, the

[14] The choice of the root mean square velocity is somewhat arbitrary. Others might be inclined to choose the mean velocity. The present choice was made to be consistent with the early work of Dehmelt (Ref. 3). No consistent convention appears in the literature, however.
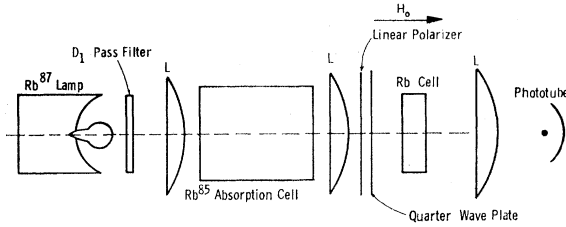
FIG. 1. Experimental arrangement for making optical pumping signal measurements. A weak dc magnetic field $H_0 = 3.6$ G is applied to the Rb cell parallel to the pumping light axis. Only the Rb $D_1$ radiation capable of being absorbed by Rb[87] reaches the cell.

rate equations become

$$(dP_1/dt) = [\sigma_0 I(x)/2] - \{[\sigma_0 I(x)/2] + 2R\}P_1$$
$$- aNv_r Q_x P_1 + aNv_r Q_x P_2 \quad (14)$$

$$(dP_2/dt) = -2RP_2 - Nv_r Q_x P_2 + Nv_r Q_x P_1. \quad (15)$$

To calculate $S_x/S$, we need the steady-state average values of the polarization of Rb[87] when $P_2$, the Rb[85] polarization, is at its steady-state value and when $P_2 = 0$ (equal population of the ground-state sublevels of Rb[85] is forced by application of an rf magnetic field at the Rb[85] frequency). The former is $\bar{P}_1$ and the latter is $\bar{G}_1$. In order to calculate these, the light distribution $I(x)$ must be known. $I(x)$ itself depends upon the Rb[87] polarization. However, a first-order solution for the polarization may be obtained through substitution of the zero-order light distribution, i.e., the light distribution in the absence of polarization. This is valid under the assumption of low polarization. The polarizations are:

$$\bar{G}_1 = \frac{1}{L} \int_0^L \frac{(\sigma_0 I_0/2)e^{-N\sigma_0 x/2}}{\dfrac{\sigma_0 I_0}{2}e^{-N\sigma_0 x/2} + 2R + aNv_r Q_x} dx \quad (16)$$

$$\bar{P}_1 = \frac{1}{L} \int_0^L \frac{(\sigma_0 I_0/2)e^{-N\sigma_0 x/2}}{\dfrac{\sigma_0 I_0}{2}e^{-N\sigma_0 x/2} + 2R + \dfrac{Nv_r Q_x(2aR)}{Nv_r Q_x + 2R}} dx. \quad (17)$$

Upon substituting the polarizations in $S_x/S = 1 - \bar{G}_1/\bar{P}_1$ and performing the integrations the following relation is obtained for low polarization.

$$(Nv_r Q_x/R) = [(1+a)/a][S_x/S/(1-S_x/S)]$$

$$+ \left[\left(\frac{1+a}{a}\right)^2\left(\frac{S_x/S}{1-S_x/S}\right)^2 + \frac{4}{a}\left(\frac{S_x/S}{1-S_x/S}\right)\right]^{\frac{1}{2}}. \quad (18)$$

Using this relation, the ratio of $Nv_r Q_x$ to $R$ can be determined by a measurement of the ratio of exchange to direct optical pumping signals and the known vapor density ratio. $N$ can be measured by the interferometric

technique described, and $v_r$ can be calculated using a measurement of the cell temperature.

$R$ must be determined in order to obtain $Q_x$. This may be accomplished by observing the time dependence of the signal at a reduced temperature. Since the exchange rate $Nv_r Q_x$, is directly proportional to the density, by reducing the density to low enough value, $Nv_r Q_x$ may be neglected in comparison to $R$. Since the signal $S$ is directly proportional to the Rb[87] polarization $P_1$, for low polarization, $R$ may be determined. Neglecting the exchange terms,

$$(dP_1/dt) = [\sigma_0 I(x)/2] - \{[\sigma_0 I(x)/2] + 2R\}P_1. \quad (19)$$

With rf on at the Rb[87] frequency, $P_1 = 0$. With the initial condition of $P_1 = 0$, the solution is

$$P_1 = P_0(1 - e^{-t/T})$$

$$P_0 = \frac{[\sigma_0 I(x)/2]}{[\sigma_0 I(x)/2] + 2R}$$

$$1/T = [\sigma_0 I(x)/2] + 2R. \quad (20)$$

The pumping rate $[\sigma_0 I(x)/2]$ at a given position in the cell is directly proportional to the incident intensity $I_0$. By observing the time dependence of the signal at two values of incident light intensity, e.g., $I_0$ and $I_0/2$, $R$ may be determined. With this additional information $Q_x$ may be determined.

## IV. EXPERIMENTAL ARRANGEMENT

Two separate types of measurements were involved in determining the cross section. These were measurements of the strengths and time dependence of optical pumping signals and spectroscopic measurements to determine the vapor density. Standard circuitry and techniques were used in both sets of measurements and will be described briefly.

Figure 1 shows the experimental arrangement for making the optical pumping signal measurements. An interference filter isolated the $D_1$ line from a Varian spectral lamp using an enriched Rb[87] bulb. The $D_1$ line was prefiltered before entering the optical pumping cell containing natural Rb. A filter cell containing 99% pure Rb[85] was used to absorb the Rb[87] light capable of being absorbed by the Rb[85] in the optical pumping cell as well as that light emitted by any Rb[85] poisoning in the lamp bulb. Polaroid linear polarizer and quarter wave plate rendered the light circularly polarized before entering the optical pumping cell. The transmitted light was monitored by an RCA 917 phototube. A pulsed rf technique was used to induce the Zeeman resonances. Phase sensitive detection was used in the measurements of the signals which were displayed on a chart recorder. Wide band detection was used in studying the time dependence of the signal to determine $R$. The signal was displayed on a CRO and photographed. Ten exposures were taken per frame to average the noise.

The density was measured using the interferometric technique. The $Rb^{85}$ filter cell, the linear polarizer, and the quarter wave plate were removed from the experimental arrangement of Fig. 1. A mirror (not shown) which deflected the transmitted light beam to the phototube was also removed which allowed the transmitted light to enter the scanning Fabry-Perot interferometer. The light beam was mechanically chopped at 150 cps. The center fringe of the interference pattern was monitored by a liquid air cooled RCA 7102 photomultiplier as air was slowly leaked back into the evacuated chamber containing the Fabry-Perot etalon. Phase sensitive detection was used and a permanent record of the spectral profiles of the $Rb^{87}$ $D_1$ line obtained by displaying the signal on a chart recorder.

## V. RESULTS

Preliminary to the measurement of $Q_x$, studies were made of the feasibility of optically pumping the $Rb^{87}$
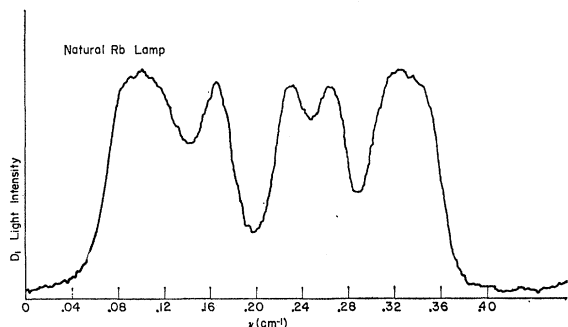
FIG. 2. The Rb $D_1$ line emitted by a Varian spectral lamp containing natural Rb metal. The peaks on the extremeties of the line are due to the two $Rb^{87}$ hyperfine components. The center is due mainly to the two $Rb^{85}$ hyperfine components.

component in a vapor of natural Rb. The first study was to examine qualitatively the dependence of both the $Rb^{87}$ and $Rb^{85}$ signals on temperature or density. In a vapor of natural Rb, $Rb^{85}$ has 2.59 times the density of $Rb^{87}$. If the direct optical signals for both isotopes were being observed, the $Rb^{85}$ signal maximum would be attained at a lower temperature than the $Rb^{87}$, due to its higher concentration in the vapor. While the $Rb^{87}$ signal is approaching its maximum, the $Rb^{85}$ signal will decline in strength as less $Rb^{85}$ light is transmitted through the cell due to the higher density of $Rb^{85}$. Thus, qualitatively, a decreasing ratio of $Rb^{85}$ to $Rb^{87}$ signal strengths would be expected as the temperature of the cell is increased. If an $Rb^{85}$ exchange signal is in fact being detected, the opposite would be expected since the $Rb^{85}$ signal depends upon the number of $Rb^{85}$-$Rb^{87}$ collisions in the vapor, which increases with increasing density (or temperature). With the pure $Rb^{85}$ filter cell in place in the apparatus, the latter situation was encountered. Upon removal of this cell, the former
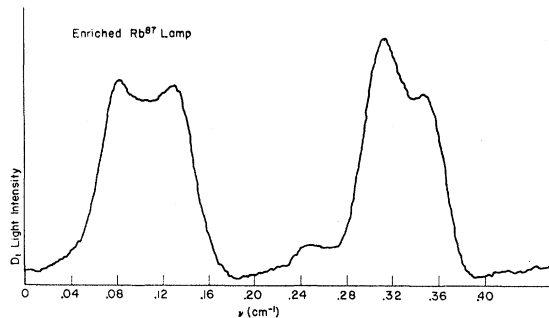
FIG. 3. The Rb $D_1$ line emitted by a Varian spectral lamp containing enriched $Rb^{87}$ metal. The component on the left arises from transitions to the $F=2$ sublevel of the ground state and the component on the right from transitions to the $F=1$ sublevel.

situation was encountered. A more direct way of showing that $Rb^{87}$ alone was optically pumped was to examine the pumping light with the scanning Fabry-Perot interferometer. Figures 2, 3, and 4 show the results of this investigation. Figure 2 is the $D_1$ line in emission from a Varian spectral lamp using a bulb containing natural Rb. The complex structure arises from the hyperfine structure of both isotopes. Figure 3 shows the $D_1$ line using an enriched $Rb^{87}$ bulb. A poisoning of $Rb^{85}$ is apparent next to the high-frequency $Rb^{87}$ hyperfine component. Also, $Rb^{85}$ is capable of absorbing the high-frequency side of the low-frequency $Rb^{87}$ hyperfine component. Figure 4 shows the action of the $Rb^{85}$ filter cell. The $Rb^{85}$ poisoning is gone and the high-frequency side of the low-frequency $Rb^{87}$ hyperfine component is attenuated. This measurement indicates that the light intensity available for direct pumping of $Rb^{85}$ and $Rb^{87}$ would provide a ratio of these direct pumping signals no larger than 1:225 (the signal is proportional to the square of the incident light intensity). The ratio observed under these pumping conditions was actually 1:9. Therefore, direct optical pumping cannot be responsible for the relatively large $Rb^{85}$ signals measured. It is felt that the contribution of direct pumping is negligible.
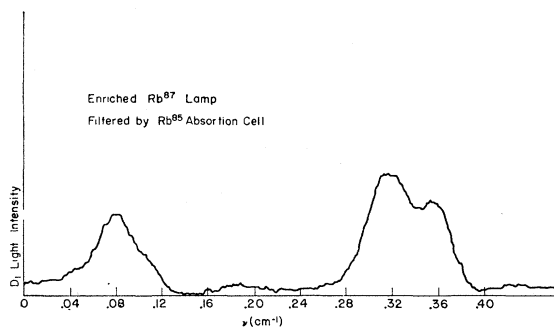
FIG. 4. The Rb $D_1$ line emitted by a Varian spectral lamp containing enriched $Rb^{87}$ metal after being filtered through a cell containing $Rb^{85}$ vapor. The component on the left arises from transitions to the $F=2$ sublevel of the ground state and the component on the right from transitions to the $F=1$ sublevel.
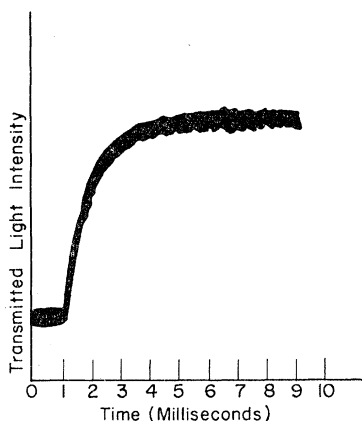
FIG. 5. A reproduction of a photograph showing the time dependence of the transmitted light intensity (the optical pumping signal). Pumping action of the light begins at about 1 msec.

Measurements of $S_x/S$ at 90°C yield a result of $(0.107\pm0.001)$. These measurements were made at low light levels and, therefore, low polarization corresponding to the assumptions in the signal calculations. Figure 5 shows a photograph used in measuring $R$. Figure 6 shows a plot of the $\ln(1-P_1/P_0)$ versus time for incident $I_0$ and $I_0/2$. These data were obtained at 50°C. Four points were plotted for each trace and the slopes determined by a least-squares fit. Measurements were also made on $Rb^{87}$ at 60°C and the direct optical pumping signal for $Rb^{85}$ at 57°C. All experimental values of $R$ determined from these measurements agreed to within 5%. It was concluded that to within this accuracy, $R$ for $Rb^{85}$ and $Rb^{87}$ were equal. The results yield $R = (413\pm21)$ sec$^{-1}$.

Measurements on the spectral traces of the transmitted $Rb^{87}$ $D_1$ high-frequency hyperfine component at room temperature and at 90°C yield a density $N = (3.33\pm0.37)\times10^{11}$ atoms/cm$^3$. At 90°C, the peak absorption was about 70%. The half-width of the absorption line was measured to be 0.039 cm$^{-1}$. This is

about twice the Doppler width of the absorption line. However, it must be noted that the hyperfine line actually contains two components in the intensity ratio of 5 to 1 separated by 0.025 cm$^{-1}$. Also, the absorption occurred in an atmosphere of 28 mm of Ne. Apparently no information is available on broadening of the Rb resonance lines in Ne, but Ch'en[15] has measured the broadening of Rb lines in argon. The result for argon indicates a half-width due to pressure broadening of 0.023 cm$^{-1}$. Under the assumption that Ne produces a similar width, the present half-width measurement seems reasonable. Other structures in emission were measured to have a half-width of 0.030 cm$^{-1}$, showing that the width observed is not predominantly instrumental. The theoretical resolving limit was calculated to be about 0.008 cm$^{-1}$. An estimated value for the resolving limit was taken to be about 0.019 cm$^{-1}$, halfway between the limits of 0.008 cm$^{-1}$ and 0.030 cm$^{-1}$. Calculations of finite resolution corrections to integrated



FIG. 7. Spectral profiles of high-frequency hyperfine component of the $Rb^{87}$ $D_1$ line transmitted through the optical pumping cell at (a) 90°C and (b) room temperature. $\Delta\nu$ is approximate resolving limit of the Fabry-Perot interferometer. These traces were used to determine $Rb^{87}$ vapor density.
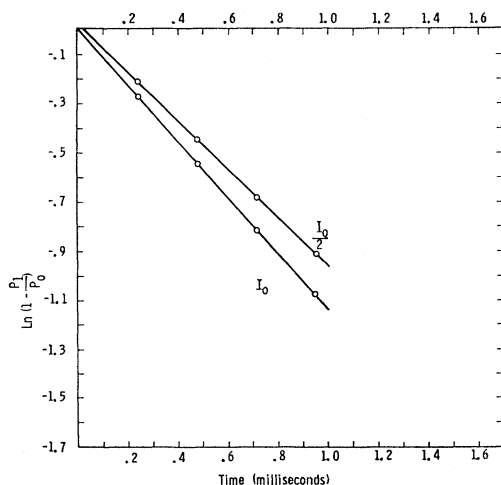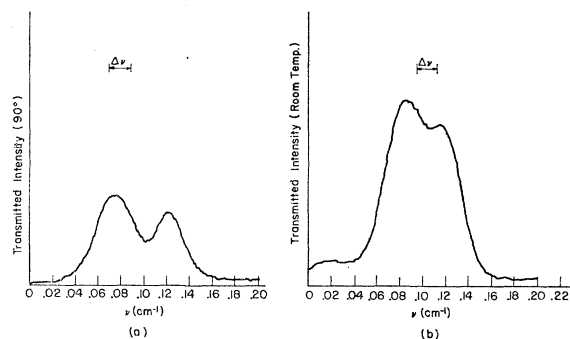


FIG. 6. Graph used to determine relaxation time. Two straight lines shown are for two different ($I_0$ and $I_0/2$) values of the pumping light intensity.

absorption coefficient measurements reported by Kostkowski and Bass[16] indicate a correction of $+3\%$ with an uncertainty of $\pm2\%$ due to the uncertainty in the width and shape of the bandpass function for the interferometer. This correction was applied to the raw data. Other sources of error were the uncertainty in the actual zero of light on the spectral traces, signal to noise considerations, and the uncertainty in the lifetime measurements. Figure 7 shows an example of traces which are compared to yield the integrated absorption coefficient.

Other numerical data needed to calculate the cross section are $a = 2.59$ obtained from the natural abundance percentages for $Rb^{85}$ and $Rb^{87}$, 72.15% and 27.85%,[17] respectively, and $v_r = (4.59\pm0.05)\times10^4$

[15] S. Y. Ch'en, Phys. Rev. 58, 1051 (1940).

[16] H. J. Kostkowski and A. M. Bass, J. Opt. Soc. Am. 46, 1060 (1956).

[17] Handbook of Chemistry and Physics (Chemical Rubber Publishing Company, Cleveland, 1960), 41st ed., p. 463.

cm/sec. The uncertainty given for $v_r$ is due to an allowed $\pm10°$C uncertainty in the cell temperature as measured by a mercury thermometer placed in the oven containing the optical pumping cell.

The data of this experiment yields a spin-exchange cross section for Rb⁸⁵-Rb⁸⁷ collisions of $(1.70\pm0.21)\times10^{-14}$ cm². The early work of Franken, Sands, and Hobart[5] and Novick and Peters[6] yielded cross sections of $5\times10^{-14}$ cm² for Na-K collisions and $2\times10^{-14}$ cm² for Na-Rb⁸⁵ collisions. These results were considered to be reliable within a factor of 3 of the quoted values. The uncertainty was primarily due to unreliable density estimates. With the use in the present work of the interferometric technique of density measurement, estimated to be reliable to $\pm11\%$, this type of uncertainty was largely overcome. The total error quoted for the cross section is closely related to a 70% confidence interval. The result presented is in reasonable agreement with measurements of Rb⁸⁵-Rb⁸⁵ and Rb⁸⁷-Rb⁸⁷ spin-exchange collision cross sections performed

by Moos and Sands[18] in this laboratory using an electron paramagnetic resonance technique.

[18] T. Stark and R. H. Sands have kindly informed us by private communication of recent results for both isotopes of Rb based on the Ph.D. thesis of H. W. Moos at the University of Michigan, 1961 (to be published).

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# Interaction of Optical and Infrared Radiation with Metastable Hydrogen Atoms

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(Received 1 August 1963)

This paper is an extension of a previous one and discusses the theory of the quenching of the metastable $2S$ state of atomic hydrogen by means of optical radiation, for example by the light from a ruby laser. The case discussed is that for which the incident intensity is sufficiently weak for the usual quantum-electrodynamical perturbation theory to be valid. A procedure developed by Schwartz and others is used to carry out the sum over intermediate states without explicit enumeration. The results are given for a range of incident wavelengths from 5000 Å to 50 $\mu$. For unpolarized light from a ruby laser (6934 Å), the total cross section for quenching is found to be $\sigma_Q = 1.27\times10^{-22}$ cm². The cross section for coherent scattering has also been calculated for the same range of wavelengths; for ruby laser light, the total cross section for scattering is found to be $\sigma_S = 1.03\times10^{-23}$ cm².

## 1. INTRODUCTION

IN a previous paper,[1] hereinafter referred to as I, an approximate calculation was reported for the quenching of the atomic hydrogen $2S$ state by means of the light from a ruby laser. It was concluded that, (a) the process can be analyzed by means of the usual quantum-electrodynamical perturbation theory[2] provided that the peak electric-field strength in the laser beam is less than about $10^7$ V/cm, and that if this is the case, then, (b) the process consists mainly of virtual excitation to the $3P$ state followed by spontaneous decay to the $1S$ ground state.

In this paper the treatment is restricted to the weak-field case but all possible intermediate states, including those in the continuum, are taken into account.

[1] W. Zernik, Phys. Rev. 132, 320 (1963).
[2] See, for example, W. Heitler, *The Quantum Theory of Radiation* (Clarendon Press, Oxford, 1954), 3rd ed.

In addition, numerical results for the quenching cross section are given for a range of incident wavelengths from 5000 Å to 50 $\mu$, essentially covering the range of currently available laser frequencies. The maximum intensity of the incident radiation for which the results are valid is a function of the frequency, as explained in I. In particular, the theory breaks down completely in the neighborhood of the Balmer frequencies.

## 2. PERTURBATION THEORY RESULTS

As indicated in I, second-order perturbation theory yields a cross section for quenching given by:

$$\frac{d\sigma}{d\Omega} = r_0^2 \left\{ k_1^3 k_0 \left| \sum_i \frac{(\boldsymbol{\varepsilon}_0 \cdot \mathbf{r}_{i0})(\boldsymbol{\varepsilon}_1 \cdot \mathbf{r}_{fi})}{E_0 - E_i + k_0} + \frac{(\boldsymbol{\varepsilon}_1 \cdot \mathbf{r}_{i0})(\boldsymbol{\varepsilon}_0 \cdot \mathbf{r}_{fi})}{E_0 - E_i - k_1} \right|^2 \right.$$
$$\left. + k_2^3 k_0 \left| \sum_i \frac{(\boldsymbol{\varepsilon}_0 \cdot \mathbf{r}_{i0})(\boldsymbol{\varepsilon}_2 \cdot \mathbf{r}_{fi})}{E_0 - E_i - k_0} + \frac{(\boldsymbol{\varepsilon}_2 \cdot \mathbf{r}_{i0})(\boldsymbol{\varepsilon}_0 \cdot \mathbf{r}_{fi})}{E_0 - E_i - k_2} \right|^2 \right\}. \quad (1)$$