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Temperature Dependence of Hyperfine Pressure Shifts. I. Deuterium in Helium from -135 to 400°C*

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Spin-exchange optical pumping has been used to measure the hyperfine pressure shift of deuterium in helium as a function of temperature. A new technique for optical pumping at low temperatures has been combined with a previously reported technique for optical pumping at high temperatures to make measurements between -135 and 400°C. The experimental results are compared with existing theoretical calculations.

I. INTRODUCTION

The precise measurements of hyperfine structure by optical pumping techniques have revealed slight frequency shifts which depend on the buffer gas. Although the initial impetus for using these buffer gases was to eliminate the Doppler shift and also to inhibit wall collisions, the shifts themselves have become of interest as a method for testing theoretical interatomic interactions. It has been found that the hyperfine intervals depend essentially linearly upon buffer gas density up to the equivalent of several atmospheres of pressure at room temperature.¹ This effect has unfortunately been called a pressure shift and for the sake of conventional usage we will continue to do so although the distinction, especially when measurements are made over an extended temperature range, can be a source of confusion.

Pressure-shift measurements have been made on the hydrogen isotopes,²⁻⁴ the alkalis,⁵⁻¹⁰ and nitrogen¹¹ and phosphorous,¹² and a number of theoretical calculations have been made in an attempt to understand these shifts.^{13,14} Recently, Das and co-workers have made extensive calculations on both the hydrogen-helium system^{15,16} and the nitrogen-helium¹⁷ system. This experiment was designed to test the theoretical results for the hydrogen-

helium system; results of a similar experiment on the nitrogen-helium system will be reported at a later date.

The theoretical interpretation of pressure shifts has, for the most part, been based on a statistical model in which the shift $\Delta A(R)$, due to a single buffer gas atom, a distance R from the atom in question is computed. It is believed the shift is the result of both van der Waals and overlap forces. This shift is then weighted with the probability $e^{-V(R)/kT}$ of finding a buffer gas atom a distance R away. Here, $V(R)$ is the interatomic potential. The final result for the shift of the magnetic dipole interaction constant A is written

$$\langle \Delta A \rangle = \rho \int e^{-V(R)/kT} \Delta A(R) dT,$$

where ρ is the buffer gas number density.

In the past, experimental values for the pressure shift could only be measured for very restricted temperature ranges. At these temperatures the theoretical predictions were only in fair agreement with experiment. It is now possible to measure the pressure shift over a greatly extended temperature range. This development enables one to test the theory in considerably more detail. In particular, it may be possible to distinguish between errors in the calculations of $\Delta A(R)$ and the

interatomic potential $V(R)$.

Recently we reported^{18,19} a technique for alkali optical pumping at high temperatures. We have discovered that the same apparatus can be modified to obtain optical pumping signals at very low temperatures as well. We have used the combination of the two techniques to study the temperature dependence of the hyperfine pressure shift of deuterium in helium from -135 to 400 °C. The D-He system is of particular theoretical interest because of its relative simplicity. Within the precision of present optical pumping experiments, the fractional pressure shift is the same for all of the hydrogen isotopes.² We chose deuterium because of the ease with which the rf field which stimulated the transitions could be generated.

In Sec. II we describe the experimental technique. This is followed by a discussion of the measurements and a comparison of our results with previous experiments and theory.

II. EXPERIMENTAL TECHNIQUE

A block diagram of the apparatus is shown in Fig. 1. Its use for high-temperature measurements has been fully described in Refs. 18 and 19. The optical pumping cell contains Rb, He buffer gas, and D_2 gas. The Rb atoms are polarized in a weak magnetic field through the absorption of circularly polarized resonance radiation. Deuterium atoms, produced in an rf discharge, are polarized by spin-exchange collisions with the optically pumped Rb atoms. When an rf field is applied at the hfs resonance frequency, the D atoms are depolarized, and the spin-exchange collisions depolarize the Rb atoms, resulting in a decrease in the intensity of the pumping light transmitted by the cell.

In the conventional optical pumping apparatus, Rb is present on the walls of the optical pumping cell, and the density of Rb atoms depends upon the vapor pressure of Rb. Because of the exponential temperature dependence of the Rb vapor pressure, such an arrangement can be used only at temperatures near room temperature. In order to perform optical pumping experiments far above or below room temperature, the Rb density must be controlled independently of the temperature of the cell.

For high-temperature measurements, the optical pumping cell is situated in an oven heated by a stream of hot air. The Rb metal is contained in an air-cooled sidearm attached to the cell. The oven determines the cell temperature, and the density of Rb atoms in the cell is controlled by adjusting the flow of air which cools the sidearm.

For optical pumping at low temperatures, the hot and cold air connections are simply interchanged. The cell is then cooled by a flow of cold nitrogen gas, and the proper Rb density is maintained by heating the sidearm with hot air. This drives Rb into the cell at an easily regulated rate. As the Rb is driven into the cell and diffuses to the walls it plates out on the walls, but the rate of deposit is so slow that it presents no problem. The nitrogen gas is cooled by bubbling it through liquid nitrogen. The dry nitrogen was used to prevent frost from forming on the cell, and the outside of the oven windows were warmed by jets of hot air to keep them frost free as well.

The optical pumping cells were 300-cm^3 Pyrex spheres with glass-covered electrodes mounted in a turret above the cell. The rf discharge was very weak and did not measurably affect the cell temperature. The cells were prepared for high-temperature use as described in Ref. 18 and could then

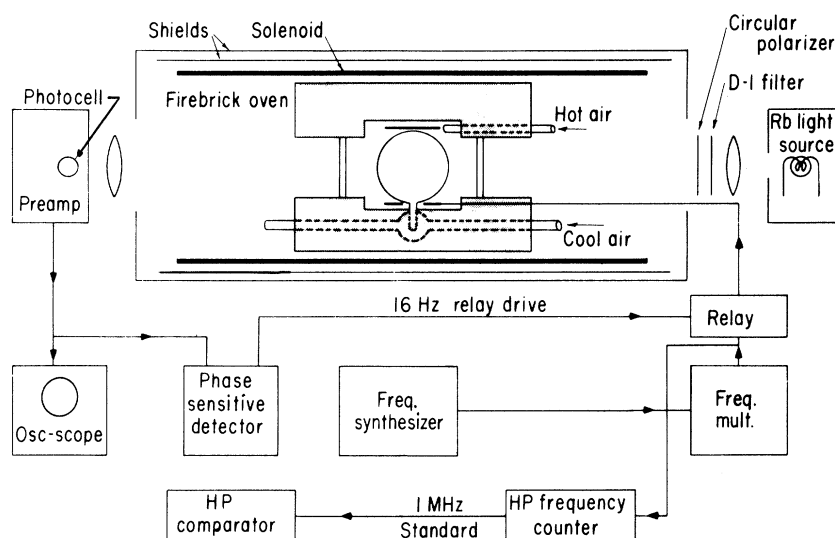


FIG. 1. Block diagram of the optical pumping apparatus.

be immediately used for low-temperature measurements as well.

Whereas, the high-temperature technique worked well in our apparatus for both high and low buffer gas pressures, optical pumping at low temperatures became more difficult with increasing pressure until the heat required at the sidearm to maintain the Rb density in the cell became excessive.

At a given pressure, essentially the same amount of sidearm heat was required at all temperatures below -10°C . Although the optical pumping signals were excellent, we could not go below -135°C because of our inefficient cooling method. Nothing indicated that the technique would not work at far lower temperatures.

III. MEASUREMENTS

The deuterium hfs was measured as a function of temperature at helium pressures of 94.4, 192.6, and 264.7 Torr at a filling temperature of 300°K . The helium pressures were measured with a Hg manometer, and the estimated error is 2 Torr. The observed temperature dependences are shown in Fig. 2. Each cell contained approximately 2 Torr of D_2 gas. This pressure was measured with an oil manometer. Measurements of the hfs in a cell containing only D_2 as a buffer gas showed that this pressure of D_2 did not contribute to the observed temperature shifts.

Measurements were made on both the ($F = \frac{3}{2}$, $M_F = \pm \frac{1}{2} \leftrightarrow F = \frac{1}{2}$, $M_F = \mp \frac{1}{2}$) and the ($F = \frac{3}{2}$, $M_F = \pm \frac{3}{2} \leftrightarrow F = \frac{1}{2}$, $M_F = \pm \frac{1}{2}$) transitions in a static field

of 4 mG. Although the former transitions were essentially field independent, and therefore preferable for determining the hyperfine splitting, they were only observable up to 250°C . Ten measurements of this transition were made at each temperature. Each measurement was the average of two half-power point determinations. The sense of circular polarization was reversed halfway through the measurements to cancel any spin-exchange frequency shifts. Between 250 and 400°C only the field-dependent transitions were observable. For this case, four measurements of the hyperfine interval were made. Each measurement consisted of the average of two transition frequencies and each transition frequency was the result of four half-power measurements. There was a surprising decrease in both Zeeman and hyperfine signals in D with increasing temperature. The linewidth of the field-dependent transitions increased from 120 Hz at 80°C to 400 Hz at 400°C . The field-independent transition behaved similarly. No signals could be measured above 400°C . This behavior was in sharp contrast to that found in a similar experiment performed concurrently on atomic nitrogen in which no strong temperature dependence of the signal amplitude was found. The apparently strong temperature dependence of the D hyperfine relaxation warrants further investigation.

With the linewidths discussed above, the transitions were reproducibly measured to better than 5 Hz at all temperatures.

The temperature of the cells was measured with two thermocouples cemented to the outside of the

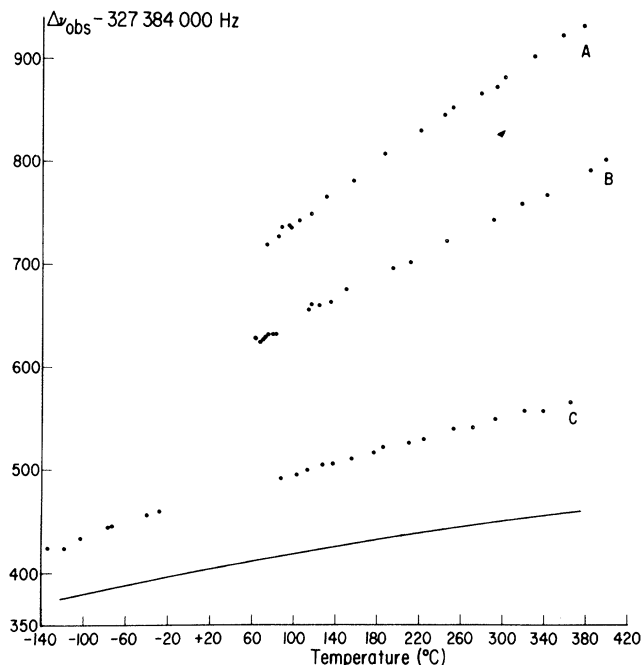


FIG. 2. Measured values for the D hyperfine splitting as a function of temperature are shown for He densities corresponding to pressures of 264.7, 192.6, and 94.6 Torr at 300°K in curves A, B, and C, respectively. Within experimental error, the observed temperature dependence of the pressure shift is proportional to the buffer gas density as is expected. A comparison between experiment and the calculations of Ray and Das need only be made at one pressure. The equivalent theoretical curves for 264.7 Torr and 192.6 Torr were omitted to avoid confusion in the figure. The solid curve is the temperature dependence predicted by Ray and Das for a He pressure of 94.6 Torr.

cell at hot and cold spots. The temperature gradient across the cells was always less than 10°C . Temperature measurements on a dummy cell with a thermocouple inside it indicated that the probable error in the temperature measurements is 10°C .

IV. COMPARISON WITH THEORY

We begin with a comparison of theory and experiment near room temperature. The experimental data above 60°C were well fitted by straight lines; these were used to compute both the fractional pressure shift (fps) and its temperature derivative. Extrapolating our data gives a fps of $(4.1 \pm 0.2) \times 10^{-9}/\text{Torr}$ at 50°C . This can be compared with the previous experimental value⁴ of $(4.4 \pm 0.1) \times 10^{-9}/\text{Torr}$ for a comparable temperature ($45 \pm 5^\circ\text{C}$). Theoretical calculations by Clarke¹⁴ and Ray, Lyons, and Das¹⁵ give $1.73 \times 10^{-9}/\text{Torr}$ and $1.9 \times 10^{-9}/\text{Torr}$, respectively. Clarke's calculation was for a temperature of 50°C ; we presume this was also true for the work of Ray *et al.*

The experimental value for the temperature derivative of the fps was $(8.26 \pm 0.61) \times 10^{-12}/\text{Torr}/^\circ\text{C}$ at 50°C . The theoretical values were $3.97 \times 10^{-12}/\text{Torr}/^\circ\text{C}$ for Clarke and $6.12 \times 10^{-12}/\text{Torr}/$

$^\circ\text{C}$ for Das and co-workers.¹⁶

Ray and Das¹⁶ have computed the fps over an extended temperature range. Their computations applied to a pressure of 94.4 Torr are shown in Fig. 2 along with our data.

V. CONCLUSION

Although the calculations of both Clarke and Ray, Lyons, and Das fail to accurately predict the pressure shift at 50°C , it is clear from Fig. 2 that the temperature dependence predicted by Ray and Das is much more accurate than their calculated fps. The observed temperature dependence should be quite helpful in making improvements in the theory. It is clear from this experiment that Clarke's calculations are much less successful in predicting the correct temperature dependence.

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