Temperature dependence of hyperfine density shifts. III. ²³Na, ³⁹K, and ⁸⁵Rb in He, Ne, Ar, and N₂

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The method of high-temperature optical pumping has been used to measure the temperature dependence of the fractional hyperfine density shifts of ²³Na, ³⁹K, and ⁸⁵Rb in He, Ne, Ar, and N₂ buffer gases over the temperature range 25–850 °C. The first definite nonlinear temperature dependence has been found. All three alkali metals showed definite maxima in Ne, as did K and Rb in N₂ and Na in Ar. In addition, Na in Ar has a zero density shift at 625 ± 25 °C. Cubic and quartic polynomial fits of the density shifts versus $1/kT$ have been calculated for each alkali metal and gas.

I. INTRODUCTION

Optical pumping has been used in the past for measurements of the hyperfine structure of many atoms.[1] Buffer gases, which were originally inserted to eliminate the Doppler shift and to decrease wall collisions, were found to cause slight shifts in the hyperfine frequencies.[2-7] These frequency shifts, which became known as pressure shifts, depend linearly on the buffer-gas pressure up to a pressure of several atmospheres.[8] The shifts also depend on the temperature.[9] With the advent of techniques for high-temperature optical pumping[10] came the possibility of pressure-shift measurements over an extended temperature range.

There have been many theoretical calculations of the temperature dependence of pressure shifts as well as experimental measurements. The most extensive theoretical work has been done for H in He,[11-13] and for N in He, Ne, and N₂.[14,15] The experimental data were furnished by Wright[16,17] for H and Weiss *et al.*[18] for N. Other experimental measurements have also been made over very limited temperature ranges. As a result of a calculation by Ray *et al.*[19] in 1970 for ²³Na, we concluded that pressure-shift measurements of the alkali metals over an extended temperature range would be useful for further understanding of the effect. We have therefore measured the fractional pressure shifts of ²³Na, ³⁹K, and ⁸⁵Rb and He, Ne, Ar, and N₂ over the temperature range 25–850 °C.

We will define the "fractional hyperfine density shift" (a more useful term than pressure shift, especially when measurements at different temperatures are taken) as $(1/\nu_0)(\nu - \nu_0)/D$, where ν is the shifted hyperfine frequency in the presence of the buffer gas, ν_0 is the free-atom hyperfine frequency, and D is the density of buffer-gas atoms. It has been calculated (assuming only two-body interactions)[20] by first considering the fractional shift $\Delta\nu(R)/\nu_0$ due to a gas atom a distance R from an alkali-metal nucleus and then taking a classical average over all possible alkali-metal-gas configurations:

$$\frac{(1/\nu_0)(\nu - \nu_0)}{D} = \int \frac{\Delta\nu(R)}{\nu_0} \exp\left(\frac{-V(R)}{kT}\right) d^3R . \quad (1)$$

The Boltzmann weighting factor contains the interatomic potential $V(R)$.

Most calculations[13,21,22] have involved treating the density shift in terms of distinct short-range and long-range effects, with a cutoff interatomic distance to separate the two effects. There have also been a few attempts[23] at unified calculations not involving cutoffs.

In Sec. II we will briefly describe the apparatus and the method of taking measurements. Then we will present the data and discuss their significance.

II. MEASUREMENT PROCESS

Diagrams of the apparatus are shown in Figs. 1 and 2. Alkali-metal resonance radiation was filtered to select the D_1 line, which was then cir-
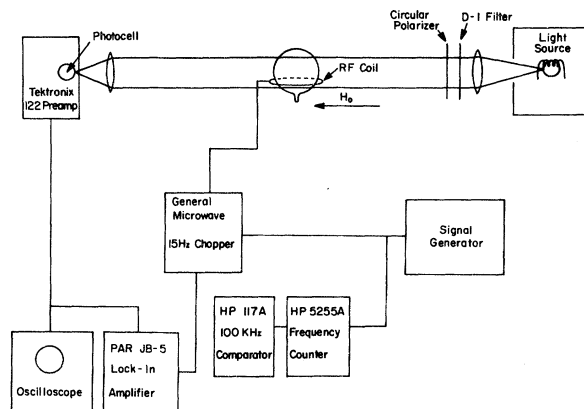

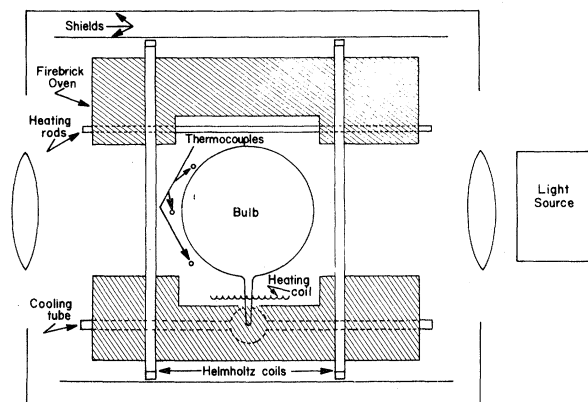FIG. 1. Block diagram of the optical-pumping apparatus.

FIG. 2. Oven used for high-temperature optical pumping.

cularly polarized. This radiation passed through an optical pumping cell which contained the alkali metal and a buffer gas. The alkali-metal atoms were polarized in a weak magnetic field through the absorption of circularly polarized resonance radiation. When an rf field was applied at the hfs resonance frequency, the alkali-metal atoms became depolarized; this resulted in a decrease in the intensity of the pumping light transmitted by
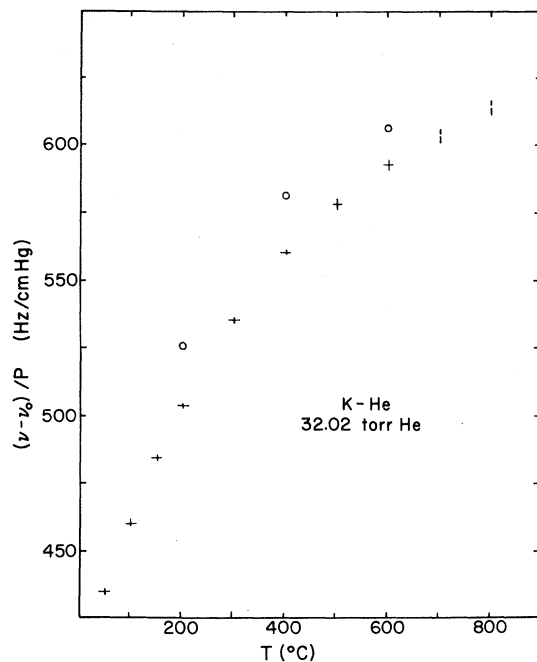

FIG. 3. Measured hyperfine pressure shift of ^{39}K in He as a function of temperature with an initial pressure of 32.02-Torr He. The open circles are data taken as the bulb was cycled from low to high temperatures, and the crosses are data taken from high to low temperatures.
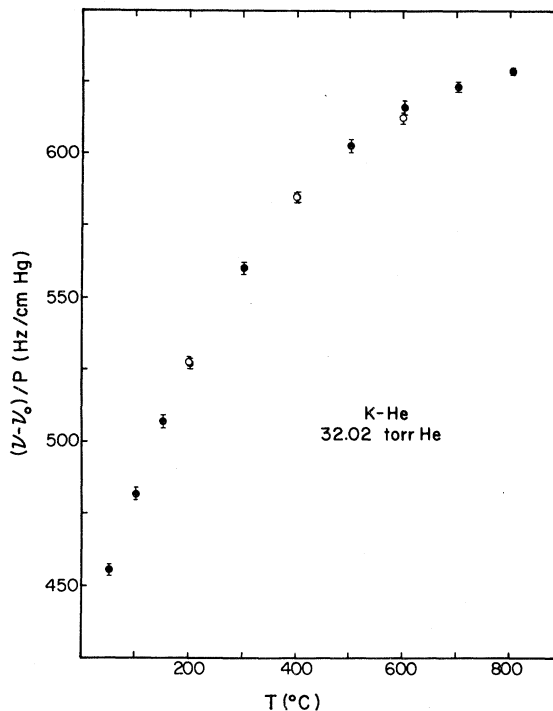

FIG. 4. Corrected hyperfine pressure shift of ^{39}K in He as a function of temperature for the same bulb. The open circles are again the first part of the temperature cycle, and the closed circles are the second part of the cycle.

the cell.

High-temperature measurements were made by situating the optical pumping cell in an oven heated by carbon rods and a coil. The alkali metal was contained in an air-cooled tip attached to the cell. The oven determined the cell temperature, and the density of alkali-metal atoms was controlled
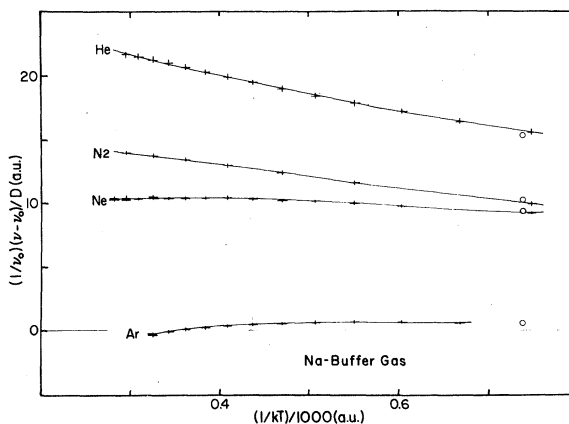

FIG. 5. Fractional hyperfine density shifts of ^{23}Na in He, Ne, Ar, and N_2 as a function of $1/kT$. The solid lines are polynomial fits to the data, and the open circles are the measurements of Ramsey and Anderson (Ref. 7)
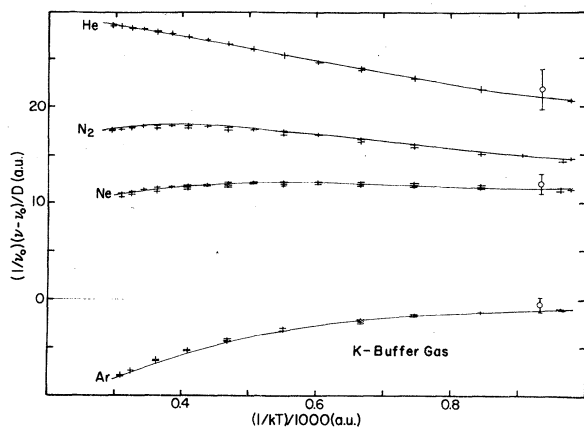
FIG. 6. Fractional hyperfine density shifts of ^{39}K in He, Ne, Ar, and N_2 as a function of $1/kT$. The solid lines are polynomial fits to the data, and the open circles are the measurements of Bloom and Carr (Ref. 4).

FIG. 8. Fractional hyperfine density shift of ^{85}Rb in Ne as a function of $1/kT$. The scale has been expanded.

by adjusting the flow of air which cooled the cell tip.

Much of the equipment used has been described.[16,18] The major differences were in the light sources and the signal generation. The light sources for Rb and K were 25-cm^3 flasks surrounded by a coil connected to the output of a 50-MHz transmitter, with the tips of the bulbs heated to give a maximum intensity of resonance radiation. For the Na experiment, a G.E. Na-1 light bulb was placed in a specially constructed oven, and the D_2 line was removed by self-reversal.[24] The rf hyperfine frequencies were generated by

three separate signal generators. For Na and Rb, these generators were PRD S712B and L712B signal sources phase locked by a Microwave Systems MOS-1 frequency stabilizer. We also used a General Microwave chopper and attenuator and PRD isolators, all connected by semirigid coaxial cable. For potassium we used a General Radio 1164A frequency synthesizer and rf Communications 805 amplifier as well as a chopper and attenuators. For all measurements, the frequency was stable to 3 Hz/h, and the frequency counter was accurate to better than one part in 10^9.

The bulbs were Pyrex or G. E. fused quartz and were prepared on a vacuum system in the usual manner.[25] For the distillation of Na, we found that if we distilled only a small amount of Na at a time, forming a fine film on the bulb, the bulb did not brown while the Na was being driven into the tip.
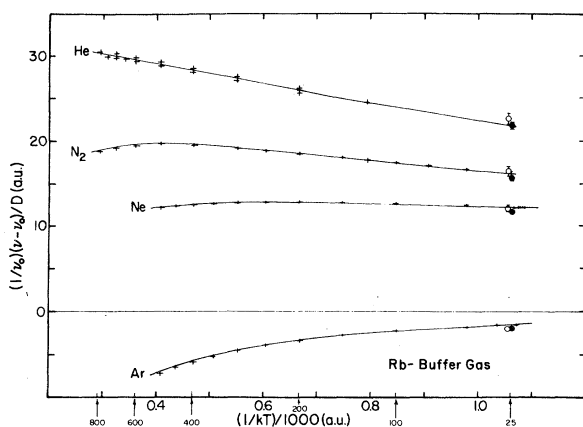
FIG. 7. Fractional hyperfine density shifts of ^{85}Rb in He, Ne, Ar, and N_2 as a function of $1/kT$. The solid lines are polynomial fits to the data. The open circles are the measurements of Bender et al. (Ref. 3), and the closed circles are the data of Vanier et al. (Ref. 27). The arrows on the x axis show the temperature in deg. centigrade.
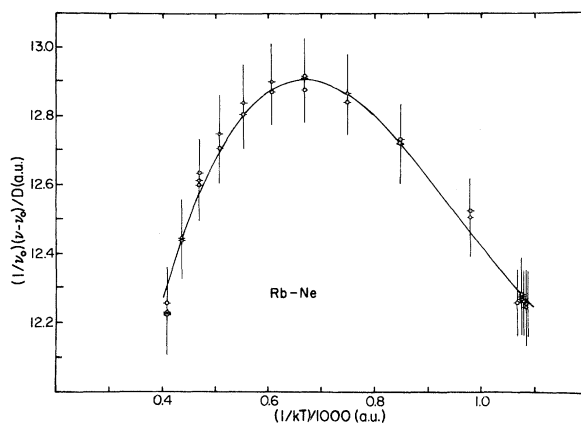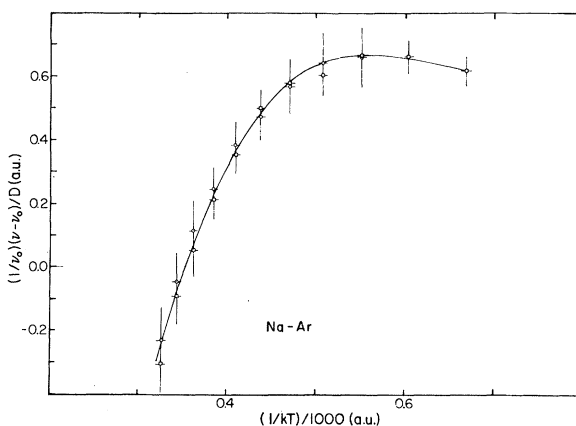
FIG. 9. Fractional hyperfine density shift of ^{23}Na in Ar as a function of $1/kT$. Again the scale has been expanded.

The measurements were made on the $(F=2,$ $M=\pm 2 \leftarrow F=1,\ M=\pm 1)$ transitions for Na and K and the $(F=3,\ M=\pm 3 \leftarrow F=2,\ M=\pm 2)$ transitions for Rb in a static field of about 5 mG. Sets of five or ten measurements were taken for each data point, and a measurement consisted of two values of each of the pair of transitions. Line-widths of the transitions ranged from 110 to 360 Hz for Na, from 60 to 160 Hz for K, and from 120 to 360 Hz for Rb.

The temperature in the cells was measured with three thermocouples in contact with the outside of the cell, and the cell was held at a given temperature for a few minutes in order to achieve thermal equilibrium. Thermal gradients from top to bottom of the cell were no greater than 25 °C at the higher temperatures and significantly smaller for lower temperatures.

The following parameters were checked for their effects upon the hyperfine frequency. First, the external magnetic field was oriented both parallel and antiparallel to the direction of the light beam. Second, the sense of the circular polarization was reversed. Third, the intensity of the resonance lamp was decreased to record any observable light shifts. Finally, the position of the rf coil was changed with respect to the bulb. None of these parameters affected the observed frequencies within the statistical error.

The measurements in He involved a calculation of the leakage of He out of the quartz bulbs at high temperatures. Each bulb was measured as the temperature was cycled from low to high and back to low temperatures, and the time was recorded as the temperature was varied. Then the leakage was calculated[26] and the density shifts fitted numerically, with the bulb thickness as a variable parameter. Figures 3 and 4 show the measured

and corrected data for one quartz bulb. Leakage of the other gases is much less[26] and could be ignored.

III. RESULTS

Graphs of the fractional hyperfine density shifts versus $1/kT$ are given in Figs. 5–7 (previous measurements[3,4,7,27] are plotted as circles), and two representative curves, for Rb in Ne and for Na in Ar, which show the behavior in more detail are given in Figs. 8 and 9. All calculations were done using atomic units $(e = \hbar = m_e = 1)$. The solid curves are polynomial fits to the data,

$$(1/\nu_0)(\nu - \nu_0)/D = c_0 + c_1 x + c_2 x^2 + c_3 x^3 + c_4 x^4,$$

$$(2)$$

where $x = \frac{1}{1000}(1/kT)$ and the polynomial coefficients are listed in Table I. In order to convert from the density shift in atomic units to the more familiar $(\text{Torr}^{-1}$ at $T = 300\,°\text{K}$, multiply the value in atomic units by 4.7464×10^{-9}. Cubic fits were required for all curves except for Na in He (quadratic fit) and for K in N_2 and Rb in N_2 (quartic fit). A graph of the raw data of hyperfine frequency versus temperature for one Rb-in-Ne bulb is also included (Fig. 10) to show distinctly the nonlinear temperature dependence.

Each alkali-metal and gas measurement involved two bulbs at different pressures, and extrapolations to zero pressure were consistent with the free-atom hyperfine values.[28,29]

The errors associated with the density-shift measurements are listed in the last column of Table I. We have calculated the error for each measurement of a bulb by including the uncertainties in the temperature (thermal gradients across the oven), the pressure (mercury and oil manometers were read to 1 mm), and the frequency (stan-

TABLE I. Polynomial fit coefficients for fractional density shift vs $(1/kT)(\frac{1}{1000})$.

| Alkali	Buffer gas	Temperature range (°C)	c_0	c_1	c_2	c_3	c_4	Error in $(1/\nu_0)(\nu-\nu_0)/D$ (a.u.)
Na	He	150–800	27.586	−22.188	8.1413			0.222
	Ne	150–850	6.8885	22.948	−45.235	25.144		0.126
	Ar	200–700	−8.1423	42.723	−68.253	35.813		0.114
	N_2	150–800	15.031	2.3090	−24.674	16.766		0.147
K	He	50–800	30.964	−3.2185	17.984	10.783		0.291
	Ne	50–750	5.1044	29.720	−39.725	16.331		0.411
	Ar	50–750	−20.831	59.825	−64.090	24.147		0.276
	N_2	50–750	8.6352	62.228	−139.31	122.34	−39.475	0.298
Rb	He	25–800	32.884	−5.1726	−11.882	6.6533		0.748
	Ne	25–800	7.6321	19.280	−22.125	7.6476		0.111
	Ar	25–800	−21.840	53.783	−50.287	16.593		0.252
	N_2	25–800	6.1642	86.223	−190.83	172.16	−57.051	0.191
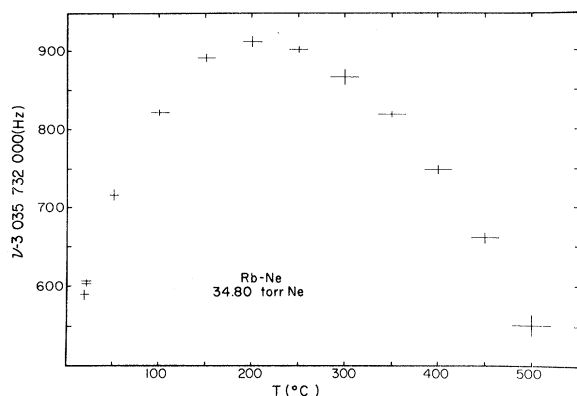
FIG. 10. Hyperfine splitting of ^{85}Rb in 34.80 Torr of Ne as a function of temperature.

dard deviation for each set of five or ten measurements).

Measurements of the temperature dependence of density shifts are extremely important for calculations of the frequency shifts. Since these calculations include both the interatomic potential and the wave function for the system, we can only check the behavior of each quantity separately if we take measurements over an extended temperature range.

The results of the measurements seem noteworthy in several respects. First, we have seen the first definite nonlinear temperature dependence. All three alkali metals showed definite maxima in Ne, as did K and Rb in N_2 and Na in Ar. The other measurements also gave varying curvatures. Second, the curve of Na in Ar passes through zero at $625 \pm 25\,°C$. This point corresponds to a rough balance of the Van der Waals and exchange forces; and this zero shift, although calculated previously for other atoms, has not been observed before. Finally, it is hoped that the results of all our measurements can lead to significantly better calculations of density shifts both for these and other atoms.

ACKNOWLEDGMENTS

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