Pressure Shifts in the Hyperfine Structure Constant of Potassium

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Optical pumping and detection methods were used to determine the resonant frequency of the K^{39} $m=0 \rightarrow$ m=0 hyperfine line in various environments. Frequency shifts were observed in noble gases and in hydrogen; no shift was observed from a paraffin wall coating. The shifts, expressed as fractional changes in the hyperfine frequency, are similar to those in rubidium though generally somewhat smaller. The hyperfine constant itself was determined for both K³⁹ and K⁴¹.

PRESSURE shifts of the ground-state hyperfine constant in alkali metal vapors are of interest because of information they can give on short-range forces between alkali and buffer atoms, and because of the possible use of the hyperfine constants as standard reference frequencies.^{1,2} We report here pressure shifts in K³⁹, obtained by an optical detection method.³ In the course of these measurements we have redetermined the zero-pressure hyperfine constant of K³⁹ and K⁴¹ and we have examined hyperfine resonances in evacuated cells containing potassium and a wall coating⁴ of dotriacontane $(C_{32}H_{66})$

The apparatus, shown in Fig. 1, was similar to that of an earlier sodium hyperfine demonstration⁵ except for the use of a reentrant cavity with two absorption cells in parallel in the optical path. Observation of the field-independent $(m=0 \rightarrow m=0)$ transition by this method depends on an intensity difference between hyperfine components of the optical resonance lines; in potassium the signal can be expected to be weak because of the closeness of the hyperfine doublet and consequent imperfect separation in resonance absorption. Since buffer gases can broaden the optical absorption, the signal amplitude might also be expected to be highly dependent on buffer pressure. We found it difficult to observe signals in cells containing more than 3 cm Hg of argon or 1 cm Hg of krypton, although up to 5 cm Hg was used with the lighter gases. That this is at least partially an optical effect, and not due to some other cause such as thermal relaxation, is shown by the fact that field-dependent signals in argon buffer observed by circularly polarized light, where the detection depends only on selection rules,3 were unimpaired by the high-pressure buffer (krypton is known to shorten thermal relaxation times and here all signals were observed to be weak).

The lamp was a small 100 Mc/sec electrodeless discharge. The absorption cells were 2×3 -in. cylinders maintained at about 65°C. The operating linewidth was about 500 cps and under these conditions the signal-to-noise ratio was about 20 with a detector bandpass of 10 cps. Frequency measurements were made by counting the crystal frequency (4th subharmonic) for one-second intervals with a Hewlett-Packard 524-C counter whose internal reference frequency is known from rubidium hyperfine resonance experiments to about 1 part in 108. In addition, the use of parallel absorption cells allowed intercomparisons without the possibility of counter drift. The consistency of results obtained on different days suggests a relative uncertainty of about 20 cps in determining line centers. The greatest uncertainty was in the buffer gas pressures,



FIG. 1. Apparatus, with front of cavity removed to show absorption cells and tuning post.

¹ M. Arditi, J. phys. radium **19**, 873 (1958); P. L. Bender, E. C. Beaty, and A. R. Chi, Phys. Rev. Letters **1**, 311 (1958); E. C. Beaty, P. L. Bender, and A. R. Chi, Phys. Rev. **112**, 450 (1958); H. Margenau, P. Fontana, and L. Klein, Phys. Rev. **115**, 87 (1959).

² Smaller shifts have also been observed in hydrogen. L. W. Anderson, F. M. Pipkin, and J. C. Baird, Phys. Rev. Letters 4, 69 (1960).

³ H. G. Dehmelt, Phys. Rev. 105, 1487 (1957).

⁴ H. G. Robinson, E. S. Ensberg, and H. G. Dehmelt, Bull. Am. Phys. Soc. **3**, 9 (1958). ⁵ W. E. Bell and A. L. Bloom, Phys. Rev. **109**, 219 (1958).

which were known only to about $\pm 1 \text{ mm Hg}$ for H₂ and He and $\pm \frac{1}{2} \text{ mm Hg}$ for the other gases.

The values of the pressure shift are shown in Table I. Uncertainties are estimated from the scatter of experimental points taken at different pressures. In addition, temperature variations in the pressure shift have been observed of the order of +1 cps (°C×mm Hg)⁻¹ in He and +0.1 cps (°C×mm Hg)⁻¹ in Ne.

If one computes proportional shift (pressure shift divided by hyperfine frequency) for the various alkalies, one finds that the results in potassium are very similar to those in rubidium and follow the trend wherein shifts for a given buffer retain the same sign and increase slowly in magnitude with increasing alkali atomic number (Table II). It is interesting that this is so, even though the hyperfine frequencies themselves vary by a factor of 20.

Measurements were made on two wall-coated cells. One, a 2×3 -in. cylinder, was freshly prepared and the other, a liter flask, was one year old. Neither showed a shift greater than experimental uncertainty from the extrapolated zero-pressure frequency, nor did they show any temperature shift. The cavity geometry provides essentially constant rf amplitude and phase over the entire absorption cell, and therefore there should be no contribution to the linewidth from Doppler effects. We observed a linewidth of about 300 cps at moderately

TABLE I. Pressure shifts in K^{39} in units of cps (mm Hg)⁻¹. The pressure is at the operating temperature of 65°C, and is assumed to have increased 10% from the filling pressure.

Buff	er gas	Frequency shift	
helin hyd neor argo kryf	um rogen n on oton	$\begin{array}{r} 43 \pm 4 \\ 33 \pm 3 \\ 24 \pm 2 \\ -0.4 \pm 1.4 \\ -42 \pm 5 \end{array}$	

TABLE II. Approximate proportional shifts in the various alkalies. The data for elements other than potassium are obtained from papers in reference 1.

Isotope	Hyperfine constant Mc/sec	Proportional shifts (mm Hg) ⁻¹ ×10 ⁹						
		He	H_2	Ne	Ar	Kr		
Na ²³ K 39	1772	04	73	34 51	0	01		
Rb ⁸⁷ Cs ¹³³	6834 9192	105 114	97 200	57 63	-8 -21	-85 -142		

high light intensities, indicating that the true linewidth in the absence of incident light is probably considerably narrower.

The frequency in a cell containing 2 mm Hg of argon is substantially the zero-pressure frequency. The magnetic field at this cell was determined from the Zeeman resonances. Correcting to zero magnetic field, we obtain, for the K^{39} hyperfine constant:

$$\Delta \nu (K^{39}) = 461~719~690 \pm 30$$
 cps,

this is in close agreement with a recent atomic beam measurement.⁶ The value for K^{41} , obtained in a wall-coated cell containing enriched K^{41} , is

$$\Delta \nu(K^{41}) = 254\ 013\ 870 \pm 35\ cps.$$

The listed uncertainties are cumulative from the uncertainties in estimate of line center, counter calibration, and magnetic field correction.

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⁶ G. Gould and M. McDermott (unpublished).