NONLINEAR HYPERFINE PRESSURE SHIFT BY OPTICAL PUMPING WITH WHITE LIGHT*

E. S. Ensberg and G. zu Putlitz†
Gibbs Laboratory, and Physics Department, Yale University, New Haven, Connecticut
(Received 22 May 1969)

Optical pumping methods have been extended to high buffer-gas pressures by replacing the customary resonance lamp by a white-light source. Rb ground-state Zeeman transitions were detected by resonance fluorescence at argon buffer-gas pressures up to 23 atm. Hyperfine-transition frequencies were measured at 4170 Torr (0°C) and at 7390 Torr (0°C) and showed the first nonlinear pressure dependence so far observed.

We have optically pumped Rb^{85} and Rb^{87} atoms in argon buffer gas at pressures up to 30 atm, by replacing the conventional resonance lamp by a high-pressure, 1-kW, xenon arc lamp. In the white light, the optical absorption rate is independent of the pressure-broadened line shape (0.4 Å per atm)[1] of the Rb atoms, and even the low spectral density of an arc lamp becomes more efficient than a resonance lamp above about 1 atm, the typical upper limit in pressure for previous optical pumping experiments.

Although tungsten-halide lamps operate near 3600°K (maximum intensity at the 7948-Å D line), the hotter Xe arc (Hanovia type 976 C-1) was found to be more efficient. The spectral width of the pumping light was reduced to about 50 Å by a number of filters in the light beam to avoid heating of the sample and instrumental scattering to our detector. With all the apparatus assembled, the short-circuit current of a solar cell in the light beam transmitted through the absorption cell was of the order of 1 mA (5×10^{15} photons/sec). Increasing the Rb vapor pressure by heating the absorption cell decreased the absorption by only a few percent, corresponding to the pressure-broadened width of the Rb D line. However, the resonance-fluorescence light detected by a photomultiplier at right angles to the transmitted beam increased in direct proportion to the Rb vapor pressure. All of our signals were detected in the resonance fluorescence, avoiding the 90% of the light not involved in the pumping process. Since both the detection of atomic polarization and the pumping process itself depend linearly on the optical absorption rate I_0, the signal strength is proportional to I_0^2 (at the intersection of the transmitted and detected beams). Maximum signal occurred near 90°C for the cells we used.

Well-annealed spherical Pyrex absorption cells 5 cm o.d. with walls roughly 4 mm thick were generally strong enough. Each sample was tested hydraulically at 50 atm before use. To avoid high pressures in the filling process, a large glass reservoir of measured volume was attached to the vacuum manifold. After evacuation and distillation of Rb metal (natural abundances) into the absorption cell, the system was filled with argon to the predetermined pressure and the pressure was measured with a Texas Instruments quartz Bourdon tube gauge. The part of the manifold carrying the cell and reservoir was then sealed off and the tip of the cell was immersed in liquid nitrogen to freeze the argon out of the reservoir before sealing off the absorption cell.

At the end of our experiment, we rechecked the pressure in our absorption cells by cracking them in an evacuated 11-liter chamber (the cells were refrozen first for safety), and measuring the final pressure. Then we assembled the cracked cells, remeasured the internal volume of each cell and the volume of the glass, and recalculated the density of argon. Our final measurements were in satisfactory agreement with our initial measurements after allowing for the cell volume change during sealoff and argon left behind in the reservoir in the initial filling process. We follow the custom of expressing the argon density ρ in terms of the pressure reduced to 0°C: "Torr (0°C)." For argon at 10 atm, the perfect gas law is correct to within $\frac{1}{2}$%.

Magnetic-resonance lines were displayed with a phase-sensitive detector and a 3-sec time constant. Unresolved Zeeman lines ($\Delta F=0$) at 180 and 270 kHz for Rb^{85} and Rb^{87}, respectively, were observed for argon pressures up to about 23 atm. Hyperfine ($\Delta F=\pm1$) transition frequencies were measured at about 5 and 10 atm or, more precisely, at $\rho=4170\pm40$ Torr (0°C) and $\rho=7390\pm70$ Torr (0°C). See Fig. 1. All transitions corresponding to $\Delta m_F=\pm1$ were observed. No transitions corresponding to $\Delta m_F=0$ were observed, as expected for complete excited-state mixing where the collision rate is large compared with the hyperfine frequency.[2] To demonstrate the $^2P_{1/2}$-$^2P_{3/2}$ mixing in the excited state[3] we observed magnetic resonance signals in the "sensitized fluorescence" (pumping with D_2

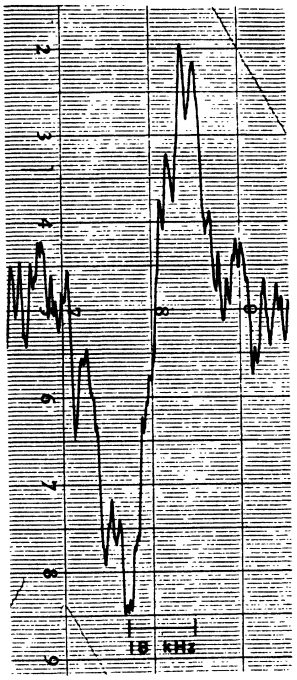

FIG. 1. Rb^{87} hyperfine resonance at 6 834 380 kHz for the superimposed transitions ($F=2, m_F=+1$) to ($F=1, m_F=0$) and ($F=2, m_F=0$) to ($F=1, m_F=+1$) in an argon buffer gas with a density of 7390 Torr (0°C) and a temperature of 94°C. The recorder time constant is 3 sec. Under these conditions, the linear part of the pressure shift is $\nu\rho a=-620$ kHz, the quadratic part is $\nu\rho^2 b=+40$ kHz, or a total $\delta\nu=-580$ kHz.

light at 7800 Å and detecting 7948-Å fluorescence).

Averaging our measurements for each of the two samples, we find the zero-field hyperfine frequency ν shifted from the zero-pressure value ν_0 by a fraction

$$\delta\nu/\nu_0=(\nu-\nu_0)/\nu_0=a\rho+b\rho^2,$$

where

$$a=(-11.5\pm0.3)\times10^{-9}/\text{Torr (0°C)},$$

$$b=(+10\pm4)\times10^{-14}/\text{Torr}^2\ (0°\text{C})$$

for measurements in argon at 80°C. The shift grows more negative with increasing temperature by $(0.60\pm0.04)\%/°$C and this temperature dependence seems linear within these limits between 70 and 130°C. Taking the results of individual samples, there is no difference between isotopes Rb^{85} and Rb^{87} to within ±0.1% and no difference between m_F levels to within ±0.1% (as expected from g_J pressure-shift experiments[4]). These results are in agreement with low-pressure measurements[5] assuming linear extrapolation in temperature to 21°C.

The uncertainties quoted in a and b are upper limits derived from our experience with systematic errors in the pressure measurement. These uncertainties are of the order of a linewidth in the transition-frequency measurements. Typical linewidths (measured between points of maximum slope) in Rb^{85} and Rb^{87} at 4170 Torr (0°C) were about 1 and 3 kHz, respectively. At 7390 Torr (0°C) they were roughly 3 and 14 kHz, respectively. Part of the increase is probably related to rf broadening because of reduced signal-to-noise ratio at higher pressures. It is likely, however, that the Rb-Ar collision broadening increases faster than linearly with pressure and faster than the linewidth in Zeeman transitions. The Rb^{87} hyperfine linewidth is always larger than that in Rb^{85}. An impact model of collision broadening, where the phase shift per two-body collision is small and proportional to frequency, predicts a collision breadth proportional to ν_0^2. Within the limits of our ability to identify the Rb-Ar collision breadth, our observations are probably compatible with that model.

The smallness of the Rb hyperfine pressure shift in argon (as opposed to other inert gases[5]) offers an advantage in this respect: Argon density gradients generated by sample temperature gradients do not dominate the linewidth. (Detection by resonance fluorescence also helps by sampling a smaller volume of atoms at the center of the absorption cell. Convection and conductivity of high-density argon tend to reduce temperature gradients there.)

Future experiments with improved lamps and gas-handling system will yield very precise information about three-body collision effects on alkali and hydrogen line shapes. The understanding of these collisions will find immediate application in reducing the uncertainty associated with the extrapolation to zero pressure in the measurement of the muonium hyperfine splitting.[6]

White-light optical pumping should find many other applications. For example, disorientation processes for alkalies in helium are so weak that very high helium pressures are desirable to compete with other relaxation processes. Pressure shifts in other transitions (e.g., g_J pressure shifts) should also be measured by this method. The white-light method possesses advantages for the measurement of g factors, i.e., the lamp need not be in the magnetic field because the Zeeman shift of the optical absorption lines will not interfere with the pumping process.

Furthermore, "light shifts" of the dispersion type[7] which depend on the displacement of structure in the lamp spectrum from the center of the absorber line cannot be caused by the broad spectrum of a white-light source. This freedom from light shifts may recommend white-light sources for high precision optical pumping at lower pressures.

We wish to thank P. Bender and V. W. Cohen for information on their unpublished work on Rb hyperfine linewidths and temperature gradients, and for enlightening comments on the theory of alkali–inert-gas collisions. We also wish to acknowledge the support and encouragement of V. W. Hughes in this work. Mr. R. J. Blume helped solve the frequency multiplication problems.

*Research supported in part by the U. S. Air Force Office of Scientific Research.

†On leave from I. Physikalisches Institut der Universität Heidelberg, Heidelberg, Germany.

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

[2]F. A. Franz and J. R. Franz, Phys. Rev. 148, 82 (1966).

[3]L. Krause, Appl. Opt. 5, 1375 (1966).

[4]G. S. Hayne and H. G. Robinson, private communication; R. M. Herman, Phys. Rev. 175, 10 (1968).

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

[6]P. A. Thompson, J. J. Amato, P. Crane, V. W. Hughes, R. M. Mobley, G. zu Putlitz, and J. E. Rothberg, Phys. Rev. Letters 22, 163 (1969).

[7]J. P. Barrat and C. Cohen-Tannoudji, Compt. Rend. 252, 93, 255 (1961), and J. Phys. (Paris) 22, 329, 443 (1961).

TUNNELING-ASSISTED NUCLEAR SPIN-LATTICE RELAXATION

P. S. Allen and S. Clough
Department of Physics, University of Nottingham, England
(Received 1 April 1969)

The tunneling splitting of the torsional-oscillator ground state of a hindered methyl group is taken into account in calculating the temperature dependence of the proton spin-lattice relaxation time. Thermal vibrations cause spin-independent transitions leading to a fluctuation in the sign of the splitting parameter. It is predicted that a second maximum in T_1^{-1} may occur at low temperature due to a tunneling-assisted process. This effect is detected in some methyl-substituted benzenes in good agreement with the theory.

Recent electron-spin resonance[1,2] and electron-nuclear double-resonance (ENDOR)[3] experiments have demonstrated important consequences of the splitting of the torsional-oscillator ground state of a hindered methyl group due to tunneling rotation. In one case the splitting has been measured by ENDOR,[3] but it may also be estimated roughly from the hindering barrier height using a relation due to Hecht and Dennison.[4] The splitting is also necessary to explain the narrow NMR lines observed at low temperatures,[5-7] but no satisfactory expression exists for calculating its effect on the temperature dependence of T_1, the spin-lattice relaxation time.

Numerous experimental studies of T_1 have been interpreted in terms of the classical Bloembergen-Purcell-Pound theory[8] which usually fits the data at high temperatures, though low-temperature anomalies have been observed.[9-12] The problem was discussed semiquantitatively by Stejskal and Gutowsky[13] who recognized the possibility of tunneling resonances when the splitting coincides with the Larmor frequency and the fact that lattice vibrations broaden the splitting spectrum. In this Letter we give a theoretical model which describes both high- and low-temperature phenomena. It leads to detailed predictions concerning a low-temperature relaxation process related to the tunneling frequency and provides an explanation for the experimental data from methyl-substituted benzenes in the range 20-200 °K.

We consider first a methyl group constrained by some static hindering potential to small oscillations about its symmetry axis. The orientation of the group is characterized by an angle φ which may be regarded as the position coordinate of a particle in a three-well potential. The wave functions are therefore linear combinations of three harmonic-oscillator functions. Two types of combinations are possible, having regard for the threefold symmetry of the potential, corresponding to the A and E representations of the group C_3. The energy splitting between these states depends on the overlap of the harmonic-oscillator functions and is closely related to the frequency for tunneling between the wells. Particle indistinguishability requires that the pro-