

FIG. 3. The double-resonance signals as a function of frequency for water lamp excitation. The OH radical is formed at an H_2 pressure of 7.6 mTorr and an NO_2 pressure of 2.4 mTorr.

From the absence of resonances above 10 G in Fig. 3(a), it is apparent that we cannot detect any levels with g values between 0.20 and 0.10. This is consistent with the OH ground-state populations expected for the $T = 320^\circ K$ Boltzmann distribution.⁶ In Fig. 3(b), four signals are observed with g values of 0.48, 0.33, 0.24, and 0.20. A tabulation of the possible g_F values for the $K' = 2, 3, 4, 5$ sublevels shows a clustering about these values, assuming Hund's case (b) coupling. Thus to fully resolve all the components, much higher fields are required than are presently obtainable with our apparatus.

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DETERMINATION OF AN ISOTOPE SHIFT IN THE RATIO OF ATOMIC g_J VALUES OF HYDROGEN AND DEUTERIUM*

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The ratio $g_J(H)/g_J(D)$ in the electronic ground state has been determined using optical pumping of Rb and spin-exchange detection of H and D atomic Zeeman resonances. The result is $g_J(H)/g_J(D) = 1 + (7.2 \pm 3.0) \times 10^{-9}$. The error includes an estimate of possible systematic effects.

Several unsuccessful attempts have been made in the past to observe a shift in the ratio of g_J values of hydrogen isotopes in the electronic ground state.¹⁻⁴ We report in this Letter an experimental determination of such an isotope shift

for the ratio $g_J(H)/g_J(D)$. A mass dependence in the shielding of the electron magnetic moment in the atom is the origin of the effect according to a recent theory by Hegstrom.⁵ It is now possible to compare theory with experiment.

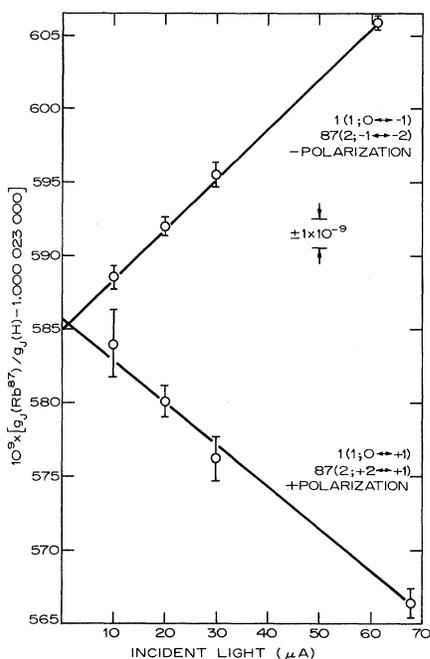


FIG. 1. Typical extrapolation of $g_J(\text{Rb}^{87})/g_J(\text{H})$ to zero Rb pumping light intensity in a 200-cm³, evacuated, Paraflint wall-coated cell. The temperature was ~35°C and the applied magnetic field was ~50 G. A straight line least-squares fit to the data was used at each sense of circular polarization of light. Zeeman transitions used are indicated by ($F; m_F \leftrightarrow m_F \pm 1$).

The experimental method used has been described in essential detail elsewhere.^{6,7} Briefly, H and D were polarized and their Zeeman resonances detected by electron-spin exchange with optically pumped Rb in a magnetic field of ~50 G. Evacuated 200-cm³ spherical Pyrex cells were used with walls coated with paraffins to maintain long relaxation times. Molecular hydrogen was dissociated by an rf discharge, and an atomic beam (nonpolarized) entered the cell through an orifice in the cell wall. Rb atoms entered through a similar orifice. The cell was continuously evacuated to maintain the vacuum under the gas load generated by the atomic hydrogen source. No wax coating was applied to any input arms leading to the spherical cell. Typical hydrogen Zeeman-resonance linewidths were ~20 Hz. Inhomogeneities in the magnetic field contributed ≤ 0.2 Hz to the linewidth. Line-shape checks indicated that H, D, and Rb⁸⁷ resonances were well represented by the Lorentzian shape; asymmetry, if it exists, was $\leq 0.5\%$ of the linewidth. A measurement procedure was designed to minimize any systematic drift effect due to the applied magnetic field. Typically, the field drift was

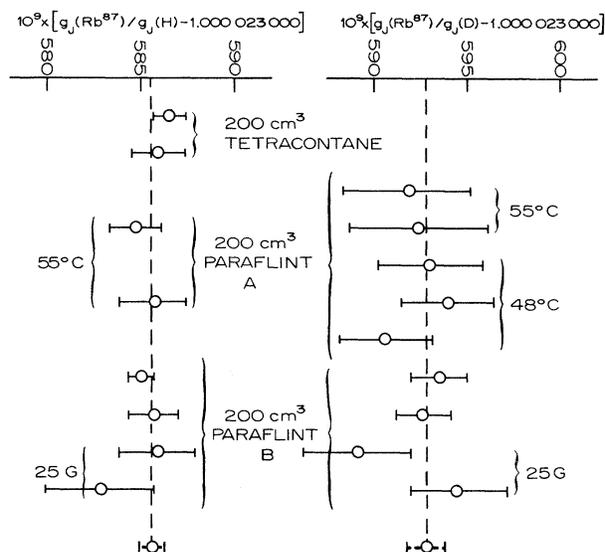


FIG. 2. Summary of $g_J(\text{Rb}^{87})/g_J(\text{H})$ and $g_J(\text{Rb}^{87})/g_J(\text{D})$ results. Data were taken at an applied magnetic field of ~50 G and at a cell temperature of ~35°C unless otherwise noted. Dotted lines refer to the weighted average and weighted rms deviation of all data.

less than 1 part in 10⁹ during the time required to determine a single pair of Zeeman-resonance transition frequencies in Rb and H. The product of g_J and the applied magnetic field H_0 was calculated for each resonance determination and the ratio $g_J(\text{Rb})/g_J(\text{H})$ was formed from pairs of $g_J H_0$ products.

Resonance frequencies were also determined as functions of Rb pumping light intensity so that extrapolation of the ratio of g_J values to zero light intensity was possible. Figure 1 shows a typical extrapolation of $g_J(\text{Rb}^{87})/g_J(\text{H})$ to zero light intensity for both senses of circular polarization. In Fig. 2 the main body of extrapolated results is presented. Unless otherwise indicated, the temperature was ~35°C and the applied magnetic field was ~50G. Weighted averages and weighted rms deviations are shown. The overall results are as follows:

$$g_J(\text{Rb}^{87})/g_J(\text{H}) = 1.000\,023\,585\,5 \times (1 \pm 0.6 \times 10^{-9}),$$

$$g_J(\text{Rb}^{87})/g_J(\text{D}) = 1.000\,023\,592\,7 \times (1 \pm 1.0 \times 10^{-9}).$$

The ratio of these two values yields

$$g_J(\text{H})/g_J(\text{D}) = 1 + (7.2 \pm 1.2) \times 10^{-9}.$$

The error again is the weighted rms deviation and represents the scatter in the results for the various runs with the experimental parameter changes indicated in Fig. 2. It contains no estimate of systematic error. Using the limit of line

asymmetry ($\leq 0.5\%$) to calculate a systematic error limit yields ≤ 1.8 parts in 10^9 . The result after consideration of possible systematic error is then

$$g_J(\text{H})/g_J(\text{D}) = 1 + (7.2 \pm 3.0) \times 10^{-9}.$$

The values used for the hyperfine frequencies (A1 time base) and the ratio of nuclear to electron g factors are given in Table I. At 50-G magnetic field, an error in $g_I/g_J(\text{D})$ of 1 part in 10^6 would cause an error in $g_J(\text{H})/g_J(\text{D})$ of 1.9 parts in 10^{10} . Hence the approximations used in obtaining $g_I/g_J(\text{D})$ are not believed to determine the final error in $g_J(\text{H})/g_J(\text{D})$. Likewise, error in the hyperfine frequencies used should not cause a significant error in the value of $g_J(\text{H})/g_J(\text{D})$.

One determination of $g_J(\text{H})/g_J(\text{D})$ was made by directly comparing H and D Zeeman-resonance data without using Rb Zeeman transitions as an intermediary. The value for this direct determination was in agreement with the result quoted in this Letter.

In order to check on the possible first-order Doppler shift, two different rf coil structures were employed to generate the rf magnetic field. Some data were taken with a simple loop of wire around the sample; other data were taken using a resistively terminated transmission line around the sample. It was expected that the first-order Doppler shift for these two coils would be different. The agreement of the reduced data is used to indicate the probable absence of first-order Doppler effect from this experiment. The second-order Doppler shift is not significant for the level of precision attained.

The possibility of frequency shifts caused by magnetic field inhomogeneity⁸ was checked by applying an even-order inhomogeneity sufficient to broaden the Rb Zeeman resonances by ~ 1 Hz.

(Under certain conditions odd-order field gradients cause no frequency shifts.⁹) No significant shift was found.

Systematic shifts were detected in H and D resonances at nonzero light intensity which were attributed to electron-spin exchange between members of the atomic ensemble. Hence extrapolation to zero electron polarization (i.e., zero light intensity) was required. This extrapolation also removes the light-induced frequency shift in Rb. Furthermore, Zeeman-resonance frequencies were determined at both senses of circular polarization of the pumping light and therefore at both senses of electron polarization. This offers another check on possible spin-exchange shifts since the shift is expected to change sign if electron polarization changes sign. No evidence for significant spin-exchange shifts was found in the extrapolated g_J -value ratios.

A possible criticism of the experiment is that the values used for hyperfine frequencies were determined elsewhere, as noted. However, by using additional Zeeman transitions, self-consistent values for the hyperfine interaction constants of H and D were found. Using these less precise values, which were in agreement with literature values, $g_J(\text{H})/g_J(\text{D})$ was found to be in agreement with our more precise result. The rms scatter in this self-consistent determination was ~ 2 parts in 10^9 .

Hegstrom⁵ has recently published a theory to describe the mass dependence of the shielding of the electron and proton in atomic hydrogen. To order $\alpha^2 m/M$,

$$g_J(\text{H})/g_J(\text{D})|_{\text{theory}} = 1 + 9.7 \times 10^{-9}.$$

This may be compared with our result,

$$g_J(\text{H})/g_J(\text{D})|_{\text{exptl}} = 1 + (7.2 \pm 3.0) \times 10^{-9}.$$

Table I. Atomic constants used in g_J -ratio determinations.

Species	Hyperfine frequency (Hz)	Nuclear-to-electron g -factor ratios $ g_I/g_J $
Rb ⁸⁷	6 834 682 614.0 ^a	4.969 914 7 $\times 10^{-4}$ ^d
H	1 420 405 751.8 ^b	1.519 270 8 $\times 10^{-3}$ ^e
D	327 384 352.3 ^c	2.332 173 3 $\times 10^{-4}$ ^f

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The experimental and theoretical values overlap only because of the increase in the error limit due to the estimated systematic error. The experimental rms deviation itself (1.2 parts in 10^9) would not allow overlap. Consideration of possible corrections to the theory of order $\alpha^2 m/M$ is presently underway.¹⁰ Further experimental work will be required to criticize systematic error. Nevertheless, the result at hand demonstrates the isotope shift in the $g_J(\text{H})/g_J(\text{D})$ ratio.

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SPIN-ECHO STUDIES OF EXCHANGE EFFECTS IN HEAVILY DOPED $\text{TiO}_2:\text{Fe}^{3+}$

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Electron-spin echoes associated with magnetic-resonance lines arising from exchange effects in heavily iron-doped rutile have been observed continuously over the frequency range from 7.7 to 10.1 GHz at zero magnetic field. Values of the phase memory time measured at zero field for various frequencies were orders of magnitude larger than expected for the spin concentrations involved, but decreased rapidly with the application of a static magnetic field.

Microwave echo signals which are associated with the exchange lines of the Fe^{3+} ions in heavily doped $\text{TiO}_2:\text{Fe}$ have been observed at 1.2 and 4.2°K using a standard two-pulse echo technique. These signals will be termed "exchange echoes" for convenience. They possess the unique property of being continuously observable throughout the entire frequency band of our measuring apparatus (7.7-10.1 GHz) in zero magnetic field,¹ even though the zero-field splittings between the three degenerate doublets of the ground manifold of the Fe^{3+} ion in rutile are 43 and 81 GHz, respectively.² Apart from these observations, however, the significant physical aspect of the experiment lies in the fact that the phase memory times T_D measured at zero field for various frequencies were orders of magnitude longer than expected (as high as 140 μsec) for the spin concentrations involved³ ($> 10^{19}$ Fe^{3+} ions per cm^3), and were at least four orders of magnitude greater than the phase-memory times of nonzero-field EPR lines in the same sample. These results serve as a dramatic indication of the way in which spin-spin phase destruction effects are depen-

dent upon the relationship between the rate of change of frequency versus applied magnetic field for the absorption lines under observation—a relationship which can vary considerably.

The ground state of the Fe^{3+} doping ion in a rutile host lattice is a ${}^6S_{5/2}$ system. By varying the magnetic field, X-band transitions between different pairs of these levels (as well as echo signals) are observed. For relatively low spin concentrations these levels are the only ones that can be observed experimentally, but when the impurity concentration is increased other lines begin to appear which apparently are a result of exchange coupling between nearby iron spins. Exchange spectra versus dc magnetic field are usually quite complicated,⁴ and in this case there is a nearly continuous array of lines over the 0- to 10-kG range of magnetic field. Echo signals have been observed in these lines. A sample of heavily iron-doped rutile was placed in a shorted piece of waveguide and cooled to liquid helium temperatures. Because of the high dielectric constant of the host material, there exist dielectric microwave-cavity modes through-