Hyperfine Separation of Tritium*

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(Received 9 January 1967)

The hyperfine separation of tritium has been measured with respect to the hyperfine separation of hydrogen by comparing the frequency of the tritium maser with that of a hydrogen maser. The result is $\Delta\nu(\mathrm{T}) = 1\,516\,701\,470.8087 \pm 0.0071$ Hz, where it is assumed that $\Delta\nu(\mathrm{H}) = 1\,420\,405\,751.8$ Hz. Wall shifts were measured for tritium and hydrogen for FEP Teflon at 35°C. For a spherical bulb, d cm in diameter, the fractional wall shift for hydrogen is $-(3.61 \pm 0.54) \times 10^{-10}/d$, and for tritium it is $-(3.14 \pm 0.47) \times 10^{-10}/d$.

I. INTRODUCTION

TRITIUM and hydrogen have similar hyperfine structures—they both have a nuclear spin of $\frac{1}{2}$ and their nuclear moments differ by less than 6%. Consequently a hydrogen maser can be readily altered to operate with tritium. This paper presents the result of a determination of the tritium hyperfine separation $\Delta\nu(\mathrm{T})$ in terms of the hydrogen hyperfine separation $\Delta\nu(\mathrm{H})$, accomplished by comparing the oscillation frequencies of a hydrogen maser with a similar maser operating with tritium. In the following sections we present some experimental details, an account of the various corrections made to the observed frequencies, and a summary of the results.

II. EXPERIMENTAL DETAILS

Since the hydrogen maser has been described in several earlier works,[1–4] we shall limit ourselves here to describing features unique to the present experiment.

The measurement consisted of comparing the oscillation frequencies of a hydrogen maser and a tritium maser. In order to correct for the wall shift described below, a series of measurements was made using storage bulbs of various sizes. A third maser, operating with hydrogen, was used as a secondary reference for purposes of tuning and determining the hydrogen wall shift.

In all cases the transition observed was $(F=1, m=0) \rightarrow (F=0, m=0)$. This occurs for hydrogen at approximately 1420 MHz and for tritium at approximately 1517 MHz.

A. Tritium Handling System

Because of tritium's scarcity and high radioactivity, the gas was recirculated. The main apparatus was pumped by two 6-in. mercury-diffusion pumps. The foreline was maintained at about 20 mTorr by a Leybold HG12 diffusion pump which pumped the tritium to a pressure of about 2 Torr. The source, a rf discharge, operated in the range 0.3 to 1 Torr. A Toepler pump was used to transfer the tritium.

The principal difficulty in the tritium measurements proved to be the unexpectedly rapid loss of tritium despite the arrangement for recirculation. In principle, only a small amount (3 to 4 Ci) of tritium should have been needed for the whole set of tritium measurements, but because of the loss, larger quantities were required. Another problem associated with the recirculation was contamination of the tritium by hydrogen and other gases. For gases other than hydrogen this was solved by the use of a liquid-helium trap whose temperature was adjusted to selectively freeze out the impurities.

Initially the loss of tritium was at such a rapid rate that it precluded observation times long enough for good measurements. Investigation of the problem with a recirculating hydrogen system revealed that the gas disappeared only when the rf discharge was operating, and the loss was apparently due to the adsorption of atomic hydrogen by the Pyrex wall of the discharge bulb. It was found that a quartz bulb adsorbed the hydrogen at a much lower rate than one of Pyrex. With a quartz bulb the adsorption was sufficiently reduced for the experiment to be possible, but the observation times were still severely limited since the tritium became mixed with hydrogen that evolved from the discharge bulb and other surfaces in the vacuum system. This contamination became less after a discharge bulb had been used for some time with tritium.

B. Frequency Comparison System

In order to determine the hydrogen wall shift, a second H maser was used as a temporary reference while the primary H maser was operated with various size storage bulbs. A straightforward heterodyne system was used to compare the frequency of these two masers. The outputs from both masers were reduced to about 5 kHz by mixing with common local oscillators.

* Work supported by the National Science Foundation and the U. S. Office of Naval Research.
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[4] Further details of this experiment are described in B. S. Mathur, thesis, Harvard University, 1965 (unpublished).

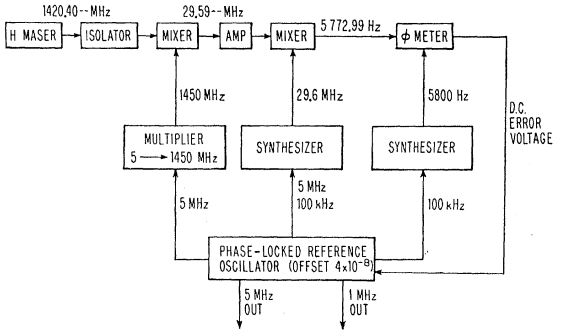

FIG. 1. System for phase-locking the reference oscillator to the hydrogen maser. The reference oscillator has been fractionally offset by approximately 4 parts in 10^8 in order to simplify the synthesizing requirements.

The audio signals were then mixed and the period of the resultant signal, typically 10 sec, was measured with an electronic counter.

The procedure for determining the tritium frequency was somewhat more elaborate because of the difference between $\Delta\nu(\mathrm{T})$ and $\Delta\nu(\mathrm{H})$. Because frequency accuracy of 10^{-4} Hz was required, all interpolation frequencies were synthesized. The system used is shown in Figs. 1 and 2. A reference oscillator was phase locked to the H maser, and its output frequency was multiplied to provide a frequency reference for the T maser. A Hewlett-Packard 5100 A frequency synthesizer formed part of the multiplier chain and allowed selection of a convenient conversion frequency. The outputs of the H and T masers were then heterodyned to an audio frequency and mixed, as above. The above synthesizer was adjusted to give a 3-sec beat period. This system allowed frequency comparisons to a precision of 3 parts in 10^{13} in 10 sec.

III. PROCEDURE

A. Wall Shifts

The major task in this experiment was determination of the wall shift, the shift in frequency due to wall collisions, which is given by[2,3]

$$\delta\nu_\omega = \varphi/2\pi\tau, \tag{1}$$

where φ is a phase shift characteristic of the surface and τ is the mean collision time. $\tau=\bar{l}/\bar{v}$, where $\bar{v}$ is the mean velocity and $\bar{l}$ is the distance between collisions. For a spherical bulb of diameter d, we have $\bar{l}=2d/3$. Consequently,

$$\varphi(4\pi/3\bar{v})\delta\nu_\omega d \tag{2}$$

and the fractional wall shift is

$$\delta\nu/\Delta\nu = 3\bar{v}\varphi/4\pi d\Delta\nu. \tag{3}$$

The wall shift was determined by measuring the maser frequency for bulbs of varying diameters and applying Eq. (2). Because of the restrictions imposed by the maser geometry, only two bulb sizes were used, approximately 10 and 15 cm in diameter. The mean diameter in each case was determined by measuring the volume of the bulb. [In principle, Eq. (2) should be corrected to account for the increased collision rate in the neck of the bulb. However, in the present case this correction was negligible.]

The major experimental difficulty was in obtaining wall shifts reproducible to the desired accuracy, and the chief burden of this experiment lay in revealing inconsistencies in the wall shift and in establishing procedures for obtaining reproducible results.

1. *Wall Coating*

The surface coating was FEP Teflon (duPont FEP Teflon, product code 120.) The coating procedure was similar to that described in Ref. (3), except that the air circulated through the bulb during curing was dried by cooling it in a dry-ice–methyl-alcohol mixture. It was found that the use of solid Teflon for the collimating plug introduced significant changes in the wall shift, and for this reason the neck of the bulb, as well as the main body, was coated.

2. *Vacuum Considerations*

Both test masers used in this experiment were pumped with 6-in. mercury-diffusion pumps baffled with liquid-nitrogen cold traps and backed with a mechanical forepump. (A sealed, rather than dynamical, pumping system is much preferable from the point of view of surface cleanliness. However, the use of the recirculating tritium system precluded this.) In spite of our concern for a possible contamination of the surface due to the vacuum systems, it was found that with care it was possible to obtain reproducible wall shifts from day to day, even in cases when the maser was left at forepressure over several days. In one case a bulb which had been in continuous use on the reference maser for a six-week period, and which had been opened to forepressure many times, was tested for contamination at

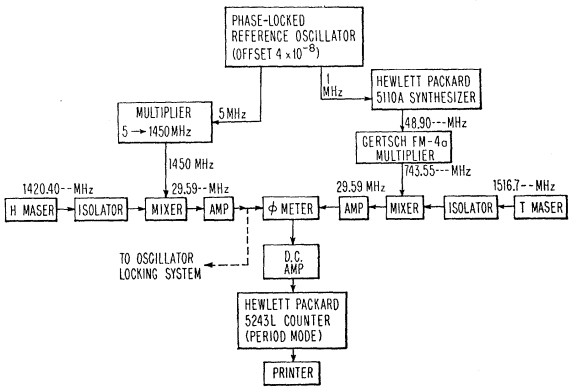

FIG. 2. System for comparing the frequencies of the hydrogen and tritium masers.

the end of the period by being baked under vacuum. This produced no significant change in its wall shift.

We did find, however, that a storage bulb which had been used on a maser, removed from the machine and maintained at atmospheric pressure for four weeks, and then returned to high vacuum after being exposed to forepressure for several days, revealed a change in the wall shift of about 25%. A 24-h bake-out at 165°C decreased this discrepancy but did not eliminate it.

B. Frequency Comparison

The procedures for demagnetizing the shields, measuring the magnetic field by double resonance, and tuning the masers were similar to those described in Ref. (3). Cavity tuning was checked by the spin-exchange method[5] and the ratio of the resonance linewidths at high and low beam flux was measured before and after each run, and occasionally during the run. This result was used to correct the small amount of observed residual mistuning.

IV. CORRECTIONS TO THE OBSERVED FREQUENCIES

The following corrections were made to the observed frequencies for the hydrogen and the tritium masers:

(*a*) *Doppler shift.* The change in frequency due to the second-order Doppler shift is given by

$$\delta\nu_D=\frac{-1}{2}\frac{v^2}{c^2}-\nu=\frac{-3}{2}\frac{kT}{Mc^2}\nu.$$

All the experiments were carried out at 35°C, which yields the following shifts:

$$\delta\nu_D(\mathrm{H})=-0.0602\ \mathrm{Hz},$$
$$\delta\nu_D(\mathrm{T})=-0.0214\ \mathrm{Hz}.$$

(*b*) *Magnetic field offset.* The quadratic-field dependence of the transitions observed can be expressed directly in terms of the Zeeman frequency ν_z.

$$\delta\nu_m(\mathrm{H})=1.417\times10^{-9}\nu_z^2\ \mathrm{Hz},$$
$$\delta\nu_m(\mathrm{T})=1.327\times10^{-9}\nu_z^2\ \mathrm{Hz}.$$

In all of the experiments the Zeeman frequency was less than 10 kc/sec, and its determination introduced negligible error.

(*c*) *Wall shift.* The wall shift and the phase shift per collision were directly determined from Eq. (2). The following values were used in determining the phase shifts:

$$\bar{v}(\mathrm{H})=2.54\times10^5\ \mathrm{cm/sec},$$
$$\bar{v}(\mathrm{T})=1.47\times10^5\ \mathrm{cm/sec}.$$

If we let $\delta\nu_{1,2}$ represent the change in frequency of a maser as its storage bulb is changed in diameter from d_1 to d_2, then

$$\varphi=\frac{4\pi}{3\bar{v}}\frac{d_2-d_1}{d_1d_2}\delta\nu_{1,2}$$

and

$$\delta\nu_\omega=\delta\nu_{1,2}\frac{d_1d_2}{d_2-d_1}\frac{1}{d}.$$

V. RESULTS

A. Wall Shift

The wall shift for hydrogen was determined on the basis of two independent series of measurements. The bulbs used in both were identical, but were freshly coated. The mean diameters were: bulb 1=9.78 cm and bulb 2=15.68 cm. All measurements were carried out at 35°C. The first series A consisted of four separate runs, and the second series B consisted of three runs. The frequency difference produced by the two bulbs was

$$\text{Series A:}\quad \delta\nu_{1,2}=-(19.53\pm0.73)\times10^{-3}\ \mathrm{Hz};$$
$$\text{Series B:}\quad \delta\nu_{1,2}=-(20.07\pm0.31)\times10^{-3}\ \mathrm{Hz}.$$

The mean is $\delta\nu_{1,2}(\mathrm{H})=(19.96\pm0.35)\times10^{-3}$ Hz. Although these results show a high degree of internal consistency, the uncertainty is larger than the 2% indicated. The data were to some degree selected, and under favorable circumstances deviations up to 25% were observed. For the present an error of 15% seems realistic. Further work should substantially reduce this.

The results are

$$\varphi(\mathrm{H})=-(8.5\pm1.3)\times10^{-6}\ \mathrm{rad},$$
$$\delta\nu_\omega(\mathrm{H})/\Delta\nu(\mathrm{H})=-(3.61\pm0.54)\times10^{-10}/d,$$

where d is the bulb diameter in cm.

The wall shifts for tritium were measured in a similar fashion, except that an H maser was used as the frequency reference. The bulb diameters were: bulb 1=11.4 cm and bulb 2=15.17 cm. Two series of measurements were made and the following results were obtained:

$$\text{Series A}':\quad \delta\nu_{1,2}(\mathrm{T})=-(9.7\pm3.0)\times10^{-3}\ \mathrm{Hz};$$
$$\text{Series B}':\quad \delta\nu_{1,2}(\mathrm{T})=-(10.7\pm1.7)\times10^{-3}\ \mathrm{Hz}.$$

The weighted mean is $\delta\nu_{1,2}(\mathrm{T})=-(10.4\pm1.5)\times10^{-3}$ Hz and leads to a value of the phase shift

$$\varphi(T)=-(13.6\pm2.1)\times10^{-6}\ \mathrm{rad},$$

and to fractional wall shift

$$\delta\nu_\omega(\mathrm{T})/\Delta\nu(\mathrm{T})=-(3.14\pm0.47)\times10^{-10}/d.$$

B. Hydrogen-Tritium Frequency Comparison

Since the H maser was used for the frequency reference in the tritium wall-shift determinations, these

[5] S. B. Crampton, thesis, Harvard University, 1964 (unpublished).

TABLE I. A comparison of the results for hyperfine splittings of the hydrogen isotopes by hydrogen-maser and optical-pumping methods. The results of references 8 and 10 have been corrected to the A.1 time scale, $\Delta\nu(Cs^{133})=9\,192\,631\,770$ Hz.

	(a) H maser	(b) Optical pumping	References (a)	(b)
$\Delta\nu$(H)	1 420 405 751.800 ±0.028 Hz	1 420 405 738.3±6.0 Hz	6, 7	8
$\Delta\nu$(D)	327 384 352.3 ±2.5 Hz	327 384 347 ±5 Hz	9	10
$\Delta\nu$(T)	1 516 701 470.8087±0.0071 Hz	1 516 701 465.4±6.0 Hz	Present article	8

measurements also provided the data for determining $\Delta\nu$(T) in terms of $\Delta\nu$(H). The maser operating frequencies were corrected for magnetic-field offset and Doppler shift and the phase shifts listed above were used to provide the wall-shift correction. $\Delta\nu$(H) was referred to the nominal value

$$\Delta\nu(\mathrm{H})=1\,420\,405\,751.8\ \mathrm{Hz},$$

which is consistent with the previous determinations of $\Delta\nu$(H) in the A.1 time scale.[6,7]

A value for $\Delta\nu$(T) was obtained for each of the storage bulbs in the two series of determinations. The results are most conveniently expressed in the form

$$\Delta\nu(\mathrm{T})=1\,516\,701\,470+\delta\ \mathrm{Hz}.$$

The following values were obtained for δ:

	Bulb 1	Bulb 2
Series A':	0.8098 Hz	0.8100 Hz
Series B':	0.8054 Hz	0.8049 Hz

Within each series the results are in good agreement, but there is a sizeable discrepancy between the series. The most likely explanation is that there was a shift in the frequency of the reference H maser. The H maser bulb was freshly coated before series A', but apparently became contaminated between series A' and series B'. To confirm this its wall shift was remeasured and found to be small by $(2.2\pm1.2)\times10^{-3}$ Hz. This correction, when referred to the tritium frequency, increases the results of series B by 2.5×10^{-3} Hz. Because of our inability to confirm the nature of this possible systematic error, the uncertainty was taken to be equal to the correction. The result is

$$\Delta\nu(\mathrm{T})=1\,516\,701\,470.8087\ \mathrm{Hz}.$$

The error in $\Delta\nu$(T) comes from the following contributions:

$\delta\nu_\omega$(H)	0.0049 Hz,
$\delta\nu_\omega$(T)	0.0043 Hz,
$\Delta\nu$(T)−$\Delta\nu$(H) comparison	0.0025 Hz.

By treating these errors as random a total error of 0.0071 Hz is obtained. The final result is

$$\Delta\nu(\mathrm{T})=1\,516\,701\,470.8087\pm0.0071\ \mathrm{Hz},$$

where it is assumed that

$$\Delta\nu(\mathrm{H})=1\,420\,405\,751.8\ \mathrm{Hz}.$$

Alternatively,

$$\Delta\nu(\mathrm{T})/\Delta\nu(\mathrm{H})=1.067\,794\,514\,9734\pm(50\times10^{-13}).$$

VI. DISCUSSION

This measurement completes the determinations of the hyperfine separations of hydrogen and its isotopes by the H-maser method. It is of interest to compare the results with those of Pipkin and his co-workers using the optical-pumping method. The results are listed in Table I.[8,9] There is a slight disagreement in the hydrogen results and the optical-pumping results all tend to be slightly low. However, there is no appreciable systematic discrepancy between the two methods.

There appears to be no significant isotope shift to the fractional wall shift. This result is consistent with the absence of a significant isotope shift to the fractional pressure shift in optical pumping.[8] Because the hyperfine separations are known to much higher accuracy than the nuclear moments of hydrogen and tritium, the present result does not alter the previous value for the hyperfine anomaly.[10]

The value for φ(H) reported here agrees with an independent determination made by Vanier,[11] using the same type of Teflon (though not the same sample) and using a somewhat different coating technique. In order to compare the results, a correction had to be made for the temperature coefficient of the wall shift -5×10^{-3}/°C in the range 25°–40°C.[11] The results agreed to 5%, which is well within the uncertainty of the present determination.

[6] S. B. Crampton, D. Kleppner, and N. F. Ramsey, Phys. Rev. Letters **11**, 338 (1963).
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[11] Jacques Vanier, Varian Laboratories (private communication).