lar theory group and his leader, Professor J. C. Slater. The author is indebted to Professor J. Van Kranendonk for correspondence and conversations and to Michael Wortis for communicating a preprint of his article.

*Work supported by the U. S. Office of Naval Research.

†Based upon the dissertation submitted by the author in partial fulfillment of the requirements for the Ph.D. degree at the Massachusetts Institute of Technology, September 1962 (unpublished).

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HYPERFINE SEPARATION OF GROUND-STATE ATOMIC HYDROGEN*

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(Received 19 August 1963)

The hyperfine separation of hydrogen in its ground state, $\Delta\nu(\mathrm{H})$, has been determined to the precision possible with currently available frequency standards by means of the hydrogen maser.[1-3] In this experiment two masers were operated simultaneously for purposes of tuning, checking internal consistency, and measuring the wall shift (the effect of collisions with the storage bulb on the transition frequency). A secondary frequency standard (National Company Model NC2001 cesium beam frequency standard) was also operated in the laboratory, and the frequency of this standard was monitored by one of the masers at half-hour intervals for a period of twenty-four hours. The average frequency of the secondary standard during this period was determined by J. A. Pierce of the Cruft Laboratory in terms of the 100-kc/sec time signal broadcast on Loran-C east-coast chain. The frequency of the Loran-C signal during the measurement period was subsequently determined by W. Markowitz and R. G. Hall of the U. S. Naval Observatory in terms of the weighted mean of a number of cesium-beam controlled frequency standards at different standards laboratories. By this method the maser frequency was referred to the mean of a number of primary standards, allowing a precision characteristic of the agreement among those standards.

Tuning a hydrogen maser involves tuning the cavity and adjusting the magnetic field to a known value. Cavity tuning was accomplished using the well-known fact that the maser oscillator frequency is "pulled" by a mistuned cavity by an amount proportional to the atomic resonance width.[3] By increasing the beam flux to allow spin-exchange collisions, the resonance width could be increased for this purpose by as much as a factor of four. The cavity was adjusted until the oscillation frequency was independent of the flux.

In addition to causing relaxation, spin-exchange collisions can introduce a small frequency shift.[4] This shift depends upon the atomic resonance width in just the same fashion as the cavity pulling, so by tuning the cavity with the above method any systematic frequency error is exactly canceled by compensating mistuning of the cavity. A preliminary experiment in which the resonance was broadened by deuterium confirms this result to well within the accuracy of concern here, and further experiments are in progress.

The magnetic field was adjusted for a Zeeman frequency of 10 kc/sec by the double resonance technique.[2] A 10-kc/sec signal from the frequency standard was introduced into the cavity, and the field could be trimmed to within 1 cps of resonance, which introduced negligible error in the frequency of the field-independent transition $(F=1, m=0) \rightarrow (F=0, m=0)$. By these means the masers could be independently and reproducibly tuned to agree to better than 1 part in 10^{12}. Fluctuations between the masers in ten-second counting periods were typically 1 or 2 parts in 10^{13}.

The following scheme was used for monitoring the local standard: The 5-Mc/sec output of the

NC2001 was multiplied and used to phase-lock a klystron at 1450 Mc/sec. The maser signal was converted to 29.594238 Mc/sec by mixing with the klystron and amplified in a conventional i.f. amplifier. (The particular i.f. frequency depends on the local standard and does not enter the final determination.) The signal was then mixed with a 29.6-Mc/sec signal derived from the standard. The resultant 5.762-kc/sec signal was multiplied to 57.62 kc/sec and this was counted on a frequency counter for 10 sec. The counting uncertainty of 1 cycle represented a frequency error of 0.01 cps which was unimportant compared to the short-term fluctuations due to the NC2001 during that time, about 0.05 cps.

A single determination of the NC2001 frequency involved about 40 readings of ten seconds each. By making separate determinationa at half-hour periods for twenty-four hours, the effect of short-term fluctuations between the masers and the NC2001 was reduced and an rms deviation of 0.007 cps was obtained, corresponding to a fractional frequency deviation of 5×10^{-12}. There were no indications of diurnal or other systematic variations in the NC2001 during the twenty-four hour run.

In order to obtain $\Delta\nu(\mathrm{H})$ from the maser oscillator frequency, three corrections must be made: magnetic field offset, second-order Doppler shift, and the wall shift. These are denoted by $\delta\nu_m$, $\delta\nu_\mathrm{D}$, and $\Delta\nu_w$, respectively.

The quadratic field dependence of the $(F=1, m=0) \to (F=0, m=0)$ transition can be expressed directly in terms of the Zeeman frequency, ν_Z (which can be assumed linear in H at the fields of interest here): $\delta\nu_m = +1.416\times10^{-9}\nu_\mathrm{Z}^2$. This expression follows from elementary theory and has been verified with the masers. For $\nu_\mathrm{Z} = 10$ kc/sec, the offset is $\delta\nu_m = +0.142$ cps with negligible error.

The second-order Doppler shift is given by

$$\delta\nu_\mathrm{D} = -(v^2/2c^2)\Delta\nu(\mathrm{H}) = -(3kT/2mc^2)\Delta\nu(\mathrm{H})$$
$$= -1.378\times10^{-13}T\Delta\nu(\mathrm{H}).$$

In this experiment the maser cavities and the storage bulbs were temperature controlled at 308°K (35°C), so that $\delta\nu_\mathrm{D} = -0.0602$ cps. The uncertainty in $\delta\nu_\mathrm{D}$ is negligible.

The storage bulbs were coated with DuPont Teflon, using DuPont 852-201 clear finish.[5] The wall shift is proportional to the collision rate and can be determined by comparing masers with different size storage bulbs. In this experiment one maser had a bulb of mean diameter 6.03 in., while the other had a bulb of mean diameter 3.88 in. The offset frequency between the masers due to the wall shift was 0.017 cps, which corresponds to a total wall shift for the maser with the 6-in. bulb of $\delta\nu_w = -0.0298$ cps (as contrasted to no collisions, i.e., free space). During the run the forepump on one machine broke and the pressure rose above foreline pressure. This resulted in a change in the wall shift of approximately 10% presumably due to contamination with forepump oil. The wall shift and this contamination effect were subsequently rechecked, and verified. The uncertainty in the wall shift, chiefly due to the contamination, is taken to be 10% (or 2 parts in 10^{12}), which is satisfactory for the present purpose since it is small compared to the uncertainty of the frequency standards.

The results of this determination will be given in the atomic time scale A.1 which is based on an assumed frequency of 9 192 631 770.0 cps for the cesium-133 hyperfine transition at zero magnetic field.[6] If we denote the experimentally determined frequency of the maser in terms of the NC2001 by ν_0, then we may write

$$\Delta\nu(\mathrm{H}) = \nu_0(1+a+b+c) - \delta\nu_m - \delta\nu_\mathrm{D} - \delta\nu_w.$$

In the present determination, $\nu_0 = 1\,420\,405\,762.468 \pm 0.007$ cps. The corrections in parentheses involve conversion of the time base from the NC2001 to the primary standards while the last three are those described above. The term a represents conversion of the NC2001 base to the A.1 time scale, b represents the measured correction of the NC2001 frequency in terms of Loran-C, and c represents the measured correction of the Loran-C signal in terms of the primary standards.

The NC2001 assumes a cesium hyperfine transition of 9 192 631 840 cps at zero magnetic field, and operates at a field which increases this by 1.39 cps, so that

$$a = [(9\,192\,631\,770 + 1.39)/(9\,192\,631\,840)] - 1$$
$$= -7.46358\times10^{-9}.$$

(Since this value of a was assumed in comparing the NC2001 to Loran-C, its actual value is not significant: Any error in it will be corrected by b.)

b corrects the NC2001 in terms of the Loran-C frequency assuming that the frequency of Loran-C is offset during 1963 from the nominal 100 kc/sec by 1300 parts in 10^{11} below the frequency of the A.1 time system. During the peried of measurement, 1:30 a.m. 11 June 1963 to 1:30 a.m. 12 June 1963, b was determined by J. A. Pierce of the Cruft Laboratory to be -2.1×10^{-11}.

The factor c represents the best estimate of the actual frequency of Loran-C during the measurement period in terms of the primary standards. The A.1 time scale is derived from the operation of cesium atomic beam time standards in eight laboratories around the world. VLF transmissions are utilized for the comparison of frequencies.[6] From such comparisons Markowitz and R. G. Hall of the U. S. Naval Observatory have determined that the frequency of Loran-C was $(1299\pm1)\times10^{-11}$ below A.1 on the date of the present determination, 11-12 June 1963. The factor c is therefore $(1\pm1)\times10^{-11}$.

The uncertainty in the result for $\Delta\nu(\mathrm{H})$ is compounded from the following sources. Uncertainties are listed fractionally:

wall shift:	0.2×10^{-11};
fluctuation in local standard:	0.5×10^{-11};
uncertainty in primary standard:	2×10^{-11}.

The uncertainty in the primary standard has been taken to be 2×10^{-11} which represents the mean deviation[6] since 1960, even though there are reasons to believe that the uncertainty may have been less at the time of the measurement. Combining these as random errors leads to a final uncertainty of 2×10^{-11}, or 0.028 cps.

If we assume $\Delta\nu(\mathrm{Cs}) = 9\,192\,631\,770.0$ cps, the final result is

$$\Delta\nu(\mathrm{H}) = 1\,420\,405\,751.800 \pm 0.028 \text{ cps.}$$

The above value agrees well with our previously published preliminary value.[2] Likewise, the result falls within the very much larger limits of the measurements by Wittke and Dicke[7] and Kusch.[8] When the results of Pipkin and Lambert[9] are referred to the A.1 time scale,[2,6] they are lower than the present result by twice their estimated experimental error of 7 cps. The preliminary hydrogen maser result of Menoud and Racine[10] is lower than our result by 1 cps, which is slightly more than double their experimental error of 0.4 cps which they attribute chiefly to the inhomogeneity of their residual magnetic field. A later unpublished value from that laboratory[11] with an experimental error of 0.3 cps agrees with our result to within their estimated error assuming their unmeasured wall shift is the same as ours. Vessot and Peters[12] in recent unpublished hydrogen maser experiments have obtained results in agreement with those of this paper assuming their unmeasured wall shift also to be the same as ours.

We wish to acknowledge contributions to the masers used in this experiment by H. C. Berg, N. Fortson, B. S. Mathur, E. Recknagel, and H. G. Robinson. The authors would like to thank J. A. Pierce for monitoring the local standard, W. Markowitz and R. G. Hall for supplying information on the Loran-C frequency, and R. Vessot for many valuable discussions. The authors are indebted to Dr. F. H. Reder and the U. S. Army Signal Research and Development Laboratory for the loan of the NC2001.

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*Research sponsored by the National Science Foundation and the U. S. Office of Naval Research.

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