

Measurement of the Unperturbed Hydrogen Hyperfine Transition Frequency

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Abstract—The results of a joint experiment aimed primarily at the determination of the frequency of the H^1 hyperfine transition ($F = 1, m_F = 0$) \leftrightarrow ($F = 0, m_F = 0$) is reported. In terms of the frequency of the Cs^{133} hyperfine transition ($F = 4, m_F = 0$) \leftrightarrow ($F = 3, m_F = 0$), defined as 9192 631 770 Hz, for the unperturbed hydrogen transition frequency the value

$$\nu_H = 1420\ 405\ 751.768\ \text{Hz}$$

is obtained. This result is the mean of two independent evaluations against the same cesium reference, which differ by 2×10^{-3} Hz. We estimate the one-sigma uncertainty of the value ν_H also to be 2×10^{-3} Hz. One evaluation is based on wall-shift experiments at Harvard University; the other is a result of a new wall-shift measurement using many storage bulbs of different sizes at the National Bureau of Standards. The experimental procedures and the applied corrections are described. Results for the wall shift and for the frequency of hydrogen are compared with previously published values, and error limits of the experiments are discussed.

I. INTRODUCTION

A SERIES of measurements involving hydrogen masers, cesium beam frequency standards, and the NBS clock system was made at the National Bureau of Standards (NBS) in Boulder, Colo., during the period from November 1969 to February 1970. The original purpose of these experiments was an evaluation of the stability performance of the involved systems and devices. A report of these results will be made elsewhere [1].

A unique opportunity thereby existed for a remeasurement of the frequency of the unperturbed hydrogen (H^1) hyperfine transition ($F = 1, m_F = 0$) \leftrightarrow ($F = 0, m_F = 0$) in terms of the cesium (Cs^{133}) hyperfine transition ($F = 4, m_F = 0$) \leftrightarrow ($F = 3, m_F = 0$), defined as 9192 631 770 Hz. This paper reports the results of our frequency measurements.

The hydrogen maser frequency differs from the unperturbed atomic transition frequency because of a variety of effects including cavity pulling, spin exchange, magnetic fields, second-order Doppler (related to the temperature of the storage vessel), and collisions with the walls of the

storage vessel. A detailed discussion of these effects is found in [2]. They can be measured and accounted for with fractional uncertainties of less than 10^{-13} with the exception of the wall-collision effect (wall shift). Thus, the measurement of the unperturbed hydrogen transition frequency involves primarily a measurement of the wall shift. We performed two different and independent¹ measurements, which are referred to hereafter as experiment 1 and experiment 2.

Experiment 1 relies on a previous determination of the wall shift at Harvard University [3]: as a result of this wall-shift evaluation the Harvard reference maser has a known wall shift. A comparison between the frequency of this maser and a cesium primary frequency standard² (NBS-III), using a different maser as a transfer standard, gave a value for the unperturbed hydrogen hyperfine transition frequency. Experiment 2 is a separate and new measurement of the wall-shift correction with, however, an important difference from any previous wall-shift measurement: the reference oscillator that was used in the measurement of the frequency of the maser equipped with storage bulbs of different sizes was directly related to the frequency of a cesium primary frequency standard (NBS-III). Wall-shift correction and hydrogen-cesium comparison in experiment 2 were thus not separate steps but were integral parts of the same measurement.

The published values of the unperturbed hydrogen hyperfine transition frequency disagree among themselves considerably more than is expected from the published values of the accuracy. In addition, there has been an almost exclusive usage of one particular wall-shift correction in the various publications of the hydrogen frequency. (See Tables I and II.) These were further motivations for our measurements.

The value for the hydrogen hyperfine transition frequency may be written as

$$\nu_H = (1420\ 405\ 751 + \nu_H^0)\ \text{Hz} \quad (1)$$

and we shall discuss in the following only ν_H^0 .

The wall-shift correction may be written³ as approximately

$$\Delta\nu_w \approx (K/D)[1 + \alpha_1(T - T_1)] \quad (2)$$

¹ They are not completely independent in the sense that a common cesium reference (NBS-III) was used.

² For our purposes a cesium primary frequency standard is an apparatus that has been experimentally evaluated in relation to all known perturbing effects [4].

Manuscript received June 5, 1970; revised July 13, 1970. This paper was presented at the 1970 Conference on Precision Electromagnetic Measurements, Boulder, Colo., and the experiments at Harvard University were supported by NASA.

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TABLE I
WALL-SHIFT RESULTS

| Author and Reference | Approximate Year of Measurement | Number of Bulbs | Teflon | $\Delta\nu_w \cdot D$ (mHz·cm) | α (K^{-1}) |
|------------------------------------|---------------------------------|-----------------|---|--|------------------------------|
| Crampton <i>et al.</i> [5] | 1963 | 2 | TFE 852-201 | 470 ± 47 at 35°C | not measured |
| Vanier and Vessot [6] | 1963-1964 | 4 | Du Pont FEP-120 | 528 ± 5 at 40°C | $-(5 \pm 1) \times 10^{-3}$ |
| Mathur <i>et al.</i> [7] | 1964 | 4 | Du Pont 1962 FEP-120 Blend 33 53.9 percent solids | 513 ± 76 at 35°C | not measured |
| Elkina <i>et al.</i> [8] | 1968 | 2 | Du Pont 1964 Teflon D | 1993 ± 75 (tempera- ture not given) | not measured |
| Zitzewitz <i>et al.</i> [3] | 1968-1969 | 18 | Du Pont FEP-120 Blend B-107 54.5 percent solids | 386 ± 8 at 40°C | $-(12 \pm 1) \times 10^{-3}$ |
| Menoud and Racine [9], [10] | 1968-1969 | 2 | Du Pont 1967 FEP-120 | 515 ± 28 at 40°C | not measured |
| Hellwig <i>et al.</i> [this paper] | 1969-1970 | 11 | TFE Blend 42 34.3 percent solids Du Pont 1969 | 528 ± 17 at 24°C | not measured |

where T_1 is the reference temperature, usually chosen at 40°C, T is the operating temperature of the storage bulb, α_1 is the wall-shift temperature coefficient, D is the diameter of the storage bulb, and K is the wall-shift coefficient.

To our knowledge only five independent wall-shift measurements have been published in the past; one reason for this must be sought in the rather tedious and time-consuming experimental effort necessary. The six published results are summarized in Table I together with the results of this paper. Table I gives the author(s) and bibliographic reference, the year(s) of the actual experiment, the number of bulbs different in coating and/or size, the type and year of purchase of the Teflon,³ and the values $\Delta\nu_w \cdot D$ and α_1 of (2) together with the accuracy claims.

In Table II we list and compare values for ν_H' . Given are the author(s) and published reference, the year(s) of the actual measurement, the Teflon that was used in the storage bulb of the hydrogen maser, the applied wall-shift correction listed by the corresponding author from Table I, the hydrogen maser type that was used, the cesium reference standard, and the value for ν_H' . The values for ν_H' are rounded in the last digit.

A discussion of Tables I and II will be postponed until the end of this paper where we will take a critical look at them in connection with a discussion of our new values.

³ Trade names and the names of manufacturers are used in this paper for the sole purpose of conveying scientific and technical information, and their citation is not to be construed as an endorsement or approval of commercial products or services by the authors' organizations.

II. MEASUREMENT PROCEDURES

Experiment 1 involved a transportation of the portable hydrogen maser of the Smithsonian Astrophysical Observatory (SAO) first to the Lyman Laboratory of Physics at Harvard University (HU) and then to the Atomic Frequency and Time Standards Section of the National Bureau of Standards (NBS). The SAO maser is described in detail in [20]. At HU its frequency was compared with the HU reference hydrogen maser. The wall shift of the HU maser was known from a previous evaluation [3]. Both masers were tuned and the appropriate bias corrections (see Section III) were applied. From the thus corrected difference frequency of both masers the wall-shift correction of the SAO maser could be inferred as $\Delta\nu_w = +20.19$ mHz. This experiment was done in December 1969. The SAO maser was brought to NBS, where its frequency was referenced to cesium on January 22 and 23, 1970.

Experiment 2 involved the NBS experimental hydrogen maser NBS-H2. Its general configuration is similar to the Varian H-10 hydrogen masers. During the period from November 1969 to January 1970 this maser was successively equipped with bulbs of different sizes ranging from 7.5 to 20 cm in diameter. A total of 15 frequency determinations was made of which 11 were used for the final analysis. Each individual measurement was made with a reference frequency source whose frequency was known in terms of cesium (NBS-III) [19]. Thus the measurement of the wall shift was simultaneously the measurement of the hydrogen-cesium ratio, and the value for zero wall shift was obtained by extrapolating

TABLE II
HYDROGEN-CESIUM MEASUREMENTS
 $\nu_H = 1420\,405\,751\text{ Hz} + \nu_H'$

| Author and Reference | Approximate Year of Measurement | Teflon Used | Wall Shift From Reference (See Table I) | Hydrogen Maser | Cesium Reference | ν_H' (mHz) |
|---|---------------------------------|---------------------------------------|--|--|---|--|
| Crampton <i>et al.</i> [5] | 1963 | TFE 852-201 Du Pont | ← Related → Crampton <i>et al.</i> (1963) | Harvard laboratory type | NC 2001 | 800 ± 28 |
| Vanier <i>et al.</i> [11] | 1963 | FEP Du Pont Lot 10144 | Vanier-Vessot (1963-1964) | Varian laboratory type | several Cs clocks via Loran C | 827 ± 20 |
| Peters <i>et al.</i> [12] | 1964 | FEP Du Pont | Vanier-Vessot (1963-1964) | Varian H-10 | HP 5060 A | 778 ± 16 |
| Peters and Kartaschoff [13] | 1964 | FEP Du Pont | Vanier-Vessot (1963-1964) | Varian H-10 | LSRH laboratory type | 785 ± 16 |
| Johnson and McGunigal [14] | 1965 | FEP Du Pont | Vanier-Vessot (1963-1964) | Varian H-10 | HP 5060 A | 781 ± 16 |
| Vessot <i>et al.</i> [15] | 1965 | FEP Du Pont | Vanier-Vessot (1963-1964) | Varian H-10 | NBS-III | 786 ± 2 |
| Becker and Fischer [16] | 1966 | TFE 852-201 Du Pont | Vanier-Vessot (1963-1964) | PTB-H2 laboratory type | HP 5060 A | 756 ± 3 |
| Becker and Fischer [16] | 1967 | TFE 852-201 Du Pont | Vanier-Vessot (1963-1964) | PTB-H2 laboratory type | PTB laboratory-type C2 and HP 5061 A | 758 ± 2 |
| Mungall <i>et al.</i> [33] | 1968 | FEP-120 Du Pont Drum 10020 | Vanier-Vessot (1963-1964) | NRC laboratory type | NRC laboratory long cesium beam standard | 778 (an explicit accuracy claim was not made) |
| Chi <i>et al.</i> [17] | 1968 | FEP-120 Interchemical vanaflex (1967) | Vanier-Vessot (1963-1964) | NASA-NX-1 laboratory type | 4 units HP 5061 A 1 unit HP 5060 A | 777 ± 3 |
| Menoud and Racine [9], [10] | 1969 | FEP-120 Du Pont | ← Related → Menoud-Racine (1968-1969) | LSRH-H2 laboratory type | Oscillatom 3 (Ebauches) | 778 ± 4 |
| Bangham [18] | 1969 | PTFE | Vanier-Vessot (1963-1964) | NPL laboratory type | NPL laboratory type | 734 ± 25 |
| Hellwig <i>et al.</i> , experiment 1 [this paper] | 1970 | FEP-120 Blend B-107 Du Pont (1967) | ← Related → Zitzewitz <i>et al.</i> (1968-1969) | portable SAO maser transferred from HU | NBS-III via NBS clock system and NASA-NP3 H-maser | 769 ± 2 |
| Hellwig <i>et al.</i> , experiment 2 [this paper] | 1970 | TFE Blend 42 Du Pont (1969) | ← Related → this paper (1969-1970) | NBS-H2 laboratory type | NBS-III via NBS clock system and NASA-NP3 H-maser | 767 ± 2 |

the measured data to $1/D = 0$ ($D \equiv$ bulb diameter).

Fig. 1 shows the measurement system used in both experiments. The receiver for the output frequency ν_M of the hydrogen maser is basically a triple-superheterodyne system. The first intermediate frequency is in the MHz range, the second in the kHz range, and the third is adjusted by means of a synthesizer (output frequency ν_S) to a slow beat frequency ν_B of the order of 1 Hz. If the external reference frequency ν_R is chosen to be nominally 5 MHz we have at the output of the second

stage an intermediate frequency of $(\nu_M - 284\nu_R)$ and for the final beat frequency

$$\nu_B = (\nu_M - 284\nu_R) - \nu_S. \quad (3)$$

By comparison with (1) we see that $\nu_S \approx 405$ kHz. The maser frequency ν_M in terms of the reference frequency ν_R can then be calculated from (3). If ν_R is given in terms of the cesium transition frequency the hydrogen-cesium ratio can be computed using the appropriate corrections. A measurement precision of a few parts in 10^{13} was

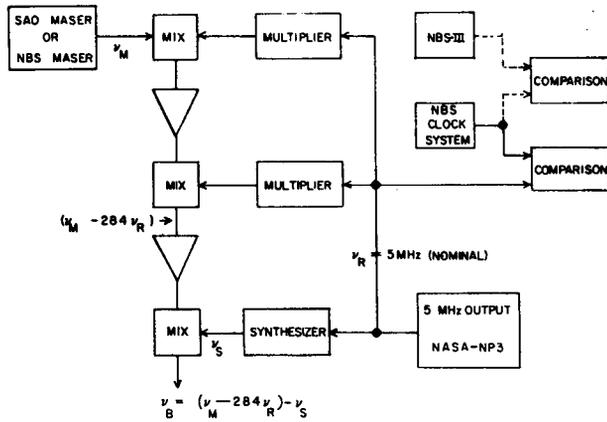


Fig. 1. Measurement system used for determining frequency ratio between two frequency standards.

desired. To take ν_R directly from the output of a cesium standard would have meant averaging times of many hours to attain this precision. This would have been awkward in experiment 1 and prohibitive for experiment 2 since the NBS-H2 maser had no temperature control, a limitation that necessitated a fast measurement technique (30 minutes maximum duration).

Fortunately we also had available the hydrogen maser standard NP3 of the National Aeronautics and Space Administration (NASA). Its design is described in [21]. The most important features of this maser for the present purpose are its stability and the provision of synthesized standard output frequencies. We used one of its outputs on nominally $\nu_R = 5$ MHz. However, the NASA maser not only served as a highly stable frequency source allowing short- and long-term measurements with a precision of a few parts in 10^{13} but also as a calibrated transfer standard. As indicated in Fig. 1, the frequency of the NASA maser was constantly monitored by the NBS clock ensemble, which consisted of six commercial cesium standards. The clock ensemble generates the atomic time scale AT(NBS) with the frequency $\nu_{AT(NBS)}$; this frequency is set by calibration with the primary frequency standard. The most recent calibration had been made in May 1969 with the NBS-III cesium beam. A coordinated universal time scale is generated from AT(NBS) and is called UTC(NBS) with a frequency of $\nu_{UTC(NBS)} = \nu_{AT(NBS)} + \Delta\nu_{UTC}$. During the course of the measurements we had $\Delta\nu_{UTC} = -299.995 \times 10^{-10} \nu_{AT(NBS)}$. The nominal output of the NASA hydrogen standard NP3 was synthesized to reflect a coordinated universal time scale (UTC) [17]. Fig. 2 shows a plot of the fractional frequency of NP3 referenced to $\nu_{UTC(NBS)}$ (zero on the vertical scale) versus time. From Fig. 2 we can derive the correction $\Delta\nu_N$ as the offset of NP3 from $\nu_{UTC(NBS)}$ evaluated at the nominal hydrogen frequency. Several additional corrections are necessary to relate the frequency of the hydrogen maser to the unperturbed transition frequency in hydrogen. They are summarized in Table III together with those already mentioned.

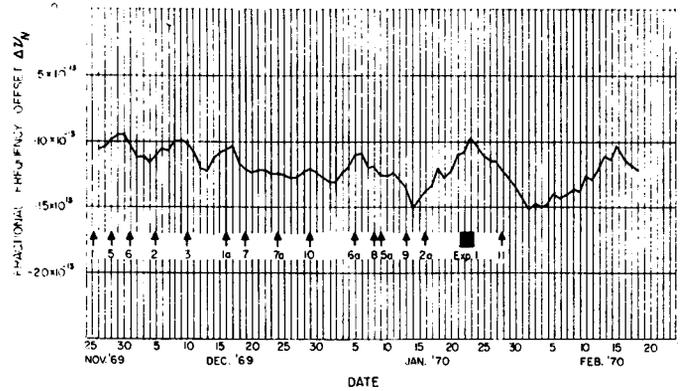


Fig. 2. Fractional frequency offset of NP3 from $\nu_{UTC(NBS)}$. Derived from a 4-day average of the time error of NP3 with respect to UTC(NBS): 6 clocks. Zero on the vertical scale corresponds to $\nu_{UTC(NBS)}$.

TABLE III
SUMMARY OF BIAS CORRECTIONS

| Correction | Symbol |
|--|-------------------|
| Offset of $\nu_{UTC(NBS)}$ from $\nu_{AT(NBS)}$ | $\Delta\nu_{UTC}$ |
| Offset of NASA-NP3 frequency from $\nu_{UTC(NBS)}$ | $\Delta\nu_N$ |
| Wall shift | $\Delta\nu_W$ |
| Second-order Doppler | $\Delta\nu_D$ |
| Thermalization | $\Delta\nu_T$ |
| Magnetic field (Zeeman) | $\Delta\nu_Z$ |
| Spin-exchange collision | $\Delta\nu_{SE}$ |
| Cavity tuning | $\Delta\nu_C$ |

The wall-shift correction was discussed previously in Section I, and (2), a semiempirical equation, was given. For (2) it is assumed that the wall shift is proportional to the wall-collision rate of the hydrogen atoms, i.e., to the inverse diameter of a spherical storage bulb.

The second-order Doppler effect in the hydrogen maser due to the thermal motion of the atoms necessitates a correction of [15]

$$\Delta\nu_D = C_1 T_s \quad (4)$$

where $C_1 = +1.9557 \times 10^{-4} \text{ Hz} \cdot \text{K}^{-1}$. We assume here that thermal equilibrium between the kinetic energy of the hydrogen atoms and the walls of the storage bulb is established. T_s is then the temperature of the storage bulb.

If the kinetic energy of the atoms is not fully in equilibrium with the temperature of the storage bulb, we will commit an error in using T_s . We should then introduce a correction $\Delta\nu_T$, which relates to the difference between the bulb temperature and the effective temperature of the stored atoms. Preliminary theoretical calculations of the thermalization process indicate [22] that $\Delta\nu_T$ should be sufficiently small to warrant $\Delta\nu_T = 0$ within our uncertainty limits. Some preliminary experimental results based on velocity selection in an atomic hydrogen beam support this assumption [23].

A magnetic field H causes a Zeeman effect on the energy level structure of hydrogen, and the corresponding frequency correction is given by [15]

$$\Delta\nu_Z = C_2 \overline{H^2} \quad (5)$$

where $C_2 = -2750 \text{ Hz} \cdot \text{G}^{-2}$, and $\overline{H^2}$ denotes the average of the squared magnetic field over the volume of the bulb. It is possible to measure the average magnetic field \overline{H} by inducing transitions among the magnetic sublevels of the $F = 1$ state and observing a change in the amplitude of the maser signal. This Zeeman frequency is given by [15]

$$f_Z = C_3 |\overline{H}| \quad (6)$$

where $C_3 = +1.4 \times 10^8 \text{ Hz} \cdot \text{G}^{-1}$. The error that one is forced to commit by substituting $\overline{H^2}$ from (6) for $\overline{H^2}$ in (5) in order to obtain $\Delta\nu_Z$ is negligible because very low and homogeneous magnetic fields ($|H| < 1 \text{ mG}$) are typically used.

The last two corrections from Table III, $\Delta\nu_{SE}$ and $\Delta\nu_C$, must be discussed together. The effects of spin exchange in combination with cavity tuning have been treated extensively in the literature [24]–[27]. The net result is that spin-exchange frequency shift and cavity pulling have a similar functional relationship to the atomic-resonance linewidth. As a consequence, cavity pulling and spin-exchange shifts cancel each other when the maser is "tuned," or

$$(\Delta\nu_C + \Delta\nu_{SE})_{\text{tuned}} = 0. \quad (7)$$

A "tuned" condition is here defined as a setting of the maser cavity such that the output frequency of the maser ν_M is independent of changes in the hydrogen pressure (beam intensity).

In experiment 1 the SAO maser was tuned in separate runs, both manually and automatically using its own automatic cavity servo, until the output frequency was unaffected by changes in the beam flux. The actual tuning element was a varactor diode mounted inside the cavity. Details of this procedure can be found in [20]. Averaging times of about 10–100 seconds were used to measure ν_B .

In experiment 2 the beat frequency ν_B for the tuned condition was calculated from four measurements of the maser frequency at two cavity settings and two beam intensities using a linear interpolation.⁴ The two cavity settings corresponded to maser frequencies that were typically a few parts in 10^{12} above and below ν_M (tuned). In this procedure, the cavity settings did not have to be known in an absolute sense but had to be reproducible to $\Delta\nu_M/\nu_M \approx 10^{-13}$. This was assured in separate experiments. The actual tuning element was also a varactor diode mounted inside the cavity. One complete measurement of ν_B took typically 15 minutes at averaging times of about 10 seconds.

From Table III and (3)–(7) we are now able to calculate the unperturbed hydrogen transition frequency referenced to NBS-III as

$$\nu_H = 284\nu_R + \nu_S + \nu_B + \Delta\nu_{UTC} + \Delta\nu_N + \Delta\nu_W + \Delta\nu_D + \Delta\nu_Z, \quad (8)$$

where $284\nu_R = 1420\,000\,000.0000 \text{ Hz}$ with $\nu_R = 5 \text{ MHz}$. All corrections $\Delta\nu$ are taken at the nominal hydrogen frequency.

III. EXPERIMENTAL RESULTS

We will now discuss the experimental results that we obtained in experiments 1 and 2 together with the uncertainty contributions associated with each of the frequency corrections. We begin with experiment 1; its results are summarized in Table IV.

The synthesizer was set at $\nu_S = 405\,794.4200 \text{ Hz}$; no uncertainty is associated with this value.

The period of the beat frequency was measured; the beat frequency ν_B is listed in Table IV. In order to obtain this value the maser had to be tuned. This can be done only with a certain precision. From the experimental results we estimate the associated uncertainty as $\pm 3 \times 10^{-13}$.

The fractional frequency offset of UTC(NBS) against AT(NBS) is nominally $\Delta\nu_{UTC} = -299.995 \times 10^{-10} \nu_{AT(NBS)}$ as listed in Table IV; no uncertainty is involved.

The actual synthesized output frequency of the NASA hydrogen maser standard deviated by a small amount $\Delta\nu_N$ from the frequency $\nu_{UTC(NBS)}$. For the date of our experiment we can take the corresponding bias correction directly from Fig. 2 and obtain $\Delta\nu_N = -0.0015 \text{ Hz}$. There is some uncertainty in this value due to the estimate of the accuracy capability of NBS-III ($1\sigma = 5 \times 10^{-13}$ [19]) and due to the frequency dispersion of AT(NBS) since it was calibrated (May 1969). The actual uncertainty (one sigma) during the time of the measurement was $\pm 9 \times 10^{-13}$.⁵

We have already discussed the fact that the wall-shift correction was obtained by a comparison between the portable SAO maser and the HU reference maser. The wall shift of the HU maser was measured in early 1969; a one-sigma confidence interval of $\pm 0.5 \text{ mHz}$ was assigned to this measurement [3]. However, we have to consider the possibility of secular changes of the physical properties of the wall coating since that time. Preliminary measurements at HU indicate that the associated uncertainty could be as large as 2 mHz . A correction of -2 mHz seems most likely [28] and would put the value of experiment 1 very close to that of experiment 2. We are not applying this correction, however, because we do not yet consider this result conclusive. The combination of the original measurement uncertainty and this bulb-aging effect thus leads to a total uncertainty of $\pm 2 \text{ mHz}$.

⁵ This value has been confirmed by comparisons between the rates of AT(NBS) and AT(U.S. Naval Observatory) as well as AT(NRC) over the past year.

⁴ This technique was also used in the comparison between the SAO maser and the HU reference maser.

TABLE IV
SUMMARY OF RESULTS FROM EXPERIMENT 1

| | ν_S | ν_B | $\Delta\nu_{UTC}$ | $\Delta\nu_N$ | $\Delta\nu_W$ | $\Delta\nu_D$ | $\Delta\nu_Z$ |
|-------------------------|---------------------|--------------------------------|----------------------------|---------------|----------------------|--|-------------------------|
| Observed quantity | synthesizer setting | electronic counter measurement | -299.995×10^{-10} | Fig. 2 | beat frequency at HU | $T_{\text{bulb}} = 47^\circ\text{C}$ (320.15°K) | $f_Z = 1020 \text{ Hz}$ |
| Bias corrections (Hz) | +405 794.4200 | -0.1193 | -42.6115 | -0.0015 | +0.0202 | +0.0627 | -0.0015 |
| Bias uncertainties (Hz) | — | ± 0.0004 | — | ± 0.0013 | ± 0.0020 | ± 0.0001 | ± 0.00002 |

$$\nu_H = 1420\,405\,751.7691 \pm 0.0024 \text{ Hz}$$

The second-order Doppler correction for the SAO maser is calculated from the bulb temperature using (4). The temperature was $(47 \pm 0.5)^\circ\text{C}$ maintained by the automatic temperature control of the SAO maser. This leads to the values for $\Delta\nu_D$ and its uncertainty in Table IV. The last correction in Table IV is the frequency change due to the Zeeman effect. A Zeeman resonance frequency of 1020 Hz was measured, and $\Delta\nu_Z$ can be calculated from (5) and (6). The Zeeman frequency was typically stable to about ± 5 Hz. This leads to a negligible uncertainty.

From (8) and Table IV we can now calculate the result for ν_H , the unperturbed hydrogen hyperfine frequency. Its uncertainty is calculated as the square root of the sum of the squared individual contributions since they are independent of each other. From

Experiment 1:

$$\nu_H = 1420\,405\,751.7691 \pm 0.0024 \text{ Hz.}$$

We now discuss the results of experiment 2. A total of 15 measurements of different coatings and bulb sizes were made. As coating material we used Du Pont's TFE Teflon, Blend 42, Lot 8842, 34.3 percent solids, purchased in 1969.

The actual coating solution consisted of 50 percent Teflon, 40 percent distilled water, and 10 percent Triton X-100 (Rohm and Haas). The bulbs were thoroughly cleaned with diluted sulfuric acid, and the coating solution was applied and then dried by circulating dry nitrogen gas through the bulb. The baking was done at 380°C for one-half hour while oxygen was circulated through the bulb. The bulbs were heated up rapidly in about 15 minutes; the cooling after baking took about 1 hour although the initial drop in temperature to below 300°C occurred rather rapidly within a few minutes. The bulbs were heated up to above 300°C immediately before setting them into the maser. They were put hot into the maser, which was then pumped down immediately. Some bulbs (indicated by a dagger in Table V) received a second Teflon coating on top of their first one. The procedure was identical to the one described previously, including the cleaning of the first coat with acid. No problems were encountered in any of the many coating

procedures. All coatings, first and second ones, passed the "water drop test" (tested *after* their use in the maser). The coatings were transparent and appeared only slightly milky. All bulbs, except bulb 1, were new and never coated before.

The first column in Table V gives the identification numbers of the bulbs. The second column lists the dates of their measurements in the hydrogen maser. In the third column we find several remarks; in the fourth, the nominal diameter is given; and in the fifth column we find the accurate inverse diameter that was determined from a volume measurement. The sixth column gives the temperature of the bulb (actually the temperature of the cavity was measured) at the time of the measurement. The NBS-H2 maser used in this experiment had no temperature control of its own. Therefore the temperatures for the various measurements differ slightly. The seventh column lists the Zeeman resonance frequency. The eighth column gives the beat frequency ν_B of the tuned maser. In the ninth column the beat frequency ν_B (corrected) is corrected for the offsets $\Delta\nu_N$ of the NASA hydrogen standard according to Fig. 2. The last column lists the standard deviation of several (more than ten, typically) independent tunings of the maser. A plot of the beat frequency ν_B (without the $\Delta\nu_N$ correction) as a function of the inverse bulb diameter is shown in Fig. 3. No oscillations were possible with bulb no. 4 since this bulb caused a significant reduction of the cavity Q . Bulbs 1*, 5*, 6*, and 10* were excluded from the final analysis (indicated by the asterisk).

They all showed obvious differences from all other bulbs, as we now describe. Bulb 1* was a previously used one, stripped of its old coating with hydrofluoric acid, and recoated. It showed up in the graph with a far too high ν_B , i.e., a larger wall shift than the other bulbs. This may be explained by its surface roughness leading to an effectively larger surface area. A second coating (†) apparently smoothed out this roughness and brought this bulb in line with the others.

Bulbs 5* and 6* received extremely thin, almost invisible coatings, but they passed the water drop test. They responded with somewhat lower values of ν_B , i.e., less wall shift than the rest of the bulbs. A second coat

TABLE V
DETERMINATION OF THE UNPERTURBED HYDROGEN FREQUENCY
EXPERIMENT 2

| Bulb No. | Date of Measurement | Remarks | Nominal Diameter (inch) | Inverse Diameter (cm ⁻¹) | T (°C) | f _Z (Hz) | ν _B (Hz) | ν _B (Hz) (corrected) | 1σ (mHz) |
|----------|---------------------|----------------------------------|-------------------------|--------------------------------------|--------|---------------------|---------------------|---------------------------------|----------|
| 1* | Nov. 25, '69 | old bulb, glass etched | 6 | 0.0608 | 24.0 | 252 | -0.7191 | -0.7206 | 1.4 |
| 1† | Dec. 16, '69 | old bulb, glass etched | 6 | 0.0608 | 23.7 | 256 | -0.7094 | -0.7107 | 0.9 |
| 2 | Dec. 5, '69 | | 6 | 0.0599 | 24.1 | 233 | -0.7114 | -0.7129 | 0.9 |
| 2† | Jan. 16, '70 | | 6 | 0.0599 | 24.1 | 215 | -0.7105 | -0.7124 | 1.0 |
| 3 | Dec. 10, '69 | | 6 | 0.0597 | 23.7 | 271 | -0.7095 | -0.7109 | 0.8 |
| 4 | | very heavy bulb | 5 | | | | | | |
| 5* | Nov. 28, '69 | very thin coating | 5 | 0.0786 | 23.8 | 255 | -0.7172 | -0.7186 | 0.7 |
| 5† | Jan. 9, '70 | | 5 | 0.0786 | 24.0 | 262 | -0.7210 | -0.7228 | 1.5 |
| 6* | Dec. 1, '69 | very thin coating | 4 | 0.0975 | 24.0 | 265 | -0.7226 | -0.7241 | 2.3 |
| 6† | Jan. 5, '70 | | 4 | 0.0975 | 23.8 | 277 | -0.7313 | -0.7328 | 1.3 |
| 7 | Dec. 19, '69 | | 4 | 0.101 | 24.0 | 255 | -0.7319 | -0.7336 | 1.0 |
| 7† | Dec. 24, '69 | | 4 | 0.101 | 23.8 | 250 | -0.7299 | -0.7316 | 0.9 |
| 8 | Jan. 8, '70 | | 4 | 0.103 | 24.1 | 263 | -0.7330 | -0.7347 | 0.6 |
| 9 | Jan. 13, '70 | | 6 | 0.0655 | 23.8 | 252 | -0.7106 | -0.7125 | 1.1 |
| 10* | Dec. 29, '69 | no spin-exchange tuning possible | 3 | 0.134 | 23.9 | 248 | -0.741 | -0.743 | 7.0 |
| 11 | Jan. 28, '70 | | 8 | 0.0504 | 23.7 | 244 | -0.7052 | -0.7069 | 1.0 |

* Indicates zero weight given in final analysis.

† Indicates a second Teflon coating.

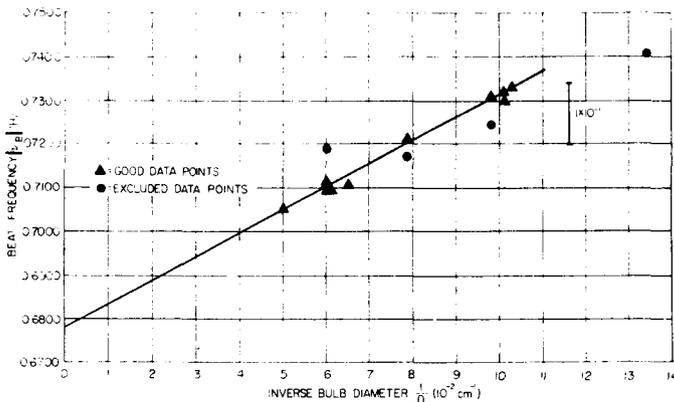


Fig. 3. Wall-shift measurement and hydrogen-cesium comparison from experiment 2 using the NBS-H₂ hydrogen maser. As plotted, the beat frequency ν_B does not contain the Δν_N correction. See Table V for both ν_B and ν_B (corrected). See Fig. 2 for the Δν_N correction.

(5† and 6†) brought them to values compatible with the majority of the bulbs. We have no good explanation for this effect.

Bulb 10* was so small that oscillations were barely possible. For this reason the spin-exchange tuning procedure, which required a reduction in beam intensity, could not be used. The uncertainty in its ν_B value was therefore prohibitively large for its inclusion in the final analysis.

The "good" bulbs were used in a linear, least-squares fit whereby each measurement point was weighted according to its variance (σ² from Table V). The intercept at 1/D = 0, which corresponds to Δν_w = 0, was obtained as ν_B (corrected) = -0.6798 Hz. The standard deviation

of the n = 11 points from the straight line was calculated to be σ = 0.00108 Hz. We can now estimate the confidence interval w of the intercept at 1/D = 0 from [29],

$$w = \left(\frac{1}{n} + \frac{(x - \bar{x})^2}{\sum x^2 - n\bar{x}^2} \right)^{1/2} t_{1-\alpha/2} \sigma \quad (9)$$

where α is the confidence level, t is the student t, and x = 1/D. For one-sigma confidence we calculate w = 0.0012 Hz.

Table VI summarizes this result and all other pertinent data analogously to Table IV. The synthesizer was set at ν_s = 405 795.0000 Hz, and the beat frequency ν_B (corrected) in Table VI is the frequency at the intercept and is thus the frequency for Δν_w = 0. It contains the correction Δν_N that was already applied in Table V. The uncertainty associated with Δν_N is the same as in Table IV and was discussed there. For the Doppler correction Δν_D we use the mean value for the temperatures listed in Table V. The uncertainty of the temperature measurement is again estimated at ±0.5°C, which well includes the systematic differences of the temperatures of the individual measurements. The mean Zeeman frequency of all measurements (Table V) is f_Z ≈ 245 Hz (175 μG), which leads to a correction of only 0.1 mHz. The individual measurements of f_Z spread around this mean by at most ±30 Hz, which corresponds to a negligible variation of the bias of ±0.02 mHz. This value is listed as bias uncertainty of Δν_Z in Table VI.

From (8) and Table VI we can now calculate ν_H, the unperturbed hydrogen hyperfine frequency. The uncertainty is the square root of the sum of the squared individual contributions, analogously to experiment 1.

TABLE VI
SUMMARY OF RESULTS FROM EXPERIMENT 2

| | ν_S | ν_B (corrected) | $\Delta\nu_{UTC}$ | $\Delta\nu_N$ | $\Delta\nu_W$ | $\Delta\nu_D$ | $\Delta\nu_Z$ |
|-------------------------|---------------------|------------------------|----------------------------|---------------------------------|---------------------------------|---|------------------------|
| Observed quantity | synthesizer setting | Fig. 2 and Table V | -299.995×10^{-10} | Fig. 2 | Fig. 3 | $T_{bulb} = 23.9^\circ\text{C}$ (297.05°K) | $f_Z = 245 \text{ Hz}$ |
| Bias corrections (Hz) | +405 795.0000 | -0.6798 | -42.6115 | included in ν_B (corrected) | included in ν_B (corrected) | +0.0581 | -0.0001 |
| Bias uncertainties (Hz) | — | ± 0.0012 | — | ± 0.0013 | — | ± 0.0001 | ± 0.00002 |

$$\nu_H = 1420\,405\,751.7667 \pm 0.0018 \text{ Hz}$$

Experiment 2:

$$\nu_H = 1420\,405\,751.7667 \pm 0.0018 \text{ Hz.}$$

Fig. 3 and Table V allow a calculation of the wall-shift coefficient K' (at 24°C), where

$$K' = K[1 + \alpha(24 - 40)]. \quad (10)$$

For experiment 2 we find (for TFE-Teflon)

$$K' = +0.528 \text{ Hz}\cdot\text{cm.}$$

From Table I (experiment 1) we calculate for the value of Zitzewitz *et al.* (FEP-Teflon) at the same temperature using $K' = +1.192K$

$$K' = +0.460 \text{ Hz}\cdot\text{cm.}$$

The difference between these values is only about 13 percent despite the fact that two different kinds of Teflon were measured: the homopolymer TFE (tetrafluoroethylene polymer) and the copolymer FEP (TFE plus hexafluoropropylene).

IV. CONCLUSIONS

The values for ν_H from experiments 1 and 2 are well within each other's error limits. The uncertainties assigned to the two values are not much different. We therefore take the mean of both as the most probable value of the unperturbed hydrogen transition frequency

$$\nu_H = 1420\,405\,751.768 \pm 0.002 \text{ Hz.}$$

This result is based on the two most extensive wall-shift evaluations that have been carried out so far, as evidenced in Table I. Furthermore, the hydrogen-cesium comparison was done while a direct link existed to the wall-shift correction data. In experiment 1 this link was provided by the preservation of the results of the Harvard wall-shift experiment [3] in the HU reference maser, and the calibration of the SAO maser against this reference. In experiment 2 the link was established by the simultaneous, integral wall-shift/hydrogen-cesium comparison experiment. In addition we used one of the best evaluated cesium standards currently in existence as

our reference (NBS-III). We feel that our quoted error limits, as documented in this paper, are realistic and meaningful.

The only question not yet completely settled is the problem of thermalization in the bulb. Although there is evidence [22], [23] that a somewhat incomplete thermalization will not cause an observable bias correction today, we encourage experimentation towards clarifying this point in view of the possibility of future, more accurate measurements.

A comparison of our results with those obtained previously is made in Table II. The range of values for ν_H totaling about 6×10^{-11} (90 mHz) far exceeds any quoted uncertainties and therefore requires some critical discussion. We surely can not explain deviations of this magnitude by differences in the cesium reference standards alone. Cesium beam tubes are extensively studied and intercompared devices. The uncertainty to be attributed to the cesium standards that have been used could be as high as 2×10^{-11} (28 mHz) before 1964, 1×10^{-11} in 1964, 3 to 5×10^{-12} (4-7 mHz) between 1965 and 1966, and 1 to 3×10^{-12} (1.4-4 mHz) since then. A larger uncertainty in the wall-shift correction as compared to those quoted in the past is the most likely explanation for most of the discrepancies. It is evident that the wall shift is not a constant of nature, but largely depends on the kind of Teflon (including differences from year to year due to the manufacturing process) and on the many complex parameters involved in the actual coating procedure. This is evidenced in Table I (compare also [3]), in the exclusion of bulbs from the wall-shift evaluation as indicated by the asterisks in Table V, and in [3] where we observed wall shifts that were up to 50 percent different from the wall shifts of "good" bulbs. Two statements can be made in consequence: 1) using only a few bulbs (e.g., two) for a wall-shift measurement can lead to highly erroneous results, and 2) the use of a wall-shift correction not directly related to the hydrogen maser that is used in a ν_H determination may also lead to errors far exceeding those quoted in Table II. If we check the values listed in Table II against the above two state-

ments, we find that the majority of the values do not have the direct experimental link required by statement 2) between the bulb used in the hydrogen maser and the applied wall-shift correction. Furthermore, they are correlated through the almost exclusive use of one particular wall-shift evaluation that we believe to be a valid one at the time of its measurement but that should not be used in the sense of a universal correction (statement 2)). Only the values of Crampton *et al.* and Menoud and Racine are based on a direct relationship between the hydrogen-cesium measurement and a wall-shift determination; unfortunately, however, only two bulbs were used in each case and statement 1) applies. The only values not affected by either statement are those of this paper.

The discussion of discrepancies in past values of ν_H that is given above should not, however, be interpreted to imply that a frequency standard based on hydrogen storage is necessarily inferior to a cesium standard. First, the uncertainties due to the cesium comparison and those due to the wall-shift correction contribute about equally to the uncertainty that we assign to our measurements of ν_H . Furthermore, a more recent measurement of ν_H has been reported [30], which was based on an independent wall-shift evaluation and which was also referenced with transfer standards to the cesium standard NBS-III. This new value of ν_H is almost identical with the results of this paper.

Second, new experimental developments that promise a reduction in the wall-shift limitation have evolved recently. They include the big storage vessel [31], the deformable storage bulb [28], and the operation at elevated bulb temperatures [30], [32]. Thus, hydrogen storage devices should be considered serious competitors for the primary standard of the future, a place now held by the cesium beam standard.

ACKNOWLEDGMENT

The following laboratories with their apparatus participated in these experiments: 1) the Atomic Frequency and Time Standards Section of the National Bureau of Standards with a laboratory-type hydrogen maser, designated NBS-H2, and the NBS clock system that was calibrated by the evaluated cesium primary frequency standard NBS-III, 2) the Smithsonian Astrophysical Observatory with a portable hydrogen maser, and 3) the Lyman Laboratory of Physics of Harvard University with the Harvard reference hydrogen maser. We are grateful for the support received from our respective organizations, which made this joint experiment possible.

We owe special thanks to H. E. Peters and E. H. Johnson for making available their NASA hydrogen maser standard NP3, which greatly facilitated our measurements. The U. S. Army Electronics Command kindly made available several storage bulbs, two of which were used in the experiment. The original design and construction of the NBS-H2 hydrogen maser is the work of

Dr. F. R. Petersen. A. S. Risley's and H. E. Bell's help in preparing NBS-H2 for the experiments is gratefully acknowledged.

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INSTRUMENTATION AND MEASUREMENT
Vol. IM-19, No. 4, November 1970

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NRC 11548