

large coils and 1.3 in 10^6 from the small coils. This estimate is not ungenerous, because as the errors are likely to be in the same sense they should afford partial compensation.

Tab. 2 lists all the known errors exceeding 1 or 2 in 10^7 .

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The Atomic Hydrogen Maser

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With 9 Figures in the Text

Abstract

The atomic hydrogen maser is described. In this device hydrogen atoms in the upper hyperfine state are focused onto the entrance aperture of a teflon coated quartz bulb in which the atoms are stored for about a second. This bulb is surrounded by a cylindrical radiofrequency cavity. When the cavity is tuned to the hyperfine frequency of atomic hydrogen, maser radiation is produced. Due to the large line Q resulting from the long storage time, the radiation is highly stable in frequency. Results are given of theoretical calculations on the threshold flux of atoms required for maser oscillations, on the various relaxation processes that limit the effective storage time, and on the possible sources of frequency shifts of the maser. Results are given on the relative stability of two hydrogen masers. Measurements of the atomic hyperfine frequency of atomic hydrogen and deuterium give $\Delta_H = 1,420,405,751.800 \pm 0.028$ cps and $\Delta_D = 327,384,352.5 \pm 1.0$ cps on the A.1 time scale with $\Delta_{cs} = 9,192,631,770.0$ cps. The method by which the deuterium has been measured depends upon the effect of a deuterium magnetic resonance transition upon the intensity of the hydrogen maser oscillation amplitude when a mixture of hydrogen and deuterium is used. This method should be capable of extension to a number of different atoms. The hydrogen maser apparatus has been used to measure the spin exchange collision cross section between atomic hydrogen and a number of different gases. Results of some of these measurements are reported. Measurements of the dependence of the hydrogen hyperfine frequency upon a strong externally applied electrostatic field are given.

I. Introduction

Most attempts to observe radiofrequency or microwave spectral lines with high precision incorporate one or more of the following features; (a) observation of the resonance over a relatively long period of time in order to obtain a narrow resonance line; (b) observation of a spectral line which is as pure as possible so that there is no broadening due to different components of the line or to the environment of the atom or molecule concerned; (c) a technique for eliminating, or at least greatly reducing, the first order Doppler shift; and (d) a means for obtaining a favorable signal-to-noise ratio such as is provided in the low-noise amplification which characterizes a maser oscillator. Although most high-precision radiofrequency and microwave experiments depend upon one or more of the above characteristics, none of them in the past has attained high quality in all of these features in a single method.

The hydrogen maser experiments described in the present paper originated in an effort to obtain a single device which was highly favorable in all of these features. Historically, the experiments were an outgrowth of the writer's previously described successive oscillatory field technique [1] and of the atomic beam experiments with stored atoms [2-4] at Harvard University. The hydrogen maser also incorporates features of the ammonia beam maser developed by Townes and his associates [5, 6]. The experiments are also related to the buffer gas experiments of Dicke [7, 8] and others although no buffer gas is used in maser. It is also related to the proposed relaxation experiments analyzed theoretically by BABB [8a]. A preliminary report on the hydrogen maser has been

published [4, 9–12] and a detailed analysis of the theory of the hydrogen maser has been given [13]. The hydrogen maser research at Harvard has been carried on in cooperation with D. KLEPPNER, H. ROBINSON, H. M. GOLDENBERG, N. FORTSON, H. BERG, E. RECK-NAGEL, and S. CRAMPTON.

II. The hydrogen maser

The hydrogen maser consists of the apparatus shown schematically in Fig. 1. Atomic hydrogen from radiofrequency discharge in the source passes through the inhomogeneous state selecting magnetic field from a 6-pole permanent magnet, as shown in Fig. 2. This field focuses atoms in the $[F=1, m=0]$ and $[F=1, m=1]$

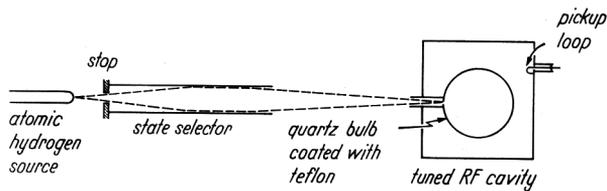


Fig. 1. Schematic diagram of atomic hydrogen maser

$m=1$] states onto an aperture in a Teflon coated quartz bulb. The energy levels for atomic hydrogen are shown in Fig. 3. The quartz bulb is located in the center of a cylindrical radiofrequency cavity, operating in the TE_{011} mode, which is tuned to the $[F=1, m=0] - [F=0, m=0]$ hyperfine transition frequency at approximately 1420.405 Mc/sec. The atoms make

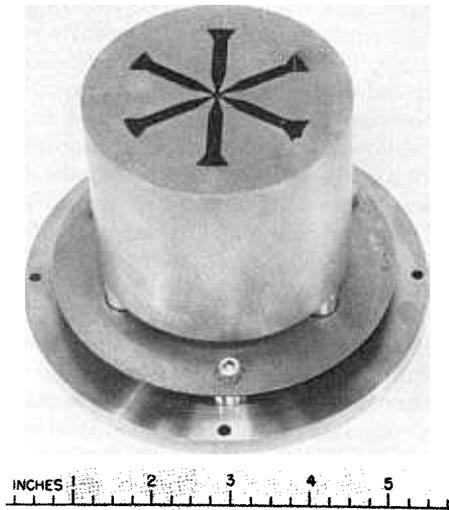


Fig. 2. Six pole permanent magnet

random collisions with the Teflon coated bulb wall and eventually leave the bulb through the entrance aperture. Due to their small interaction with the Teflon surface the atoms are only slightly perturbed even though they are retained in the bulb for several seconds and undergo approximately 10^6 collisions with the wall during the storage time. Under these conditions the resonance line is so sharp that self-excited maser oscillations at the hyperfine frequency can take place.

The hydrogen maser has advantages in the desirable features listed in the Introduction: (a) since the transition time is longer than one second, the reso-

nance line is narrow: (b) the hydrogen atom spends most of its time in free space where it has a simple unperturbed hyperfine spectrum and the effects of wall collisions are small due to the low electric polariz-

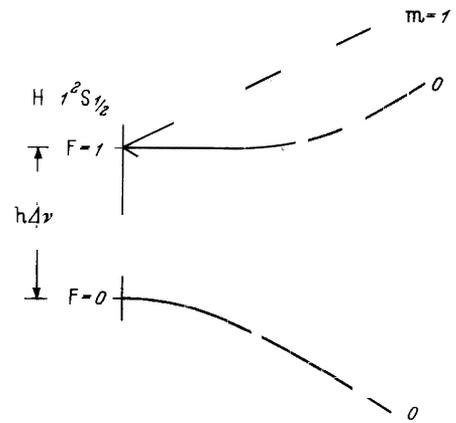


Fig. 3. Energy levels for hyperfine structure of atomic hydrogen in the electronic ground state $1^2S_{1/2}$. The electron and proton spins are parallel for the $F=1$ state and antiparallel for $F=0$. The indicated Zeeman splitting corresponds to the external magnetic field being increased toward the right of the figure.

zability of atomic hydrogen and the wall material: (c) the effect of the first-order Doppler shift is greatly reduced by the fact that the velocity of the atom in the bulb, when suitably averaged, is close to zero: and (d) the ability of the device to operate as a self-excited maser oscillator provides the advantages of low noise amplification which characterizes masers.



Fig. 4. Photograph of hydrogen maser. The apparatus is about four feet tall. The magnetic shields are removed

A photograph of the hydrogen maser is shown in Fig. 4. In these figures the cylinders with vertical axes are the diffusion pumps used to evacuate the hydrogen. They are much larger than necessary because one of the experiments to be done with this apparatus is to investigate the effects of excessive

amounts of gas flow. The cylinder with the horizontal axis is the tuned silverplated radiofrequency cavity. Inside the cavity is the quartz bulb of about 10 cm diameter which is coated with Teflon. In this apparatus the focusing magnet is a small permanent magnet. The earth's magnetic field is cancelled with concentric mu-metal shielding cylinders not shown in Fig. 4. A schematic view of a complete hydrogen maser used as a frequency standard is shown in Fig. 5. A photograph of such a maser is shown in Fig. 6.

A determination of these values is useful in the highest precision experiments as a means of making higher order corrections for field variations in the transition which is field independent to the first order.

Since the field dependence of the transition most studied is quadratic in the magnetic field, the effect of the magnetic field is markedly reduced at lower values of the field. Consequently magnetic shielding is ordinarily used to diminish the magnetic field to approximately a milligauss or less.

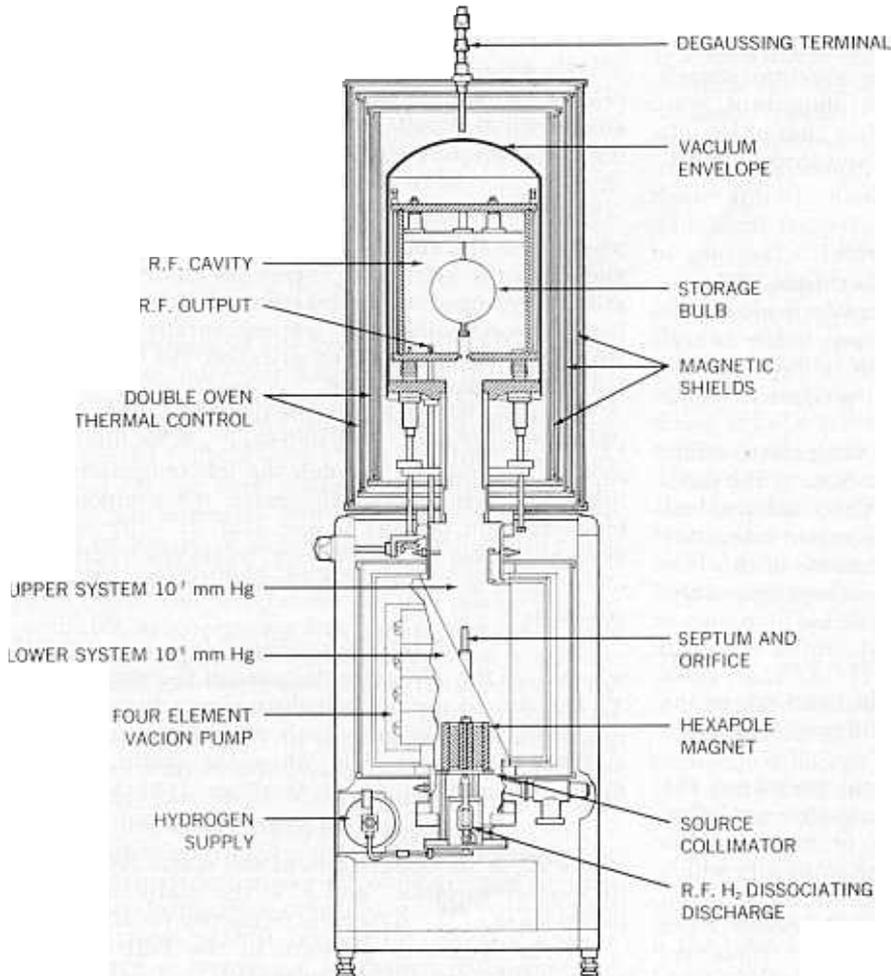


Fig. 5. Diagram of a complete hydrogen maser for use as a frequency standard [20]



Fig. 6. Photograph of a hydrogen maser frequency standard [20]

The hydrogen maser is normally used for transitions between the $[F = 1, m = 0]$ and $[F = 0, m = 0]$ energy levels of Fig. 3 because this energy difference is magnetic field independent to the first approximation. However, it has also been found possible to operate the maser between the $[F = 1, m = 1]$ and $[F = 0, m = 0]$ levels. Such operation provides a means of measuring the average strength of the magnetic field inside the cavity. This information can also be obtained by operating the maser on the field independent transition with a separate oscillatory field inducing transitions between the $[F = 1, m = 0]$ state to the $[F = 1, m = \pm 1]$ state. These ZEEEMAN transitions also provide a measure of the average magnetic field. Furthermore, the line observed in this case should be a doublet and the separation of the doublet provides a measurement of the mean square magnetic field.

III. Threshold for oscillation

For oscillation to occur the power delivered to the cavity by the beam must equal the power dissipated in the cavity. If I_{th} is the threshold intensity of the atomic beam, ν the hyperfine frequency, Q the quality factor of the cavity, η the geometrical factor approximately equal to 3 which depends on the distribution of the radiofrequency magnetic field in the cavity, V_c the volume of the cavity, H the oscillatory field amplitude, μ_0 the Bohr magneton and γ the relaxation constant of the atom in the bulb, so that γ is approximately the effective storage time in the bulb, then the above condition directly gives

$$I_{th} \left(\frac{1}{2} h\nu \right) = \frac{1}{Q} \frac{H^2}{8\pi} V_c 2\pi\nu \quad (1)$$

provided the oscillatory field is sufficiently strong for

the transition between the hyperfine states to be induced. The condition [12] for this is

$$\frac{\mu_0 H \sqrt{\eta}}{(\hbar/2\pi)} (1/\gamma) = 1. \quad (2)$$

On the elimination of H between these equations, the beam intensity at threshold becomes

$$I_{th} = \hbar V_c \gamma^2 / 8 \pi^2 \mu_0^2 Q \eta. \quad (3)$$

If typical values suitable for the hydrogen maser are substituted in this relationship, the threshold flux becomes about 10^{12} atoms per sec. An intensity of this magnitude can easily be achieved with an atomic beam apparatus employing a 6-pole focusing magnet. If the apparatus is operated under conditions such that spin exchange broadening is important, the threshold condition will be greater than that of Eq. (3) by a factor that varies between one and three depending on the exact circumstances [19].

IV. Relaxation processes

In Eq. (3) it is apparent that the threshold flux is strongly dependent upon the relaxation constant γ . Likewise the accuracy of the hydrogen maser is also dependent upon γ . For this reason it is important to consider the various relaxation processes which contribute to γ .

A variety of processes can limit the radiative lifetime of a beam in the storage bulb. Most of the processes are random and lead to time independent relaxation rates, so that the total relaxation rate is the sum of the rates for each process. Because of this it is possible to analyze the relaxation processes separately. The total relaxation rate is then given by.

$$\gamma = \gamma_0 + \gamma_s + \gamma_r + \gamma_{H1} + \gamma_{H2} + \gamma_{se} \quad (4)$$

where the subscripted γ 's on the right hand side of the above equation correspond to the different relaxation processes as defined subsequently.

In the case of nuclear magnetic resonance the dynamical equations of the magnetization are often described by the Bloch equations in terms of the relaxation times T_1 and T_2 , the time constants which describe the return of magnetization in a given direction to its equilibrium value, and the decay of the oscillating dipole moment, respectively. These relaxation times are not used in the present analysis because the Bloch equations do not apply due to the presence of hyperfine structure. It is important to remember, however, that a given perturbation frequently causes relaxation by both changing the magnetization along the axis of quantization and by causing loss of coherence between the oscillating moment and the radiofrequency field, and that these two rates may be considerably different. To emphasize this, the subscripts 1 and 2 are used to identify decay rates due to each of these processes, respectively. A detailed description of the different relaxation processes has already been given in the literature [13] along with suitable derivations. Consequently, in the present article merely the results of the derivations will be given.

The escape rate of atoms from the bulb through its hole is a basic source of relaxation designated γ_0 . It may easily be seen [13] that

$$\gamma_0 = \bar{v} A_e / (4 K V_b) \quad (5)$$

where \bar{v} is the mean velocity of the atoms, A_e the total escape area, K a numerical factor depending on the geometry of the hole (unity for a thin hole), and V_b the volume of the storage bulb.

Although the atom spends most of its time in the free space of the bulb, a small fraction is spent on the wall surface and during this time the hyperfine frequency is slightly altered. If Φ is the average phase shift per collision caused in this way and if \bar{v}/l is the collision rate, the relaxation rate γ_s by this adiabatic wall process is given [13] by

$$\gamma_s = \frac{1}{2} (\bar{v}/l) \Phi^2. \quad (6)$$

In addition to the above adiabatic wall relaxation process, a non-adiabatic chemical reaction of the atom with the wall is equivalent to escape from the bulb. The effective relaxation from this is given [13] by

$$\gamma_r = (2\bar{v} P / \pi^2 l) \exp(-E_a/kT) \quad (7)$$

where P is the steric factor [13] often taken as 0.1 and E_a is the activation energy for the reaction. For atomic hydrogen on hydrocarbon walls, $\gamma_r \approx 0.7 \text{ sec}^{-1}$ both theoretically and experimentally. However, with fluorocarbon walls such as Teflon, the decay rate is found to be much smaller.

Magnetic field inhomogeneities cause relaxation in two different ways. One of them, γ_{H1} , is due to the motion of the atom through the inhomogeneous field inducing transitions which change the component of magnetization parallel to the field. If $\langle H_t^2 \rangle$ is the average square of the varying transverse component of the field and if t_0 is the mean time between wall collisions

$$\gamma_{H1} = 2 \gamma_F^2 \langle H_t^2 \rangle t_0 \quad (8)$$

where γ_F is the gyromagnetic ratio of the atom in state F . The second process, which produces the relaxation γ_{H2} , arises from the loss of coherence between the atom and the oscillatory field when the static magnetic field is not uniform. It can be shown [13] that

$$\gamma_{H2} = t_0 (16 \alpha^2 H_0^2 \Delta H^2) \quad (9)$$

where H_0 is the magnitude of the static field, ΔH is its typical variation, and α is the coefficient of the dependence of the hyperfine frequency on H_0^2 .

If the hydrogen pressure in the bulb is raised sufficiently there will be a relaxation γ_{se} by the process of spin exchange in the hydrogen-hydrogen collisions where [13]

$$\gamma_{se} \approx 5 \cdot 10^{-10} N \text{ sec}^{-1} \quad (10)$$

with N being the number of hydrogen atoms per cubic centimeter.

In addition to the above, relaxation can also be produced by DOPPLER and pressure broadening but these are normally too small to justify reproducing the theoretical expressions here [13].

When all the above relaxation processes are combined by Eq. (4), to yield the resultant relaxation γ , it is found that $\gamma \sim 0.5 \text{ sec}^{-1}$ should be achieved, i.e., storage times of several seconds should be obtainable. Experimentally this is found to be the case when atomic hydrogen is stored in Teflon-coated bulbs.

V. Frequency stability and accuracy

The frequency stability and accuracy of the hydrogen maser is determined in part by the relaxation

times discussed in the previous section but also by other factors as well. One of these is thermal noise since with thermal noise the apparent position of the resonance peak will deviate slightly from the true resonance. It can be shown that the root mean square deviation of the frequency is given [6, 13] by

$$\langle \Delta \omega^2 \rangle^{1/2} / \omega_0 = \frac{1}{2\pi\sqrt{2}} \frac{1}{Ql} \sqrt{\left(\frac{kT}{Pt}\right)} \quad (11)$$

where $Ql = \omega_0 / (2\gamma)$ is the line quality factor, P is the power delivered by the beam to the cavity, and t is the observation time. For observation times of 1 second and for values characteristic of the hydrogen maser the above fractional deviations should be about 10^{-15} .

In addition to thermal noise in the frequency output, there are several potential sources of frequency shift. Since the hyperfine frequency will ordinarily be shifted when the atom is in the immediate vicinity of the bulb walls, the average frequency will be slightly shifted as well by the relative amount

$$\frac{\Delta \omega_w}{\omega_0} = \Phi / (\omega_0 t_0) \quad (12)$$

From a comparison of the frequencies of masers with different sized bulbs the magnitude of the wall shift can be experimentally determined. In this way it has been found that the frequency shift with a 6-inch Teflon coated bulb is -2.1 parts in 10^{11} . A search for a wall coating that produces a smaller shift is in progress. Furthermore, the shift can be markedly reduced by the use of larger diameter cylindrical bulbs and by the operation of the maser at a higher temperature. Since the magnitude of the phase shift is measurable by comparing frequencies of masers with different sized bulbs, the hydrogen hyperfine frequency is much more accurately measurable than indicated by the magnitude of the wall shift. Furthermore the stability is not limited by this shift since even the present wall shift is sufficiently small that no reasonable assumptions as to its variation produces any significant limitation to the stability.

The first order Doppler shift should be negligibly small in the hydrogen maser since the average velocity of the atoms during their time of radiation is essentially zero, as a result of their leaving by the same hole as they entered a second or so earlier. However, the second order Doppler shift is important. It is [13]

$$\frac{\Delta \omega_0}{\omega_0} = \frac{3kT}{2mc^2} = 1.4 \cdot 10^{-13} T \quad (13)$$

where m is the mass of the hydrogen atom. This means that the temperature must be stabilized to 0.01°C for a stability of 10^{-15} to be achieved.

A further source of frequency shift is the Zeeman effect on the hyperfine frequency. Fortunately, the $[F=1, m=0] - [F=0, m=0]$ transition in atomic hydrogen is independent of the magnetic field to first order as seen in Fig. 3. However, there is a second order of dependence of frequency upon field. If the magnetic field differs by an amount ΔH_0 from the assumed value H_0 , the frequency error will be [13]

$$\frac{\Delta \omega_z}{\omega_0} = 3.9 \cdot 10^{-6} H_0 \Delta H_0 \quad (14)$$

Hence, if H_0 is 1 milligauss it must be known to about 1 percent if this error is to be 10^{-14} .

One of the most important sources of frequency shift is cavity pulling. If the cavity is tuned to a frequency ω_0 the maser oscillation will be pulled an amount $\Delta \omega_c$ where [13, 19]

$$\frac{\Delta \omega_c}{\omega_0} = 2 \frac{(\omega_c - \omega_0)}{\omega_0^2} QK \quad (15)$$

with K being approximately $\omega_0/2 Q_l$ where Q_l is the quality factor of the emitted resonance line. More exactly and including effects of spin exchange collisions [19].

$$K = r + U/4 + 3D/8 + \gamma_2$$

where r is the rate of escape of an atom from the bulb, U is the average value of $2s \sin^2(\Phi/2)$, s is the hydrogen collision rate for a given atom, Φ is the phase shift induced between the $^1\Sigma$ and $^3\Sigma$ hydrogen wave functions induced by the collision, D is defined as for U except for hydrogen atoms striking other atoms such as deuterium which may be present, and γ_2 is an arbitrary additional transverse relaxation included for the sake of generality. Due to the narrowness of the line and hence the small value of K , the cavity pulling is much less for the hydrogen maser than for other oscillators. On the other hand this feature is used to provide greater stability, so great care must be still used with regard to cavity pulling if the ultimate stability of the maser is to be achieved. As a result the cavity must be thermally stabilized to better than 0.01°C to diminish drifts due to thermal expansion of the cavity. It is also helpful to design the cavity for approximate temperature compensation. Cavity detuning can also result from atmospheric pressure changes so it is best to surround the cavity with an evacuated cylinder to eliminate such detuning. Even when cavity tuning drifts are eliminated special care must be taken to assure that the cavity is tuned correctly. Means of doing so are discussed two paragraphs below.

An additional source of frequency shift is spin exchange collisions as have been discussed by BENDER [18] and CRAMPTON [19]. The spin exchange collisions will pull the frequency an amount $\Delta \omega_{se}$ where

$$\frac{\Delta \omega_{se}}{\omega_0} = \frac{1}{4} \left(\frac{V}{U}\right) \lambda \frac{K}{\omega_0} \quad (15a)$$

In the above V is the average value of $s \sin \Phi$ so (V/U) is the ratio of the rate of spin exchange phase shifting to the rate of spin exchange relaxing collisions. λ is given by the following

$$\lambda = \frac{V_c}{4\pi} \frac{\hbar}{\mu_0^2} \frac{1}{\eta Q} \frac{v_{HH} \sigma_{HH}}{V_0} < 1 - \cos \varphi > \quad (15b)$$

where v_{HH} is the mean relative hydrogen velocity and σ_{HH} is hydrogen-hydrogen cross section. For a given bulb and temperature V/U and λ are constants as the hydrogen pressure is changed, and consequently in Eq. (15a) as the hydrogen pressure is altered to change K , the frequency shift is altered proportionally to K just as is the case in Eq. (15) for cavity pulling.

The cavity is ordinarily tuned by varying the atomic hydrogen pressure and consequently the quantity K in Eqs. (15) and (15a); the cavity tuning is then adjusted until the maser frequency is independent of K . From Eqs. (15) and (15a), it is apparent that for such a setting the cavity mistuning exactly compensates for the spin exchange frequency pulling so there is no net frequency shift from these two sources

together even though each alone contributes a frequency shift. Independent of the details of the above analysis it is apparent that an adjustment to make the output frequency of the maser independent of the hydrogen pressure, if achievable, will lead to a compensation of pressure dependent effects which vanish at zero pressure and are larger at the pressures of the observations since with pressure independence the frequency will then be the same at the actual pressure and at zero pressure. The accuracy to which this compensation can be achieved depends on the accuracy of relative frequency measurements. An accuracy of 10^{-14} should eventually be achievable in this respect.

From a consideration of the above sources of frequency shifts, it appears that an accuracy of better than 10^{-13} should be achievable with the hydrogen

In these experiments it was found that if one assumes for the A.1 time standard that $\Delta\lambda(Cs) = 9,192,631,770.0$ cps, then for atomic hydrogen corrected for second order Doppler shift to 0°K

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

The measurements were made in terms of the Loran-C frequency. However, at the same time W. MARKOWITZ and R. G. HALL measured the Loran-C frequency in terms of the A.1 time scale as derived from the operation of cesium atomic beam standards in eight laboratories around the world (with VLF being used for their intercomparison). The hydrogen was then referred to the A.1 time scale.

The uncertainties in the measurement are discussed in detail by CRAMPTON, KLEPPNER and RAMSEY [22].

The uncertainty in the primary A.1 time scale provided the largest contribution. This fractional uncertainty was estimated to be $2 \cdot 10^{-11}$. The next largest error was due to short term fluctuations of the NC 2001 Cs beam signal that was used as a local secondary standard in the intercomparison. The error introduced from this source was estimated to be $0.5 \cdot 10^{-11}$.

Of the uncertainties arising from the hydrogen maser itself, the largest was due lack of exact knowledge of the frequency shift caused by interactions of the hydrogen atoms with the teflon-coated quartz containing vessel. The total wall shift for the 6" bulb was -0.0298 cps. as contrasted to no collisions in free space. This wall shift can be measured by observing the dependence of the frequency upon the bulb diameter [13, 22]. In the experiment described in reference [22], the uncertainty was larger than necessary since the

coating of the storage bulb had been partially contaminated with forepump oil in an accident during the course of the experiment. However, even with this unnecessary complication the uncertainty due to the wall shift was $0.2 \cdot 10^{-11}$, or only one tenth of that due to the A.1 time scale.

Adjusting a hydrogen maser to yield the correct frequency involves tuning the cavity and adjusting the magnetic field to a known value. Cavity tuning was accomplished by the technique discussed in Section V. With this technique any systematic frequency error due to spin exchange collisions is exactly cancelled by a 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. By these means the masers could be independently and reproducibly tuned to better than $1 \cdot 10^{-12}$.

The magnetic field within the maser was kept to a low value by means of cylindrical magnetic shields and was measured by observing the frequency of the field dependent Zeeman lines by the double resonance technique [2, 6]. The shift in frequency due to the magnetic field used in the experiment was 0.142 cps,

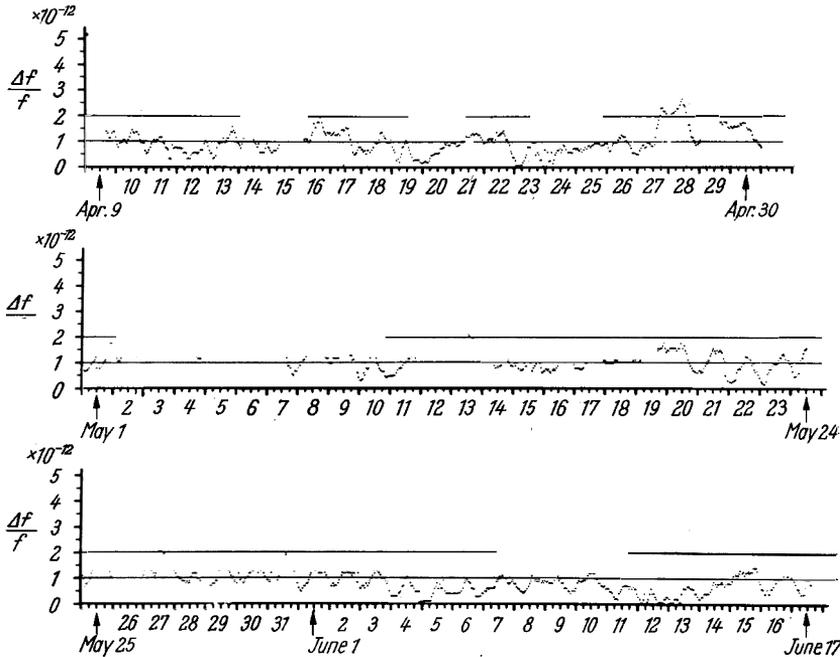


Fig. 7. Typical curve showing relative variation of frequencies of two hydrogen masers [20]

maser if sufficient care were taken. An accuracy of 10^{-13} is the objective with the present hydrogen masers. So far independent resettability to 10^{-12} has been achieved and rms frequency deviations of $5 \cdot 10^{-14}$ have been found over a 5-day period and of $4 \cdot 10^{-14}$ over a fifteen minute period. A curve showing the frequency variation of two masers over a two month interval is given in Fig. 7. The largest frequency variations are known to be due to large temperature variations in the room containing the masers and to inadequate temperature stabilization of the cavity. Improvements in mechanical stability, temperature stability, magnetic shielding, electronic stabilization of the cavity tuning, beam stability, etc., should improve all of the stability measurements to below the desired 10^{-13} .

VI. Measurement of atomic hydrogen hyperfine frequency

The atomic hydrogen maser has recently been used to measure the hydrogen hyperfine frequency in terms of the A.1 time scale based on Cs. These measurements are reported by CRAMPTON, KLEPPNER, and RAMSEY [22].

measured with a negligible error. The hydrogen maser is often operated at much lower magnetic fields where this shift is much smaller.

The correction for the second order Doppler shift when the masers are operated at 308 °K is -0.0602 cps. The temperature is measured with sufficient accuracy for this to yield a negligible error in the experiment.

The measured value of the atomic hydrogen hyperfine frequency agrees well with the previously published preliminary value [9] obtained with the first hydrogen maser when the earlier measurements are corrected to the A.1 time scale [21] by subtracting 10.6 cps. Likewise, the result falls within the very much larger limits of the measurements by WITKE and DICKE [15] and KUSCH [23]. When the results of LAMBERT and PIPKIN [24] are referred to the A.1 time scale [21] 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 [25] 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 [26] 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. R. F. C. VESSOT and H. C. PETERS [27] 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 and when it is recognized that the observations were taken at different times so that the intercomparison can be no more accurate than the Cs standard to which each was compared.

VII. The hydrogen maser as a frequency and time standard

As a frequency and time standard the hydrogen maser possesses many marked advantages over other devices. The only significant disadvantage is the small frequency shift which results from the atoms spending a fraction of their time on the walls of the containing bulb. With a teflon-coated 6" diameter bulb this fractional shift is $-2.1 \cdot 10^{-11}$. However, it can be measured by comparing the frequencies of bulbs of different diameter since the fraction of the time spent in wall collisions is inversely proportional to the diameter. Even with the present teflon-coated 6" spherical bulbs the uncertainty due to the wall shift should be no more than a few parts in 10^{13} . Several promising new materials for wall coatings will soon be tried and these may have smaller shifts and the maser operates well with considerably larger cylindrical bulbs for which the wall shift is correspondingly reduced. Furthermore, it has recently been found that the wall shift can be considerably reduced by operating the maser at a higher temperature.

The atomic hydrogen maser provides a radio-frequency radiation that is more stable than the radiation from any other source. This feature in combination with other favorable characteristics makes the hydrogen maser particularly suitable as a frequency and time standard.

The intrinsic narrowness of the resonance makes it

difficult to pull the maser frequency from the correct value and contributes to the maser's stability, reliability and accuracy. Furthermore, the atomic hydrogen spectrum is particularly simple and well spaced which diminishes perturbations from neighboring states. The first order Doppler shift is negligibly small and correction for the small second order shift can easily be made by measurement of the cavity temperature. In addition the low noise characteristic of maser amplification assures that the frequency of oscillation will be close to the peak of the resonance curve. The method of cavity tuning compensates for the frequency effects of spin exchange collisions.

Since the maser is an active oscillator, no external electronics are required in the basic frequency determining elements. The danger of hunting, the complications, and the reduced reliability associated with servo-circuits are avoided. As a result of the intrinsic simplicity of the hydrogen maser it has been relatively easy to make it reliable. Although the hydrogen maser is an atomic beam device the rate of gas flow is sufficiently low that several years' supply of hydrogen can easily be provided and a closed vacuum system with a titanium style pump should operate continuously without servicing for years.

As a result of the above characteristics, the short term stability, the long term stability, and the reliability of the maser are high and the maser can conveniently be operated continuously for long periods of time. Consequently the hydrogen maser is suitable as a direct continuously operating frequency and time standard, as opposed to being merely a device occasionally to monitor subsidiary oscillators. These properties make it suitable for use as a time standard as well as a frequency standard.

The hydrogen maser by its very newness should be subject to further improvements in subsequent years. Some of these improvements are sufficiently obvious and simple — like improved temperature stabilization — that they should lead to improved results almost immediately, while others may come only after more extensive research. Included in the probable improvements are installation of improved magnetic shields that have already been tested in one maser, development of wall coating materials with smaller wall shifts, reduction of wall shifts by use of larger storage bulbs and higher temperatures, improved temperature stability, improved mechanical stability, use of a solid quartz radiofrequency cavity, simplification of the vacuum system, electronic stabilization of cavity tuning, etc. It is reasonable to expect that with further development the independent resettability, the short and long term stability, and the absolute accuracy should all be $1 \cdot 10^{-13}$, or better, for the hydrogen maser.

VIII. The hyperfine frequency of atomic deuterium

The ratios of the atomic hyperfine structure separations for the three isotopes of atomic hydrogen can be measured with the hydrogen maser to much greater accuracy than they are known at present. Two quite different methods can be used for these measurements. One method — the one originally conceived and the most accurate method — involves the construction of separate masers for the intercomparison. In the case of deuterium the maser cavity would have to be much larger than that for hydrogen due to the lower

frequency of the deuterium hyperfine separation. Although such a maser should be feasible, there has not been an opportunity to construct it so far, so the measurements up to this time have been by the method discussed in the next paragraph.

Professor HUGH ROBINSON has suggested an alternative method of measuring the hyperfine separations. If hydrogen and deuterium are mixed in the source, the cavity will contain both H and D atoms. If sufficient H atoms are present, the maser can operate under such circumstances as a hydrogen maser. However, if the D pressure is sufficiently high, the H maser signal is limited in amplitude by spin exchange collisions [14–16] between H and D atoms. It has been found that the effectiveness of the D atoms in quenching the H maser oscillations is modified if hfs transitions of D are induced by an additional oscillatory field. Consequently the magnitude of the H maser oscillation can be used as a detector of the hfs transition in D . In this manner the hyperfine separation of D has been measured. Since all the necessary experimental checks have not as yet been made, the quoted error is much larger than that which should eventually be achieved. On the same scale as used above for H ,

$$\Delta_D = 327,384,352.5 \pm 1.0 \text{ cps.}$$

This method is applicable to other atoms as well. Even if the atom can not be stored for as long a time as H , the hfs should be measurable if even a few hundred wall collisions can be tolerated, as is already known to be possible, say with Cs . In this case, of course, the precision of the measurement is decreased with the reduced storage time, but even so the accuracies should ordinarily be better than those of past measurements. The hyperfine structure of atomic nitrogen has recently been studied in this fashion with much greater accuracy than was possible in any previous experiments.

An experiment to measure the hyperfine frequency of atomic tritium is now in progress.

IX. Measurements of spin exchange cross sections

The atomic hydrogen maser can be used to measure the spin exchange collision cross sections between

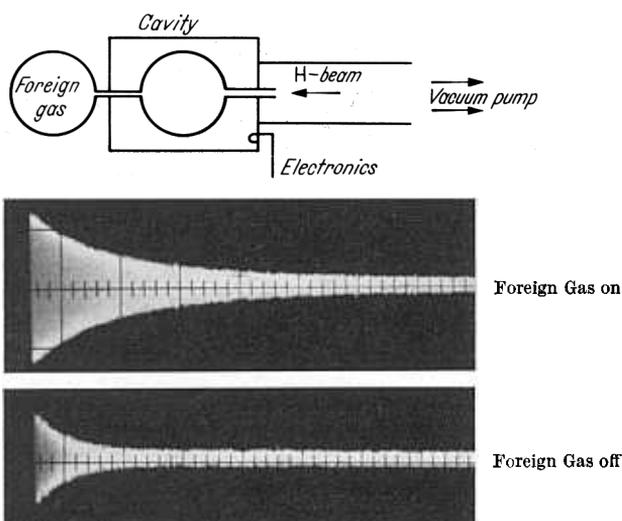


Fig. 8. Hydrogen maser apparatus adapted to the measurement of spin exchange cross sections and typical signal decay curves.

atomic hydrogen and other gases. The gas to be measured is introduced into the storage bottle along with the atomic hydrogen, as shown in Fig. 7. In these experiments the coupling loop is adjusted to diminish the cavity Q to such an extent that spontaneous oscillations no longer occur. A pulse at the hyperfine frequency of hydrogen is then introduced and the decaying signal is observed as in Fig. 8. The decay rate of the curve is observed and from this the increment γ' to the decay rate due to the foreign gas is obtained. In addition the strength of the signal is observed and the ratio \bar{d} of the signal without and with the foreign gas can be obtained. The quantity \bar{d} may then be plotted as a function of γ' when these quantities are varied by changing the pressure of the foreign gas. From the slope of this curve information can be obtained as to the nature of the collision process, as discussed by H. BERG [17]. The results are consistent with the dominant mechanism of relaxation being that of spin exchange collision with the amount of phase memory after the collision being that to be expected for spin exchange collisions [14–17].

From the dependence of the incremental decay rate γ' on the pressure of foreign gas, the mutual spin exchange cross sections can be obtained. The measurements of these quantities have just begun and only a few preliminary values are so far available.

In the future it is planned to extend these decay measurements not only to other molecules but also to collisions between hydrogen atoms and various solid surfaces as well.

X. Stark shift of hydrogen hyperfine structure

It has been theoretically predicted for many years that there should be a small shift of the atomic

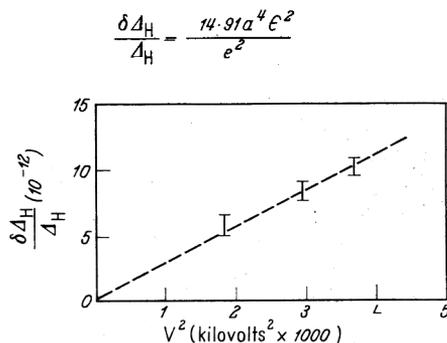


Fig. 9. Dependence of hydrogen hyperfine frequency on the square of the voltage applied to parallel plates inside the cavity

hydrogen hyperfine frequency with a strong externally applied electric field. However, even in the strong electric field used in the present experiment this shift is only a few parts in 10^{11} and has consequently been unobservable in the past. With the precision of the hydrogen maser, this effect has now been observed. The dependence of the hydrogen hyperfine frequency upon the voltage applied to the parallel plates in the cavity is shown in Fig. 9. It can be seen that the shift is proportional to the square of the applied voltage, as should be the case theoretically. Since the actual electric field distribution throughout the bottle has not been accurately determined as yet, a comparison between theory and experiment can not as yet be made to better than ten percent accuracy, though much

better accuracy should eventually be achieved. To within the present 10 percent accuracy, the measured frequency agrees well with that predicted theoretically.

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Scientific Metrology on the International Plane and the Bureau International des Poids et Mesures

By

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Convention du Mètre and Related Organizations

The "Convention du Mètre" is a treaty which was signed in Paris on 20th May 1875 by the plenipotentiaries of 18 states; it was revised on 6th October 1921 and others having joined there are now, in 1964, 40 adhering states. Any other may join simply by notification to the French government, with whom the treaty is deposited.

By this treaty, the Bureau International des Poids et Mesures was created, with the principal task of making, keeping and using one standard of length and one standard of mass, in order to provide the badly needed uniformity of measurement in science, trade and industry of the whole world. At that time, most of the desired standards of measurement could be easily derived from these two international standards. As the precision of the new international standards was about one hundred times better than the preceding ones, the Bureau International was immediately faced with difficulties such as poor definition of temperature scales and poor knowledge of physical constants (thermal expansion coefficient of materials, compressibility, density of water and mercury, acceleration due to gravity, etc.) and it therefore started scientific researches to fulfil these needs.

After the ninety years which have elapsed since the beginning of the Bureau International, its aims are still the same to a remarkable extent, despite the huge growth of metrology, the importance of the measurements made, their precision, their diversity and their extension throughout the world. The Bureau Inter-

national has grown up as a modern laboratory, its scope having been extended to thermometry, electricity, photometry and ionizing radiations. But the aim remains to promote uniformity and precision of physical measurements, by means of a few selected standards or procedures from which most others can be derived, and by related physical research.

The Bureau International des Poids et Mesures has also grown up as the centre for international cooperation in the field of scientific metrology, under the leadership of the Comité International des Poids et Mesures. This Comité International has great powers: not only does it nominate the director and the higher staff of the Bureau International and survey the work to be done; but it nominates also the laboratories and individuals expert in special fields who meet within the framework of the six Comités Consultatifs which exist to-day (definition of the metre, definition of the second, thermometry, electricity, photometry and standards of ionizing radiations). In these committees the work of the national laboratories towards improved standards of measurements can be discussed and planned and decisions of international importance can be discussed and prepared. A seventh one, dealing with units and the International System of Units, was created in October 1964. These Comités Consultatifs report to the Comité International des Poids et Mesures. The Comité International has the privilege of calling the governments participating in the Convention du Mètre to meet in a Conférence Générale des Poids et Mesures, at least once every six years.