from this crystal. The temperatures at which these events take place is graphically shown on the two channel recording.

Figs. 27 through 31 show some standard models and components of the Time-of-Flight Mass Spectrometer manufactured by The Bendix Corporation.

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D. B. Harrington

MICROWAVE SPECTROSCOPY

ATOMIC FREQUENCY STANDARDS

General Considerations

A discussion of frequency immediately involves a discussion of time because of the reciprocal relationship between the two quantities. Astronomical events such as the mean solar day and, since 1956, the tropical year have been used for reasons of permanence and continuity as standards for the time scale, that is the origin and the size of the unit. The need, however, to interpolate these rather large units has led to quartz oscillators of great stability and to techniques of intercomparing frequencies to greater precision than any other physical
quantity, and such oscillators can thus be used to provide very uniform time scales if properly calibrated against the standard. In calibrating these oscillators against the mean solar day, for example, variations were detectable in the latter. In using astronomical standards, furthermore, a very long time is required to attain high precision for the fundamental reason that in counting cycles many counts are required to reduce the random errors in marking the beginning and end of a cycle.

As a possible alternative, the observed transition frequencies of atomic systems, given by the Bohr relation,

\[ h \nu = \Delta E, \tag{1} \]

appeared capable of satisfying the general requirements of a standard so well that it became conceivable to take the corresponding period as the standard of the unit of time, or even to make frequency a basic quantity and consider time a derived quantity. In the standard for any unit we require constancy of the determination of the size of the unit with time. In an astronomical standard the size of the cycle may vary; or if this objection is overcome by specifying one particular cycle, such as the tropical year for 1900, the determination of this unit from subsequent observations may fail from inadequate knowledge of the motion. The requirement of constancy is more likely to be met in a small system of elementary particles such as an atom than in a macroscopic system such as the sun-earth-moon system because of the smaller number of particles involved and because of the possibility of arranging that the perturbing energies be much smaller than the system energy.

A good standard must also be observable with precision. If we suppose that the process of measuring a frequency is equivalent to taking the mean of the distribution of frequencies comprising a spectral line such as shown in Fig. 1, we have

\[ \bar{\omega} = \int o g(\omega) \, d\omega. \tag{2} \]

The line, \( g(\omega) \), may be expressed as

\[ g(\omega) = y_0(\omega - \omega_0) + \eta y(\omega - \omega_0), \tag{3} \]

where \( \eta y(x) \) is one of the ensemble of functions describing departures from the ideal shape, \( y_0(x) \), because of noise or other disturbance, and \( \eta \) is a parameter of smallness. The resonant frequency of any one determination is \( \omega_0 \), also considered one of an ensemble to account for experimental variations. Clearly \( \bar{\omega} \) will have a distribution, \( f(\bar{\omega}) \), due to variations in \( \omega_0 \) (drifts) and in the form of \( y \) (disturbances). For a good standard we seek to achieve the smallest value of

\[ \sigma^2 = (\bar{\omega} - \bar{\omega})^2 = \bar{\omega}^2 - \bar{\omega}^2, \tag{4} \]

where

\[ \bar{\omega} = \int \omega f(\omega) \, d\omega \quad \text{and} \quad \bar{\omega}^2 = \int \omega^2 f(\omega) \, d\omega. \tag{5} \]

This problem may be attacked in special cases by usual statistical methods; but we can say immediately that narrow \( y_0(\omega - \omega_0) \), small \( \eta \) or good signal-to-noise ratio, and stable \( \omega_0 \) or freedom from drift and perturbations will help. Atomic frequency standards offer all these possibilities.

Astronomical standards offer the advantages of permanent availability and continuity. Atomic standards offer an equivalent advantage of renewability in case of loss, but in case of a lapse of continuity the origin may be lost. This is a disadvantage, how-

![Fig. 1. Hypothetical spectral line showing possible variations in observation.](image-url)
ever, only in experiments extending over decades, as conducted in positional astronomy.

A good standard must be of optimum size for comparison, as are the meter and the kilogram. Since time standards always are nearly of the form \( f(t) = f(t + 2\pi n/\omega) \) and we have to average over large values of \( n \) for precision or to take the Fourier frequency transform of a large number of cycles, \( \omega \) should be large so that these operations can be applied to conveniently small intervals. Furthermore, because of the characteristics of practical electrical circuits, frequencies of many cycles per second are much more convenient to multiply and divide electronically than are frequencies of one cycle per day or per year. Since frequency measurement is essentially a counting process, we also note that the standard must not be too rapid for counting in some fashion. This effectively limits us to frequencies below about 300 kMc at the present state of the art.

To summarize, we seek a narrow, intense transition in the range of microwave or radio frequency spectroscopy, insensitive to perturbing fields, and observable with apparatus that remains stable for times necessary to secure a sufficiently narrow band width of observation, typically of the order of some tens of seconds.

Two transitions exist with outstanding characteristics. These are the \((J = 3, K = 3)\) inversion of \(N^{14}H_3\) at 23,870 Mc useful for its high intensity and convenient frequency, and the \((F = 4, m_F = 0) \leftrightarrow (F = 3, m_F = 0)\) transition between hyperfine levels in the ground state of \(Cs^{133}\) at 9,192 Mc arising from electron spin-nuclear spin interaction, useful for its insensitivity to electric and magnetic fields and also its convenient frequency. Other transitions which have been studied are the \((J = N \pm 1) \rightarrow (J = N)\) transitions near 60,000 Mc in the ground state of oxygen arising from change of electronic spin momentum with respect to rotational momentum, and the hyperfine transitions in the ground state of the alkali metals Na\(^{23}\) at 1,772 Mc and Rb\(^{87}\) at 6,835 Mc.

**Techniques of Observation**

**Gas Absorption.\(^1\)** The gas absorption cell was historically the first method of utilizing molecular resonances for a frequency standard and was used for \(NH_3\) and \(O_2\). For a well isolated pressure broadened line a sufficiently good expression is given by the Van Vleck-Weisskopf formula for the absorption per unit length, \(\gamma\):

\[
\gamma = \frac{8\pi e^2 N f}{3ekT} |\mu_{ij}|^2 \\
\cdot \left[ \frac{1/2\pi}{(\nu - \nu_0)^2 + (1/2\pi)^2} + \frac{1/2\pi}{(\nu + \nu_0)^2 + (1/2\pi)^2} \right],
\]

where \(N\) is the number of molecules per unit volume; \(f\) is the fraction of molecules in the lower state \(i\), of energy \(W_i\), usually given as

\[e^{-W_i/kT} / \sum_i e^{-W_i/kT}\]

\(|\mu_{ij}|^2\) is the mean square matrix element for transitions from \(i\) to \(j\); \(c, k, T, \) and \(\nu\) have their usual significance; and \(\tau\) is the mean time between collisions, varying inversely as pressure. The half width of the line at the half intensity point, \(\Delta\nu\), is 1/2\(\pi\). Standard techniques of microwave spectroscopy are used, namely, a microwave generator, absorption cell containing gas under low pressure for well resolved lines, and a microwave power detector arranged to display absorption vs frequency. Many refinements have been devised to improve the precision of measurement such as modulation of the source and the absorption and various bridge arrangements to improve minimum detectable frequency change.

A practical \(NH_3\) device gave frequency precision of about 2 parts in \(10^9\) over 8 days, and an \(O_2\) spectrometer gave actual frequency measurements to 2 parts in \(10^9\) and evidence of greater precision at the cost of engineering refinements to reduce residual systematic errors.
The limitations of the gas absorption standard are large $\Delta \nu$ of some tens of kilocycles due to pressure and Doppler broadening and consequent inability to localize the line precisely because of systematic errors which usually limit measurement to a fixed fraction of a line width. Consequently the gas absorption standard has essentially been abandoned as an atomic frequency standard.

**Atomic Beam.** The atomic beam frequency standard has proved the most satisfactory instrument to date probably because it most closely approaches the ideal of a single atom in field-free space, unperturbed by collisions and free of Doppler effect. Fixed laboratory installations serving as national standards and also portable commercial models have been made. The usual arrangement is shown in Fig. 2. Atoms in all sublevels of both states $F = 3$ and $F = 4$ leave the oven with a distribution of velocity vectors and are deflected in the moderately strong non-uniform Stern-Gerlach field by virtue of an effective component of dipole moment along the field, dependent on both $m_F$ and field. For the two $m_F = 0$ levels the deflection is equal and opposite. The atoms then drift in the low-field space C and are subject to a Ramsey-type excitation using separated r-f fields. At resonance change of state occurs by absorption or stimulated emission depending on the initial state, and upon traversing the second identical deflecting field only those atoms having undergone transitions are focused on the detector. If resonant transitions do not occur, the beam is deflected away from the detector. Atoms with $m_F \neq 0$ undergo no transitions and never reach the detector. Detection is commonly accomplished by ionization of the alkali atoms striking a hot wire and observation of the resulting current by as convenient and sensitive means as possible. The line width is governed by the uncertainty principle, $\Delta E \Delta t \geq \hbar / 2$ or $\Delta \nu \Delta t \geq 1 / 4 \pi$, where $\Delta t$ is the time of flight of the atom.
The Cs beam has been found to be self-checking as to correct phase of the two r-f exciting fields and satisfactorily insensitive to experimental conditions such as value of oven temperature, beam flux, chamber pressure, Stern-Gerlach field, Stark fields, r-f power level, mechanical alignment, and C field. Only the latter parameter is corrected for by the relation,

$$\nu = (\nu_0 + 427 \text{ Hz}) \sec^{-1}, \quad (7)$$

representing an accurate correction of a few parts in $10^{10}$. Precision may be increased by lengthening the beam until various non-fundamental systematic effects such as attainable vacuum, focusing, and spectral impurity, that is, phase jitter of the exciting radiation, become important. First-order Doppler shift or broadening is absent since the particle direction and photon direction are perpendicular.

Results with several beams of independent design of 50 cm length have shown that the resonance can be reproducibly observed on a given apparatus to about 1 part in $10^{10}$, and that these apparatuses agree among themselves to 3 or 4 parts in $10^{10}$. With additional care in construction and testing it has recently been possible to obtain precision of measurement of 2 parts in $10^{12}$ as estimated by the standard deviation of the mean, to obtain agreement between two apparatuses to 2 parts in $10^{11}$, and to assign the uncertainty of approaching the idealized Cs resonance to 2 parts in $10^{11}$.

As to current developments, somewhat
longer beams of 1.5 to 5 m length have been made recently; and the resonance of $^{14}$NH$_3$ at 21, 311 Me has been suggested as worth investigating.

**Maser.** The gas maser may also be considered an atomic frequency standard. Figure 3 shows one experimental arrangement. Ammonia atoms leave the oven in a beam and are prepared in the upper inversion state by the quadrupolar electrostatic focuser which focuses atoms in the upper state and defocuses those in the lower state; the focused atoms enter the microwave cavity where they are stimulated to emit by the existing microwave field. This energy is stored in the cavity to produce further stimulated emission and to supply losses of the cavity and external loads. The maser can selectively amplify an applied signal in the neighborhood of resonance or it can oscillate. In the former case the line width depends on experimental conditions of beam flux, cavity $Q$, and applied signal strength and may be of the order of a few kilocycles. In the latter case the condition for oscillation is that the energy input per unit time equal or exceed the power losses $P$, or

$$nP_{2-1}h\nu \geq P,$$  

where $n$ is the number of excited molecules entering the cavity per unit time and $P_{2-1}$ is the probability that a molecule undergoes stimulated emission while in the cavity. Expressing $P_{2-1}$ in terms of the dipole matrix element $\mu$ connecting states 1 and 2, the energy density, the time spent in the cavity $\tau = 1/\nu$, and the line width $\Delta \nu \sim 1/\tau$, and expressing $P$ in terms of the loaded $Q$ and the stored energy in the volume $V$, we find the minimum beam flux for oscillation to be

$$n_{\text{min}} \sim Vh/\mu^2Q^{1/2}. \quad (9)$$

$P_{2-1}$ may be made of the order of $1/2$ for strong oscillations, and some $10^{-9} \text{ w}$ may be extracted. The spectral output of the maser oscillator is exceedingly monochromatic; its relative half-half width is given by

$$\frac{\delta \nu}{\nu} = \frac{4\pi kT(\Delta \nu)^2}{P\nu} \quad (10)$$

and observed in practice as a few parts in $10^{12}$—better than any other r-f source. The actual frequency is sensitive to experimental conditions of cavity tuning, cavity $Q$, beam flux, and Doppler shift due to possible existence of traveling waves in the cavity which supply localized losses such as an exit iris. These conditions must be specified more
carefully than the Cs conditions in order to achieve comparable reproducibility to parts in $10^6$.

An interesting application may be to solve the limitation of spectral purity in the Cs exciting radiation by deriving it from a maser oscillator.

**Optical Pumping.** As in the atomic beam and the maser, atoms are prepared in a pure state arranged to have a long lifetime and are stimulated to emit by microwave radiation in a manner free of Doppler effect; and the change of state is detected. Here the state preparation consists of selective excitation of a vapor at partial pressure of about $10^{-7}$ mm Hg from some of its ground state magnetic or hyperfine sublevels to an upper electronic state by specially filtered or polarized optical resonance radiation. Excited atoms become more or less equally distributed among the sub-levels of the upper state by collisions and spontaneously radiate to all lower levels. In the case of the alkali atoms it is possible to enhance the upper hyperfine level of the ground state at the expense of the lower.

This situation is preserved because collisions in the $^2S$ ground state with either a buffer gas introduced at about 100 mm Hg or a special wall coating are not disorienting because of absence of magnetic dipole or spin exchange interactions, and the requisite long lifetime of the prepared state is accomplished. Doppler width reduction occurs essentially by a mechanism in which the radiating atom is confined by buffer gas collisions to a region small compared to a wavelength, so that the motion of the source does not cumulatively affect the phase of the emitted wave, as is ordinarily responsible for Doppler effect. If $\Delta F = 1$ transitions are induced between these hyperfine levels by microwave radiation, the fact can be detected by a change in the absorption, scattering, or polarization of the exciting optical radiation because of the altered populations produced.

Microwave responses as narrow as 400 cps for Na, 400 cps for Cs, and 200 cps for Rb have been observed. Present limitations are a non-negligible shift in line frequency with buffer gas composition, pressure, and temperature, so that the device does not seem to provide as ideal a standard as an atom in a beam, but nevertheless does provide a very stable frequency with relatively small apparatus.

**Utilization of Resonance**

The utilization of an atomic resonance as a frequency standard may consist of passive use, as a cavity resonator might be used as a wavemeter, or of use of the frequency discrimination available in the line as a part of a control mechanism to regulate an oscillator continuously. Such control mechanisms may possess considerable electronic complexity and sophistication, but they may usually be brought into the standard form shown in Fig. 4 with either phase or frequency as the controlled variable. Figure 5 shows a loop which may be used to phase lock an oscillator to a maser. The reference quantity is the phase of the maser output, $\omega t$. To simplify analysis it is convenient to assume that the reference frequency is re-supplied through the disturbance input, so that inside the loop we deal only with quantities proportional to phase error. The relative stability of the auxiliary conversion oscillator introduced into the sum point, $\delta \omega_L/\omega_L$, enters into the system relative stability, $\delta \omega/\omega$; but it is reduced by the factor $\omega_L/\omega$, which may be chosen as small as $10^{-3}$ or $10^{-4}$. From the condition on the figure, $(\omega - \omega_r - \omega_L)t < \pi$, and the assumption $\delta \omega_r = 0$, we have at sufficiently long times $\delta \omega = \delta \omega_L$ or $\delta \omega/\omega = (\delta \omega_L/\omega_L)(\omega_L/\omega)$. The same loop might be used to control an oscillator from the Cs resonance. The reference frequency would be provided passively by the property of Cs; the sum point would be a convenient schematic fiction containing no apparatus; and the phase transducer would be replaced by one of a variety of frequency...
Fig. 4. Standard form of control mechanism.

e = b - r

\[ e = G_1G_2(Hc - r) + u \]

Fig. 5. Oscillator phase locked to a maser, drawn as a control mechanism. Phase is the controlled quantity.

discriminators, transducing frequency difference into a control voltage.

Applications

Atomic frequency standards have provided orders of magnitude improvement in the scientific time scale. When compared with the most refined mean solar second, the Cs beam confirmed variations in the latter of the order of 5 parts in 10^9 in the course of a year, and contributed to a redefinition of the second in 1956 by the Comité International des Poids et Mètres (CIPM) as the fraction 1/31,556,925.9747 of the tropical year for January 0, 1900, at 12 hours Ephemeris Time. This unit, although constant by definition, is very cumbersome to recover from current astronomical observations; therefore as a result of a recent measurement yielding

\[ \nu_{Cs} = (9,192,631,770 \pm 20) \text{ sec}^{-1} \text{ (of E.T.)} \]

the second may be considered to be provided immediately by the Cs resonance to the stated accuracy. Because different Cs resonators are now constant among themselves to a precision of a few parts in 10^10, with early expectation of order of magnitude improve-
ment, the CIPM may eventually define a unit of time based on an atomic frequency standard, similar to its intended action with respect to an atomic unit of length in 1960.

Several applications to physical experiments exist. First, a signal of great spectral purity such as that available from a maser may be used as a high resolution analyzer of other spectra such as those produced by electronic oscillators and multipliers. For if \( f_1(t) \) is the signal from the oscillator and \( f_2(t) \) is the signal from the maser, we may form \( f_1(t)f_2(t) \) whose Fourier transform is the convolution integral
\[
\frac{1}{2\pi} \int F_1(s) F_2(\omega - s) \, ds,
\]
where \( F(s) \) is the Fourier transform of \( f(t) \); and if \( F_2 \) may be approximated by the Dirac delta function, we may arrive at \( |F_1(\omega)|^2 \), the power spectrum of \( f_1 \).

The great precision in frequency measurement does not, of course, contribute to measurement of physical quantities involving dimensions other than time; for these are limited by the lesser precision available in length, mass, or current, as the case may be. The precision may, however, be utilized by selecting quantities involving frequency or time alone, such as the cyclotron frequency of the electron or proton, or the frequency of nuclear precession in a magnetic field, or dimensionless ratios of such frequencies. One such experiment has tested anew the postulate of special relativity prohibiting a preferred frame among frames in uniform relative motion by observing the rate of a beam maser for molecular velocity along and against the orbital velocity of the earth. The experiment is equivalent to the Michelson-Morley experiment, which gave a null result of 1/20 of the expected ether drift. The present experiment improved this to 1/1000 by virtue of the ability to compare frequencies precisely.

In addition, the precision inherent in frequency determination may be used to obtain a number of quantities external to the atom upon which \( \Delta E \) in Equation (1) depends, such as Stark or Zeeman fields, initial momentum \( \mathbf{m} \mathbf{u} \) of the system (Doppler effect), and the gravitational scalar and vector potential, \( \chi \) and \( \gamma \), at the emitter, depending on the metric tensor \( g_{ik} \). Calculations may most conveniently be carried out separately according to the predominant effect. Møller gives the observed frequency of emission in the absence of electric and magnetic fields:
\[
h v = \frac{[\tilde{m}_0^2 - m_0^2]c^3}{2E(1 - c'm \cdot c/E)} \quad \text{(11)}
\]
where \( \tilde{m}_0 \) and \( m_0 \) are rest masses in an inertial frame for initial and final states; \( c' = c(1 + 2\chi/c^2)^{1/2} \) is the velocity of light in an inertial frame; \( E = mc'^2(1 - \gamma \cdot \mathbf{u}/c') \) is the energy of the initial state;
\[
m = \frac{m_0}{[\sqrt{1 + 2\chi/c^2} - \gamma \cdot \mathbf{u}/c'}^2 - u^2/c^2]^{1/2};
\]
and \( e \) is the unit vector in the direction of photon emission. For systems at rest at places differing by gravitational potential \( \Delta x \), Equation (11) predicts a relative frequency shift of \( \Delta x/c^2 \), the Einstein gravitational red shift. This effect is 1.76 parts in \( 10^{13} \) per mile at the surface of the earth. If one of the systems is put into an artificial satellite, the result is complicated by the relativistic Doppler effect arising from the velocity dependence in Equation (11) and the need to integrate both effects over the orbit; but the effect has been calculated as a few parts in \( 10^9 \) for a typical satellite. Both magnitudes are within reach by present atomic frequency standards. Such implications of general relativity as to the alteration of time scales may have practical application to accurate timekeeping among space stations.

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**John M. Richardson**

**THEORY, INSTRUMENTATION, APPLICATIONS**

The portion of the electromagnetic spectrum extending approximately from one millimeter (300,000 megacycles) to 30 centimeters (1,000 megacycles) is designated the microwave region. This region lies between the far infrared and the conventional radio-frequency regions. Spectroscopic applications of microwaves consist almost exclusively of absorption work in gaseous samples, not of emission work since emission spectra have been observed only from astronomical sources.

With some exceptions the various types of spectra are distinguished by the energy origins. In the visible and ultraviolet regions the transitions between electronic energy states are directly measurable as characteristic of elements with vibrational and rotational energies of molecules observed only as perturbation effects. In the infrared region the vibrational spectra are observed directly as characteristic of functional groups with rotational energies observed as perturbation effects. In the microwave region transitions...