Considerations on the Design of a Molecular Frequency Standard Based on the Molecular Beam Electric Resonance Method*

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The use of a rotational state transition as observed by the molecular beam electric resonance method is discussed as a possible frequency standard particularly in the millimeter wavelength range. As a promising example the 100-kMc transition between the \( J = 0 \) and \( J = 1 \) rotational states of \( LiF \) is considered. The relative insensitivity of the transition frequency to external electric and magnetic fields and the low microwave power requirements appear favorable; the small fraction of the molecular beam that is in a single rotational state is a limiting factor.

1. INTRODUCTION

In recent years frequency standards based on microwave transitions in atoms and molecules have had great success. In particular, the cesium frequency standard which is based on the observation of a transition between the hyperfine structure levels of the cesium atom occurring at about 9192 Mc by the atomic beam magnetic resonance method has been found to perform as an absolute frequency standard to an accuracy of about 1 part in \( 10^{10} \) over a long period of time. The ammonia maser which utilizes an inversion frequency at 23870 Mc is less reliable as an absolute frequency standard because of the dependence of the output frequency on the resonant frequency of a cavity, but its relative short time stability has been observed to be as high as 1 part in \( 10^8 \). The gas cell frequency standard, which is based on a magnetic dipole hyperfine structure transition in an alkali atom and which utilizes a buffer gas to reduce the line width, exhibits a large dependence of the transition frequency on the type and pressure of the buffer gas and hence does not appear easily capable of the absolute accuracy achieved by the cesium atomic beam frequency standard.

For the future development of more accurate frequency standards it is generally believed that the use of an atomic or molecular transition which occurs in the millimeter wavelength range may be important. The largest known hf transition for a stable atom occurs for thallium, \( Tl \), at a frequency of 21311 Mc. A fine structure transition of a molecule is a possible frequency standard particularly in the millimeter wavelength range. As a promising example the 100-kMc transition between the \( J = 0 \) and \( J = 1 \) rotational states of \( LiF \) is considered. The relative insensitivity of the transition frequency to external electric and magnetic fields and the low microwave power requirements appear favorable; the small fraction of the molecular beam that is in a single rotational state is a limiting factor.

2. MOLECULAR BEAM ELECTRIC RESONANCE METHOD

The molecular beam electric resonance method, is the electric analog of the well-known atomic or molecular beam magnetic resonance method which is used in the cesium atomic beam frequency standard. A schematic diagram of the molecular beam electric resonance method is shown in Fig. 1. Deflection of the molecule occurs through the electric force of an inhomogeneous electric field on the electric dipole moment of the molecule,

\[
F = \mu_0 \nabla E. \tag{1}
\]

The effective electric dipole moment, \( \mu_0 \), depends on the rotational state of the molecule. If a transition is induced state of boron which occurs at a wavelength of 0.63 mm—may be found useful; however, the high power requirements for this transition and the inefficiency for detection of the atom are not encouraging.

The use of a rotational state transition in a molecule which can be observed by the molecular beam electric resonance method appears to offer some attractive possibilities, and it is the purpose of this article to discuss the design of a molecular frequency standard based on the molecular beam electric resonance method.

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‡ L. Essen and J. V. L. Parry, Trans. Roy. Soc. (London) 250, 45 (1957). The National Company of Malden, Massachusetts, now manufactures a cesium atomic frequency standard with a guaranteed absolute accuracy of about 3 parts in \( 10^8 \).


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in the C region from one rotational state to another, it is observed through the change in trajectory of the molecule as a change in beam intensity at the detector. Thus far the electric resonance method has been applied only to alkali halide (and thallium halide) molecules, largely because these are the only molecules which are known to be detected with high efficiency by the hot wire surface ionization detector.

Design of the deflection system for an electric resonance apparatus requires a knowledge of the effective electric dipole moment, \( \mu_e \), appearing in Eq. (1). This quantity is the electric dipole moment induced by the applied electric field and it depends on the rotational state, \( J \), of the molecule and on the component, \( m_J \), of rotational angular momentum in the field direction. The ratio of \( \mu_e \) to the permanent electric dipole moment, \( \mu_0 \), is shown in Fig. 2 as a function of electric field for the rotational states \( J=0 \), \( 1 \), and \( 2 \). Known values of the permanent electric dipole moments, \( \mu_0 \), of the alkali halide molecules are given in Table I. Thus far transitions have been studied only for rotational states \( J=0 \), \( 1 \), and \( 2 \). Although there is no reason in principle why higher rotational states cannot be studied, in practice such experiments will be more difficult because \( \mu_e \) is smaller for higher \( J \) values. The magnitude of \( \mu_e \) and of useful values of electric field are such that the deflection properties of a molecular beam electric resonance apparatus are similar to those of an atomic beam magnetic resonance apparatus where the atom has a magnetic moment of the order of a Bohr magneton.

In the C region of a molecular beam electric resonance apparatus a static electric field is applied to maintain the state of quantization of the molecules. A microwave field is also applied to induce the electric dipole transition from one rotational state to another.

Designs of several molecular beam electric resonance apparatuses have been reported in detail in the literature.\(^7\)–\(^9\)

### 3. MICROWAVE TRANSITIONS FOR ALKALI HALIDE MOLECULES

Rotational state transitions have been studied for most of the alkali halide molecules either by the molecular beam electric resonance method,\(^8\) by conventional microwave absorption spectroscopy with a high-temperature spectroscope,\(^10\) or by microwave absorption at millimeter wavelengths by a beam of alkali halide molecules.\(^11\) The frequency for a transition between the rotational states \( J \) and \( J+1 \) is given approximately by the equation,

\[
\nu = 2B_e(J+1).
\]

Table II gives values of the rotational constant \( B_e \) for alkali halide molecules.\(^5\) In the cases designated by stars the \( B_e \) values were determined from measurements of the spectrum at radio-frequencies,\(^12\) and no microwave rotational state transition has been observed.

Transitions at frequencies of 100 kMc or higher are available as transitions between high \( J \) rotational states for all the alkali halide molecules. Of especial interest is the LiF molecule for which the transition \( J=0 \rightarrow J=1 \) occurs at about 100 kMc.

A transition with a narrow line width can be obtained in a molecular beam apparatus provided the transit time of the molecule through the transition region is sufficiently long to give a small natural line width and provided line broadening due to inhomogeneity of external fields is small. In order to obtain a line width for an alkali halide molecule of about 200 cps which is comparable to that of the cesium

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\(^1\) H. K. Hughes, Phys. Rev. 72, 614 (1947).
atomic beam frequency standard it is necessary to have a transition region several hundred centimeters in length. Since this length is very long compared to the wavelength of the radiation, it would appear necessary to use the method of separated oscillating fields\(^{1}\) to induce the transition. This method employs two short regions with oscillating fields, one at the beginning and the other at the end of the transition region. It has the favorable property that the line is not broadened by field inhomogeneities in the region between the two oscillating fields. The separated oscillating fields method has been successfully applied in many magnetic resonance experiments; it has not yet been used in electric resonance experiments, but no fundamental difficulties in its application are anticipated.

4. USE OF J = 0 \rightarrow J = 1 TRANSITION IN Li\(^6\)F\(^{19}\) FOR A FREQUENCY STANDARD

One of the most promising transitions for a frequency standard to operate at about 100 kMc and based on the molecular beam electric resonance method is the transition \(J = 0 \rightarrow J = 1\) for the Li\(^6\)F\(^{19}\) molecule.\(^{12}\) Detailed consideration of the energy levels, resonance line shape, and special features of the molecular beam electric resonance apparatus will be given for this case and should serve to illustrate more generally the design problems of a frequency standard based on the molecular beam electric resonance method.

The complete Hamiltonian for LiF which pertains to a rotational state transition can be written\(^{6,15}\)

\[
H = H^{(0)}(v, J) + c_1 \mathbf{I}_1 \cdot \mathbf{J} + c_2 \mathbf{I}_2 \cdot \mathbf{J}
\]

\[
- \frac{eqQ_i}{2I_1(2I_1 - 1)(2I_2 - 1)(2J + 3)} \left[ 3(I_1 - J)^2 + \frac{3}{2}(I_1 + J) - I_1^2 J^2 \right]
\]

\[
+ \frac{2g_1 g_2 \mu_0^2}{R^3} \left[ 3(I_1 - J)(I_1 + J) - (I_1 - I_2) + I_1^2(J + 1) \right]
\]

\[
- \mathbf{u} \cdot \mathbf{E} + \mu g_1 \mathbf{I}_1 \cdot \mathbf{H} + \mu g_2 \mathbf{I}_2 \cdot \mathbf{H} + \mu g_3 \mathbf{J} \cdot \mathbf{H}. \tag{3}
\]

The term \(H^{(0)}(v, J)\) gives the energy level of the molecule in the ground electronic state, \(v\), and in the rotational state, \(J\), in the absence of interactions which involve the nuclear spins or external fields. The interactions involving \(c_1\) and \(c_2\) (1 refers to the Li nucleus and 2 refers to the F nucleus) are the spin-rotation interactions. \(I_1\) and \(I_2\) are the nuclear spins. The term involving \(eqQ_i\) is the electric quadrupole interaction for the Li nucleus. The term involving \(g_1 g_2 \mu_0^2 / R^3\) is the magnetic dipole-dipole interaction between the two nuclei.

\(^{15}\)N. F. Ramsey, Phys. Rev. 78, 695 (1950).


\(^{19}\)P. Kusch, Phys. Rev. 75, 887 (1949).
The rotational constant \( B_r \) is known only through the determination\(^9\) of the internuclear distance, \( R \), from the measurement of the nuclear magnetic dipole-dipole interaction constant \( g g_{2} \mu_{2} / (h R^3) \) for \( Li^6F^5 \). \( B_r \) has the value (49 000 \( \pm \) 4000) Mc.

The energy levels of the \( Li^6F^5 \) molecule in zero electric and magnetic fields can be calculated by a perturbation theory based on the known relative orders of magnitude of the interaction terms,

\[
(h^2/2A) > c_3, c_4, c_0, \text{ or } (g g_{2} \mu_{2}^2 / R^6),
\]

in which \( A \) is the moment of inertia of the molecule. The zero field representation defined by the quantum numbers \( (I_1, I_2, F_1, F_2, F, M) \) is used in which \( F_2 = I_2 + J, F = F_2 + I_1, \) and \( M \) is the component of \( F \) in the \( z \) direction. The energy levels are given by the expression\(^9,10\)

\[
W = H_0(J,J) + \frac{c_3 K_3}{2} + \frac{c_4 K_4 K}{4 F_1(F_1+1)} + \frac{g g_{2} \mu_{2}^2}{2 R^4(2J-1)(2J+3)} \left[ \frac{3 K_3 K_4}{2 F_2(F_2+1)} \right] \left[ \frac{J(J+1)K_2''}{F_2(F_2+1)} \right] K
\]

\[
- \frac{c_0 Q_1}{2 I_1(2I_1-1)(2J-1)(2J+3)} \left[ \frac{3 K_3 K_4}{8 F_2(F_2+1)} \right] I_1(I_1+1)J(J+1),
\]

where

\[
K_3 = F_2(F_2+1) - I_2(I_2+1) - J(J+1),
\]

\[
K_4 = F_2(F_2+1) - I_2(I_2+1) + J(J+1),
\]

\[
K_4' = F_2(F_2+1) + I_2(I_2+1) - J(J+1),
\]

\[
K = F(F+1) - I_1(I_1+1) - F_2(F_2+1),
\]

\[
M_0 = 3 F_2^2 F_1^2 + M_3^2 + M_4^2,
\]

\[
M_3 = \left[ \frac{F_2(F_2+1)}{16(F_2+1)^2(2F_2+1)2F_2+3} \right] \times \left[ (F+F_2-I_1+1)(F-F_2+I_1)(F+F_2+I_1+2)(F_2+I_1-F_1+1) \right],
\]

\[
M_4 = \left[ \frac{K_2''}{4 F_2(F_2+1)} \right] \times \left[ \frac{(F_2-I_2+J)(F_2+I_2-J)(F_2+I_2+J+1)(I_2+J-F_1+1)}{16 F_2^2(F_2+1)^2(2F_2+1)} \right] \times \left[ (F+F_2-I_1)(F-F_2+I_1+1)(F+F_2+I_1+1)(F_2+I_1-F_1) \right].
\]

The zero field energy levels for the \( J=1 \) state, obtained from Eq. (5) and the known interaction constants, are shown in Fig. 3. For the \( J=0 \) state there is only a single energy level. Each \( F \) level has a \((2F+1)\)-fold degeneracy.

In the presence of an electric field the degeneracy of levels with different \( |M| \) is removed. If the electric field is weak so that \( \mu E^2 / (h^2/2A) \ll (\text{internal molecular interactions involving the } Li^6 \text{ nucleus}) \) then the energy levels are obtained\(^9\) by the addition of a term of order \( \mu E^2 / (h^2/2A) \) to Eq. (5). For the \( J=1 \) levels with \( F_2=\frac{1}{2} \) this quadratic Stark term actually has the coefficient zero. For the \( J=0 \) state the electric field dependence is given by

\[
W_E = - \mu E^2 / 6 (h^2/2A).
\]

In the presence of a magnetic field the degeneracy is completely removed. If the magnetic field is weak so that \( \mu g H \ll (\text{internal molecular interactions involving the } Li^6 \text{ nucleus}) \), then the energy contribution of the magnetic field is given by the addition to Eq. (5) of the term

\[
W_H = \mu g \gamma H M.
\]

The total \( g \) value, \( g_F \), is obtained from a generalized Landé formula for the three vector system of \( I_1, I_2, \) and \( J \) and will be of the order of a \( g \) value for a nucleus \((\sim -0.003)\).

A favorable transition for a frequency standard may be the transition from the \( J=0 \) state to the level designated by \( (F_2=\frac{1}{2}, F=\frac{1}{2}) \) in the \( J=1 \) state, which will occur at a frequency of about 100 kMc. Both the upper and lower levels are single levels in the absence of a magnetic field. The upper level is sufficiently far from the adjoining levels in the \( J=1 \) state so that the resonance line shape of a
The electric field dependence of the transition frequency is given from Eq. (6) as

$$\nu = \nu_0 + 38E^2 \text{(cps)}, \quad (8)$$

in which \(\nu_0\) is the transition frequency at zero field and \(E\) is the field expressed in \(v/cm\). Hence if the transition occurs in a field \(E\) of 0.1 \(v/cm\), the frequency shift will be only 0.4 cps and a 10\% change in the field will only alter the frequency by 0.1 cps. Transitions in such weak fields have been observed without undue loss of quantization. In order that the frequency shift due to a magnetic field shall be less than a few cycles per second, it is necessary to keep \(H\) about 1 milligauss or less which should be possible.

The specification of the line width will determine major features of the apparatus design. The vapor pressure of LiF is low and customarily an oven temperature of about 1200°K might be used. Hence the most probable velocity \(\alpha\) for a molecule of mass \(m\) in the oven will be given by

$$\alpha = (2kT/m)^{1/2} = 0.9 \times 10^4 \text{ cm/sec.} \quad (9)$$

The line width of the central peak of the line obtained by separated, in-phase oscillating fields is given by

$$\delta \nu = 0.6\alpha L / L, \quad (10)$$

in which \(L\) is the distance between the two oscillating fields. Hence in order that \(\delta \nu = 200\) cps, \(L\) must be 300 cm. The over-all length of the apparatus might then be some 400 cm.

The microwave field required to induce the transition with near unity probability is determined from the condition,

$$V_{pq} \tau \approx \hbar, \quad (11)$$

where \(V_{pq}\) is the amplitude of the matrix element of the interaction

$$V = - \mu \cdot E = \mu \cdot E \text{e}^{|t^\nu|} \quad (12)$$

of the microwave field \(E\) with the molecular electric dipole moment between the initial and final states, and \(\tau\) is the time molecule \(\alpha\) spends in an oscillating field region of length \(L\). For a length \(L\) of one cm, the amplitude \(E_1\) is of the order of \(3 \times 10^{-4}\) esu or 0.1 \(v/cm\). Use of a cavity with dimensions of roughly 1 cm which operates in a higher mode and which has a \(Q\) of 1000 would yield the proper amplitude of the microwave electric field provided the cavity is fed with a power of the order of a microwatt. Such an input power should be available from crystal harmonic generation from a klystron output.

The principal difficulty in the use of the molecular beam electric resonance method as compared with the use of the magnetic resonance method is the reduced useful intensity of the beam. The fraction of the molecules in the beam that are in the rotational state \(J\) is given by

$$(N_J/N) \approx (2J+1) (h^2/2kT), \quad (13)$$

in which \(T\) is the oven temperature and \(k\) is Boltzmann’s constant. For Li\(^{6+}\) as observed by the molecular beam electric resonance method appears favorable for obtaining a standard frequency in the 100-kMc range, but the useful beam intensity will be less than that for a cesium atomic frequency standard due principally to the many rotational states present in the molecular beam.

In conclusion, the use of the transition \(J=0 \rightarrow J=1\) in Li\(^{6+}\) as observed by the molecular beam electric resonance method appears favorable for obtaining a standard frequency in the 100-kMc range, but the useful beam intensity will be less than that for a cesium atomic frequency standard due principally to the many rotational states present in the molecular beam.

The molecular beam electric resonance method may also prove useful in extending the frequency range of frequency standards by use of higher rotational state transitions than \(J=0 \rightarrow J=1\). At present due to limitations of the efficiency of molecular detectors other than the surface ionization detector the molecular beam electric resonance method has been used only for alkali halide molecules. Further development of molecule detectors would extend the transitions available for a frequency standard using polar molecules and the molecular beam electric resonance method.

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Footnote: