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Determination of Atomic Masses by Microwave Spectroscopy[*][†]

S. Geschwind,[‡] G. R. Gunther-Mohr,[§] and C. H. Townes

Columbia University, New York, New York

I. INTRODUCTION

MICROWAVE spectroscopy gives information about atomic masses from the isotopic shift in the pure rotational spectrum of molecules. Shifts of a spectral line due to a change of isotopic mass are quite familiar. One recalls the discovery of deuterium in 1932 by Urey, Brickwedde, and Murphy[1] by observation of an isotopic shift of 1.70 A in the electronic spectrum for the H_α-line of the Balmer series. In the same year, Hardy, Barker, and Dennison[2] determined the deuteron mass to 0.1 mMU by measuring the separation of the rotational lines in the DCl^{35} vibrational bands which lie in the infrared region. The isotope shift in this case was very large, since the rotational spectrum of a diatomic molecule depends on the reduced mass of the molecule, which for DCl is roughly twice that for HCl. For heavier nuclei, however, even the most favorable cases give isotopic shifts which are considerably less pronounced. For example, in ICl, the shift in rotational frequency for the two isotopes Cl^{35} and Cl^{37} is only 5 percent. With the limited resolution obtainable by infrared techniques, the precision measurement of nuclear masses is thus difficult, if not impossible.

However, with the development of microwave techniques in the last decade, direct observation of the pure rotational absorption spectra of molecules (many of which fall in the region near 1 cm^{-1}) became possible, and the very high resolution and accuracy characteristic of microwave spectroscopy have made accurate mass determinations practical. As an illustration, the aforementioned shift of 5 percent in ICl corresponds to about 1000 Mc. Absolute frequencies and frequency intervals in the region near 24 000 Mc can be measured with an error at least as small as 0.01 Mc. Therefore this 1000 Mc shift for a change of two mass units can be measured to 1 part in 10^5, or the Cl^{37} mass determined to 0.05 thousandths of a mass unit (0.05 mMU) relative to Cl^{35}.

The most general variety of molecule which has so far been used for mass determination by microwave techniques is the symmetric top for which rotational energy levels are given by

$$W_r = hBJ(J+1) + h(A-B)K^2. \qquad \text{(I.1)}$$

Here $A = h/8\pi^2 I_A$ and $B = h/8\pi^2 I_B$; I_A and I_B are the moments of inertia parallel and perpendicular to the symmetry axis, respectively. $[J(J+1)]^{\frac{1}{2}}\hbar$ is the total angular momentum of the molecule and $K\hbar$ is its projection on the symmetry axis. If the molecule possesses a permanent dipole moment, it will have a pure rotational absorption spectrum with the selection rules $\Delta J = +1$ and $\Delta K = 0$, and hence the pure rotational absorption frequencies will be given by

$$\nu = 2BJ, \qquad \text{(I.2)}$$

where J is the angular momentum quantum number for the upper state of the transition. If a different isotope is substituted for an atom lying along the axis of symmetry, I_B will change and thereby change the absorption frequency. Isotopic shifts can range from a few Mc to many thousands of Mc. With the high-resolution spectrometer described in Sec. III, frequency separations have been measured to an accuracy of about 0.01 Mc. For typical isotopic shifts of 100 Mc per mass-unit, this corresponds to an accuracy of 0.1 mMU in mass determinations. Current improvements in techniques allow measurement of frequency intervals to 0.002 Mc, so that future mass measurements by microwave methods may be improved by a factor of five, or to an accuracy near 0.02 mMU. This accuracy compares favorably with the best mass spectrographic and nuclear reaction measurements recently obtained in the middle mass region ($A = 60$ to 130).[3]

Some molecular rotational spectra are complicated by hyperfine structure associated with reorientation of the nuclear spin. In this case the energy may be written[4]

$$W = W_r + W_i(I,J,K,F), \qquad \text{(I.3)}$$

where W_r is the rotational energy as in (I.1) and W_i is the hyperfine energy, which depends on the nuclear spin I, the rotational quantum numbers J and K, and the quantum number $F = |\mathbf{I}+\mathbf{J}|$. The observed ab-

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[‡] Present address, Bell Telephone Laboratories, Murray Hill, New Jersey.

[§] Present address, IBM Watson Laboratories, Columbia University, New York, New York.

[1] Urey, Brickwedde, and Murphy, Phys. Rev. **39**, 164 (1932).

[2] Hardy, Barker, and Dennison, Phys. Rev. **42**, 279 (1932).

[3] Collins, Nier, and Johnson, Phys. Rev. **94**, 398 (1954).

[4] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

sorption frequencies are

$$\nu = 2BJ + \frac{W_i - W_i'}{h}, \tag{I.4}$$

where $W_i - W_i'$ corresponds to the change in hyperfine energy during the transition. Usually W_i is much smaller than W_r and does not depend on the rotational constant B, so that B is easily isolated and evaluated from the observed spectrum. In some cases, W_i is sufficiently large that it perturbs the molecular rotation[5] and is not quite independent of B, but even in these cases the rotational frequency $2BJ$ can be obtained rather readily from the observed spectra. In subsequent discussion we shall assume that no hyperfine structure occurs, or that its effects have been eliminated so that only the rotational energy of the molecule need be treated.

The following section (II) presents the theory involved in determination of masses from rotational spectra of diatomic molecules, and of molecules which are linear or symmetric rotors. Section III is devoted to a brief description of experimental techniques and in Sec. IV results of mass measurements by microwave methods are tabulated and discussed.

II. THEORY OF MASS DETERMINATION FROM ROTATIONAL SPECTRA

The program of mass determination by microwave spectroscopy is to correlate the very accurately measured rotational frequencies of various isotopic species of a molecule with mass ratios for the isotopes involved. Such a correlation can be done most simply and accurately for diatomic molecules.

Diatomic Molecules

The pure rotational absorption frequencies of a polar diatomic molecule are to a very good approximation given by

$$\nu = 2J[B_e - \alpha(v + \tfrac{1}{2})], \tag{II.1}$$

where

$B_e = h/(8\pi^2 I_e)$, where I_e is the equilibrium moment of inertia assuming the nuclei are stationary at their equilibrium separation r_e. $I_e = \mu r_e^2$, with μ the reduced mass of the molecule.

α = rotation-vibration correction representing the change in effective value of B due to the vibration of the molecule.

v = vibrational quantum number.

In calculating the reduced mass of the molecule, it is usually assumed that the mass of an entire neutral atom, i.e., nucleus plus electrons, is concentrated at a point. It will be seen below that this assumption introduces an even smaller error than one might at first expect.

By measuring the frequency separation of two absorption lines with different values of v (for example the same rotational transition in the ground vibrational and first excited states) α_e can be determined, and hence B_e can be evaluated. If the excited vibrational state of one of the isotopic species is insufficiently populated so that the transition is too weak to be observed, α and B_e can still be determined if the α and B_e for the more abundant species can be measured. This is because α is known to be proportional to $1/\mu^{\frac{3}{2}}$, and B_e is proportional to $1/\mu$.

Once B_e has been determined for two isotopic species of a molecule containing masses M and $m^{(0)}$ or M and $m^{(1)}$, respectively, the ratio of reduced masses is given directly by the ratio of the B_e's:

$$\frac{\mu^{(1)}}{\mu^{(0)}} = \frac{B_e^{(0)}}{B_e^{(1)}} = \frac{m^{(1)}(M + m^{(0)})}{m^{(0)}(M + m^{(1)})},$$

or

$$\frac{m^{(1)}}{m^{(0)}} = \frac{M}{m^{(0)}} \frac{B_e^{(0)}}{B_e^{(1)}} \Big/ \left(1 + \frac{M}{m^{(0)}} - \frac{B_e^{(0)}}{B_e^{(1)}}\right). \tag{II.2}$$

By substituting the microwave determination of $B_e^{(0)}/B_e^{(1)}$ in Eq. (II.2), the mass ratio $m^{(1)}/m^{(0)}$ can be determined with great accuracy. The mass ratio $M/m^{(0)}$ in the numerator tends to compensate its appearance in the denominator so that it need be known with only moderate accuracy. Note that no information about internuclear distance or atomic constants such as h is needed. By this method, for example, the mass ratio $\mathrm{Cl}^{35}/\mathrm{Cl}^{37}$ has been determined to several parts in 10^6 in several diatomic molecules. Specific examples will be discussed in Sec. IV.

Factors Contributing to Error in Mass Ratio Determinations from Spectra of Diatomic Molecules

There are a number of possible sources of error in precise determination of masses from expression (II.2).[6,7] Most of these correspond to inaccuracies in the approximations under which this expression is derived. The more important sources of errors are listed below.

(a) *Anharmonicity of the Potential Function*

The representation of effective B values in terms of equilibrium B values and α as given by Eq. II.1 does not take into complete account the anharmonicity of the potential function in which the nuclei move. Dunham[8] has calculated the energy levels for a vibrating rotator by a W.K.B. method for any potential which can be expanded as a series in powers of $(r - r_e)$ near the potential minimum. He shows that the energy

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[5] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 627 (1948).

[6] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy of Gases* (to be published by McGraw-Hill Book Company, Inc., New York).

[7] J. H. Van Vleck, J. Chem. Phys. **4**, 327 (1936).

[8] J. L. Dunham, Phys. Rev. **41**, 721 (1932).

levels can be written as

$$F_{v,J}=\sum_{l,j}Y_{lj}(v+\tfrac{1}{2})^{l}J^{j}(J+1)^{j}, \qquad \text{(II.3)}$$

where l and j are summation indices, v and J are, respectively, vibrational and rotational quantum numbers, and Y_{lj} are coefficients. If the ratio of B_e/ω_e is small (ω_e is the vibrational frequency), so that terms of order $(B_e/\omega_e)^2$ may be neglected; the Y's can be related to the ordinary band spectrum constants as follows:

$$Y_{01}\sim B_e, \quad Y_{11}\sim -\alpha_e, \quad Y_{10}\sim\omega_e, \quad Y_{02}\sim D_e, \qquad \text{(II.4)}$$

where D_e is the term which takes into account the change in moment of inertia due to the centrifugal distortion of the rotating molecule. Neglect of terms of order $(B_e/\omega_e)^2$ gives an error of about 5×10^{-7} in the mass ratio Cl^{35}/Cl^{37} obtained from ICl. Since this ratio has been measured to an accuracy of about 5×10^{-6} and could now be improved by almost a factor of 10, this type of correction may be significant in the future.

(*b*) *Uncertainties in Electronic Distribution*

It was assumed in calculating the moment of inertia of the molecule that each atom has the necessary number of electrons to make it neutral, and that the entire mass of the atom is concentrated at a point. Since the electrons are arranged more or less spherically about their respective nuclei, one might expect the moment of inertia to be greater than that given by the point mass assumption by an amount approximately equal to the moments of inertia of the electrons about their respective nuclei. This contribution to the moment of inertia would be rather large but is fortunately not really present because the orientation of a completely spherical shell of electrons remains fixed in space as the molecule rotates.[6,9] The slipping of the electrons as the molecule rotates can be compared to motion of a chair on a ferris wheel.

However, the valence shell of electrons is not completely spherical and part of it does not slip as the molecule rotates, giving a contribution approximately $n\epsilon r^2$ to the moment of inertia. Here n is the number of rotating valence electrons, ϵ the electron mass and r some average of their distance from the nuclei with which they are associated. If n is taken as one and $r=r_e$ the equilibrium internuclear distance, this error in moment of inertia has about the same magnitude as the change in moment of inertia which would be produced by removing or adding an electron to one of the atoms. An error in the moment of inertia of similar magnitude ($\sim\epsilon r_e^2$) is produced if the molecule is composed of two ions rather than two neutral atoms, for then an electron has been lost by one atom and gained by the other. Present knowledge of molecular structure gives some information about the ionic character of a molecule, so that errors of this type may be partially corrected by using ionic rather than atomic masses, or values intermediate between the two.

If uncertainty in the valence electrons does produce an error in the moment of inertia as large as ϵr_e^2, the resulterror in the mass ratio $m^{(1)}/m^{(0)}$ is $(m^{(1)}-m^{(0)})\epsilon/[m^{(0)}]^2$, where ϵ is the electron mass. For the mass ratio Cl^{35}/Cl^{37} in ICl, this error is 8×10^{-7}. For Li^6/Li^7 in LiI this type of error would be as large as 10^{-5}. or about 0.06 mMU in the mass difference between Li^6 and Li^7. Since LiI is known to be almost completely ionic, this error is largely eliminated and the Li^6/Li^7 mass ratio determined from the LiI spectra found to be in excellent agreement with other determinations if ionic rather than atomic masses are used for this molecule.[10]

(*c*) *L-Uncoupling*

Electrons in a $^1\Sigma$ molecule have angular momentum when the molecule is rotated, and hence are not strictly in a $^1\Sigma$ state. Their effects on the kinetic energy of rotation discussed under the above heading (*b*) may in a sense be regarded as due to partial excitation of the electrons to a series of high-energy electronic states. This concept of electronic excitation caused by molecular rotation is much more useful and natural, however, in treating the perturbation between the ground $^1\Sigma$ state and the lowest $^1\Pi$ state of a molecule. Such a perturbation of the molecular electronic state is a type of L-uncoupling. It results in a decrease in rotational energy given by

$$\Delta W_R=-4J(J+1)\frac{hB_e^2}{\nu}|(\Sigma|L_x|\Pi)|^2, \qquad \text{(II.5)}$$

where ν is the frequency of transition between the ground ($^1\Sigma$) electronic state and the lowest $^1\Pi$ state and $|(\Sigma|L_x|\Pi)|^2$ is the matrix element between the Σ and Π states for one component of the electronic orbital momentum perpendicular to the molecular axis. L_x is expressed in units of $\hbar$, so that $|(\Sigma|L_x|\Pi)|^2$ is of order unity.

Since the energy ΔW_R is proportional to $J\,(J+1)$, the electronic excitation simply decreases the effective value of B_e by a fractional amount of the order of B_e/ν. If L-uncoupling is neglected, as it is in expression (II.2), an error of about 10^{-6} is produced in the Cl^{35}/Cl^{37} mass ratio obtained from ICl or FCl. This is large enough to be of importance in accurate microwave measurements. Lighter molecules, which rotate faster, would in general involve larger errors from L-uncoupling.

In some cases it is practical to correct for the effect of L-uncoupling on mass determinations. Excitation of electronic angular momentum by molecular rotation is also largely responsible for magnetic moments of $^1\Sigma$ molecules associated with rotation and for magnetic hyperfine interactions in these molecules. Thus, if L-uncoupling dominates in these effects, one can show

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[9] G. C. Wick, Phys. Rev. **73**, 51 (1948).

[10] Honig, Mandel, Stitch, and Townes, Phys. Rev. (to be published).

that[6]

$$\Delta W_R = gJ(J+1)hB_e(\mu_n/\mu_0), \tag{II.6}$$

where g is the molecular g-factor in terms of nuclear magnetons, μ_n and μ_0 are nuclear and Bohr magnetons, respectively. In addition,[6]

$$\Delta W_R = \frac{CJ(J+1)hB_e}{2\mu_n\mu_0 g_I\langle 1/r^3\rangle_{\mathrm{Av}}}, \tag{II.7}$$

where the magnetic hyperfine interaction between the molecule and a nucleus of spin I and g-factor g_I is given by $W_M = C\mathbf{I}\cdot\mathbf{J}$. $\langle 1/r^3\rangle_{\mathrm{Av}}$ is the average inverse cube of the distance between nucleus and the electrons which carry orbital momentum in the excited state.

Rosenblum and Nethercot[11] have measured the rotational spectra of deuterium and tritium iodide and discussed the role of L-uncoupling in the mass ratio determination. These molecules and the similar compounds of Br are the only cases so far measured by microwave techniques for which the L-uncoupling affects the mass ratios by an amount larger than the uncertainty due to errors in frequency measurement.

(*d*) *Errors in Reference Masses*

In determining $m^{(1)}/m^{(0)}$ it may be seen from Eq. (II.2) that $M/m^{(0)}$ is assumed known. If the uncertainty in $M/m^{(0)}$ is Δ, then the corresponding uncertainty in $m^{(1)}/m^{(0)}$ is

$$\simeq \frac{m^{(1)}\Delta}{M}\left[\frac{m^{(0)}-m^{(1)}}{m^{(0)}+M}\right],$$

assuming $m^{(0)}-m^{(1)}$ is small. Thus, $M/m^{(0)}$ need not be known to especially high accuracy in order to make its contribution to the uncertainty in $m^{(1)}/m^{(0)}$ negligible. For example, in ICl, an uncertainty of one mMU in both M and $m^{(0)}$ produces an error in the $\mathrm{Cl}^{35}/\mathrm{Cl}^{37}$ ratio of only 1 part in 10^7.

The accuracy of present microwave measurements is just at the threshold of the theoretical uncertainties discussed above. Since improvement in the accuracy of measurement by a factor of 10 is already possible and will probably be commonplace in the future, these theoretical uncertainties will set a limit on the accuracy of mass ratio determination in diatomic molecules of about 1 part in 10^6. This corresponds to errors of about 0.1 mMU in the region of atomic mass 100, or somewhat less for lighter mass. In some favorable cases corrections for these errors will be possible, and then still better accuracy can be obtained.

Polyatomic Linear and Symmetric Top Molecules

In molecules more complex than a diatomic molecule zero-point vibrations make it necessary to determine accurate mass information in terms of *mass difference ratios* rather than mass ratios.

The one structural parameter of a diatomic molecule, i.e., its internuclear distance, does not appear explicitly in the expression for isotopic mass ratios given by Eq. (II.2). One may consider that it has been determined and eliminated from this equation by measurement of the B value of the first isotopic species. Similarly in a more complex molecule with n structural parameters, i.e., internuclear distances and bond angles, the B_e's corresponding to n isotopic species can in principle determine these parameters and allow their elimination from a suitable equation for the masses of other isotopes. Mass ratios would then be determined in terms of B_e values and other mass ratios.

As an obvious extension of vibrational effects in diatomic molecules, the effective rotational constant $B_0 = h/8\pi^2 I$ for polyatomic linear molecules and symmetric tops is written as

$$B_0 = B_e - \sum_i \alpha_i\left(v_i + \frac{d_i}{2}\right), \tag{II.8}$$

where α_i, v_i, and d_i are the rotation-vibration constants, the vibrational quantum number, and the degree of degeneracy respectively of the ith vibrational mode.

To determine B_e from the measured rotational frequencies, all the α_i's must be determined by measuring rotational frequencies of excited vibrational states. However, even for the simplest polyatomic molecule of the linear XYZ type, this usually involves severe experimental difficulties. It has so far been done for only one isotopic species of OCS. This is because the energy of one or more of the excited vibrational states is usually so great that only a very small fraction of the molecules are in the excited state at ordinary temperatures and consequently the corresponding absorption line is too weak for detection by present microwave spectrographs. Often more than one excited state of a given mode of vibration is needed in order to correct for "Fermi resonance" effects.[12,13] Moreover, for polyatomic molecules the quantities depend in a rather complex way upon the vibrational frequencies and the anharmonic force constants, so that even if the values were known for one isotopic form of the molecule, the theory is not complete enough to allow their prediction for another isotopic species. Hence it is not practical to obtain values for B_e and thus determine mass ratios. On the other hand, the situation is much more favorable for ratios of mass differences.

The moment of inertia through the center of mass of a molecule and along a direction fixed in the molecule and defined as the z axis is

$$I = \sum_i m_i(x_i^2 + y_i^2).$$

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[11] B. Rosenblum and A. H. Nethercot, Jr., Phys. Rev. (to be published).

[12] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).

[13] W. Low and C. H. Townes, Phys. Rev. **79**, 224 (1950).

If an isotopic substitution is made for the jth atom replacing the original mass $m_j^{(0)}$ by $m_j^{(1)}$, the shift in the center of gravity will be

$$\delta=\frac{m_j^{(1)}-m_j^{(0)}}{M^{(1)}}(x_j^2+y_j^2)^{\frac{1}{2}}, \tag{II.9}$$

where $M^{(1)}$ is the total mass of the molecule with isotope $m_j^{(1)}$. By the parallel axis theorem the moment of inertia $I^{(1)}$ is given by

$$I^{(1)}+M^{(1)}\delta^2=I^{(0)}+(m_j^{(1)}-m_j^{(0)})(x_j^2+y_j^2). \tag{II.10}$$

Substituting (II.9) into (II.10) gives

$$I^{(1)}-I^{(0)}=\frac{(m_j^{(1)}-m_j^{(0)})M^{(0)}(x_j^2+y_j^2)}{M^{(1)}}. \tag{II.11}$$

A similar equation applies for isotope $m_j^{(2)}$, so that

$$\frac{m^{(1)}-m^{(0)}}{m^{(2)}-m^{(0)}}=\frac{M^{(1)}}{M^{(2)}}\frac{I^{(1)}}{I^{(2)}}\frac{(1/I^{(0)}-1/I^{(1)})}{(1/I^{(0)}-1/I^{(2)})}. \tag{II.12}$$

This type of expression was given by Strandberg' Wentink, and Hill[14] for a somewhat specialized case. However, it is quite general and might even be applied to asymmetric rotors. No mass measurements have yet been made by use of asymmetric top molecules because of the complexity of their spectra.

If (II.12) is applied only to linear molecules and symmetric tops with isotopic substitutions along the symmetry axis, and if the z axis referred to is taken in a direction perpendicular to the axis of the molecule or the symmetry axis, then it may be written

$$\frac{m^{(1)}-m^{(0)}}{m^{(2)}-m^{(0)}}=\frac{M^{(1)}}{M^{(2)}}\frac{B_e^{(2)}}{B_e^{(1)}}\frac{(B_e^{(0)}-B_e^{(1)})}{(B_e^{(0)}-B_e^{(2)})}. \tag{II.13}$$

Note that structural parameters of the molecule do not appear explicitly. The B_e quantities appearing in Eq. (II.13) are the values of the rotational constant for equilibrium internuclear distances, while the measured rotational frequencies give the effective rotational constants B_0 when zero-point vibrations are present. Since the quantities B_e are so difficult to determine, the effective rotational constants B_0 are actually used in Eq. (II.13). The error which is thereby introduced is quite small, as will be shown in the next sections. Thus, if three rotational frequencies of a molecule corresponding to three isotopic substitutions of the same atom are measured and if the masses of two of these isotopes are known, then the mass of the third isotope can be determined to very good accuracy. Use of two isotopes of known masses might be regarded as a calibration of the isotope shift in the molecule and the effect of zero-point vibrations so that the mass of the third atom can be determined. Note that about all that need be known concerning the molecule is the mass of the other atoms it contains, and even that is not required to high precision.

(a) *Error in Mass Difference Ratio Caused by Neglect of Zero-Point Vibrations*

If α and B had the same functional dependence upon mass variation, then

$$\frac{B_e^{(1)}-B_e^{(0)}}{B_e^{(2)}-B_e^{(0)}}=\frac{B_0^{(1)}-B_0^{(0)}}{B_0^{(2)}-B_0^{(0)}} \quad\text{and}\quad \frac{B_e^{(2)}}{B_e^{(1)}}=\frac{B_0^{(2)}}{B_0^{(1)}},$$

so that no error at all is introduced in the mass difference ratio by using the effective B values, B_0, instead of the equilibrium B values, B_e. However, even though α and B do not have the same functional dependence upon mass, to a first approximation α and B vary linearly with small fractional changes of mass, and since $\alpha \ll B$, the error introduced by α is small. An estimate of this error can be made by expanding α and B about their values when $m=m^{(0)}$ in powers of the change in isotopic mass Δm_j.

Let $\alpha_i^{(0)}$, $\alpha_i^{(1)}$ and $\alpha_i^{(2)}$ be the rotation-vibration constants in the ith vibrational mode for isotopic masses $m_j^{(0)}$ and $m_j^{(2)}$ and $\alpha^{(0)}=\sum_i \alpha_i^{(0)}d_i$. Expanding α and B_e in a Taylor series about $\alpha^{(0)}$ and $B_e^{(0)}$

$$\alpha=\alpha^{(0)}+\alpha'\Delta m+\tfrac{1}{2}\alpha''(\Delta m)^2+\cdots, \tag{II.14}$$

$$B_e=B_e^{(0)}+B'\Delta m+\tfrac{1}{2}B''(\Delta m)^2+\cdots, \tag*{(II.15)*}$$

then

$$\frac{B_0^{(1)}-B_0^{(0)}}{B_0^{(2)}-B_0^{(0)}}\simeq\left[1-\frac{1}{4}\frac{\alpha'}{B'}\left(\frac{B''}{B'}-\frac{\alpha''}{\alpha'}\right)\times(m^{(2)}-m^{(1)})\right]\left[\frac{B_e^{(1)}-B_e^{(0)}}{B_e^{(2)}-B_e^{(0)}}\right]. \tag{II.16}$$

Similarly, expanding $B_e^{(2)}$ and $\alpha^{(2)}$ about $B_e^{(1)}$ and $\alpha^{(1)}$, one finds

$$\frac{B_0^{(2)}}{B_0^{(1)}}\simeq\left[1+\frac{1}{2}\frac{\alpha}{B}\left(\frac{B'}{B}-\frac{\alpha'}{\alpha}\right)(m^{(2)}-m^{(1)})\right]\frac{B_e^{(2)}}{B_e^{(1)}}. \tag{II.17}$$

With these expansions, the mass difference ratio can be written as

$$\left(\frac{m^{(1)}-m^{(0)}}{m^{(2)}-m^{(0)}}\right)_{\text{exp}}=\left(\frac{m^{(1)}-m^{(0)}}{m^{(2)}-m^{(0)}}\right)_{\text{true}}\left[1-\frac{1}{4}\frac{\alpha'}{B'}\left(\frac{B''}{B'}-\frac{\alpha''}{\alpha'}\right)(m^{(2)}-m^{(1)})+\frac{1}{2}\frac{\alpha}{B}\left(\frac{B'}{B}-\frac{\alpha'}{\alpha}\right)(m^{(2)}-m^{(1)})\right. \tag{II.18}$$

$$\left.+\text{terms in higher powers of the mass differences.}\right]$$

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[14] Strandberg, Wentink, and Hill, Phys. Rev. **75**, 827 (1949).

* Here and in Eqs. (II.16) and (II.18) B' and B'' should be B_e' and B_e'', however as they appear as corrections and the differences between them and B_0' and B_0'' are small one may use B_0' and B_0'' in Eq. (II.18).

B_0'' and B_0' are easily determined experimentally. An exact evaluation of α'' and α' is very difficult. In fact, if they could be evaluated properly, the error in the ratio of mass differences due to neglect of zero-point vibrations could be eliminated. However, even an approximate knowledge of α' and α'' would allow a reasonable estimate of the error. B and α are positive in all known cases, B' and α' are negative, and B'' and α'' positive. In this respect α and B are similar, if not identical functions of m, so that the two terms in each bracket

$$\left(\frac{B''}{B'}-\frac{\alpha''}{\alpha'}\right) \quad \text{and} \quad \left(\frac{B'}{B}-\frac{\alpha'}{\alpha}\right)$$

will partially cancel. In addition, the two error terms in Eq. (II.18) are of opposite sign and also tend to partially cancel. The extent to which cancellation occurs in a polyatomic molecule is, however, difficult to establish. Discussion of the molecule OCS below may be helpful as an example of the magnitudes of these terms.

The three vibrational modes of the linear molecule OCS are shown in Fig. 1, where the relative directions and amplitudes of motion of the different atoms are indicated by arrows. The behavior of the first mode (ν_1) may be approximated by regarding the molecule as diatomic, with O and C replaced by a combined atom of weight equal to the sum of these two. If one now uses the fact that α in a diatomic molecule varies with reduced mass μ as $1/\mu^{\frac{3}{2}}$, the following results are obtained for the variation of α_1, with variation in the sulfur mass number:

$$\begin{aligned} \partial\alpha_1/\partial m_1=\alpha_1'&=-0.022\alpha_1, \\ \alpha_1''&=+0.0015\alpha_1. \end{aligned} \tag{II.19}$$

For variation of the Se mass in the similar molecule OCSe

$$\begin{aligned} \partial\alpha_1/\partial m_1=\alpha_1'&=-0.0049\alpha_1, \\ \alpha_1''&=+0.0013\alpha_1. \end{aligned}$$

As a check on the reliability of this diatomic molecule approximation, one may use the experimental values[15] $\alpha_1=18$ Mc for OCS and $\alpha_1=13.4$ Mc for OCSe to obtain $\alpha_1'(\text{OCS})=-0.5$ and $\alpha_1'(\text{OCSe})=-0.065$. These values are in reasonable agreement with the measured values of -0.25 and -0.07 for OCS and OCSe, respectively. For the degenerate mode ν_2 and for ν_3, the amplitudes of vibration of the S atom are of the same order of magnitude and considerably less than that for the ν_1 mode. One would therefore expect an isotopic substitution to have effects on α_2 and α_3 which would be considerably less than for α_1. This indicates that an upper limit for α' ($\alpha'=\alpha_1'+2\alpha_2'+\alpha_3'$) may be obtained by using Eqs. (II.19) to express α'' and α' in terms of α ($\alpha=\alpha_1+2\alpha_2+\alpha_3$). Using the experimental value[16] of α, one obtains by this method $\alpha'\sim 0.7$ and $\alpha''\sim 0.005$. In addition, the following experimental values are known for OCS:

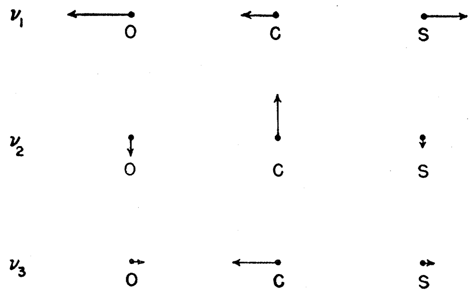

FIG. 1. Vibrational modes of the linear molecule OCS.

$$B_0\sim 6000,\quad B_0'\sim -74 \text{ Mc/Mass Unit},$$
$$B_0''\sim 4 \text{ Mc/(Mass Unit)}^2.$$

If the above values of B and α and their derivatives are substituted in Eq. (II.18), one finds that the largest of the four error terms in (II.18) is the second, involving α'', which produces an error of 1/2500 in the mass difference ratio $(\text{S}^{33}-\text{S}^{32})/(\text{S}^{34}-\text{S}^{33})$. The first error term is about two-thirds as large, and is of opposite sign so that the first two terms result in an error of about one part in 7500. The last two terms are smaller, and result in an error about half as large as the sum of the first two and of opposite sign. Hence the sum of all four terms produces an expected error of about one part in 15 000 in the mass difference ratio, or about 0.03 millimass unit in the mass of S^{33}. Although one cannot be certain of the amount of cancellation in the various terms of Eq. (II.18), this estimate of the errors due to zero-point vibrations is probably not overly optimistic for the particular case of OCS.

It is of course possible to find exceptional cases for which the errors given by Eq. (II.18) are serious. These can be expected to occur primarily where the masses being compared are located near the center of gravity of the molecule, such as the central nitrogen in NNO. This would make B' very small but α' and α'' would not necessarily be small so that the error terms may be quite large.

A numerical estimate for more complex molecules such as GeH_3Cl and SiH_3Cl is almost impossible. One can only surmise that in most cases the error would be of the same order of magnitude as in the linear molecule OCS just discussed.

Further evidence for the smallness of errors due to zero-point vibrations in determining mass difference ratios comes from a comparison of results with those obtained from mass spectrographs and nuclear reactions. Such comparisons, as shown by Table II of Sec. IV, give good evidence that the errors made by

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[15] P. Kisliuk and C. H. Townes, National Bureau of Standards, Circular 518 (1952).

[16] M. Peter and M. W. P. Strandberg, M.I.T. Research Laboratory of Electronics Quarterly Report, April, 1954.

neglecting zero-point vibrations are not appreciably larger than the above estimate. The case of O^{16}, O^{17}, and O^{18} measured in OCS affords a particularly good comparison because the O atom is light and its vibrational motion large, and because the O masses are rather accurately known from other measurements.

(*b*) *Error in Mass Difference Ratio Caused by Uncertainty in Assumed Reference Masses and Remaining Masses in the Molecule*

If $M^{(1)}/M^{(2)}$ is written as $(M+m^{(1)})/(M+m^{(2)})$, then it is easily shown that an uncertainty ΔM in M produces an error in $M^{(1)}/M^{(2)}$ equal to

$$\Delta M(m^{(2)}-m^{(1)})/(M+m^{(2)})^2.$$

Since ΔM is usually known to a few milli-mass units, the resultant error in mass difference ratio is of the order of 1 part in 10^6 and is therefore negligible.

On the other hand, an uncertainty δ in the difference between the two reference masses, $m^{(2)}-m^{(1)}$, produces an error equal to $\delta/(M+m^{(2)})$ in the mass difference ratio. Since the maximum uncertainty in δ is a few milli-mass units, the resulting maximum error will be of the order of 1 part in 25 000, and it is generally much less.

Information on the odd-even mass difference of isotopes can be obtained which is not subject to errors due to zero-point vibration. As an illustration of this and of the general application of the method, consider the relative mass determination of the Se isotopes from the microwave spectrum OCSe. In the $J=2\rightarrow3$ transition in OCSe the frequency separations between the six isotopic lines, corresponding to the six stable Se isotopes, were measured to an accuracy of 15 kc/sec or better.[17] From these frequency differences the Se mass difference ratios were calculated by use of Eq. (II.13). Since the measurement yields information only on mass difference ratios, the masses of two of the isotopes must be assumed from which the remaining masses can be determined. Taking the masses of Se^{76} and Se^{80} given by Collins, Nier, and Johnson,[3] the remaining Se masses were determined and are plotted in Fig. 2. (This plot includes the radioactive isotopes Se^{75} and Se^{79} measured by L. C. Aamodt and W. A. Hardy as discussed in Sec. IV.)

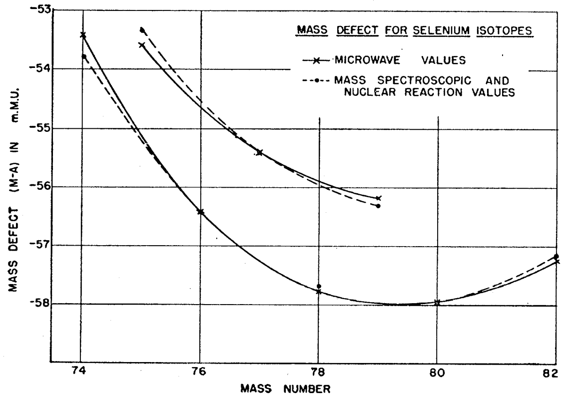

FIG. 2. Masses of the Se isotopes, showing odd-even mass differences.

The even masses lie on a smooth curve while the odd isotopes Se^{75}, Se^{77}, and Se^{79} lie above this curve. The distance that the odd isotopes lie above the curve of even masses (the odd-even mass difference) is essentially unaffected by errors in the assumed Se^{76} and Se^{80} masses or by uncertainties due to zero-point vibrations. Hence the accuracy of determination of the odd-even mass differences is limited only by the experimental errors in frequency measurement.

III. METHODS FOR MEASUREMENT OF MICROWAVE ABSORPTION LINES

Since there exists a considerable literature[6,18–20] describing microwave spectrometers, we shall simply review those features which distinguish the different instruments used to obtain the data given in Sec. IV of this report.

In the most widely used microwave spectrometer, illustrated schematically by Fig. 3, the gas whose absorptions are to be studied is enclosed in a length of rectangular wave guide containing a thin metallic septum which is insulated from the wave guide and midway between its broad sides. The gas, which is at a pressure of $\sim10^{-2}$ mm Hg, absorbs power from the microwaves being transmitted down this cell at frequencies characteristic of its molecules. To avoid spurious signals from guide reflections and from discontinuities in the mode pattern of the microwave source klystron, the characteristic gas absorption frequencies are modulated by the application of a square wave of voltage between the septum and the guide proper which produces a Stark effect. After detection in a silicon crystal rectifier, the modulated absorption signal is amplified by a narrow band amplifier tuned to the Stark modulation frequency and then detected in a phase-sensitive detector. This scheme of detection greatly reduces spurious signals since the amplitude of noise or spurious signals which fall in the pass band of the amplifier is small. Low frequency Stark modulation does not give good sensitivity because of interfering low-frequency noise generated in the crystal. On the other hand, a high modulation frequency tends to produce broad absorption lines, which cannot be narrower than about twice the frequency of modulation.[21] A Stark modulation frequency near 100 kc/sec represents a common and reasonable compromise.

This type of spectrometer has been operated in a frequency range from about 1000 Mc/sec to over 60 000

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[17] Geschwind, Minden, and Townes, Phys. Rev. **78**, 174 (1950).

[18] Gordy, Trambarulo, and Smith, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953).

[19] M. W. P. Strandberg, *Microwave Spectroscopy* (Methuen and Company, Ltd., London, 1954).

[20] "Microwave spectroscopy," Ann. N. Y. Acad. Sci., **55** (1952).

[21] R. Karplus, Phys. Rev. **73**, 1027 (1948).

Mc/sec and has been used to detect molecular lines with absorption coefficients as small as 5×10^{-10} cm^{-1}. Absorption lines in the region near 24 000 Mc typically have total widths at half-maximum intensity between 150 and 300 kc/sec. Pressure broadening, Stark modulation, or power saturation may each contribute to these line breadths.[22] Microwave power as large as a few tens of microwatts must be received by the silicon crystal for best sensitivity. However, this much power will saturate the absorption lines being observed if the gas pressure is reduced too far.

With this type of spectrometer, it is possible to measure absorption line frequencies to an accuracy of 10 to 25 kc/sec in the 24 000 Mc region. Better accuracy is prevented partly by the line width, and partly by the difficulty of avoiding distortion or displacement of the absorption line by Stark effects. In order to avoid displacement of the line, it is important that the electric field be accurately clamped to zero during half the cycle of the modulating square wave.

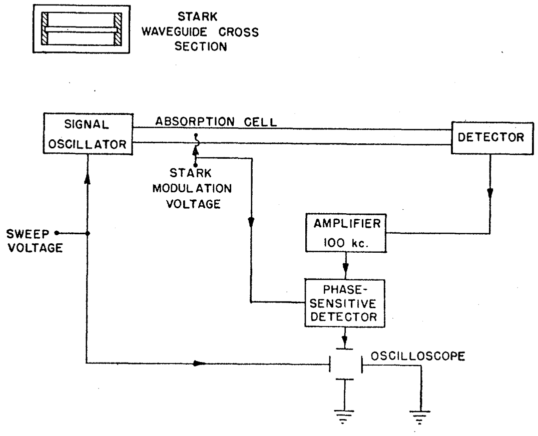

FIG. 3. A microwave spectrometer using Stark modulation.

Narrower lines have been obtained by using a balanced microwave bridge with heterodyne detection.[23] This construction allows the use of very low gas pressures and low power levels to avoid saturation without loss of sensitivity at the detecting crystal since the optimum power necessary to give sensitive detection is furnished by the beat oscillator. Also the use of a 30 Mc/sec intermediate frequency allows the low-frequency crystal noise to be avoided without broadening the absorption lines by high frequency modulation. Line widths in such a spectrometer are limited mainly by the Doppler effect and by collisions of the molecules with the guide walls. At room temperature for such typical molecules as OCS and SiD$_3$F line widths (total widths at half-maximum intensity) range from 70 to 100 kc/sec. If the signal microwave oscillator is stabilized so that its frequency can be carefully controlled, it is possible to measure absorption line frequencies to an accuracy of about 2 kc/sec in the 24 000 Mc/sec region, if Stark modulation is not used or if it is very accurately based on zero.[24]

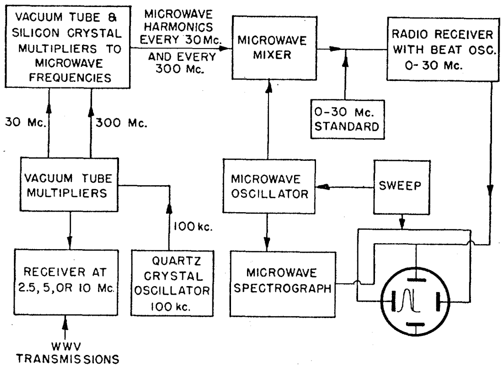

FIG. 4. Block schematic of circuits for measurement of frequencies of microwave lines (from Schawlow and Townes). (See reference 6.)

Precise frequency measurements are generally made by comparing the signal oscillator frequency with a set of frequency markers obtained by multiplying directly to microwave frequencies the output of a standard quartz crystal oscillator. Harmonics of the quartz crystal oscillator (Fig. 4) are fed at various stages of multiplication together with part of the output of the klystron source into a crystal mixer. The beating of the various harmonics in the crystal produces a set of standard frequencies 30 Mc apart in the *K*-band region. When the difference between the swept klystron frequency and a standard marker is equal to the frequency setting of a calibrated communications receiver connected to the crystal, a "pip" is generated in the receiver output. This pip is viewed simultaneously with the absorption line on an oscilloscope. By tuning the receiver, the pip can be superimposed on the peak of the line. The calibrated receiver frequency setting together with the standard marker frequency can thus be used to determine absorption frequencies in the microwave region.

Molecular Beam Methods

As is well known, molecular beam experiments usually depend on detecting a change in the states of the molecules in a beam as they pass through a fixed radiation field.[25] The more common variety of molecular beam experiment which uses a change in the component of the molecular magnetic moments in a given direction as the molecules pass through a radiation field is not well suited for measurement of molecular rotational energies. The electric resonance method,[26,27] depending on changes of molecular electric moment in a given

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[22] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).

[23] S. Geschwind, Ann. N. Y. Acad. Sci. **55**, 751 (1952).

[24] R. L. White, J. Chem. Phys. (to be published).

[25] J. B. M. Kellogg and S. Millman, Revs. Modern Phys. **18**, 323 (1946).

[26] H. K. Hughes, Phys. Rev. **72**, 614 (1948).

[27] J. W. Trischka, Phys. Rev. **74**, 718 (1948).

direction, allows one to select molecules in one or a few rotational states and therefore it can be used to study rotational transitions and molecular moments of inertia. It is this method which is of present interest.

The electric resonance apparatus, illustrated in Fig. 5, makes use of two inhomogeneous electric fields (A, B fields) to select for detection polar molecules in a given rotational state (J state) with a particular component of their electric moments along the Z direction. A strategically placed wire stop eliminates molecules with large J values which are not appreciably deflected in the A and B fields. In passing through a field-free region (C-field in Fig. 5) between the A and B fields, the molecules can change their quantization under the influence of a superimposed oscillating field tuned to a frequency ν_{nm} given by

$$\nu_{nm}=(E_n-E_m)/h,$$

where E_m and E_n are the energies, respectively, of the initial and final molecular rotational states. The resulting change in molecular rotation is observed by a change in the beam intensity arriving at the detector.

The frequency resolution of such an apparatus depends primarily on the length of time the molecule is acted upon by the radiation field. Thus if a molecule is acted on by a radiation field of approximately uniform intensity in the C-field region for a time $\Delta\tau$, the width $\Delta\nu$ of the transition observed will be approximately $\Delta\nu=1/\Delta\tau$. This leads to line widths from 10 to 20 kc with the design of apparatus which has been used. We assume that the observed line is not broadened by power saturation. This line width represents a better resolution than can be achieved by the usual types of microwave absorption spectrometers. However, the molecular beam electric resonance method is probably limited to those molecules which can be detected by an ion gauge because of the low intensity of the beam. Resolution may be improved if a longer interaction region is used, or if the interaction region is split into two widely separated parts.[28] It thus appears practical to obtain line widths as narrow as 1 kc or less, with the possibility of very high accuracy in measurement of frequency.

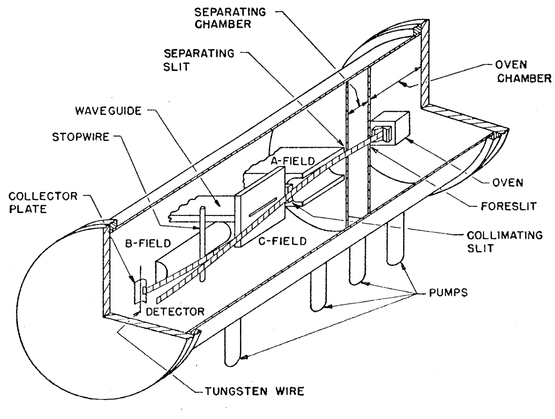

FIG. 5. Molecular beam apparatus (from Lee, Fabricand, Carlson, and Rabi, Phys. Rev. **91**, 1395 (1953)).

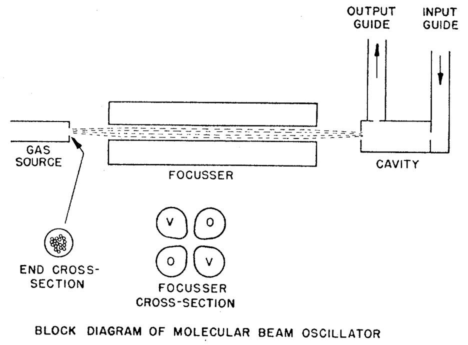

FIG. 6. A molecular beam-microwave emission spectrometer (from Gordon, Zeiger, and Townes).

Combined Methods

It is possible to detect directly the change in radiation intensity due to emission or absorption by a dense beam of molecules. This allows a type of spectroscopy which is similar to microwave gas absorption in that changes in radiation power are detected, and similar to molecular beam spectroscopy in that molecules move essentially in one direction so that the Doppler effect can be reduced and very narrow lines obtained. Absorption of microwaves in an unfocused beam of NH_3 has been demonstrated and narrow lines obtained by Strandberg *et al.*[29,30] Very narrow lines and better signal-to-noise ratios have been obtained by Gordon, Zeiger, and Townes[31] in a device illustrated by Fig. 6.

In the experimental arrangement indicated by Fig. 6, a beam of molecules passes through a set of electrodes which focus those molecules in a particular energy state into a tuned cavity. Transitions from the given molecular state which are induced by the radiation field in the cavity change the radiation intensity thus detected. As in the normal molecular beam case, the line width is given by $\Delta\nu\sim 1/\Delta\tau$, where $\Delta\tau$ is the time required by the molecule to traverse the cavity. Under the experimental conditions actually employed a line width of 6–8 kc was obtained for the NH_3 spectrum at room temperature. Use of this method promises to make it possible to determine transition frequencies to a few parts in 10^8 in the 24 000-Mc region. Since this technique involves detection of radiation rather than of molecules, it should be applicable to a range of molecules which cannot be studied by the molecular beam technique described above.

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[28] N. F. Ramsey, Phys. Rev. **76**, 996 (1949).

[29] N. R. Johnson and M. W. P. Strandberg, Phys. Rev. **85**, 503 (1952).

[30] M. W. P. Strandberg and H. Dreicer, Phys. Rev. **94**, 1393 (1954).

[31] Gordon, Zeiger, and Townes, Phys. Rev. **95**, 282 (1954).

IV. EXPERIMENTAL RESULTS

With the exception of Ge^{73} and Te^{120} mass information has been obtained from microwave spectra for all the stable isotopes of Li, C, O, Si, S, Cl, K, Br, Ge, Se, Rb, and Te, as well as a small but growing list of radioactive isotopes, i.e., H^3, S^{35}, Cl^{36}, Se^{75}, and Se^{79}. This information is compiled in Tables I and II, with mass ratios obtained from diatomic molecules listed in Table I, and mass difference ratios obtained from polyatomic molecules in Table II. The tables are supplemented by a discussion of the results listed in order of increasing atomic number. This section also includes hitherto unpublished microwave data.

Comparison of the microwave results with the listed results obtained by mass spectrometers and nuclear reactions indicates excellent agreement in most cases. The few discrepancies which do exist are discussed in the individual sections devoted to each atom.

H.—HBr and HI have considerably smaller moments of inertia than any of the other molecules listed. Hence their rotational motion is particularly violent and L-uncoupling may be expected to be important. It is primarily uncertainties in the L-uncoupling and in the experimental values of the rotation-vibration constants α which are responsible for the error in the H^2/H^3 mass ratio from microwave spectra. These have been discussed to some extent by Rosenblum and Nethercot.[11] Precision of the microwave measurements corresponds to an error of only ±18 in the ratio stated. The constants α come at present from infrared measurements, which can probably be improved to allow an interesting evaluation of the effects of L-uncoupling in these two molecules.

Li.—The microwave value for the Li mass ratio calculated from Eq. (II.2) was corrected for the 85 percent ionic character of the Li—I bond. This ionic character could be estimated to an accuracy of about 10 percent from the quadrupole coupling in the molecule.[32] L-uncoupling probably gives no appreciable error in the Li mass ratio nor does it affect mass ratios in the other alkali halides in which it is of relatively less importance because of their larger moments of inertia. The microwave mass ratio so calculated is in excellent agreement with that obtained from nuclear data.

C.—The C^{13} mass can be accurately related to the C^{12} mass by a (d,p) reaction,[33] and there is now fair agreement between the various mass-spectroscopic determinations[34–36] of C^{12} and C^{13}. Hence the disagreement of the microwave mass ratio[37] C^{12}/C^{13} with the other determinations is puzzling.

O.—The oxygen masses were obtained while studying the hyperfine structure of the $J=1\rightarrow2$ transitions in $O^{17}C^{12}S^{32}$ to determine the spin and quadrupole moment[38] of O^{17}. Since the frequencies involved have never been published elsewhere they are presented here. The absorption frequencies of the $J=1\rightarrow2$ transition in $OC^{12}S^{32}$ are

$$O^{16} \quad 24\,325.921\pm0.003,$$
$$O^{17} \quad 23\,534.661\pm0.007,$$
$$O^{18} \quad 22\,819.400\pm0.006.$$

These frequencies yield

$$(O^{17}-O^{16})/(O^{18}-O^{16})=0.501042\pm8.$$

The most accurate comparison with the microwave value is had by taking an average of Ogata *et al.*[35] and Ewald's[36] O^{18} value and by using Klema's O^{17} value[39] obtained from nuclear reactions. These give

$$(O^{17}-O^{16})/(O^{18}-O^{16})=0.501044\pm7,$$

in excellent agreement with the microwave value.

As a result of zero-point vibrations, the O atom undergoes relatively large displacements from its equilibrium position. Hence one might expect the neglect of zero-point vibrations to show up in this case. The

TABLE I. Mass ratios from the spectra of diatomic molecules.

Mass ratio	Molecule in which measured	Values from microwave spectra	Ref.	Best other values	Ref.
H^2/H^3	HBr	0.6678051±100	a	0.6677942±20	b, c
	HI	0.6678046±100			
Li^6/Li^7	LiI	0.8573423±20	d	0.8573425±30	b
C^{12}/C^{13}	CS	0.9228447±20	e	0.9228395±11	f, g, c
S^{32}/S^{33}	CS	0.9696909±32	e	0.9696905±10	c
				0.9696896±12	h
				0.9696838±14	g
S^{32}/S^{34}	CS	0.9412462±23	e	0.9412446±6	c
				0.9412428±14	i
				0.9412414±15	g
Cl^{35}/Cl^{37}	ICl	0.9459801±50	j	0.9459777±20	c
	FCl	0.9459775±40	k	0.9459779±9	g
	CsCl	0.9459781±30	d		
	$K^{39}Cl$	0.9459803±15	l		
K^{39}/K^{41}	KI	0.9512250±70	d		
	KCl^{35}	0.9512189±15	l	0.9511890±700	m
Br^{79}/Br^{81}	$Rb^{85}Br$	0.9752999±65	d		
	CsBr	0.9753068±45	d	0.9753075±10	o
	KBr	0.9753088±20	n		
Rb^{85}/Rb^{87}	RbI	0.9770177±45	d	0.9770100±300	m
	$RbBr^{79}$	0.9770146±55	d		

[a] See reference 11.
[b] Li, Walling, Fowler, and Lauritsen, Phys. Rev. **83**, 512 (1951).
[c] See reference 35.
[d] See reference 10.
[e] See reference 37.
[f] See reference 33.
[g] See reference 34.
[h] See reference 42.
[i] See reference 36.
[j] Townes, Merritt, and Wright, Phys. Rev. **73**, 1334 (1948).
[k] Gilbert, Roberts, and Griswold, Phys. Rev. **76**, 1723 (1949).
[l] See reference 27a.
[m] Hays, Richards, and Goudsmit, Phys. Rev. **82**, 345A (1951); Phys. Rev. **84**, 824 (1951).
[n] Fabricand, Carlson, Lee, and Rabi, Phys. Rev. **91**, 1403 (1953).
[o] See reference 3.

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[32] B. P. Dailey, and C. H. Townes, J. Chem. Phys. (to be published).

[33] Buechner, Strait, Sperduto, and Malm, Phys. Rev. **76**, 1543 (1949).

[34] Collins, Johnson, and Nier, Phys. Rev. **84**, 717 (1951).

[35] K. Ogata and H. Matsuda, Phys. Rev. **89**, 27 (1953).

[36] H. Ewald, Z. Naturforsch, **6a**, 293 (1951).

[37] R. C. Mockler and G. R. Bird, Phys. Rev. (to be published).

[38] Geschwind, Gunther-Mohr, and Silvey, Phys. Rev. **85**, 474 (1952).

[39] E. D. Klema and G. C. Phillips, Phys. Rev. **86**, 951 (1952).

TABLE II. Mass difference ratios.

Atom	Molecule in which measured	Mass difference ratio	Microwave value	Other values
O	$OC^{12}S^{32}$	$\frac{O^{17}-O^{16}}{O^{18}-O^{16}}$	0.501042 ± 8[a]	0.501032 ± 9[b] 0.501044 ± 7[c]
Si	SiH_3Cl	$\frac{Si^{30}-Si^{29}}{Si^{30}-Si^{28}}$	0.49941 ± 5[d]	0.499426 ± 15[e, f] 0.49934 ± 20[g] 0.49943 ± 3[i]
	SiD_3F	$\frac{Si^{30}-Si^{29}}{Si^{30}-Si^{28}}$	0.49934 ± 3[h]	
S	$O^{16}C^{12}S$	$\frac{S^{33}-S^{32}}{S^{34}-S^{32}}$	0.500714 ± 30[d]	0.500727 ± 20[i] 0.500820 ± 30[j] 0.500735 ± 30[k] 0.500726 ± 20[l]
		$\frac{S^{35}-S^{32}}{S^{35}-S^{34}}$	2.993825 ± 85[m]	2.993375 ± 75[n]
		$\frac{S^{36}-S^{32}}{S^{36}-S^{34}}$	1.998320 ± 30[o]	
Cl	CH_3Cl	$\frac{Cl^{36}-Cl^{35}}{Cl^{37}-Cl^{36}}$	1.001761 ± 400[p]	1.001790 ± 66[q]
	ClCN	$\frac{Cl^{36}-Cl^{35}}{Cl^{37}-Cl^{36}}$	1.002260 ± 800[r]	
Ge	GeH_3Cl^{35}	$\frac{Ge^{76}-Ge^{74}}{Ge^{76}-Ge^{72}}$	0.500127 ± 35[d]	0.500111 ± 20[s]
		$\frac{Ge^{72}-Ge^{70}}{Ge^{74}-Ge^{70}}$	0.499852 ± 35[d]	0.499776 ± 20[s]
Se	$O^{16}C^{12}Se$	$\frac{Se^{74}-Se^{76}}{Se^{74}-Se^{80}}$	0.333125 ± 18[t]	0.333082 ± 25[s]
		$\frac{Se^{77}-Se^{76}}{Se^{80}-Se^{77}}$	0.333947 ± 23[t]	0.333943 ± 35[s]
		$\frac{Se^{78}-Se^{76}}{Se^{80}-Se^{78}} =$	0.999510 ± 50[t]	0.999380 ± 100[s]
		$\frac{Se^{82}-Se^{76}}{Se^{82}-Se^{80}} =$	2.998441 ± 110[t]	2.998541 ± 160[s]
		$\frac{Se^{75}-Se^{76}}{Se^{75}-Se^{80}}$	0.1995660 ± 120[p]	0.199601 ± 100[u]
		$\frac{Se^{79}-Se^{76}}{Se^{80}-Se^{79}}$	3.00557 ± 21[v]	3.00525 ± 18[w]
Te	$S^{32}C^{12}Te$	$\frac{Te^{128}-Te^{122}}{Te^{124}-Te^{122}}$	3.00127 ± 60[x]	3.00100 ± 25[y] 3.00300 ± 90[z]
		$\frac{Te^{128}-Te^{123}}{Te^{124}-Te^{123}}$	5.00826 ± 100[x]	5.00731 ± 160[y]
		$\frac{Te^{128}-Te^{125}}{Te^{125}-Te^{124}}$	2.99509 ± 60[x]	2.99645 ± 70[y]
		$\frac{Te^{128}-Te^{126}}{Te^{126}-Te^{124}}$	1.00030 ± 14[x]	1.00043 ± 10[y]
		$\frac{Te^{128}-Te^{130}}{Te^{124}-Te^{130}}$	0.33346 ± 3.5[x]	0.33337 ± 2.2[y] 0.33351 ± 11[z]

[a] See discussion of oxygen.
[b] See reference 36.
[c] See discussion of oxygen.
[d] See reference 40.
[e] See reference 42.
[f] Van Patter, Sperduto, Endt, Buechner, and Enge, Phys. Rev. **85**, 142 (1952).
[g] Duckworth, Preston, and Woodcock, Phys. Rev. **79**, 188 (1950); Phys. Rev. **79**, 402 (1950).
[h] See reference 41.
[i] See reference 35.
[j] See reference 34.
[k] See Table I and reference 37.
[l] See discussion of sulfur.
[m] See reference 44.
[n] See discussion of sulfur.
[o] See reference 45.
[p] See reference 47.
[q] See discussion of chlorine.
[r] Low and Townes quote R. G. Schulman, Phys. Rev. **80**, 608 (1950).
[s] See reference 3.
[t] See reference 17.
[u] C. C. Trail and C. H. Johnson, Phys. Rev. **91**, 474 (1953).
[v] Hardy, Silvey, Townes, Burke, Strandberg, Parker, and Cohen, Phys. Rev. **92**, 1532 (1953).
[w] Hollander, Perlman, and Seaborg, Revs. Modern Phys. **89**, 375 (1953).
[x] W. A. Hardy and G. Silvey, Phys. Rev. **95**, 385 (1954).
[y] See reference 48.
[z] B. G. Hogg and H. E. Duckworth, Can. J. Phys. **30**, 628 (1952).

excellent agreement between the microwave value and the best other values, however, may be taken as good evidence for the smallness of this type of error.

Si.—Microwave measurement of the Si mass difference ratio given by Geschwind and Gunther-Mohr[40] is in better agreement than that of White and Townes[41] with the best value from other sources. This may be because of a small systematic error in the latter measurement due to Stark effects (see Sec. III). Geschwind and Gunther-Mohr did not use Stark modulation, and hence were not subject to this type of error.

S.—The excellent agreement between the microwave S^{32}/S^{33} mass ratio[37] and the values of references 35 and 42 indicates that perhaps the value of reference 34 is in error. The situation is less clear for the S^{34}/S^{32} ratio where one finds somewhat less consistent results. However, using an average of all the S^{32}/S^{34} results and an

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[40] S. Geschwind and G. R. Gunther-Mohr, Phys. Rev. **81**, 882 (1951).
[41] R. L. White and C. H. Townes, Phys. Rev. **92**, 1256 (1953).
[42] Strait, Van Patter, Buechner, and Sperduto, Phys. Rev. **81** 747 (1951).

average of the three best S^{33}/S^{32} results, one gets

$$(S^{33}-S^{32})/(S^{34}-S^{32})=0.500722\pm 20$$

compared with the microwave value[40] determined from OCS of 0.500714±30.

The S^{35} mass can be rather accurately determined relative to Cl^{35} from the end-point[43] of the β decay of S^{35}. If one uses Ogata's value[35] for Cl^{35}, he obtains 34.980244±22 for the S^{35} mass. From it and Ogata's values for S^{32} and S^{34}, one obtains $S^{35}-S^{32}/S^{35}-S^{34}=2.993360\pm 75$. The microwave value[44] is 2.993806 ±85, corresponding to a disagreement by 0.4 mMU in the S^{35} mass. This discrepancy would require an error in the microwave frequency measurement of about 100 kc, which is enormously greater than the stated error. Unfortunately, the microwave measurement cannot easily be redone, since radioactive S^{35} in the form OCS is necessary.

No mass measurement other than the microwave one exists for S^{36}. The frequency of the $J=1\rightarrow 2$ transition in $O^{16}C^{12}S^{36}$ is 23 198.76±0.02 Mc.[45]

Cl.—The best microwave value for the Cl^{35}/Cl^{37} ratio is most probably that obtained from molecular beams and is in good agreement with the best mass spectroscopic determinations. The internal consistency of the microwave values determined in four different molecules where corrections due to electronic structure should differ demonstrates that these effects are not important to the accuracy quoted.

Cl^{36} is very accurately connected by the end point of its β-decay spectrum to A^{36}. By use of Collin *et al.*'s value[34] for A^{36} and Feldman and Wu's value[46] for the β-decay end point one obtains $Cl^{36}=35.979764\pm 30$. This value taken with Ogata's[35] Cl^{35} and Cl^{37} gives the quoted result 1.001790±66.

K.—The best mass ratio from microwave spectra, determined by the molecular beam technique, is an order of magnitude more accurate than the present mass spectroscopic value, which was obtained in a time-of-flight mass spectrometer.

Ge.—The discrepancy of 0.6 mMU between the microwave and mass spectroscopic value of Ge^{70} is an interesting one. Ge^{72} has 40 neutrons for which the closing of a subshell is expected. The value for Ge^{70} given by Collins *et al.*[3] seems to indicate such a break in the mass defect curve for Ge at 40 neutrons of approximately 600 Kev, while the microwave value indicates a maximum break of 100 Kev.

No microwave mass data are available for Ge^{73} because the rotational transition for this isotope is split by quadrupole hyperfine structure. As a result, the intensity of each hyperfine component was too weak for measurement in the spectrometer used.

Se.—The Se masses determined by microwaves as quoted in reference 17 contain errors due to zero-point vibration as well as the experimental error in frequency measurement. Since the errors allowed for zero-point vibration represent an absolute upper limit and may be too large, we have listed only the experimental errors in Table II. By plotting the mass defect of the Se isotopes, one obtains the following odd-even mass differences

$$Se^{75}-1.5\pm 0.3\text{ mMU},$$
$$Se^{77}-2.0\pm 0.12\text{ mMU},$$
$$Se^{79}-1.8\pm 0.05\text{ mMU}.$$

The frequency of $O^{16}C^{12}Se^{75}$ as measured by Aamodt[47] is 24 491.535±0.030 Mc.

Br.—There is excellent agreement between the microwave and mass spectroscopic values. The internal consistency between the microwave measurements should be noted.

Rb.—The microwave spectroscopic value for this ratio is at present the most accurate available, being an order of magnitude better than the mass spectroscopic one.

Te.—There is good agreement between the microwave values and Halsted's values[48] with the exception of $(Te^{128}-Te^{130})/(Te^{124}-Te^{130})$. This discrepancy amounts to almost 1 mMU for Te^{130} if one assumes Te^{124} and Te^{128} as known.

CONCLUSION

In certain cases the precision of mass determination by microwave methods is as good or better than that obtained by better known methods. In other cases it is inferior by a small factor. Although the precision of mass spectrometric measurements is often very high, deviations between the various mass spectrographic measurements is often considerably greater than the errors in precision, indicating the presence of troublesome systematic errors. Microwave determinations have not yet been pushed to the point where systematic errors, such as lack of complete enough knowledge of the molecular electronic structure, are commonly encountered. However, the continuing development of microwave methods now allows considerable improvement in the precision of microwave measurements. This should yield improved mass determinations in cases where systematic uncertainties of the various types discussed above are not too large.

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