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Isotopic Mass Ratios, Magnetic Moments and the Sign of the Electric Dipole Moment in Carbon Monoxide*

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Precision measurements of the $J=1\leftarrow 0$ rotational frequencies and the molecular magnetic moments for various isotopic species of carbon monoxide have been made in order to determine isotopic mass ratios. A correction amounting to several hundred micromass units and evaluated from the magnetic moment has been applied for the fact that the electrons are not spherically distributed about their respective nuclei. It is also shown that the rapidly precessing electronic angular momentum causes a "wobbling" motion of the nuclei which in turn produces a stretching of the molecule ("wobble stretching") inversely proportional to the reduced mass of the molecule, but independent of J. This stretching cannot be accurately evaluated from theory and therefore appears to be the ultimate limitation on microwave determinations of mass ratios. This correction amounts to about 20 micro-mass units and is evaluated by the use of the nuclear reaction value for the $C^{14}-C^{12}$ mass ratio. The final mass ratios agree very closely with the nuclear reaction values.

The sign of the electric dipole moment was determined from the relative magnetic moments of the several isotopic species and corresponds to the charge distribution, C^-O^+. This appears to be the first measurement of the sign of the electric dipole moment in any molecule.

INTRODUCTION

MEASUREMENTS of the rotational frequencies of molecules can be made with very high accuracy in the microwave region. Since the rotational frequency of a diatomic molecule is approximately inversely proportional to the reduced mass of the molecule, the measurement of the rotational frequencies of two isotopic species of a molecule could determine the ratio of the masses of the two isotopes involved with high accuracy if the precise dependence of the rotational frequency of a molecule on the atomic mass were known. From these mass ratios, mass differences could readily be computed. In this work the $J=1\leftarrow 0$ rotational frequencies of a number of isotopic species of carbon monoxide have been measured, and the dependence of these frequencies on isotopic mass is analyzed in order to determine isotopic mass ratios for the carbon and oxygen isotopes.

The rotational energy of a diatomic molecule is usually written (see for example, Townes and Schawlow[1])

$$\frac{W(v,J)}{h}=B_eJ(J+1)-\alpha_e(v+\tfrac{1}{2})J(J+1)+\gamma_e(v+\tfrac{1}{2})^2J(J+1)-D_eJ^2(J+1)^2, \quad (1)$$

where v and J are, respectively, the vibrational and rotational quantum numbers, h is Planck's constant, and $B_e=h/(8\pi^2\mu r_e^2)$. Here μ is the reduced mass of the molecule and r_e the equilibrium internuclear distance, i.e., the internuclear distance in the absence of vibration or centrifugal distortion.[2] The terms in α_e and γ_e correct for the change in internuclear distance due to vibration and that in D_e corrects for centrifugal distortion. Coefficients of higher powers of v and J are negligibly small in most cases (including the present one).

A more refined method of calculating the energy levels of a rotating vibrator was given by Dunham,[3] who assumed a fixed electronic potential for the molecule which could be expanded in a power series in $(r-r_e)/r_e$ in the neighborhood of the potential minimum. Application of a WKB approximation then gives for the rotational energy the expression

$$\frac{W(v,J)}{h}=\sum_{\substack{m\\ n\neq 0}} Y_{m,n}(v+\tfrac{1}{2})^mJ^n(J+1)^n. \quad (2)$$

The Y_{mn} are given in terms of the coefficients in the expansion of the molecular potential, the rotational constant (B_e), and the vibrational frequency of the molecule (ω_e). The dependence of the Y_{mn} on the reduced mass of the molecule is thereby determined. It is found that Y_{01}, the coefficient of $J(J+1)$, is not exactly proportional to $(1/\mu)$, as is B_e. However, since the difference between B_e and Y_{01} is quite small and since B_e is a far more common notation, reference will be made throughout this paper to B_e and the small correction given by Dunham will later be applied for the fact that it is Y_{01} which is actually determined experimentally. Since α_e, γ_e, and D_e are small compared to B_e, the differences between these constants and their corresponding Y_{mn} are too small to be significant. They can be measured for a single isotopic species and computed for the other species by the usual relationships[4]

$$\alpha_e\propto(1/\mu)^{\frac{3}{2}},\quad \gamma_e\propto(1/\mu)^2,\quad\text{and}\quad D_e\propto(1/\mu)^2, \quad (3)$$

where approximate values of the reduced mass may be used. The B_e of the various isotopic species can then be calculated from the rotational frequencies and used to determine the ratios of the reduced masses.

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[1] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), p. 11.

[2] The definition of r_e will be considered in greater detail later.

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

[4] The limits of the validity of Eqs. (3) will be discussed later.

For a diatomic molecule, μ is approximately given by

$$\mu = M_A M_B/(M_A+M_B), \tag{4}$$

where M_A and M_B are the atomic masses of the two atoms in the molecule. This approximation corresponds to the assumption that the mass of each electron is effectively concentrated at its respective nucleus. This is a better approximation than might appear at first since the electrons are primarily in spherical shells about their respective nuclei and spherical shells can be shown to "slip," i.e., the motion of such shells is similar to that of the chairs on a Ferris wheel. In this paper a distribution in which the electrons are all in spherical shells about their respective nuclei will be referred to as a "spherical distribution of electrons." In this approximation, if M_1 and M_2 are the masses of two isotopes of one of the atoms in the molecule, then

$$\frac{M_1}{M_2} = \frac{(M/M_2)(\mu_1/\mu_2)}{1-\mu_1/\mu_2+M/M_2}, \tag{5}$$

where M is the mass of the other atom in the molecule and μ_1 and μ_2 are, respectively, the reduced mass of the molecule containing M_1 or M_2. The ratio M/M_2 generally does not have to be known with great precision to determine a precise value of M_1/M_2 since it appears in the numerator and the denominator with the same sign.

For $^1\Sigma$ molecules it has been shown[5,6] that the error introduced by the assumption of a spherical distribution of electrons can largely be corrected for if the rotational magnetic moment of the molecule is known. This correction will be discussed in detail in a later section of this paper. The essential result, however, can be seen in a simple, classical manner, essentially by Larmor's theorem and the constant charge-to-mass ratio of electrons. The magnetic moment caused by rotation is proportional to the product of the deviation of the moment of inertia of the molecule from that of the idealized molecule composed of spherically distributed electrons (ΔI) and the speed of rotation of the molecule (ω). Hence it can easily be shown that

$$\Delta B/B = -\mu_J/\mu_0 J, \tag{6}$$

where μ_J is the rotational magnetic moment, μ_0 the Bohr magneton, and J the rotational quantum number. ΔB is just the difference between the actual B value and the B value of an idealized molecule in which Eq. (5) for the mass ratio of two isotopes would hold exactly. Thus, a measurement of μ_J allows a correction for the moment of inertia of the electrons to be made.

An additional correction, apparently untreated previously, is also found to be required. The rapidly precessing electronic angular momentum in a molecule causes the nuclei to "wobble." This motion of the nuclei, which is dependent on the reduced mass, stretches the molecule, thus changing its moment of inertia. The correction for this stretching cannot be evaluated accurately without prior knowledge of an isotopic mass ratio. In this work it is evaluated with the $C^{14}-C^{12}$ mass ratio as determined from nuclear reaction data. This effect will be discussed in detail in the perturbation treatment of a nonrigid rotor below.

There are thus three corrections which must be applied to the B_e's before their ratios are equal to the ratios of the reduced masses. These reduced mass ratios are then substituted in Eq. (5). In the order of their size, the corrections are: the correction for the nonspherical distribution of electrons; the correction for "wobble stretching," which is almost an order of magnitude smaller; and the Dunham correction, which is still another order of magnitude smaller. Since they are all small compared to B_e, they can be applied successively and independently. However, since the Dunham correction has the same dependence on the reduced mass as has the wobble stretching, it is not necessary to make this correction explicitly.

The measured frequencies of the $J=1\leftarrow 0$ transitions for $C^{12}O^{16}$ and $C^{13}O^{16}$ to be described below are in agreement with a previous measurement,[7] but are about fifty times more accurate. The $C^{12}O^{16}$ frequency is also in agreement with a very recent measurement[8] and is three times as accurate. The magnetic moment for $C^{12}O^{16}$ is in agreement with values previously reported,[9,10] but is also more accurate. The measurements have also been extended to $C^{12}O^{18}$, $C^{12}O^{17}$, $C^{14}O^{16}$, and $C^{13}O^{18}$.

From the magnetic measurements made on the various isotopic species of carbon monoxide, it was also possible to determine the sign of the electric dipole moment of carbon monoxide. This is, apparently, the first time the sign of the electric dipole moment of any molecule has been experimentally determined.

EXPERIMENTAL PROCEDURE

The rotational constant of each isotopic species of carbon monoxide was determined by the measurement of the frequency of the $J=1\leftarrow 0$ rotational transition. These transitions occur in the region of 110 000 Mc/sec. Power at these frequencies was produced by harmonic generator crystals driven by the Raytheon klystrons QK463 or 2K33, which operate near 25 000 Mc/sec. Techniques for the production and detection of high-frequency power have been previously described.[11–14]

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[5] M. W. P. Strandberg, *Microwave Spectroscopy* (Methuen and Company, Ltd., London, 1954), p. 62.

[6] C. H. Townes and A. L. Schawlow, reference 1, p. 207.

[7] Gilliam, Johnson, and Gordy, Phys. Rev. **78**, 140 (1950).

[8] W. Gordy and M. Cowan, Bull. Am. Phys. Soc. Ser. II, **2**, 212 (1957).

[9] B. Rosenblum and A. H. Nethercot, Bull. Am. Phys. Soc. Ser. II, **1**, 13 (1956).

[10] J. T. Cox and W. Gordy, Phys. Rev. **101**, 1298 (1956).

[11] Klein, Loubser, Nethercot, and Townes, Rev. Sci. Instr. **23**, 78 (1952).

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

[13] C. H. Townes and A. L. Schawlow, reference 1, Chap. 16.

[14] A. H. Nethercot, Jr., Trans. Inst. Radio Engrs. **MTT, 2**, 17 (1954).

The first measurements[9] were made with a 1% concentration of C^{13} and O^{18} and with an absorption cell consisting of a thirty-two foot length of RG53/U wave guide. This wave guide was coiled into a double helix and immersed in liquid nitrogen. The later measurements were made with more highly enriched isotopic samples and the absorption cell could then be reduced to a six foot length of RG98/U wave guide.

The absorption lines were observed on a cathode-ray oscilloscope with the klystron swept in frequency. A frequency-marker pip was superimposed on the center of the absorption line. The sweep repetition rate was about one cycle per second and the final band width of the phase-sensitive detector was kept relatively large (about 100 cycles per second) to reduce phase shift. To eliminate the effect of the residual phase shift, the frequency of the klystron was swept in both directions and the two frequencies thus measured were averaged.

It was found to be quite difficult to achieve a frequency sweep which was sufficiently linear in time by electrical modulation of the klystron. This was particularly true at slow sweep rates and is probably caused by thermal effects in the klystron. The klystron was, therefore, mechanically swept in frequency by distorting the klystron cavity with a rubber band driven by a small variable-speed motor. The same motor also drove a potentiometer which controlled the x axis of the oscilloscope which displayed the absorption line. The system gave a sweep of excellent linearity.

The sensitivity of millimeter-wave spectrometers is usually limited by the small amount of microwave power available at such high frequencies rather than by reflections. Therefore, there is little advantage in using Stark modulation. Also, Stark-modulation systems are quite lossy at these frequencies.

If absorptions are weak and reflections annoying, a square-wave frequency modulation of the klystron somewhat greater in amplitude than the width of the absorption line is advantageous. This reduces the part of the low-frequency noise which is dependent on the power level (and probably originates in the harmonic generator crystal), as well as the low-frequency amplifier noise. It also eliminates the major errors in frequency measurements caused by the absorption line appearing on a sloping base line due to reflections. In this work a four-kilocycle modulation frequency was employed. The four-kilocycle signal from the crystal detector was amplified in a tuned receiver and fed to a phase-sensitive detector which received its phase reference signal from the klystron modulator.

The half-width at half maximum of the absorption lines observed was about 100 kc/sec at a frequency of 110 000 Mc/sec. The major sources of this width were Doppler broadening and wall-collision broadening. Pressure broadening was made small by reducing the pressure in the absorption cell. It may be noted that the ratio of line width to frequency is $1/10^6$. The reasons for this small width are the absence of Stark broadening, the fairly low-modulation frequency, and the reduction of wall collisions and Doppler broadening at liquid nitrogen temperatures. In order to sweep the klystron over the absorption line is approximately one-half second without appreciable drift or frequency noise, several precautions had to be taken. However, electronic frequency stabilization was not necessary. A carefully selected klystron was shock-mounted in an oil bath, powered by a well-regulated supply, and protected from drafts.

The signal-to-noise ratio on all lines except for $C^{13}O^{18}$ and $C^{12}O^{17}$ was greater than 40. The signal-to-noise ratio on $C^{13}O^{18}$ was about 10. In the case of $C^{12}O^{17}$, the low concentration of this isotopic form (1%) and the hyperfine splitting into three partially resolved components due to the O^{17} nuclear quadrupole moment[15] reduced the signal-to-noise ratio to about unity. This low signal-to-noise ratio accounts for the large error assigned to the measurements on this molecule.

The isotopic enrichment and chemical preparation of the various samples of carbon monoxide was as follows:

$C^{14}O^{16}$.—A 15% C^{14} sample of barium carbonate (one millicurie) was obtained from the Oak Ridge National Laboratory. The barium carbonate was thoroughly mixed with approximately six times stoichiometric proportions of lead chloride. This mixture was then heated at 500°C in a furnace for three hours. Carbon dioxide was evolved in the reaction[16]:

$$BaCO_3+PbCl_2 \rightarrow BaCl_2+PbO+CO_2.$$

The carbon dioxide was then transferred to a tube containing acid-washed asbestos fibers impregnated with a fairly large amount of powdered zinc.[17] This mixture was heated for three hours at about 420°C. The carbon dioxide was thereby reduced to carbon monoxide in the reaction:

$$Zn+CO_2 \rightarrow ZnO+CO.$$

$C^{13}O^{16}$.—A sample of carbon monoxide containing about 66% $C^{13}O^{16}$ was supplied by Dr. T. F. Johns of the Atomic Energy Research Establishment, Harwell, England.

$C^{12}O^{18}$, $C^{12}O^{17}$.—A sample of oxygen enriched to 10% O^{18} and 1% O^{17} by thermal diffusion by Professor A. O. Nier was available. This oxygen was heated for about three hours at 520°C in the presence of an excess of powdered carbon which was obtained by crushing spectrometer electrodes. At 520°C the equilibrium constant is such that almost all the oxygen is converted to carbon dioxide. This was then reduced to carbon monoxide as described above for $C^{14}O^{16}$.

$C^{13}O^{18}$.—The sample of carbon monoxide obtained from Harwell was actually enriched in all the stable heavy isotopes of carbon and oxygen. This sample

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[15] B. Rosenblum and A. H. Nethercot, J. Chem. Phys. **27**, 828 (1957).

[16] Zweibel, Turkevich, and Miller, J. Am. Chem. Soc. **71**, 376 (1949).

[17] R. B. Bernstein and T. I. Taylor, Science **106**, 498 (1947).

contained about 66% $C^{13}O^{16}$, 4.6% $C^{12}O^{18}$, but only 0.4% $C^{13}O^{18}$. As suggested by Dr. Johns, this sample was placed in contact with a hot tungsten filament for a few hours to equilibrate the isotopic distribution. This resulted in about a 3% concentration of $C^{13}O^{18}$.

The frequency standard used in these measurements was a stable, crystal-controlled oscillator whose output was multiplied to a frequency close to that of the klystron. This standard was periodically compared with the 5-Mc signal transmitted by the National Bureau of Standards station WWV and was also intercompared with two other stable local standards. Care was taken to ensure that errors caused by the diurnal shifts of the ionosphere were averaged out.

The actual frequency-measurement technique used in this experiment has been described in detail elsewhere.[18] Briefly, a frequency-marker pip is formed whenever the klystron frequency, f_k, is swept past the point $f_k = f_{\text{std}} \pm f_{\text{rec}}$, where f_{std} is an appropriate multiple of the standard frequency and f_{rec} is the frequency to which a receiver is tuned. The receiver is tuned until the pip is coincident with the maximum of the absorption line. The frequency of the receiver is then measured. Care was taken to ensure that the intermediate frequency stage of the receiver did not distort the frequency-marker pip; also, a ferrite isolator assured the noninteraction of the frequency standard with the klystron. Two different electronic systems were used at various times to multiply the standard frequency.

In Fig. 1, the frequencies measured in each "run" are plotted as differences from the weighted average of all the runs. The errors shown for each run are the probable errors of the run calculated from the deviations of the individual measurements in the run. The error shown by the bold line is the assigned error in the final averaged frequency. The difference between successive runs on the same isotopic species is seen to be somewhat larger than might be expected from the stated probable error of the run. This is most likely caused by the average WWV frequency not yielding the true absolute frequency. This error should, however, be quite random since any unidirectional Doppler shift over a week or more is not reasonable. The psychological factor in deciding on the coincidence of the marker pip and the absorption line under different conditions and at different times may also play a role. The assigned final errors are believed to allow for these effects. In the case of $C^{13}O^{18}$ only one run was made. The standard deviation of the individual measurements was 0.4 kc/sec and the assigned error ±8 kc/sec.

For the measurements of the magnetic moments of the various isotopic species, the absorption cell was a six-foot length of RG98/U wave guide. Four turns of this guide, bent in the E plane, were wound on a diameter of 5.5 inches in two layers. A small bag made of Koroseal plastic sheet and Scotch electrical tape was placed around the guide and used as a container for the liquid nitrogen. The rf power transmission was approximately 25%. The wave guide and liquid-nitrogen container were placed in the 0.8-inch gap between the eight inch diameter pole faces of a magnet, the faces being thermally insulated from the liquid nitrogen with asbestos. The effect of any possible paramagnetic liquid oxygen on the magnetic field was considered and found to be negligible. The magnet provided a field of about 8000 gauss. The magnet current (11 amperes) was supplied by six naval submarine cells and was therefore quite stable. The magnetic field was monitored with two rotating flip coils driven by a single synchronous motor, one of which was rotated in the experimental field and the other in a shielded reference magnet. The voltages they produced were compared in a bridge. With this system, the field could be monitored for relative changes to a few parts in 10 000.

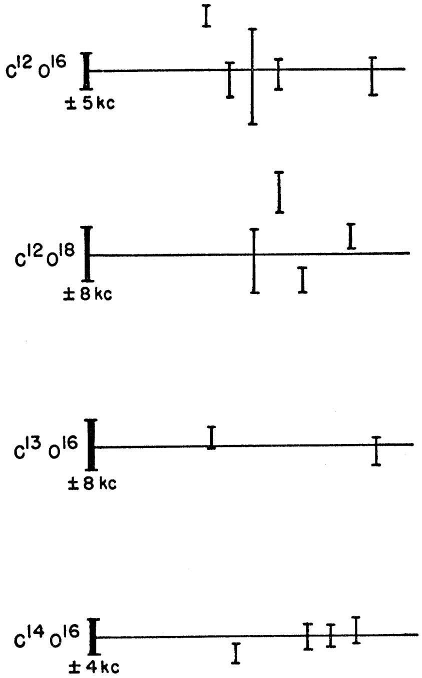

FIG. 1. Reproducibility and errors of the frequency measurements. The final assigned error is shown by the heavy line. The deviations and probable errors of the individual runs are also shown for the various days on which measurements were made.

The orientation of the dc magnetic and rf electric fields was such that only the $\Delta M = \pm 1$ transitions were induced, where M is the magnetic quantum number. For the $J = 1 \leftarrow 0$ transition, the absorption line was split by about 3 Mc/sec into two components, symmetric about the unsplit line.

In none of the isotopic species for which the Zeeman effect was observed was there a nucleus with a quadrupole moment. In only one case was there a nucleus with a magnetic moment (C^{13}). Here the 8000-gauss

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[18] C. H. Townes and A. L. Schawlow, reference 1, Chap. 17.

TABLE I. The magnetic moment of $C^{12}O^{16}$ in the $J=1$ rotational state as measured at four different times and in different magnetic fields.

Field (gauss)	Magnetic moment (nuclear magnetons)
7071±15	0.2690
7355±15	0.2689
7171±15	0.2692
3805±10	0.2691
Final value	0.2691±0.0005

field corresponds to an extreme strong-field case and therefore the nuclear spin is essentially uncoupled and does not take part in the molecular transition (i.e., $\Delta M_I=0$).[19] The Zeeman splitting is therefore unaffected except for a slight broadening of the Zeeman components.

The magnet was allowed to come to equilibrium and then a number of measurements of the Zeeman splitting were made. The frequencies of the two Zeeman components were measured as described above for the unsplit lines. The absorption cell was then removed from the magnet gap without turning off the field. The region of the field previously occupied by the absorption cell was plotted with a Numar proton-resonance probe and averaged. The maximum variation in the magnetic field over the region of the absorption cell was ±0.2% During the measurements, changes in the field, as monitored by the rotating coils, were of the order of ±0.1%. Actually, a direct measurement of the magnetic moment against the proton resonance was only made for $C^{12}O^{16}$, for which the data of four individual runs and the final value are shown in Table I. The magnetic moments of the other isotopic species were measured relative to that of $C^{12}O^{16}$.

RESULTS

The measured values of the frequencies and the assigned errors for the $J=1\leftarrow0$ rotational transitions in the ground vibrational state of the six isotopic species of carbon monoxide are given in Column II of Table II. From these measurements of the rotational frequencies, the equilibrium rotational constants, B_e, can be calculated from Eq. (1) if α_e, γ_e, and D_e are known. The coefficients of powers of $(v+\frac{1}{2})$ and $J(J+1)$ higher than those written in Eq. (1) can be shown to be too small to be significant.

The small amount of microwave power available at these frequencies precludes the microwave measurement of α_e and γ_e. However, very accurate infrared measurements have been made on the $C^{12}O^{16}$ molecule,[20–22] and α_e, γ_e, and D_e are known with sufficient accuracy for our purposes. Microwave measurements[23–25] of the $J=2\leftarrow1$ and $J=3\leftarrow2$ rotational transitions in $C^{12}O^{16}$ have also been made which give even more accurate values for D_e and which are in essential agreement with the infrared measurements. The standard deviation of the measurement by Plyler *et al.* of $B_0-B_1\cong2\alpha$, as computed on the SEAC,[26] is 0.16 Mc/sec. The value of α_e of 525.24 Mc/sec measured by Plyler *et al.* is in perfect agreement with the value measured by Goldberg and Müller. Professor Goldberg has kindly estimated that the possible systematic error in his measurements might be about one part in one thousand, or about six times the standard deviation quoted by Plyler. Considering the perfect agreement between the two measurements, the value $\alpha=525.24\pm0.5$ Mc/sec was adopted. The adopted values of $\gamma_e=0.0887$ Mc/sec and $D_e=0.1853$ Mc/sec are small and their errors are not of significance. The α_e, γ_e, and D_e for other isotopic species were computed from those of $C^{12}O^{16}$ from Eqs. (3). The error in α_e results in an error of about 0.25 Mc/sec in the B_e given in Column III of Table II. These errors are, of course, not independent, and they largely cancel out when ratios of the B_e's are taken for the determination of isotopic mass ratios. Furthermore, in the empirical correction made for wobble stretching, a correction for the error in α_e is automatically included. Since α_e does not have quite the same dependence on reduced mass as does wobble stretching, the correction is not complete, but it does insure that the error in α_e is not significant in the final mass-ratio determination. The same situation exists for any error introduced by the use of Eqs. (3) for the determination of α_e, γ_e, and D_e for isotopic species other than $C^{12}O^{16}$.

The final value of the magnetic moment of $C^{12}O^{16}$ is -0.2691 ± 0.0005 nm, where "nm" is the nuclear magneton. The sign of the magnetic moment was not directly measured in the present work. However, a negative sign is expected for almost all molecules other

TABLE II. Rotational frequencies, rotational constants, and magnetic moments of carbon monoxide.

Isotopic species	$J=1\leftarrow0$, $v=0$ Rotational frequencies (Mc/sec)	B_e (Mc/sec)	μ_J (nuclear magnetons)[a]
$C^{12}O^{16}$	115 271.204±0.005	57 898.568	−0.26910±0.0005
$C^{13}O^{16}$	110 201.370±0.008	55 346.447	−0.25704±0.0005
$C^{12}O^{18}$	109 782.182±0.008	55 135.449	−0.25622±0.0005
$C^{14}O^{16}$	105 871.110±0.004	53 166.936	−0.24664±0.0005
$C^{13}O^{18}$	104 711.416±0.008	52 583.288	−0.24418±0.0005[b]
$C^{12}O^{17}$	112 359.276±0.060[b]	56 432.675	−0.26227±0.0005[b]

[a] The errors given are absolute errors; the relative errors are about three times smaller.

[b] Calculated.

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[19] H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., New York, 1934), p. 376.

[20] Plyler, Blaine, and Tidwell, J. Research Natl. Bur. Standards **55**, 183 (1955).

[21] L. Goldberg and E. A. Müller, Astrophys. J. **118**, 397 (1953).

[22] Rank, Guenther, Saksena, Shearer, and Wiggins, J. Opt. Soc. Am. **47**, 686 (1957). This new value of α (525.70 Mc/sec) is within the adopted error and was received too late to be included in the calculations.

[23] Bedard, Gallagher, and Johnson, Phys. Rev. **92**, 1440 (1953).

[24] M. J. Cowan and W. Gordy, Phys. Rev. **104**, 551 (1956).

[25] W. Gordy and M. J. Cowan, Bull. Am. Phys. Soc. Ser. **II**, **2**, 212 (1957). Received too late to be included, but would produce no significant change in calculated results.

[26] E. K. Plyler (private communication).

than hydrides, and in this case a positive magnetic moment would lead to completely unreasonable mass ratios. The magnetic moment was measured both at about 4000 gauss and at about 7000 gauss. Thus it was verified that the Zeeman splitting is linear in magnetic field to the above accuracy. The magnetic moments of the three other isotopic species ($C^{14}O^{16}$, $C^{13}O^{16}$, $C^{12}O^{18}$), which were measured relative to $C^{12}O^{16}$, as well as the magnetic moments calculated for $C^{12}O^{17}$ and $C^{13}O^{18}$ are given in Column IV of Table II.

To a good approximation it would be expected that the magnetic moments of the various isotopic species of a molecule would be proportional to their speed of rotation. Vibrational effects and higher orders in the perturbation theory would be expected to be small and to be functions only of the speed of rotation. However, if the molecule has an electric dipole moment, the magnetic moment is not only dependent on the speed of rotation, but also on the position of the center of gravity of the molecule. It has been shown[27,28] that since this dependence is linear in the dipole moment, it can be used to determine the sign of the electric dipole moment of a molecule. The equation obtained for the change in the magnetic moment due to the change in center of gravity when the mass of one of the nuclei in a diatomic molecule is changed is[27]

$$\Delta\mu = 2JM\Delta M_1(\text{nm})d/(M_1+M_2)M_1 e r_0, \tag{7}$$

where M_1 and M_2 are the masses of the two atoms in the molecule, ΔM_1 is the change in the mass of M_1, r_0 is the internuclear distance, d the dipole moment, e the electronic charge, (nm) the nuclear magneton, and M the proton mass.[29] Equation (7) should give the only significant variation of magnetic moment which is not a monotonic function of the rotational frequency.

In Fig. 2(a) a plot of the ratio of magnetic moment to rotational frequency, ν_0, *versus* rotational frequency for the four measured isotopic species is given. The probable error is indicated by the arrows. This error is the relative error of the magnetic moments. The absolute error is about three times larger. Figure 2(b) and Fig. 2(c) show the same data as does Fig. 2(a), but with the effect of the change in the center of gravity removed by the application of Eq. (7) with d equal to 0.1 debye. In Fig. 2(b) it has been assumed that the carbon atom carries the excess negative charge and the oxygen atom the excess positive charge, while in Fig. 2(c) the dipole moment has been assumed to be in the other direction. Since, except for the variation given in Eq. (7), the variation of μ_J/ν_0 with frequency would be expected to be slow and monotonic, the choice of sign made in Fig. 2(b) (C^-O^+) appears to be correct. This is opposite to the sign which might be predicted for the dipole moment on the basis of electronegativity differences, but since the dipole moment is so small, there is no strong reason for believing that other molecular factors should not determine its direction. Most experimentally measurable effects of molecular dipoles depend on the square of this moment or on its absolute value. Hence magnitudes of many dipole moments have been measured, but it appears that there has been no previous experimental determination of the sign of a molecular dipole moment.

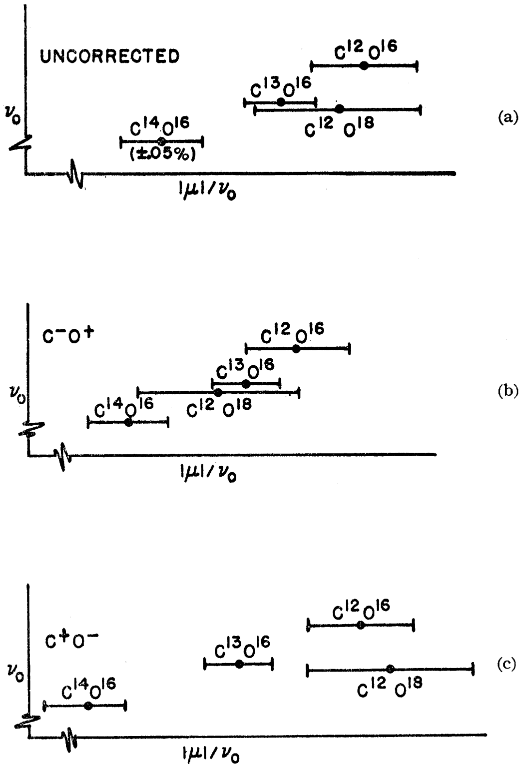

FIG. 2. The ratio of magnetic moment to rotational frequency *vs* rotational frequency. After the proper correction for electric dipole moment, the points should lie on a straight line.

TABLE III. Rotational constants corrected, respectively, for higher excited states and also for wobble stretching. B_e^a is the value of the rotational constant B_e after correction (by adding ΔB) for higher excited states. B_e^b is the value after further corrections for wobble stretching.

Isotopic species	ΔB (Mc/sec)	B_e^a (Mc/sec)	B_e^b (Mc/sec)
$C^{12}O^{16}$	8.4828	57 907.0508	57 907.9692
$C^{13}O^{16}$	7.7457	55 354.1927	55 355.0322
$C^{12}O^{18}$	7.6913	55 143.1401	55 143.9731
$C^{14}O^{16}$	7.1393	53 174.0751	53 174.8497
$C^{13}O^{18}$	6.9904	52 590.2779	52 591.0355
$C^{12}O^{17}$	8.0581	56 440.7331	56 441.6055

The magnetic moment for each isotope can now be substituted into Eq. (6) [or Eq. (20)] and ΔB determined. ΔB is added to the equilibrium B value, B_e, to give the equilibrium B value, B_e^a, for the idealized molecule consisting of atoms with a spherical distribution of electrons. ΔB and B_e^a are listed in Columns II

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[27] Townes, Dousmanis, White, and Schwartz, Discussions Faraday Soc. **19**, 62 (1955).

[28] C. H. Townes and A. L. Schawlow, reference 1, p. 296.

[29] The same equation can be derived classically starting from Eq. (6).

TABLE IV. Mass ratios of the carbon and oxygen isotopes. The exact agreement of the microwave and nuclear reaction values for the $C^{14}-C^{12}$ ratio is forced by the evaluation of the wobble stretching as explained in the text.

Isotopes	Isotopic species used	Microwave mass ratio[a]	Nuclear reaction mass ratio[b]	Mass spectroscopic mass ratio[c]
$C^{14}-C^{12}$	$C^{14}O^{16}$, $C^{12}O^{16}$	1.166 937 43±23	1.166 937 43±23 (1.166 937 55±23)	
$C^{13}-C^{12}$	$C^{13}O^{16}$, $C^{12}O^{16}$ $C^{13}O^{18}$, $C^{12}O^{18}$ Average	1.083 612 83±27 1.083 612 90±28 1.083 612 86±25	1.083 613 08±20 (1.083 612 78±20)	1.083 613 09±03
$O^{18}-O^{16}$	$C^{12}O^{18}$, $C^{12}O^{16}$ $C^{13}O^{18}$, $C^{13}O^{16}$ Average	1.125 304 71±35 1.125 304 71±38 1.125 304 71±28	1.125 304 19±70	1.125 305 27±05
$O^{17}-O^{16}$	$C^{12}O^{17}$, $C^{12}O^{16}$	1.062 784 72±105	1.062 783 38±30 (1.062 783 25±25)	1.062 783 52±11

[a] Calculated by Eq. (5).
[b] See reference 30.
[c] See Scolman *et al.*, reference 30.

and III of Table III for each isotopic species. It is noted that the magnetic moment was measured with sufficient accuracy to make the error in ΔB negligible compared to the error in the frequency measurements.

The correction to B_e for wobble stretching is almost an order of magnitude smaller than the correction for nonspherically distributed electrons, but it is still large enough to be significant in this experiment. However, its evaluation requires information from other measurements of nuclear masses. The nature of the effect is considered in detail in the following section of this paper. It is shown there that the contribution of this effect to the rotational energy is proportional to $(1/\mu)^2$. In order to evaluate this wobble-stretching correction, the B_e^a values for $C^{12}O^{16}$ and $C^{14}O^{16}$ are properly adjusted to give the accepted nuclear reaction value for the $C^{14}-C^{12}$ mass ratio. The correction thus evaluated can then be applied to the B_e^a values for the remaining isotopic species. The B_e^a values corrected for wobble stretching, B_e^b, are given in Column IV of Table III. Dunham's correction and a correction for any error in α_e are automatically taken into account in evaluating B_e^b as has been explained above.

The isotopic mass ratios are computed with the B_e^b (which are proportional to the reduced mass) from Eq. (5). They are listed in Column III of Table IV. The errors listed include both the errors in the nuclear reaction and the microwave determination of the $C^{14}-C^{12}$ mass ratio. In Column IV of Table IV are listed the nuclear reaction values for the mass ratios.[30] The exact correspondence of the microwave and nuclear reaction values for the $C^{14}-C^{12}$ ratio is, of course, forced by the choice of the value for the wobble stretching. The very good agreement in the other cases serves as an excellent check on the consistency of the nuclear reaction values with each other. The two sets of nuclear reaction values[30] (computed from essentially the same data) agree very well with each other and with the microwave results except for $C^{13}-C^{12}$, where the microwave value lies between the two nuclear reaction results. The agreement of the microwave values with the mass spectroscopic results[31] is fairly good. The disagreement for $O^{18}-O^{16}$ may perhaps not be significant. The close agreement of the two microwave determinations of the $C^{13}-C^{12}$ and $O^{18}-O^{16}$ mass ratios serves as a check of the microwave-frequency measurements and demonstrates that there are no effects of significant magnitude which vary rapidly with reduced mass. No such effects are expected theoretically.

PERTURBATION TREATMENT OF A NONRIGID ROTOR

This treatment is an extension of one given by Townes and Schawlow[32] for rigid rotors. The dependence of the rotational energy on the masses of the nuclei will be considered for nonrigid $^1\Sigma$ diatomic molecules.

The Hamiltonian for the n electrons in a molecule with fixed (or infinitely heavy) nuclei may be written:

$$H_e=\frac{1}{2m}\sum_n\sum_g p_{ng}^2+V+X, \tag{8}$$

where m is the electron mass, p_{ng} is the gth component of the momentum of the nth electron in Cartesian coordinates, and $V+X$ is the potential energy of the electrons. Here,

$$X=\sum\nolimits_n \sum\nolimits_g a_{ng}s_{ng}l_{ng},$$

where s_{ng} and l_{ng} are, respectively, the gth Cartesian component of the spin and orbital angular momentum of the nth electron, and a_{ng} is a constant. V is the remainder of the potential energy. This separation is

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[30] The nuclear reaction values for the $C^{13}-C^{12}$, $C^{14}-C^{12}$, and $O^{17}-O^{16}$ mass ratios are from the work of A. H. Wapstra [Physica **21**, 367 (1955)]. The $O^{18}-O^{16}$ ratio is the one computed by Scolman, Quisenberry, and Nier [Phys. Rev. **102**, 1076 (1956)] and is based on new and more accurate nuclear reaction data. Also, the values computed by Mattauch, Waldmann, Bieri, and Everling [*Annual Review of Nuclear Science* (Annual Review, Inc., Stanford, 1956), Vol. 6, p. 179] are included in parentheses for ready comparison.

[31] Scolman, Quisenberry, and Nier, reference 30.

[32] C. H. Townes and A. L. Schawlow, reference 1, p. 207.

made so that X may be treated as part of the perturbation, and the unperturbed system may be considered as having pure Russell-Saunders coupling. If the molecule rotates, the Hamiltonian for the electrons is of the same form as above, but p_{ng} then refers to the generalized momentum referred to a set of axes fixed in the molecule. The eigenvalues of this operator are therefore the same for the rotating and the nonrotating molecule. The Hamiltonian of the nuclei in a diatomic molecule may be written

$$H_n=(O^2/2A)+G, \qquad (9)$$

where O is the angular momentum of the nuclei about an axis perpendicular to the internuclear axis and A is the moment of inertia of the nuclei about the same axis. G is the vibrational energy of the nuclei. The total Hamiltonian for the molecule is then

$$H=H_e+H_n.$$

When the molecule rotates, the angular momentum of the electrons cannot be strictly zero since the electrons at least partially rotate with the molecule. The total angular momentum, $\hbar J$, is equal to the sum of the nuclear angular momentum, O, and the electronic angular momentum, $\hbar L$, or[33]

$$O=(J-L)\hbar. \qquad (10)$$

The Hamiltonian can then be written

$$H=\frac{\hbar^2J^2}{2A}-\frac{\hbar^2\mathbf{J}\cdot\mathbf{L}}{A}+\frac{\hbar^2L^2}{2A}+G+X+\frac{1}{2m}\sum_n\sum_g p_{ng}{}^2 +V+\mu_0\mathcal{H}\cdot\mathbf{L}. \qquad (11)$$

Since the electrons are rotating with the molecule, electronic states with orbital angular momentum must be mixed into the ground state. The presence of these states will cause a molecular magnetic moment. The last term in the above Hamiltonian was added to give the interaction energy of the electronic magnetic moment with an applied magnetic field, $\mathcal{H}$ (μ_0 is the Bohr magneton). The additional magnetic moment caused by the rotation of the nuclei can be computed straightforwardly and will be considered later.

In the above Hamiltonian all terms except the sixth and the seventh are considered part of the perturbation Hamiltonian, H'. The perturbation consists of allowing the nuclei in the molecule to rotate and vibrate, i.e., allowing the masses of the nuclei to become noninfinite, and letting the a_{ng} be nonzero.

The first-order correction to the molecular energy is:

$$W^{(1)}=\hbar^2J(J+1)\langle 0|1/2A|0\rangle+\langle 0|G|0\rangle +\hbar^2\langle 0|L^2/2A|0\rangle, \qquad (12)$$

where 0 designates the wave function in the rotating coordinate system of the ground vibrational and electronic state. The first term is just the rotational energy a rigid molecule would have if the mass of the electrons were neglected compared to the mass of the nuclei. The second term gives the zero-point vibrational energy of the nuclei. The third term is the energy of a "wobbling" motion of the nuclei. This wobbling is caused by the electronic angular momentum which, although averaging to zero, has an instantaneous value perpendicular to and precessing rapidly about the internuclear axis. This term can be of the same order of magnitude as the first term in $W^{(1)}$. This motion and its consequences will be discussed below. Both the second and third terms in Eq. (12) are independent of J and therefore will not themselves be of further concern. All other terms in the perturbation Hamiltonian have zero diagonal values.

The second-order correction to the energy is given, as usual, by

$$W^{(2)}=\sum_{n\neq 0}\frac{|\langle 0|H'|n\rangle|^2}{W_0-W_n}, \qquad (13)$$

where n designates the wave functions in the rotating coordinate system of all the excited states of the molecule. This includes all the vibrational states in each electronic state, including the ground electronic state. W_0-W_n is the energy difference between the ground state and the excited state, n. The six terms in H' give rise to twenty-one terms in the second-order energy. Fortunately, most of these either do not depend on J, or are zero, or both.

In the following, the moment of inertia of the nuclei, A, must be considered as an operator. This operator causes excitation of higher vibrational and electronic states by the motion of the nuclei in vibration. Since this vibration is along the internuclear axis, it cannot excite angular momentum about this axis, and therefore can only connect the ground state with vibrational states in higher $^1\Sigma$ electronic states. The operator L can only connect the $^1\Sigma$ ground state with $^1\Pi$ states. The operator L^2 can connect the ground state only with $^1\Sigma$ or $^1\Delta$ states. The operator X does not connect states of the same multiplicity. It will, therefore, not contribute to the rotational or magnetic energy in the second order. (Its contribution in the third order will be considered below.) From such considerations, many cross terms vanish since their individual operators never connect the same states. The only nonzero terms which involve J are given below.[34]

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[33] It would be more complete to write $O=(J-L-S)\hbar$, where S is the electronic spin angular momentum. However, since the unperturbed molecular electronic states are diagonal in the spin and the ground state is a $^1\Sigma$, S will not contribute any nonzero terms in the second order. The effect of spin in the third order will be discussed below.

[34] In the treatment of Townes and Schawlow, the second, third, and fourth terms in Eq. (14) do not appear since that treatment was for the case of the rigid rotor.

$$W^{(2)}=\sum_{n\neq 0}\frac{\hbar^4|\langle 0|\mathbf{J}\cdot\mathbf{L}/A|n\rangle|^2}{W_0-W_n}+2\sum_{n\neq 0}\frac{\hbar^2\langle 0|J^2/2A|n\rangle\langle n|G|0\rangle}{W_0-W_n}+2\sum_{n\neq 0}\frac{\hbar^4\langle 0|J^2/2A|n\rangle\langle n|L^2/-2A|0\rangle}{W_0-W_n}+\sum_{n\neq 0}\frac{\hbar^4|\langle 0|J^2/2A|n\rangle|^2}{W_0-W_n}-2\mu_0\sum_{n\neq 0}\frac{\hbar^2\langle 0|\mathbf{J}\cdot\mathbf{L}/A|n\rangle\langle n|\mathcal{H}\cdot\mathbf{L}|0\rangle}{W_0-W_n}. \quad (14)$$

If the internuclear axis is chosen as the z axis, $\langle 0|L_z|n\rangle=0$. Cross products of the form $\langle 0|L_x|n\rangle\times\langle n|L_y|0\rangle$ which arise in Eq. (14) when the dot products are squared must also be zero: upon rotation of the coordinate axis about the z axis by $\pi/2$, the sign of such a term changes; but since the x and y directions are equivalent, the value of the term must not change. From these considerations and the equivalence of the x and y directions, Eq. (14) can be rewritten:

$$W^{(2)}=\hbar^4J(J+1)\sum_{n\neq 0}\frac{|\langle 0|L_x/A|n\rangle|^2}{W_0-W_n}+\hbar^2J(J+1)\sum_{n\neq 0}\frac{\langle 0|1/A|n\rangle\langle n|G|0\rangle}{W_0-W_n}+\tfrac{1}{2}\hbar^4J(J+1)\sum_{n\neq 0}\frac{\langle 0|1/A|n\rangle\langle n|L^2/A|0\rangle}{W_0-W_n}+\tfrac{1}{4}\hbar^4J^2(J+1)^2\sum_{n\neq 0}\frac{|\langle 0|1/A|n\rangle|^2}{W_0-W_n}-2\mu_0\mathbf{J}\cdot\mathcal{H}\hbar^2\sum_{n\neq 0}\frac{\langle 0|L_x/A|n\rangle\langle n|L_x|0\rangle}{W_0-W_n}. \quad (15)$$

The sum of the first term of $W^{(1)}$ plus $W^{(2)}$ gives the total rotational energy of the molecule, both electronic and nuclear, to the second order plus the interaction energy of the electronic magnetic moment with the field, $\mathcal{H}$. The negative of the first term of $W^{(2)}$, $-W_1^{(2)}$, is essentially the rotational energy of the electrons. The physical significance and the evaluation of the various terms in $W^{(2)}$ will now be discussed.

For the case of a rigid rotor with all the electrons in spherical shells about their respective nuclei, $W_1^{(2)}$ has been evaluated[35] as

$$W_1^{(2)}=\hbar^4\frac{J(J+1)}{A^2}\sum_{n\neq 0}\frac{|\langle 0|L_x|n\rangle|^2}{W_0-W_n}=-\hbar^2\frac{J(J+1)}{2A}\sum_i r_i^2m, \quad (16)$$

where r_i is the distance of the ith nucleus from the center of gravity of the molecule. $\sum_i r_i^2m$ is the moment of inertia of the spherical-shell electrons, and $\hbar^2J(J+1)/A^2$ is the square of the angular speed of rotation. In Eq. (16) above, the average A has been removed from the matrix elements; since the electrons are assumed to stay in the same spherical shells at all times, A cannot mix the electronic wave functions.

A new moment of inertia, A_{eff}, which includes the effect of $W_1^{(2)}$ can be written as

$$\frac{1}{A_{\text{eff}}}=\frac{1}{A}+\hbar^2\sum_{n\neq 0}\frac{|\langle 0|L_x/A|n\rangle|^2}{W_0-W_n}. \quad (17)$$

In order to evaluate the added term accurately, the molecular Zeeman effect is measured. The matrix elements appearing in $W_5^{(2)}$ are almost identical to those in Eq. (17). However, the Zeeman measurement yields the molecular magnetic moment, μ_J, where μ_J is the sum of the magnetic moment of the rotating nuclei, μ_R, and the electronic magnetic moment, μ_e. It is convenient to equate μ_R to the negative of the moment that would be produced by spherical shells of the electrons about their respective nuclei:

$$\mu_R=\frac{J\mu_0}{A}\sum_i r_i^2m. \quad (18)$$

Therefore,

$$\mu_J=2J\hbar^2\mu_0\sum_{n\neq 0}\frac{\langle 0|L_x/A|n\rangle\langle n|L_x|0\rangle}{W_0-W_n}+\frac{J\mu_0}{A}\sum_i r_i^2m. \quad (19)$$

Let it be assumed that

$$\frac{1}{A}\sum_{n\neq 0}\frac{\langle 0|L_x/A|n\rangle\langle n|L_x|0\rangle}{W_0-W_n}=\sum_{n\neq 0}\frac{|\langle 0|L_x/A|n\rangle|^2}{W_0-W_n}.$$

The error introduced by this assumption is small and will be discussed later.[36] Then, on elimination of the matrix elements between Eq. (17) and Eq. (19), and using the condition that $A\gg\sum_i r_i^2m$,

$$\mu_J/\mu_0J=\Delta A/A=-\Delta B/B. \quad (20)$$

Here $\Delta A=A+\sum_i r_i^2m-A_{\text{eff}}$, and is therefore the difference between the moment of inertia of the actual molecule (however, still neglecting $W_3^{(2)}$ and $W_4^{(2)}$) and an idealized molecule composed of bare nuclei and spherical shells of electrons. This is just the equation whose classical derivation was indicated in the Introduction.

The second term in the second-order energy, $W_2^{(2)}$, is the vibration-rotation correction. The matrix elements are nonzero only when n designates vibrational states in $^1\Sigma$ electronic states. This sum can be divided into two separate sums, one over the ground and one over the excited electronic states. It would not seem

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[35] C. H. Townes and A. L. Schawlow, reference 1, p. 213.

[36] See Appendix I.

unreasonable that the average matrix element of $1/A$ and G in the first sum would be of the same order as in the second sum. Since the vibrational energy level spacing in carbon monoxide is about thirty times smaller than the electronic energy level spacing, it might be expected that the sum over excited electronic states would be as much as a few percent of the total vibration-rotation interaction. Dunham, in assuming an electronic potential fixed in space for the molecule, does not fully treat the contribution of excited electronic states to the vibration-rotation interaction. The larger sum is the part whose dependence on reduced mass was deduced as $1/\mu^{\frac{3}{2}}$. The dependence of the smaller sum would be somewhat different. Measurements of the vibration-rotation interaction in $C^{13}O^{16}$ are, unfortunately, not accurate enough to determine the size of the second sum. The error in the mass ratios caused by the uncertainty in the reduced mass dependence of the vibration-rotation interaction might not be insignificant, but would be largely corrected in the present case by being included in the adjustment made for wobble stretching. In principle, this uncertainty could be eliminated by measuring α for each isotopic species.

The fourth term in the second-order energy, $W_4^{(2)}$, is the change in rotational energy caused by the centrifugal stretching of the molecule. Again, the only nonzero matrix elements are those connecting vibrational states in the ground and excited $^1\Sigma$ states. As in the case of the vibration-rotation interaction, the contribution of excited electronic states to $W_4^{(2)}$ is not explicitly considered by Dunham. However, since D_e is very small and since the contribution of these terms is probably not more than a few percent, no significant error in mass ratios would be introduced. As with the vibration-rotation interaction, the effect could be eliminated by measuring D_e for each isotopic species.

D_e is often considered a "determined constant" of the molecule: if ω_e and B_e are known, D_e can be computed from

$$D_e = 4B_e^3/\omega_e^2. \qquad (21)$$

The more refined treatment by Dunham gives a negligibly small correction to Eq. (21) and also permits the calculation of D_0. Since equation (21) is derived on the basis of an electronic potential fixed in space, it could be in error by as much as the contribution of the excited electronic states to $W_4^{(2)}$. This error might then be as much as a few percent. However, it is possible that a partial correction for the effect of excited electronic states on D_e may be automatically included by deriving the molecular potential constants from observed spectral constants (α_e, γ_e, etc.). These observed spectral constants also contain effects of higher electronic states similar to those in $W_4^{(2)}$ and hence do not obey the idealized Dunham relations, but it is not clear that the deviations must invariably, if ever, compensate each other. It is also true that Eq. (21) would be in error correspondingly less than a few percent if the matrix elements to the excited electronic states are less than those within the ground electronic state. It is possible that these matrix elements are considerably smaller.

The value of D_0 computed from (21) for CO is 0.1835 ± 0.0001 Mc/sec, where the error is that due to the error in B_e, ω_e and to the error in the molecular potential constants used in computing the Dunham correction. The experimental situation here is not completely clear. Microwave measurements by Bedard, Gallagher, and Johnson[23] on the $J=1 \leftarrow 0$ and $J=2 \leftarrow 1$ transitions give a value for D_0 of 0.1890 ± 0.0007 Mc/sec. This value deviates in the expected direction from the one calculated from Eq. (21) by 3% and the deviation is about eight times the stated experimental error. A paper by Cowan and Gordy[24] on the $J=1 \leftarrow 0$, $J=2 \leftarrow 1$ and $J=3 \leftarrow 2$ transitions reports a value of 0.1888 Mc/sec, in excellent agreement with Bedard *et al.* However, a later measurement by Gordy and Cowan[25] gives 0.1838 ± 0.0005 Mc/sec, which is in agreement with the value calculated from Eq. (21). The infrared values of D_e are 0.1878 Mc/sec,[20] 0.1854 Mc/sec,[21] and 0.1836 Mc/sec.[22] D seems to be somewhat larger than given by Eq. (21), but the exact amount of the discrepancy is uncertain.

The remaining term in the second-order energy $W_3^{(2)}$, is not a familiar one. Measurements of vibrational and rotational levels in only one isotopic species of a molecule would reveal no effects caused by this term. It would merely be treated as a part of B_e. However, since it is proportional to $(1/\mu)^2$ instead of $1/\mu$, as is expected for B_e, its effect will appear when measurements in two different isotopic species are compared. This term is seen to be quite similar in appearance to $W_4^{(2)}$, the centrifugal-distortion term. In the approximation that L^2 can be removed from the matrix element and set equal to $L(L+1)$, $W_3^{(2)}$ and $W_4^{(2)}$ are almost identical. The matrix elements connect the ground state to the same excited states as in $W_4^{(2)}$. The largest contribution would similarly be expected from the ground electronic state.

A brief digression will be made to discuss this angular momentum, L. L can be considered to be the resultant of the two atomic orbital angular momenta which are coupled together when the two atoms form a molecule. Because of the large electric field along the internuclear axis, L precesses rapidly about this axis. In a $^1\Sigma$ molecule it always remains perpendicular to the internuclear axis. Since this precession is very rapid, the molecular electronic states cannot be considered characteristic of L, but only of its projection on the internuclear axis. However, the average value of L^2 is not necessarily small, but would be expected to be of the order of one or two units of squared angular momentum. Indeed, for CO, from a comparison of $W_3^{(2)}$ and $W_4^{(2)}$, $L(L+1) = 2.5$ if $\langle n | L^2/A | 0 \rangle = L(L+1) \langle 0 | 1/A | n \rangle$. Since the total angular momentum, J, is a constant, this rapidly precessing electronic angular momentum must be

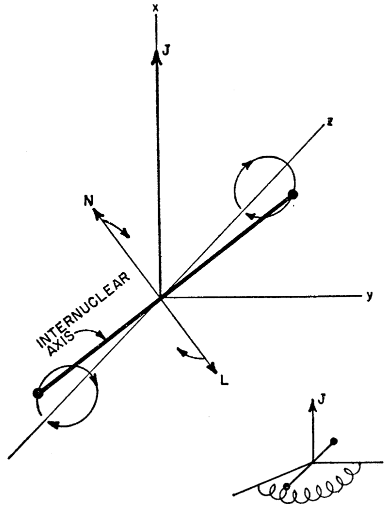

FIG. 3. The "wobbling" motion of the nuclei caused by the rapid precession of L (the large figure represents rotating coordinates; the inset represents space-fixed coordinates).

exactly canceled by an equal and opposite angular momentum of the nuclei, N. It is readily seen that the motion of the nuclei corresponding to the precessing angular momentum N is a "wobbling" motion in which the nuclei move in small circles about what otherwise would be the internuclear axis. This is illustrated in Fig. 3 in a coordinate system rotating with the molecule. The resultant motion of the nuclei in a fixed coordinate system due to J and N is shown in the inset of Fig. 3. The curved arrows on L and N in Fig. 3 indicate the precession of these vectors. The energy of this motion, which is of the order of the rotational energy of the nuclei for $J\simeq 1$, is given by the third term in the first-order energy, Eq. (12). Since this energy is independent of J, it is not of direct concern. However, the precessing angular momentum has an indirect effect which is important.

As the nuclei move in small circles about the z axis in Fig. 3, they will experience a centrifugal force proportional to L^2. This centrifugal force is balanced by forces on the particle perpendicular to and along the internuclear axis. The component of the centrifugal force along the internuclear axis (which stretches the molecule) is just equal to the force caused by simple rotation of the molecule with an angular momentum of L. The stretching caused by this wobbling of the nuclei thus changes the moment of inertia of the molecule by an amount which is to a first-order independent of the rotational or vibrational quantum numbers. It will therefore cause a change in the rotational energy proportional to $J(J+1)$ which is just that given by $W_3^{(2)}$.

Since this change of moment of inertia is independent of vibrational or rotational states, it cannot be evaluated from measurements on only one isotopic species. In this work both $W_3^{(2)}$ and corrections such as those caused by the contribution of higher electronic states to α have been evaluated by assuming the value of the $C^{14}-C^{12}$ mass difference from nuclear reaction data to be correct. $W_3^{(2)}$ is probably considerably larger than the other effects.

B_e is usually considered to be proportional to $1/\mu$ except for the very small correction given by Dunham. Because of the wobble stretching, the rotational constant deviates from this proportionality. B_e is often defined as $B_e=h/(8\pi^2\mu r_e^2)$, where r_e is the internuclear distance in the absence of vibration or centrifugal stretching, i.e., it is the internuclear distance in the $J=0$, $v=0$ state with the effect of zero-point vibration subtracted out. The quantity r_e is therefore generally regarded as a constant of the molecule which is the same for all isotopic species. If it is desired to consider r_e as such a constant of the molecule, the term $W_3^{(2)}$ must be added to Eq. (1). In this case r_e must be defined as the internuclear distance when N is also equal to zero. This is equivalent to saying that r_e is the internuclear distance for a molecule with infinitely heavy nuclei. Alternatively, Eq. (1) can be kept intact and the condition that r_e is exactly the same for all isotopic species must be relaxed. The latter situation is probably to be preferred in view of the small difference in r_e from one isotopic species to another (e.g., $\Delta r_e\cong 10^{-6}$ A for a $C^{12}\rightarrow C^{14}$ substitution; the change would be 10^{-5} A if the Zeeman correction were not made).

The third-order energy is given by the expression:

$$W^{(3)}=\sum_{k\neq 0}\sum_{n\neq 0}\frac{\langle 0|H'|k\rangle\langle k|H'|n\rangle\langle n|H'|0\rangle}{(W_0-W_k)(W_0-W_n)}-\sum_{k\neq 0}\frac{\langle 0|H'|k\rangle\langle 0|H'|0\rangle\langle k|H'|0\rangle}{(W_0-W_k)^2}, \quad (22)$$

where the notation is analogous to that in Eq. (17). In the third order there are a number of nonzero terms which depend on J. However, all the terms in H', with the exception of G and X are extremely small compared to the electronic energy. Third-order terms not involving G or X will, therefore, be negligibly small.

Since X only connects states of different multiplicity,[37] and since it is the only operator in H' that can connect such states, it must appear in the numerator twice or not at all for the numerator to be nonzero. There are, therefore, two types of terms which might be large enough to be significant: first, those involving G with $J^2/2A$ or with $J^2/2A$ and $L^2/2A$; and second, those involving X twice and a term containing J. Terms of the first type are higher order corrections to the vibration-rotation interaction, to the centrifugal distortion, or are vibrational corrections to the wobble stretching. The effects of such higher terms have already been included in the empirical evaluation of

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[37] X connects both the ${}^3\Sigma_0^-$ and the ${}^3\Pi_0^+$ states with the ground ${}^1\Sigma$ state. The matrix element with the ${}^3\Sigma_0^-$ may be as large as 100 cm^{-1} while the matrix element with the ${}^3\Pi_0^+$ probably is of the order of 30 cm^{-1}. W. Lichten (private communication).

these corrections and will not be considered further. Of the second type there are terms involving X twice with $\mathbf{J}\cdot\mathbf{L}/A$, or $\mathbf{J}\cdot\mathbf{S}/A$. For the case of $\mathbf{J}\cdot\mathbf{L}/A$, the second sum in Eq. (22) is zero. Consider a typical term in the numerator of the first sum involving $\mathbf{J}\cdot\mathbf{L}/A$:

$$\mathbf{J}\cdot\langle 0|X|{}^3\Lambda\rangle\langle{}^3\Lambda|\mathbf{L}/A|{}^3\Lambda'\rangle\langle{}^3\Lambda'|X|0\rangle,$$

where ${}^3\Lambda$ and ${}^3\Lambda'$ denote triplet electronic states. The operator X cannot induce any angular momentum about the internuclear axis (the z axis). Therefore, X can connect ${}^1\Sigma$ states only with triplet states having zero angular momentum about the z axis (${}^3\Lambda_0$ states). The operators L_x and L_y change the projection of the orbital angular momentum, and therefore also that of the total electronic angular momentum along the z axis by one unit. Since the electronic states are diagonal in this projection of the total electronic angular momentum (Ω),

$$\langle{}^3\Lambda|L_x|{}^3\Lambda'\rangle=\langle{}^3\Lambda|L_y|{}^3\Lambda'\rangle=0.$$

The matrix element $\langle{}^3\Lambda|\mathbf{L}|{}^3\Lambda'\rangle$ is not necessarily zero, but since X did not induce angular momentum along the internuclear axis, J_z is zero and $J_z\langle{}^3\Lambda|L_z|{}^3\Lambda'\rangle=0$. Terms of this type are, therefore, zero. A similar argument shows that terms containing $\mathbf{J}\cdot\mathbf{S}/A$ and X twice are also zero. This was expected since otherwise there would be an energy term which changed its sign for a change in the direction of rotation of the molecule. In the case of terms containing X twice and $J^2/2A$, neither sum in Eq. (27) is expected to be zero. These terms correspond to a change in the internuclear distance (and a change in B_e proportional to $1/\mu$) due to the admixture of other electronic states into the ground ${}^1\Sigma$ state by the operator X. The empirical determination of B_e includes this effect. Terms of higher order than third should be negligibly small regardless of which operators they contain.

DISCUSSION OF HYDROGEN IODIDE

The authors have previously discussed[38] the tritium-deuterium mass ratio as derived from measurements on tritium iodide[38] and deuterium iodide.[39,40] However, at that time magnetic moment measurements could not be made and the correction for the nonspherical distribution of electrons was estimated by assuming the pure precession hypothesis. It now appears that the consequent discrepancy was caused by the pure precession hypothesis giving far too large an estimate for the magnetic moment in this case.

The magnetic moment of tritium iodide in the $J=1$, $v=0$ state was experimentally determined to be less than 0.05 nm during the course of the work on CO. Therefore the moment of inertia of the molecule is not very different from that of the idealized molecule with a spherical distribution of electrons. Since this is the case and since the moment could not be exactly determined experimentally, in order to calculate the deuterium-hydrogen mass ratio it was decided to make an empirical correction (inversely proportional to the reduced mass squared) such that agreement is obtained between the tritium-hydrogen mass ratio from the microwave measurements and that from nuclear reaction data.[41] The recent microwave measurements on hydrogen iodide[23] were used. This empirical correction (amounting to 0.000161 in the tritium-hydrogen mass ratio) takes care of the nonspherical distribution, the wobble stretching, and also tends to correct for any possible inaccuracies in the infrared constants used. In fact, any error in α is overcorrected by five percent. The microwave value of the deuterium-hydrogen mass ratio is then calculated to be 1.998 468±0.000 009 (including the correction of 0.000 081) and can be compared with the nuclear reaction value of 1.998 463±0.000 002. The error in the microwave value is primarily caused by the rather large errors in both the microwave frequency measurements and in the infrared value of α. Both these measurements could be improved in accuracy.

The values of the rotational frequencies of the various isotopic species used in the above calculation were 385 293.27±0.70; 195 068.15±0.30 and 131 501.50 ±0.40 Mc/sec, respectively. The infrared constants[42] used were $\alpha_{\mathrm{HI}}=0.1698\pm0.0013$ cm^{-1}, $\gamma_{\mathrm{HI}}=-0.00068$ cm^{-1}, and $D_{\mathrm{HI}}=2.03\times10^{-4}$ cm^{-1}.

DISCUSSION

Before the B_e values were used to compute the isotopic mass ratios, three corrections were applied. These were a correction for the nonspherical distribution of electrons, a correction for wobble stretching, and the corrections given by Dunham.

The first and largest correction was the contribution of the nonspherical distribution of electrons to the moment of inertia of the molecule, and was about one hundred times greater than the error contributed by the frequency measurements. This correction corresponds to the moment of inertia of about three electron masses at a distance of one angstrom. To evaluate this correction, the molecular magnetic moment was measured with sufficient accuracy that no significant error in the isotopic mass ratios resulted from this effect. This is the first case in which this correction has been evaluated with high accuracy from Zeeman measurements and applied in the determination of isotopic mass ratios.

The second correction and a basic limitation on the accuracy of the microwave method of nuclear mass determination is the effect described above as "wobble

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stretching." It depends on the square of the electronic orbital angular momentum, L^2, whose average value cannot be evaluated accurately. The correction required in the isotopic mass ratios resulting from the wobble stretching is about ten times the error contributed by the frequency measurements. In the present work the wobble stretching has been evaluated by use of the nuclear reaction value for the $C^{14}-C^{12}$ mass ratio. This limits the accuracy of the microwave determination of the $C^{13}-C^{12}$ and $O^{18}-O^{16}$ mass ratios to about that of the nuclear reaction determination of the $C^{14}-C^{12}$ ratio.

The third type of correction, that given by Dunham, is about the same size as the error due to the frequency measurement. The Dunham correction is, therefore, considerably smaller than the correction for wobble stretching. In the empirical correction for wobble stretching, corrections for any small effects which do not vary extremely rapidly with reduced mass are automatically included. Since the Dunham correction is proportional to $1/\mu^2$ as is the wobble stretching, it is unnecessary to include the Dunham correction explicitly. The close agreement of the two determinations of both the $C^{13}-C^{12}$ and the $O^{18}-O^{16}$ mass ratios indicate experimentally that there are no unknown effects of significant size which vary very rapidly with reduced mass.

Actually, the corrections to the various molecular constants given by Dunham are also smaller than errors to be expected in these same constants because of the excitation of higher electronic states by the vibration of the molecule. Dunham, in assuming an electronic potential fixed in space for the molecule, did not fully take into account such effects. This is perhaps illustrated by the difference in the value of the centrifugal stretching constant predicted by the Dunham treatment with the experimental value as discussed above.

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APPENDIX I

In order to derive Eq. (20), one of the A's in the matrix element in Eq. (17) was removed from the matrix element and then the sums in Eq. (17) and Eq. (19) were equated. This introduced an error, ϵ, in Eq. (22), where

$$\epsilon=\hbar^2\left[\sum_{n\neq 0}\frac{|\langle 0|L_x/A|n\rangle|^2}{W_0-W_n}-\frac{1}{A}\sum_{n\neq 0}\frac{\langle 0|L_x/A|n\rangle\langle n|L_x|0\rangle}{W_0-W_n}\right]. \tag{23}$$

If, in both of the summations of Eq. (23), an "average electronic energy" W is factored out, ϵ may be written

$$\epsilon=\frac{\hbar^2}{W}\left[\sum_{n\neq 0}|\langle 0|L_x/A|n\rangle|^2-\frac{1}{A}\sum_{n\neq 0}\langle 0|L_x/A|n\rangle\langle n|L_x|0\rangle\right]. \tag{24}$$

The assumption made was that the average denominator in both sums is the same. Since the molecule is actually quite rigid, the change in each matrix element in the sum caused by factoring out $1/A$ should be small and to a first order proportional to the size of the matrix element, thus leaving the average denominator unchanged. The sum rule for matrix products is now applied and it yields (noting that matrix elements involving $n=0$ are zero)

$$\epsilon=\frac{\hbar^2}{W}\left[\langle 0|(L_x/A)^2|0\rangle-\frac{1}{A}\langle 0|L_x^2/A|0\rangle\right]. \tag{25}$$

If the sum rule is again applied to the first matrix element in Eq. (25), it yields

$$\epsilon=\frac{\hbar^2}{W}\left[\sum_n\langle 0|1/A|n\rangle\langle n|L_x^2/A|0\rangle-\frac{1}{A}\langle 0|L_x^2/A|0\rangle\right]. \tag{26}$$

The $n=0$ term in the above sum is now written separately, and it is noted that $\langle 0|1/A|0\rangle=1/A$. The n in Eq. (26), of course, designates all of the excited states in the molecule, including the vibrational states of the ground electronic state. Since $L_x^2=1/2L^2$,

$$\epsilon=\frac{\hbar^2}{2W}\sum_{n\neq 0}\langle 0|1/A|n\rangle\langle n|L^2/A|0\rangle. \tag{27}$$

It is seen that Eq. (27) is quite similar to the expression for the change in rotational energy due to wobble stretching, $W_3^{(2)}$. However, since the major contribution to $W_3^{(2)}$ comes from the vibrational states in the ground electronic state and in Eq. (26) W is an electronic energy, then ϵ should be about 6% of $W_3^{(2)}$. Therefore ϵ was automatically included as a small contribution in the empirical correction for wobble stretching.