The Spin and Quadrupole Moment of O^{17}*

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Measurements of the quadrupole splitting caused by the O^{17} nuclear spin in the $J=1\rightarrow 2$ transition of the $O^{17}C^{12}S^{32}$ pure rotational spectrum show that the spin of O^{17} is 5/2 and its quadrupole coupling constant is -1.32 ± 0.07 mc. From this coupling constant, the quadrupole moment of the O^{17} nucleus can be estimated as $Q=-5\times 10^{-27}$ cm^2. O^{17} appears to fit the extreme single particle model of the nucleus exceptionally well.

I. INTRODUCTION

THE energy of interaction of a nuclear electric quadrupole moment with the gradient of the electric field of the molecule in which it is situated varies with the orientation of the nucleus in the molecule. For a nucleus with spin I and a molecule in a rotational state J, the rotational energy level will be split into $2J+1$ levels for $I>J$ and $2I+1$ levels for $I<J$, corresponding to the quantum-mechanically allowed orientations of the nucleus in the molecule. This splitting of the rotational levels gives rise to a hyperfine splitting in the pure rotational absorption spectrum, whose magnitude is proportional to the product of the nuclear quadrupole moment and the electric field gradient. However, the relative separations and intensities of the hyperfine structure components, for a given rotational transition, depend solely on the nuclear spin I. Hence, by observing the quadrupole hyperfine structure one can uniquely determine the nuclear spin.

Two earlier groups of investigators[1,2] observed the $J=1\rightarrow 2$ rotational transition of the molecule $O^{17}CS$ and reported no detectable hyperfine structure. This failure to find hyperfine structure might be taken as an indication that the O^{17} spin is 1/2, since then the quadrupole moment is necessarily zero. However, as Low and Townes[1] pointed out, even with a larger spin, the O^{17} nucleus might be expected to have such a small quadrupole moment that hyperfine structure would not be observed with the conventional Stark-modulation spectrometers which were used. Recently Alder and Yu,[3] using nuclear induction techniques, have obtained a value of 5/2 for the spin of O^{17} from intensity measurements. We have succeeded in resolving the quadrupole hyperfine structure caused by O^{17} in the $J=1\rightarrow 2$ transition of $O^{17}C^{12}S^{32}$ with a high resolution microwave spectrometer. The results described below allow an estimation of the O^{17} quadrupole moment and confirm the spin value of 5/2.

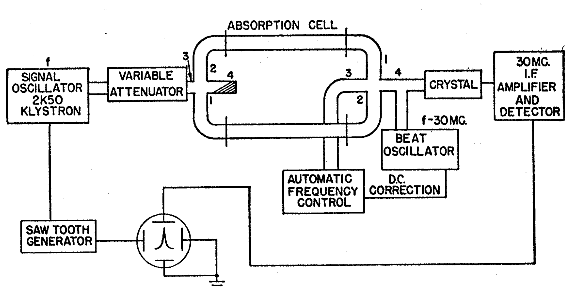

FIG. 1. Simplified block diagram of high resolution microwave spectrograph.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The main components of the hyperfine structure of the $J=1\rightarrow 2$ transition of $O^{17}CS$ are confined to a frequency range of about 0.3 megacycle/sec. The high resolution needed to view this structure was afforded by a balanced microwave bridge spectrometer with superheterodyne detection illustrated in Fig. 1. (Details of this apparatus will appear in a forthcoming paper on mass determinations by microwave spectroscopy. This paper will also contain an O^{17} mass determination.) The $O^{17}C^{12}S^{32}$ was made from oxygen kindly supplied by Professor A. O. Nier which was enriched in O^{17} to slightly more than 1 percent. The 5-meter K-band absorption cell was cooled to $-78°$C to enhance the line intensities threefold above their intensities at room temperature.

Figure 2 shows the spectral pattern observed together with the theoretical patterns calculated for different values of spin. In computing the theoretical patterns a Lorentz line shape was assumed with a line width of 70 kc. In each case the value of the quadrupole coupling constant eqQ was taken to fit the experimentally measured intervals as well as possible. Though the resolution was not sufficiently great to permit the splitting of all the lines, yet it is clear from Fig. 2 that the spin of 5/2 best fits the experimental pattern and measured intervals. The weaker lines in the pattern were only a few times noise. It was not possible to completely eliminate reflections in the absorption cell and comparison arms of the bridge. As those reflections imparted a steep slope to the base line on which the pattern was viewed, the weak $F=5/2\rightarrow 3/2$ line on the extreme right of the pattern could not be observed.

In Table I are listed the experimental and theoretical

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[1] W. Low and C. H. Townes, Phys. Rev. **75**, 529 (1949).
[2] Bianco, Matlack, and Roberts, Phys. Rev. **76**, 473 (1949).
[3] F. Alder and F. C. Yu, Phys. Rev. **81**, 1067 (1951).

line frequencies and intensities assuming $I=5/2$ and assuming a coupling constant $eqQ=-1.32$ Mc. Frequencies were measured by the usual method of comparison with the harmonics of a quartz crystal oscillator monitored with WWV. The intervals between the lines which stood out most clearly (numbered 2, 3, 4) were most accurately measured. They were thus more heavily weighted in obtaining the value of eqQ. It is believed that any systematic errors present are less than the quoted statistical errors. The experimental intensities given are those compared with the strongest observed line (numbered 4) and were obtained viewing the spectrum on a 5-inch oscillograph.

III. PREPARATION OF OCS

The sample of $O^{17}CS$ was prepared from 10 ml (STP) of oxygen enriched in O^{17} to 1.35 percent. The oxygen was introduced into a Pyrex vessel which contained a stainless steel bar coated with carbon as lampblack. The bar, supported by quartz rods was heated to about 950°C for 15 minutes by an industrial rf generator. The CO thus produced was removed from the vessel to a small Pyrex tube containing sulfur. The tube was heated to 500°C to produce OCS.

IV. QUADRUPOLE MOMENT OF O^{17}

To determine the quadrupole moment, Q, from the quadrupole coupling constant $-eqQ$, an estimate of $q=\partial^2V/\partial z^2$ along the molecular axis at the oxygen

TABLE I. Observed frequencies and intensities compared with theoretical values for a spin of 5/2 and a quadrupole coupling constant of -1.32 Mc.

Line number	Transition $J=1\rightarrow2$	Frequency (Mc) Observed	Frequency (Mc) Theoretical	Intensity relative to line 4 Observed	Intensity relative to line 4 Theoretical
1	$F=3/2\rightarrow5/2$	23,534.101±0.014	23,534.106	0.2_0	0.21
2	$7/2\rightarrow7/2$	23,534.164±0.012	23,534.159	0.2_2	0.26
	$7/2\rightarrow5/2$[a]	—	23,534.226	—	0.04
3	$3/2\rightarrow1/2$	23,534.308±0.012	23,534.295	0.2_1	0.28
4	$7/2\rightarrow9/2$, $5/2\rightarrow7/2$	23,534.422	23,534.422	1.0	1.00
5	$3/2\rightarrow3/2$, $5/2\rightarrow5/2$	23,534.481±0.014	23,534.489	0.5_6	0.53
	$5/2\rightarrow3/2$[a]	—	23,534.691	—	0.11

Intervals in kc	$1\rightarrow2$	$2\rightarrow3$	$3\rightarrow4$	$4\rightarrow5$
Experimental	63±9	144±6	114±12	59±14
Theoretical	53	136	127	67
$eqQ=-1.32$ Mc				

[a] Not observed.

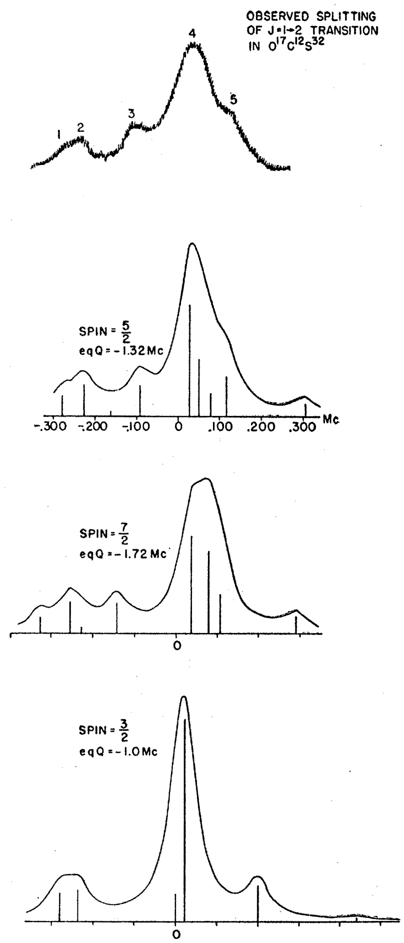

FIG. 2. Comparison of observed splitting of $J=1\rightarrow2$ transition in $O^{17}C^{12}S^{32}$ with theoretical patterns due to nuclear quadrupole.

nucleus was made, following the method outlined by Townes and Dailey.[4] $\partial^2V/\partial z^2$ was estimated for a p electron in the atomic ground state and was then multiplied by the fraction of unbalanced p electron along the molecular axis to allow for the modification caused by molecular binding.

For a single valence electron outside a closed atomic shell or for one electron less than a closed shell $\partial^2V/\partial z^2$ may be readily evaluated from the fine structure doublet separation $\Delta\nu$, i.e.,

$$\frac{\partial^2V}{\partial z^2}=-\frac{2le\Delta\nu}{[Z_iR\alpha^2a_0^3(l+\frac{1}{2})(2l+3)]},$$

where the symbols are explained in reference 4. For oxygen one can estimate, in the following way, an equivalent $\Delta\nu$ (which is proportional to $1/r^3$) to be substituted into the above expression for $\partial^2V/\partial z^2$. For triply ionized oxygen $\Delta\nu=386.5$ cm^{-1} and for quadruply ionized fluorine $\Delta\nu=746$ cm^{-1} or just 1.85 times the value of $\Delta\nu$ for neutral F. Thus an equivalent $\Delta\nu$ for oxygen may be taken as $386.5/[1+\frac{3}{4}(0.85)]$ cm^{-1},

[4] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

TABLE II. Fraction of unbalanced p-electron associated with each resonant structure, and their averages.

Resonating structure	Percentage importance	Fraction of unbalanced p-electron for pure p-bonds	Average	Fraction of unbalanced p-electron for 25% s-hybridization	Average
$O=C=S$	58	-0.5		-0.25	
$O^{-}-C\equiv S^{+}$	14	-0.8	-0.4	-0.60	-0.14
$O^{+}\equiv C-S^{-}$	28	0		$+0.31$	

giving a value for atomic oxygen of $eq=6.75\times10^{6}$ esu^2/cm^3.

From the bond distance determined by microwave spectroscopy,[5] using the method outlined by Pauling,[6] it may be deduced that the molecule resonates between the structures, $O=C=S$, $O^{-}-C\equiv S^{+}$ and $O^{+}\equiv C-S^{-}$ with percentage importances of 58, 14, and 28, respectively. The fraction of unbalanced p-electron associated with each resonant structure and their averages are listed on Table II for both pure p-bonds and for 25 percent s-hybridization of the p-bonds (see Table VIa of reference 4). The minus sign denotes a deficiency of p electrons.

Strong evidence exists for considerable s-p hybridization in compounds of the lighter elements, an average value of this hybridization being about 20 percent. Thus an average value, slightly weighted in favor of the hybridized structure, of the number of unbalanced p electrons was taken as $-0.24p$ electrons. Multiplying by eq for atomic oxygen one gets $eq=1.62\times10^{6}$ esu^2/cm^3, which combined with the experimentally determined coupling constant $eqQ=-1.32$ Mc gives $Q=-0.005\times10^{-24}$ cm^2. The nature of the approximations made in the estimate of q are such that we believe the value of Q to be correct within a factor of 2.

V. O^{17} AND NUCLEAR SHELL THEORY

It is of some interest to consider the spin and quadrupole moment of O^{17} in the light of the extreme "one particle model" recently proposed by Mayer[7] and Haxel, Jensen, and Suess.[8] In this model, it is assumed that each nucleon moves in an average nuclear potential which extends over the nuclear volume and which is intermediate between that of a square well and a three-dimensional isotropic oscillator well. If in addition strong spin-orbit coupling is assumed, the succession of energy levels so obtained gives rise to closed shells which correspond exactly to the "magic numbers." An even number of neutrons or protons pair off to give zero spin and moment, so that for odd A nuclei the spin, magnetic moment, and quadrupole moment are attributed to the odd nucleon. While this model is rather successful in predicting nuclear spins, most of the observed magnetic moments lie between the theoretical values or "Schmidt lines." The deviation of the magnetic moments from the Schmidt limits may be taken as a measure of the departure of nuclei from the extreme single particle picture. However, it is expected that a nucleus with one particle more or less than a closed shell should be well represented by this model. O^{17}, containing a closed shell of 8 protons, and one neutron more than the closed shell of 8 neutrons, provides a very fine test of the theory and indeed the following empirical results seem to indicate that it is a very good "single particle nucleus."

(1) The spin value of 5/2 is in agreement with the theory which assigns a $d_{5/2}$ orbit to the ninth neutron or proton in the potential well.

(2) The quadrupole moment is very small as would be expected if the positive charge is confined to a spherical core. If one assumes that the odd neutron, moving in a $d_{5/2}$ orbit at a radius approximately equal to the core radius, and the spherically symmetric core rotate about their common center of gravity, the quadrupole moment to be expected from the motion of the core is $Q\sim-0.002\times10^{-24}$ cm^2. This is not much smaller than the observed value, indicating very little distortion of the core.

(3) Its magnetic moment is 1.8928 nm.[3] The Schmidt limit value is -1.91 nm corresponding to the magnetic moment of the odd neutron. Since the core shares some of the angular momentum of the odd particle, a correction of $+0.06$ nm must be made for this giving the theoretical value of -1.85 in good agreement with the observed value.

Fluorine 19, another possible example of this type of one-particle model, with 9 protons and 10 neutrons, should have its 9th proton in a $d_{5/2}$ level, yet, the spin of F^{19} is definitely 1/2. The $1d_{5/2}$ and $2s_{1/2}$ levels are evidently very close to each other and the two neutrons beyond the closed shell of eight are sufficient to cause an inversion of the order of these levels as compared to O^{17}.

VI. SPHEROIDAL NUCLEAR MODEL

As the odd particle in O^{17} is a neutron, the observed quadrupole moment must be due solely to the core. O^{17} thus furnishes a simple example for comparison with the quadrupole moment calculated according to the spheroidal nuclear model recently proposed by Rainwater.[9] Using Feenberg's[10] expression, obtained from first-order perturbation theory, for the shift in the energy of the odd particle outside the core and taking a well of depth 37 Mev[11] and radius $R=1.46\times10^{-13}A^{\frac{1}{3}}$ cm, we find a predicted quadrupole moment for O^{17} of $Q=-2.2\times10^{-25}$ cm^2. Bohr[12] has pointed out that if the nucleus is a spheroid with a component of angular

[5] C. H. Townes, Phys. Rev. **74**, 1113 (1948).
[6] L. Pauling, *Chemical Bond* (Cornell University Press, Ithaca, New York, 1945), p. 197.
[7] M. Mayer, Phys. Rev. **78**, 16 (1950).
[8] Haxel, Jensen, and Suess, Phys. Rev. **75**, 1766 (1949).
[9] J. Rainwater, Phys. Rev. **79**, 432 (1950).
[10] E. Feenberg, Phys. Rev. **81**, 285 (1951).
[11] The well depth was adjusted to bind the odd neutron with approximately 3.8 Mev, its binding energy according to the $O^{17}-O^{16}$ mass difference.
[12] A. Bohr, Phys. Rev. **81**, 134 (1951).

momentum $m=l$ along its axis, it will precess about the total angular momentum I, so that the experimental quadrupole moment, Q, referred to an axis fixed in space for the substate $M=I$, will be smaller than the intrinsic quadrupole moment Q_0, defined with respect to the axis of the nucleus, by a factor $I(2I-1)/I+1)\times(2I+3)$. For a spin of 5/2 this reduces the above calculated value of Q by a factor 5/14 to -0.79×10^{-25} cm^2, still a factor of 16 larger than the experimentally determined value.

Evidently still further corrections must be applied to this type of calculation of the quadrupole moment. If allowance is made for the possibility of the odd nucleon moving in an orbit with radius somewhat greater than the radius of the core, the discrepancy might be further reduced. In addition the use of perturbation theory for such large distortions gives a larger distortion than an exact calculation would yield for the level $n=1$, $1=2$, $m_1=2$ as indicated by Granger and Spence.[13] With the above mentioned modifications, the quadrupole moment calculated for O^{17} from the spheroidal model may possibly become small enough to agree with the measured values.

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[13] S. Granger and R. D. Spence, Phys. Rev. 83, 460 (1951).