A. MOLECULAR-BEAM RESEARCH

Prof. J. R. Zacharias	V. Jaccarino
Prof. B. T. Feld	J. G. King
Dr. J. Levinson	C. Koster
J. T. Eisinger	W. B. Pohlman

Investigation of Quadrupole Interaction in Homonuclear Diatomic Molecules of Spin 3/2

The perturbation of the energy levels due to the quadrupole interaction operator of the form

$$H_{q} = -\frac{e^{2}Qq}{2J(2J-1)i_{1}(2i_{1}-1)} \frac{J}{2J+3} \left[3(i_{1} \cdot J)^{2} + \frac{3}{2}(i_{1} \cdot J) - i_{1}^{2}J^{2} \cdot 3(i_{2} \cdot J) + \frac{3}{2}(i_{2} \cdot J) - i_{2}^{2}J^{2} \right]$$

where J = rotational quantum number of molecule and $i_1 = i_2 = 3/2$ spin of identical nuclei

was investigated. It was found that a given J-level was split into a number of levels corresponding to different values of F, the total angular momentum quantum number of the molecule. In some cases there were two levels corresponding to a given J and F value. Due to the difference in symmetry properties of the unperturbed J-levels corresponding to odd and even values of J, different expressions for the energy levels arise in these two cases. The following results were obtained.

$$J = 0 ; \frac{\Delta E}{e^2 Q q} = 0$$

 $\mathbf{J} = \mathbf{1}$



 $J \ge 2$ (J even) $\frac{\Delta E}{e^2 \, Q \, q}$ $\frac{\Delta E}{e^2 Q q}$ \mathbf{F} (J large) J - 2 0 0 0 **J** - 1 0 $+\frac{1}{6}\sqrt{\frac{J(J+1)}{(2J-1)(2J+3)}}$ $\frac{1}{12}$ J J + 10 0 J + 2 0 0 $J \ge 3$ (J odd) $\frac{\Delta E}{e^2 Q q}$ \mathbf{F} $J - 3 - \frac{J + 1}{2(2J - 1)}$

$$J - 2 = -\frac{3}{2(2J - 1)} \qquad 0$$

$$J - 1 = -\frac{1}{6(2J + 3)(2J - 1)} \left[\frac{-15(2J^2 - J - 12) \pm \sqrt{(6J^2 - 75J - 216)^2 + 24(4J^2 - 9)(J^2 - 1)}}{10} \right] + \frac{1}{8} \pm \frac{\sqrt{33}}{120}$$

$$J = -\frac{1}{2(2J + 3)(2J - 1)} \left[6 \pm \frac{\sqrt{16(2J^2 + 2J - 9)^2 + (J - 1)(J + 2)(2J - 1)(2J + 3)}}{5} \right] \pm \frac{\sqrt{17}}{20}$$

$$J + 1 = \frac{1}{2(2J + 3)(2J - 1)} \left[\frac{-2J^2 - 5J + 9}{2} \pm \sqrt{\frac{(2J^2 + 29J - 45)^2 + \frac{8}{3}J(2J - 1)(2J + 5)(J + 2)}{10}} \right] - \frac{1}{8} \pm \frac{\sqrt{11}}{360}$$

$$J + 2 = \frac{3}{2(2J + 3)} \qquad 0$$

$$J + 3 = -\frac{J}{2(2J + 3)} - \frac{1}{4}$$

C. Koster

 $\frac{\Delta E}{e^2 Q q} (J \text{ large})$

 $-\frac{1}{4}$

References

- 1. For the form of quadrupole operator in a symmetric top type molecule, J. M. Jauch: Phys. Rev. 72, 715 (1947).
- 2. For matrix elements necessary in calculation, H. M. Foley: Phys. Rev. 71, 747 (1947).

B. NUCLEAR MAGNETIC RESONANCE

Prof. F. Bitter	J. Brossel
Dr. W. C. Dickinson	P. Sagalyn
N. I. Adams III	T. Wimett

1. The Double Resonance Method for the Investigation of Atomic and Nuclear Moments

Work on the optical detection of r-f resonance has been continued, and it has been decided to adopt the name above for the method, since the essential feature is the simultaneous application of two resonant frequencies which have a common energy level.



Fig. V-1 Resonance curve for angular momentum quantum member unity. Experimentally the work has been confined to increasing the sensitivity of the apparatus, and to the construction of equipment for accurate field measurements. A detailed theoretical analysis of effects to be expected in mercury has been completed, and a report is being prepared. An unexpected result is the complex structure of the resonance lines predicted by the Rabi-Majorana (1) formula for angular momenta greater than one-half. For example, the average probability of finding a particle having a resultant angular momentum quantum number unity, and known to be at some time in

a state with m = 0, in a state m = \pm 1 at some much later time, is shown in Fig. V-1. The transitions are produced by an r-f rotating field of angular frequency ω and amplitude H₁ perpendicular to a constant field H₂. The parameter

$$\delta = \frac{\omega - \gamma H_z}{\gamma H_1}$$

measures the approach to the resonance condition $\omega = \gamma H_{z}$, where γ is the gyromagnetic ratio.

Experimental verification of predicted results is being undertaken.

F. Bitter, J. Brossel, P. Sagalyn

Reference

1. I. I. Rabi: Phys. Rev. 51, 652 (1937).



Fig. V-2 Two views of the new barrel-type electromagnet.



Fig. V-3 Cross section of the electromagnet.

2. A New Barrel-Type Electromagnet

A magnet designed jointly by one of us and Everett Reed of Arthur D. Little Inc. has been completed and installed. Two photographs of the instrument are shown in Fig. V-2, and a cross-section is shown in Fig. V-3. Preliminary tests have yielded the results summarized in Fig. V-4. The maximum temperature of the copper for full power



Fig. V-4 Field in kilogauss using 11-inch diameter pure iron pole pieces.

(20 kw) was about 70°C, or 160°F. Field measurements were made with a new type of gaussmeter constructed at our suggestion by the Rawson Instrument Company, and now commercially available. The gaussmeter consists of a coil rotated at constant frequency in the unknown field. The induced current is rectified and measured on a meter calibrated to read directly in gauss on scales of 0-500; 5,000; or 50,000. Preliminary data on the uniformity of the field produced by 11-inch diameter pure iron pole-pieces may be summarized by stating that for gaps up to almost one-half of the pole diameter, the field was uniform to better than 1 percent in a centrally located volume with a diameter about one-half that of the poles themselves. At points about three-fourths of the way out from the middle, the field in general differs by less than 5 percent from its maximum value. At small separations and low inductions the uniformity is considerably better than is indicated above.

A complete report is being prepared.

F. Bitter, N. I. Adams

3. Factors Influencing the Positions of Nuclear Magnetic Resonances

A doctoral thesis entitled "A Study of the Time Average Magnetic Field at the Nucleus in Nuclear Magnetic Resonance Experiments" has been written and submitted to the physics department. W. C. Dickinson

4. Deuteron-Proton Moment Ratio

Our major effort has been directed toward adjusting the Helmholtz coils for maximum field homogeneity and obtaining reproducible narrow proton resonance lines. Line widths of less than a hundredth of a gauss have been obtained (see Fig. V-5), and the remaining





Fig. V-5 (top) Very sharp nuclear magnetic resonance absorption line obtained in a circuit without modulation. (bottom) Dispersion line obtained under similar conditions.

line broadening due to the field might be reduced by a factor of five or more if a more sensitive probe arrangement were used for measuring field variations. Experience indicates that adequate adjustments may very probably be made with the position screws and relative current control on the two field coils to produce a field uniform to one part in a million over a volume of about a cubic centimeter.

The main difficulty encountered in homogenizing the field has been in displaying and examining the field variations while making the adjustments. The method used has been to observe on an oscilloscope the proton nuclear resonance from a small oil sample in a probe which is moved about in the sinusoidally modulated field. The precision of this scheme is limited by the broadness of the "wiggles" which are observed and also by field fluctuations with time.

The problem of field instability resulting from rapid temperature fluctuations (as high as 0.1°C in five minutes) in the cooling system for the coils has been solved by passing tap water through a 150-gallon mixing tank before running it through the cooling system. Still remaining is a slow drift of the order of a quarter of a degree per hour. The resulting field drift (one gauss per hour) is sufficient to make it impossible to maintain the field at a resonance position long enough to make adjustments of the order of one part

in a million.

In order to eliminate the possibility of line broadening due to both the amplitude and frequency of the field modulation which is generally used in nuclear resonance experiments, a circuit has been developed which requires no modulation and makes possible the direct observation of a resonance line. The circuit consists of a bridged-T null network (mentioned in the Quarterly Progress Report, April 15, 1950) containing the sample coil and followed by an r-f amplifier, a rectifier and balanced d-c amplifier which drives a recording milliammeter directly. Stability of the unbalanced voltage from the null circuit is very important in obtaining accurate line shapes, a requirement adequately fulfilled by the null-T circuit. Examples of resonance lines obtained with this recording arrangement are shown in Fig. V-5. The resonances were obtained from protons in an oil sample about 4 mm in diameter and length at a thousand gauss.

T. F. Wimett

C. MICROWAVE SPECTROSCOPY

Prof. M. W. P. Strandberg	Dr. R. B. Lawrance	H. R. Johnson
Dr. R. E. Hillger	J. R. Eshbach	C. C. Loomis
Dr. G. W. King	B. V. Gokhale	M. T. Weiss
	J. G. Ingersoll	

1. Hydrogen Deuterium Sulphide

The resonant molecular absorption between rotational energy levels was measured for hydrogen deuterium sulphide (HDS) in the microwave region. Twelve lines were observed in the frequency range 7000 Mc/sec to 76,000 Mc/sec for HDS³², five lines were observed for HDS³⁴, and one line for HDS³³. Stark-effect measurements on several of these lines yield the permanent electric dipole moment of HDS³² to be 1.02 ± 0.01 debye units. The calculated absorption coefficient is given for each line. The data is summarized in the tables on p. 41.

A simple theory, correct to the first order, was developed to correct for the centrifugal distortion of a molecule. Using the matrix elements derived by H. H. Nielsen (1) for the general polyatomic molecule, the true absorption frequency is obtained in terms of a rigid rotor frequency and five centrifugal distortion constants. The theory was evolved for immediate application to the asymmetric HDS molecule, but the formulation is perfectly general and can be used for other types of molecules. The value of this theory lies in the fact that these same distortion constants can be calculated with a knowledge of the vibrational spectra and structure of the molecule which allows one either to correct doubtful assignments in infrared and Raman spectra or to predict with greater accuracy the existence of new rotational absorption lines. The experimental values of the centrifugal distortion constants were determined for HDS³² by a least-squares fitting

Initial State	Final State	Frequency (Mc/sec)	Absorption (T = 195°K)(cm ⁻¹)
1 _{1,1}	¹ 1,0	51,073.27	2.9×10^{-4}
² 2,1	² 2,0	11,283.83	2.3×10^{-5}
³ 2,2	³ 2,1	53,200.93	3.0×10^{-4}
⁴ 3,2	⁴ 3,1	10,861.07	1.3×10^{-5}
⁵ 3,3	⁵ 3,2	40,929.20	1.1×10^{-5}
6 _{4,3}	⁶ 4,2	7,936.74	3.2×10^{-6}
7 _{4,4}	7 _{4,3}	27, 566. 31	2.1×10^{-5}
⁸ 4,5	⁸ 4,4	75, 551.73	7.6×10^{-5}
⁹ 5,5	⁹ 5,4	17,212.61	2.2×10^{-6}
¹⁰ 5,6	¹⁰ 5,5	47,905.36	8.0×10^{-6}
¹¹ 6,6	¹¹ 6,5	10,235.81	1.5×10^{-7}
¹² 6,7	¹² 6,6	28,842.84	4.8×10^{-7}

Rotational Absorption Frequencies of HDS³² in the Microwave Region

Absorption Frequencies of HDS^{34} and HDS^{33}

Compound	Transition	Frequency (Mc/sec)	Absorption (T = 195°K)(cm ⁻¹)
HDS^{34}	¹ 1,1 ^{→ 1} 1,0	50,912.27	1.3×10^{-5}
HDS^{34}	$2_{2,1} \rightarrow 2_{2,0}$	11,235.45	1.0×10^{-6}
HDS^{34}	${}^{3}2, 2 \xrightarrow{\rightarrow} {}^{3}2, 1$	52,979.67	1.4×10^{-5}
HDS^{34}	4 _{3,2} → 4 _{3,1}	10,802.36	5.9×10^{-7}
HDS^{34}	⁷ 4,4 [→] ⁷ 4,3	27,392.00	1.1×10^{-6}
HDS ³³	$2_{2,1} \rightarrow 2_{2,0}$	11,258.21	9.1 $\times 10^{-8}$

The HDS^{33} line is the most intense of a group of lines.

Distortion Coefficient	Calculated Value (cm ⁻¹)	Experimental Value (cm ⁻¹)
R ₅	$+2.21 \times 10^{-4}$	$+ 8.02 \times 10^{-5}$
6 _J	-2.69×10^{-5}	-2.531×10^{-5}
$^{\mathrm{D}}\mathrm{_{JK}}$	+ 9.16 \times 10 ⁻⁴	+ 9.133 × 10 ⁻⁴
D _K	-1.64×10^{-4}	-1.403×10^{-4}
R ₆	-1.90×10^{-5}	- 1.067 × 10 ⁻⁵

process and are compared with the calculated values from vibrational data.

The inertia defect Δ , which exists for all planar molecules, was computed from vibrational data and used with the data obtained from the rotational absorption spectrum to obtain the effective moments of inertia of HDS³². The known microwave spectrum does not provide sufficient information to make this calculation directly. The resulting values are

$$\Delta = -0.244 \times 10^{-40} \text{ gm/cm}^2$$

$$I_a = 9.682 \text{ cm}^{-1} \equiv 2.890 \times 10^{-40} \text{ gm/cm}^2$$

$$I_b = 4.844 \text{ cm}^{-1} \equiv 5.777 \times 10^{-40} \text{ gm/cm}^2$$

$$I_c = 3.140 \text{ cm}^{-1} \equiv 8.910 \times 10^{-40} \text{ gm/cm}^2$$

The equilibrium values of the moments of inertia were not determined because of lack of knowledge of the anharmonic force constants of the molecule.

Reference 1. H. H. Nielsen: Phys. Rev. 60, 794 (1941).

2. Nuclear Magnetic Moment of S^{33}

The nuclear magnetic moment of S^{33} has been measured by means of the Zeeman effect on the molecule carbonyl sulphide (OCS). The observed line intensity of the largest line of the hyperfine pattern (the coincident $F = 5/2 \rightarrow 7/2$ and $3/2 \rightarrow 5/2$ line and nearby $1/2 \rightarrow 1/2$ line) of the rotational absorption J = 1 to J = 2 is shown in Fig. V-6 plotted as a function of the magnetic field. Theoretical curves are also shown for several values of the parameter $g_N - g_{mol}$. From this plot we obtain $|g_N - g_{mol}| = 0.57 \pm 0.04$ nuclear units. g_{mol} is given by Jen (1) and by Coles (2) and from their measurements is found to be about |0.03| with the sign undetermined. Since the sign of $g_N - g_{mol}$ is undetermined in our experiment, the correction for g_{mol} cannot be applied at this time. The



Fig. V-6 Relative peak intensity vs. magnetic field for the coincident $F = 3/2 \rightarrow 5/2$, $F = 5/2 \rightarrow 7/2$ transitions of the J = 1 $\rightarrow 2$ absorption of OCS³³ (including contributions from the nearby $F = 1/2 \rightarrow 1/2$ transition).

spin of S^{33} is known to be I = 3/2 (ref. 3) and the nuclear magnetic moment is given by $\mu_N = g_N I$. Thus we find for S^{33} that $\mu_N = 0.85 \pm 0.10$ nuclear magnetons, where part of the inaccuracy is due to the undetermined signs. A similar measurement with which we are in agreement has been made by Jen (1).

J. R. Eshbach, R. E. Hillger

References

- 1. C. K. Jen: Harvard Univ., Cruft Lab. Progress Report No. 14, p. 41 (Jan. 1, 1950).
- 2. D. K. Coles: Advances in Electronics 23, 313 (1950).
- 3. C. H. Townes, S. Geschwind: Phys. Rev. 74, 626 (1948).

3. Stibine

The search for the $J = 0 \Rightarrow 1$ transition in the molecule SbD_3 has been completed. The process of this search was interrupted to find transitions in the impurity molecules, phosphine and arsine. With the finding of these transitions the spectroscope could be used to purify the sample positively and thus to ensure that the search was conducted with stibine in the absorption cell. The following dipole moments have been measured for these three molecules.

Molecule	Dipole Moment (debye units)
phosphine	0.55 ± 0.01
arsine	0.22 ± 0.02
stibine	0.116 ± 0.003

A report on the quadrupole coupling in these molecules, and their structure, is in progress.

4. Ketene

Twelve lines in the microwave spectrum of ketene, $H_2^1 C_2^{12} O^{16}$, have been observed and identified, and the frequencies of these lines have been measured to six figures.

Nine of the lines are J = 0+1, 1+2, and 2+3 rotational transitions for the molecule in the ground vibrational state (Table I). The corresponding undistorted reciprocal moments are a = 280,000 Mc/sec (assumed the same as that for formaldehyde, $H_2^1C^{12}O^{16}$); b = 10,293.28 Mc/sec; and c = 9,915.87 Mc/sec (from measured lines, corrected for centrifugal distortion). Symmetric top centrifugal distortion theory, carried to first order, gives a good fit to the observed lines, except the 0+1 line, with D_J = 0.0015 Mc/sec, and D_{JK} = 0.478 Mc/sec. (There is a 0.63-Mc discrepancy between measured and calculated values of the 0+1 line frequency.) Stark-effect measurement gives for the dipole moment in the ground vibrational state, for the 0+1 transition, the value 1.35 \pm 0.05 debye units. This is thought to be in reasonable agreement with previous studies using the temperature dependence of the susceptibility, which yield 1.45 debye units (1).

Three of the observed lines are 0+1 transitions with the molecule in an excited vibrational state (Table II). Relative intensity measurements on these lines at room temperature give the associated vibrational frequencies as 420, 460, and 570 cm⁻¹, within about 20 cm^{-1} . Start-effect measurement gives for the dipole moments of these states 1.31, 1.31, and 1.37 debye units respectively, and line frequencies give for (b + c), extrapolated to zero centrifugal distortion, the values 20,267.18 Mc/sec, 20,220.65 Mc/sec, and 20,232.34 Mc/sec respectively. There is some correlation with infrared absorption measurements on the same molecule, but more microwave line-intensity measurement, including temperature dependence studies, is definitely indicated.

Predictions of approximate frequencies to be expected for heavy ketene $(D_2^2 C_2^{12} O^{16})$ have been made; measurement of the 0+1 and 1+2 transitions of this isotopic molecule will enable the average structure in the ground vibrational state to be completely determined. (Two values of b and two values of c enable calculation of three bond distances and one angle.) Measurement of the vibration satellites on the 1+2 transition of ordinary ketene will yield the average reciprocal moments for the excited vibrational states, and measurement of these satellites for heavy ketene will enable calculation of the complete average structure in each of the accessible vibrational states. Intensity calculations

Table I

Lines in the Ground Vibrational State

Transition	Calculated Intensity cm ⁻¹	Measured Frequency Mc/sec [*]	Calculated Frequency Mc/sec	Literal Frequency
$0_{00} \rightarrow 1_{01}$	3.14×10^{-6}	20,209.76	20,209.13	(b + c) - 4D _J
$l_{01} \rightarrow 2_{02}$	25.1 $\times 10^{-6}$	40,417.90	40,417.84	$2(b + c) - 0.75(b - c) \delta - 32 D_{J}$
$1_{11} \rightarrow 2_{12}$	52.9 $\times 10^{-6}$	40,038.80	40,038.91	$2(b + c) - (b - c) - 4D_{JK} - 32D_J$
$1_{10} \rightarrow 2_{11}$	55.0 $\times 10^{-6}$	40,793.62	40,793.73	2(b + c) + (b - c) - 4D _{JK} - 32D _J
$2_{02} \rightarrow 3_{03}$	84.7 $\times 10^{-6}$	60,625.68	60,625.70	$3(b + c) - 3(b - c) \delta - 108 D_J$
$2_{12} \rightarrow 3_{13}$	212.0×10^{-6}	60,057.92	60,058.03	$3(b + c) - 1.5(b - c) - 0.469(b - c) \delta - 6D_{JK} - 108D_{J}$
$2_{11} \rightarrow 3_{12}$	220.0 ×10 ⁻⁶	61,190.24	61,190.27	$3(b + c) + 1.5(b - c) - 0.469(b - c)\delta - 6D_{JK} - 108D_{J}$
$2_{21} \rightarrow 3_{22}$	39.3 $\times 10^{-6}$	60,615.88	60,615.78	$3(b + c) - 24D_{JK} - 108D_{J}$
$2_{20} \rightarrow 3_{21}$	39.3 $\times 10^{-6}$	60,617.30	60,617.34	$3(b + c) + 3(b - c) \delta - 24 D_{JK} - 108 D_{J}$

*Experimental errors are ± 0.05 Mc/sec at 20,000 Mc/sec, ± 0.10 Mc/sec at 40,000 Mc/sec, and ± 0.15 Mc/sec at 60,000 Mc/sec.

Table II

The Vibrational Satellites on the $0_{00} \neq 1_{01}$ Transition

Measured Frequency Mc/sec	Measured Relative Intensity	Measured Dipole Moment (Debye units)	Calculated Vibration Line Frequency (cm ⁻¹)
20,209.76	1.00	1.35	ground state
20, 267. 17	0.41	1.31	420 ± 20
20,220.64	0.30	1.31	460 <u>+</u> 20
20,232.33	0.18	1.37	570 <u>+</u> 20

indicate that these lines will be detectable in present systems. Measurements of the $\Delta J = 0$, $\Delta K = 0$ lines, of which a large number occur in the microwave region, will give a measured value for a. These latter measurements, plus measurements of the 3-4 and higher lines with $\Delta J = 1$, will yield data from which a more complete analysis of the centrifugal distortion could be made.

Intensity measurements quoted in this report were made by Dr. J. Goldstein at Harvard, who first found the lines of the 0+1 transition in Spring, 1949. Stark-effect measurements and frequency measurements of the 0+1 and 1+2 transitions were made by Prof. M. W. P. Strandberg.

Further investigation of the microwave spectrum of ketene is continuing.

H. R. Johnson

Reference

1. N. B. Hannay, C. P. Smyth: J. Am. Chem. Soc. 68, 1357.