

Microwave Spectra: The Hyperfine Structure of Ammonia*

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USING a 12-meter wave-guide cell, a sensitive detecting system, and a pressure of approximately 10^{-5} mm Hg, we have re-examined¹ $N^{14}H_3$ spectra in the region of 1.25 cm, with the result that the small satellites of certain of the lines first detected by Good¹ are strikingly resolved. The upper curve in the accompanying photograph (Fig. 1) is a cathode-ray scope display of the 3,3 line² with its satellite pairs on opposite sides. These satellites are believed³ to be a splitting of the center line by the nuclear quadrupole moment of N^{14} . The wide separation of the satellite pair which are only about 0.6 Mc apart, illustrates the remarkable resolution now obtainable with electronic techniques in the microwave region. We have also made photographs showing the similar splitting in the 1,1; 2,2; 4,4; 5,5; 6,6; and 8,8 lines.² The lower curve in the figure shows that obtained for the 6,6 line. The satellites are closest to the center line for the 1,1 case and move out from the center line as the quantum numbers of angular momenta increase. Accurate measurements of their positions⁴ are being made and will be reported later. The intensity of the satellites, as compared with that of the center line, decreases with increasing quantum numbers of angular momenta. We have not yet photographed the fine structure of the 7,7 and 9,9 lines because our oscillator would not operate in their regions. We observed several

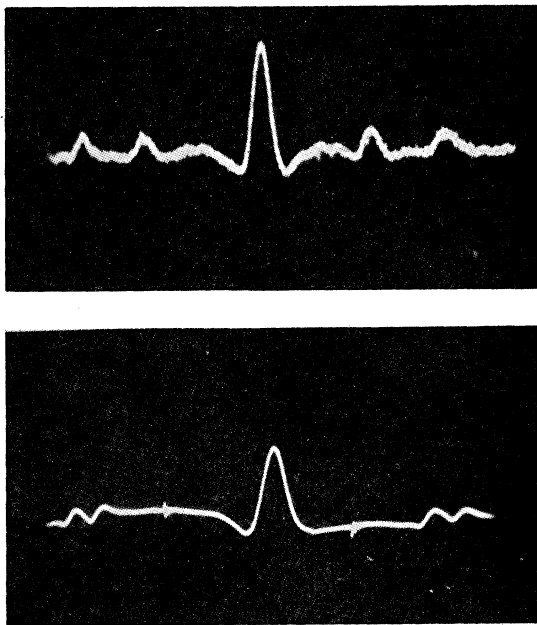


FIG. 1. Upper curve: 3,3 line of ammonia with satellite structure. Lower curve: 6,6 line, with satellite structure. Pressure $\approx 10^{-5}$ mm of Hg.

strong lines for which J and K are unequal but did not detect any satellite structure.³

In this work we did not observe the broadening caused by saturation which was reported by Townes.¹ The sharp lines shown in the photographs were observed when approximately 10 milliwatts of power were flowing through the cell.

These results were obtained by a single crystal, unbalanced detecting system which we have evolved. In brief, we use a slowly changing reflector voltage to modulate the source and a low frequency filter in the amplifier so that the indicator does not respond to the gradual change of voltage over the envelope of the oscillator mode but is very sensitive to the abrupt changes in output caused by the sharp absorption lines. This system has the additional advantage that spurious signals caused by reflections are largely eliminated, since they are usually much broader than the absorption lines of a gas at low pressure. Our tests indicate that this system is superior to the balanced detectors which employ either two crystals and cancellation in the video stage or a single crystal and cancellation in the r-f stage.

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¹ C. E. Cleeton and N. H. Williams, *Phys. Rev.* **45**, 234 (1934); B. Bleamy and Penrose, *Nature* **157**, 339 (1946); W. E. Good, *Phys. Rev.* **70**, 213 (1946); C. H. Townes, *Phys. Rev.* **70**, 665 (1946); M. W. P. Strandberg, R. Kyhl, T. Wentink, Jr., and R. E. Hillger, *Phys. Rev.* **71**, 326 (1947).

² Strandberg, Kyhl, Wentink, and Hillger (reference 1) and W. E. Good and D. K. Coles (*Phys. Rev.* **71**, 383 (1947)) have provided accurately measured frequencies of the centers of the first six of these lines.

³ B. P. Dailey, R. L. Kyhl, M. W. P. Strandberg, J. H. Van Vleck, and E. B. Wilson, Jr., *Phys. Rev.* **70**, 984 (1946); D. K. Coles and W. E. Good, *Phys. Rev.* **70**, 979 (1946).

⁴ Dailey, Kyhl, Strandberg, Van Vleck, and Wilson (reference 3) have measured the satellite separations for the 1,1; 2,2; 3,3; and 4,4 lines.

Bond Distances in OCS from Microwave Absorption Lines

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THE rotational absorption line for the $J=1$ to $J=2$ rotational transition of the OCS linear molecule was reported by Dakin, Good, and Coles.¹ Absorption at higher pressures caused by the transition had been reported previously by Hershberger.² The absorption line reported above was caused by the molecule composed of the abundant isotopes: carbon 12, oxygen 16, and sulfur 32. Of these three elements, only sulfur has another isotope with an abundance of more than 1 percent of the total naturally occurring element. The sulfur isotope 34 has an abundance of about 3 percent. It was believed that the sensitivity of our microwave absorption apparatus described by Good,³ with a wave-guide absorption cell 36 feet long, was just about enough to detect the absorption line caused by the OCS molecule with the sulfur 34 isotope, and after a preliminary calculation of the approximate frequency of this line, using the bond distances reported by Cross and Brockway,⁴ it was searched for and eventually found. The resolution of this isotopic absorption line was

TABLE I. Data on bond distances in OCS.

Constant	Value	Effect of uncertainty on	
		CO distance	CS distance
Atomic weight S ³²	31.9823 ± 0.00030	± 0.00002 × 10 ⁻⁸ cm	∓ 0.00002 × 10 ⁻⁸ cm
Atomic weight C ¹²	12.003861 ± 0.000024	± 0.00005	∓ 0.00004
Atomic weight O ¹⁶	16.0000		
Atomic weight difference S ³⁴ - S ³²	1.9957 ± 0.002	± 0.0047	∓ 0.0038
Mass of atom of unit atomic weight	(1.66035 ± 0.00031) × 10 ⁻²⁴ g	∓ 0.00011	∓ 0.00015
Planck's Constant	(6.6242 ± 0.0024) × 10 ⁻²⁷ erg sec.	± 0.00022	± 0.00030
Calculated values from the observed frequencies:			
Moment of inertia (S ³² molecule)	(137.9540 ± 0.0001) × 10 ⁻⁴⁰ g cm ²	± 0.000009	∓ 0.000005
Moment of inertia difference (S ³⁴ mole - S ³² mole)	(3.4564 ± 0.0003) × 10 ⁻⁴⁰ g cm ²	∓ 0.00075	± 0.00062
Probable error		± 0.0058	± 0.0049

first reported by us at the National Research Council Conference on Insulation in November, 1946.

The frequencies of these two absorption lines have since been measured more accurately by comparison with a harmonic of an oscillator which was heterodyned to zero beat with the 5-megacycle WWV National Bureau of Standards station as used by Good and Coles.⁵ The frequencies of the absorption lines can thus be determined to about one part per million. They are $f(\text{S}^{32} \text{ line}) = 24,325.92 \pm 0.02 \text{ Mc/sec.}$, $f(\text{S}^{34} \text{ line}) = 23,731.33 \pm 0.03 \text{ Mc/sec.}$ Unfortunately, because the nature of the calculation and the uncertainty of other constants necessary, all of this accuracy is not available in the two bond distances which may be calculated from these two frequencies.

In Table I there is a list of all the constants used in the calculation of the bond distances from the frequencies. The values of these constants, together with their uncertainties are given, and the effect of these uncertainties on the calculated bond distances is given. It will be observed that in most cases the effect of the error is in the opposite direction on the two bond distances so that their sum can be calculated more accurately than either separately. It was hoped that this very accurate frequency measurement would give a much more accurate value of the bond distance. An examination of Table I shows that the principal uncertainty is the difference in atomic weight of the sulfur isotopes. This contributes by far the largest amount to the uncertainty of the bond distance. The possible error in the frequency difference between the absorption line of the two isotopic molecules is the next largest uncertainty.

The bond distances C-O, $(1.1612 \pm 0.0058) \times 10^{-8} \text{ cm}$, and C-S, $(1.5604 \pm 0.0049) \times 10^{-8} \text{ cm}$ calculated here are the average interatomic distances in the lowest vibrational state. The atoms are assumed to be point masses and the centrifugal stretching has been approximated from the expressions given by Nielsen⁶ and the vibrational frequencies of Penney and Sutherland⁷ and found to be less than one part per million for the rotational levels involved here. The uncertainty in these bond distances can be reduced to about 0.1 percent when the difference in mass of the two sulfur isotopes is known to be better than

± 0.0001 atomic weight units. The isotope atomic weight values used were obtained from the table of Evans.⁸ The values of interatomic distances given here compare very well with the values obtained by Cross and Brockway from electron diffraction measurements: C-O = $1.16 \pm 0.02 \times 10^{-8} \text{ cm}$, C-S = $1.56 \pm 0.03 \times 10^{-8} \text{ cm}$.

¹ T. W. Dakin, W. E. Good, and D. K. Coles, Phys. Rev. **70**, 560 (L) (1946).

² W. D. Hershberger, R.C.A. Review **7**, 422 (1946); J. App. Phys. **17**, 814 (1946).

³ W. E. Good, Phys. Rev. **70**, 213 (1946).

⁴ P. C. Cross and L. O. Brockway, J. Chem. Phys. **3**, 821 (1935).

⁵ W. E. Good and D. K. Coles, Phys. Rev. **71**, 383 (1947).

⁶ A. H. Nielsen, J. Chem. Phys. **11**, 160 (1943).

⁷ W. G. Penney and G. B. M. Sutherland, Proc. Roy. Soc. **156**, 654 (1936).

⁸ R. D. Evans, *Introduction to the Atomic Nucleus* (M.I.T. 1944).

High Energy Ions in Crystal Lattices

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MANY complex anions are known to give rise to a Szilard-Chalmers effect when irradiated with slow neutrons.¹ In the case of a perchlorate, after neutron capture the activity is found entirely in the chloride fraction. This means more than the simple fact that the recoil separates the central chlorine from its surrounding oxygens. It is customary to consider the ClO_4^- ion as having a composition intermediate between the formulae Cl^+O_4 and $\text{Cl}^{7+}(\text{O}^{2-})_4$, but either all the activated chlorine is ejected as negative ions or, if part is ejected with a positive charge or as a neutral atom, it takes up electrons before it can react with any of the oxygen in the lattice. In other cases (e.g., arsenates and arsenites) the radioactivity is found entirely in ions of the same formula as those of which the crystal consists. Thus the capture of a neutron by a nucleus causes either a chemical reduction or it leaves the valency of the activated ion unchanged. Comparison between different reactions of this type is complicated by the fact that both the chemical conditions of atoms ejected by recoil and their chances of subsequent reactions depend on the crystal lattice.

In a note giving some preliminary figures,² it has been pointed out that the position is quite different in case the radioactive nucleus originates from an (n,p) or an (n,α) reaction. If fast neutrons of normal energy are used in such a process the kinetic energy of the recoil of the activated nucleus is very roughly 100 to 1000 times as large as the energy of a nucleus which has captured a neutron. Now this energy is not only sufficient to break the chemical bonds which connect the activated atom with the surrounding oxygens but even to strip it of many of its electrons during a series of collisions with neighboring particles. The highest positive charge which the activated atom attains will depend on the energy it has been given by the nuclear reaction and will be influenced very little by the composition of the lattice. In general, this highly charged ion will be very unstable chemically, and after