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Nuclear Quadrupole Moment Effects in the Inversion Spectrum of Ammonia*

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Satellite lines have been observed near lines 11, 22, 21, 33, 44, 55, 66, and 76 in the inversion spectrum of ammonia. The relative intensities and displacements of these satellites are in excellent agreement with Van Vleck's recent theory. From the observed separations of the satellites from the main lines can be calculated the interaction energy between the electrical quadrupole moment of the nitrogen nucleus and the electric field of the ammonia molecule.

THE presence of satellite lines constituting a hyperfine structure in the "inversion spectrum" of ammonia was first reported by Good.[1] These satellite lines were observed close to the fine-structure lines in the neighborhood of 0.8 cm^{-1}. Their existence has been confirmed by further experiments in other laboratories. The presence of these satellite lines has been explained by the recent theories developed by Van Vleck *et al.*[2] and by Coles and Good.[3] According to these theories, the observed satellite lines result from the interaction of the electrical quadrupole moment of the N^{14} nucleus and the electric field of the other charges in the ammonia molecule.

Van Vleck's equations for the separations of satellites from the central line are as follows:

$$h\Delta\nu = \pm\frac{3}{16}Q\frac{\partial^2 V}{\partial z^2}\left[1-\frac{3K^2}{J(J+1)}\right]\left[\frac{J+1}{2J+3}\right],$$

$$h\Delta\nu' = \pm\frac{3}{16}Q\frac{\partial^2 V}{\partial z^2}\left[1-\frac{3K^2}{J(J+1)}\right]\left[\frac{J}{2J-1}\right],$$

where $\Delta\nu$ and $\Delta\nu'$ denote frequency separations of satellites from the main line, Q is the nuclear quadrupole moment of N^{14} as defined by the expression $\{\rho(3z^2-r^2)\}_{\mathrm{Av}}$, and J and K are rotational quantum numbers associated with the total molecular angular momentum and angular momentum about the figure axis of the molecule, respectively.

The agreement of predicted separations with the experimentally observed values was found to be excellent for lines 11, 22, 33, and 44.[2] Another aspect of Van Vleck's theory indicates that the intensity of the satellite lines should decrease rapidly with increasing values of J. The experimental results thus far published in detail[2] are in agreement with this prediction, and no satellite lines have been reported for lines with J greater than 4.

The purpose of the present note is to report the results of recent studies conducted in this laboratory, in which satellite lines have been observed for J values as high as 7. The techniques are similar in essentials to those used earlier by other investigators. A modulated Klystron oscillator was used as a source of radiation, and single-crystal detection was employed. The ammonia under study was in a rectangular wave guide equipped with mica

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[1] W. E. Good, Phys. Rev. **70**, 213 (1946).

[2] B. P. Dailey, R. L. Kyhl, M. W. P. Strandberg, J. H. Van Vleck, and E. B. Wilson, Jr., Phys. Rev. **70**, 984 (1946).

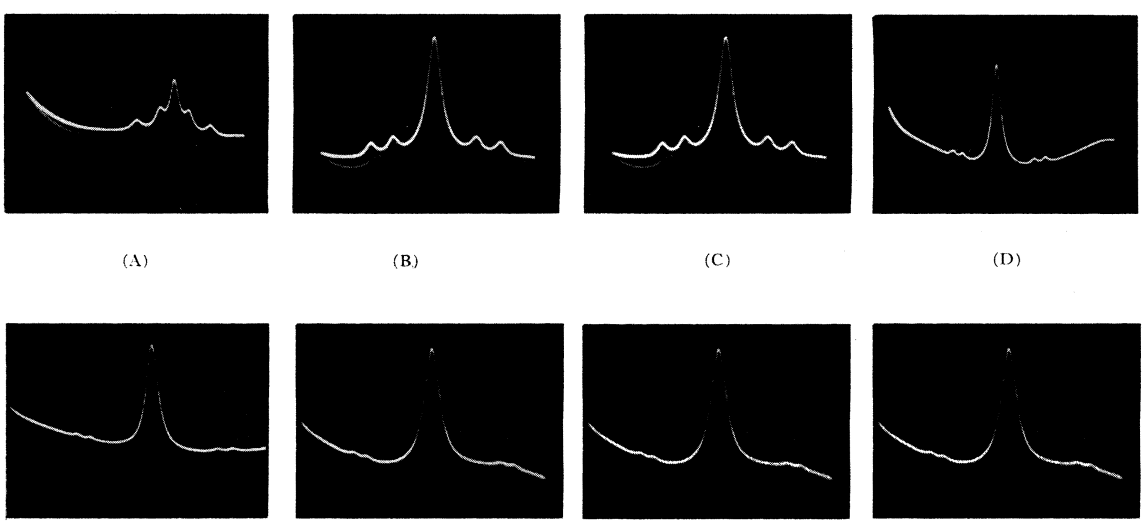
[3] D. E. Coles and W. E. Good, Phys. Rev. **70**, 979 (1946).

windows. The length of the section of wave guide forming the "absorption cell" was 100 ft., and pumping was accomplished through a $\frac{1}{16}$-in. slot in the wall. The length of this slot was 5 ft. With an oil diffusion pump, pressures as low as 5×10^{-3} mm of mercury could be attained; these pressures could be maintained for several hours after the absorbtion section was isolated from the pumps.

Spectral lines were observed from an oscillograph trace. The modulating voltage was plotted horizontally and transmitted power vertically on the cathode-ray screen. The results obtained for lines 11, 22, 33, 44, 55, 66, 21, and 76 are given in Fig. 1 in which photographs of the oscilloscope trace are shown. The satellite lines are readily discernible for all these lines except 21 and 76, in which they are barely discernible in the noise. The 21 line itself is rather weak, and the intensities of the satellites relative to the main lines are comparable with the relative intensities of the satellites near the 22 line. However, the intensity of satellites relative to the strong 76 is extremely low.

Measurements of the relative separations $\Delta\nu$ and $\Delta\nu'$ were made by two methods. The first involved measurements of separations of the satellite lines from the main lines on the oscillograph trace; ratios of the separations were then taken to give $\Delta\nu'/\Delta\nu$. This method requires that the oscilloscope separation be directly proportional to frequency difference. Measurements made under different conditions of modulating voltage, horizontal amplifier gain, etc., gave fairly consistent results for the $\Delta\nu'/\Delta\nu$ ratio. Since the satellite pattern is found by other methods to be symmetrical in frequency, it is simple to detect radical departures from linearity. The second method of determining $\Delta\nu'/\Delta\nu$ involves determination of the actual frequency separations by introducing modulating radiofrequency signals from a variable-frequency oscillator. If such a radiofrequency modulation of the order of a few megacycles is applied to the Klystron repeller, small "ghosts" appear near an absorption line on the oscillograph trace. The frequency separation of the "ghost" and the main line is a multiple of the modulation frequency. By comparison of "ghost" and satellite positions, the absolute values of $\Delta\nu$ and $\Delta\nu'$ may be determined. This method of measuring frequency differences has been used by Strandberg *et al.*[2] The accuracy with which frequency differences can be measured by this method is ±0.05 megacycles.

The results obtained for satellite separations



(A) (B) (C) (D)

(E) (F) (G) (H)

FIG. 1. Photographs of oscilloscope traces showing ammonia absorption lines as follows: A, line 11; B, line 22; C, line 33; D, line 44; E, line 55; F, line 66; G, line 76; H, line 21. All photographs except G and H were obtained with ammonia at identical pressure $\sim10^{-2}$ mm Hg; the pressure was only slightly different when photographs G and H were taken.

TABLE I. Separations of satellites from main lines.

Line	$\Delta\nu$	$\left(\frac{\Delta\nu_{JK}}{\Delta\nu_{11}}\right)_{\text{obs.}}$	$\left(\frac{\Delta\nu_{JK}}{\Delta\nu_{11}}\right)_{\text{calc.}}$	$\Delta\nu'$	$\left(\frac{\Delta\nu_{JK}'}{\Delta\nu_{11}'}\right)_{\text{obs.}}$	$\left(\frac{\Delta\nu_{JK}'}{\Delta\nu_{11}'}\right)_{\text{calc.}}$	$\left(\frac{\Delta\nu'}{\Delta\nu}\right)_{\text{obs.}}$	$\left(\frac{\Delta\nu'}{\Delta\nu}\right)_{\text{calc.}}$
11	0.62^5 Mc	1.00	1.00	1.61 Mc	1.00	1.00	2.55	2.50
22	1.33	2.13	2.14	2.10	1.30	1.33	1.56	1.56
21	0.72	1.15	1.07	1.07	0.66	0.66	1.52	1.54
33	1.74	2.79	2.78	2.39	1.48^5	1.50	1.36	1.35
44	1.98	3.17	3.18	2.54	1.58	1.60	1.28	1.26
55	2.31	3.70	3.47	2.79	1.67	1.67	1.21	1.20
66	2.28	3.65	3.67	2.64	1.64	1.72	1.18	1.17
76	1.38	2.21	2.19	1.72	1.07	1.00	1.20	1.14

are summarized in Table I. It will be noted that the experimental results are in agreement with Van Vleck's theory within the limits of experimental error. The values given in the table for $\Delta\nu'/\Delta\nu$ combine the results obtained by the two methods listed above.

The experimentally obtained results can be fitted to Van Vleck's equations to give a value for the interaction energy $Q\partial^2 V/\partial z^2$ between the nuclear quadrupole moment and the electric field. In obtaining the value for the interaction energy, we have obtained the frequency which when multiplied by h gives $Q\partial^2 V/\partial z^2$ as defined above. This frequency is:

$$\frac{1}{h}Q\frac{\partial^2 V}{\partial z^2} = 17.05 \pm 0.11 \text{ megacycles.}$$

Stated in wave numbers, this frequency is

$$5.67 \pm 0.04 \times 10^{-4} \text{ cm}^{-1}.*$$

Note added in proof:* This frequency should be divided by 4 for direct comparison with the "quadrupole coupling" terms given by Townes [Phys. Rev. **71, 909 (1947)].

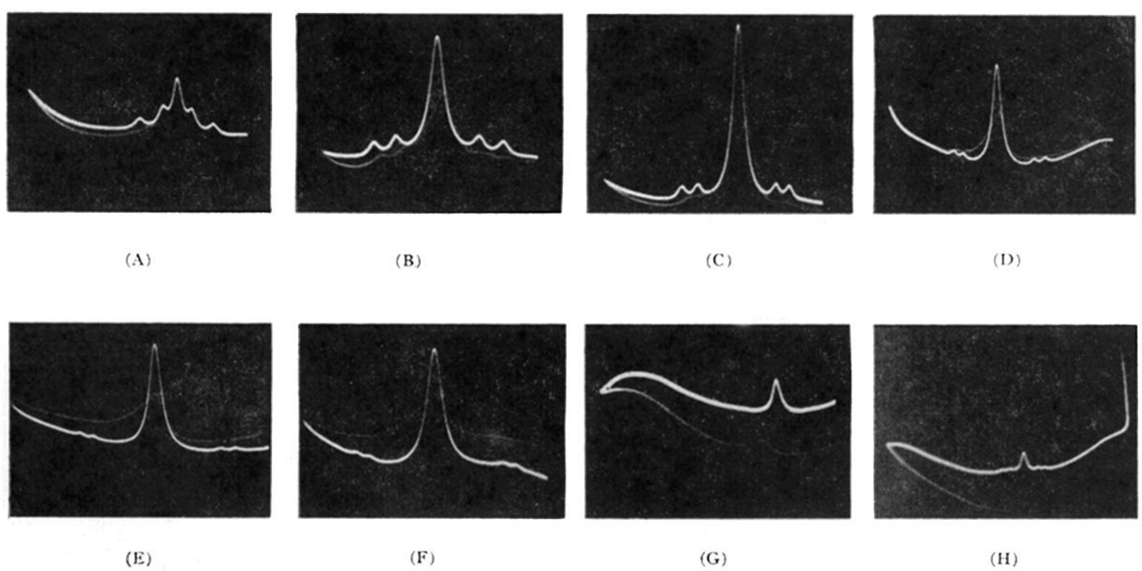


FIG. 1. Photographs of oscilloscope traces showing ammonia absorption lines as follows: A, line 11; B, line 22; C, line 33; D, line 44; E, line 55; F, line 66; G, line 76; H, line 21. All photographs except G and H were obtained with ammonia at identical pressure $\sim 10^{-2}$ mm Hg; the pressure was only slightly different when photographs G and H were taken.