

The Raman Effect in Ammonia and Some Other Gases

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(Received August 30, 1933)

The Raman rotation spectra of polyatomic molecules can be interpreted in terms of the polarizabilities of the molecule, without explicit knowledge of the electronic states. This point of view makes possible the calculation of the relative intensities of all rotation lines to be expected. The spectrum of gaseous ammonia shows the calculated intensity relations when a suitable shape is assumed for the molecule. The measurements are good enough to exclude the possibility of the case with three equal moments of inertia, and tend to support the flat pyramid inferred from

infrared data. The larger moment of inertia is $2.79 \cdot 10^{-40}$ g cm². Methane shows no pure rotation band in spite of the presence of a vibration-rotation band. Ethane shows a rotation band which has not been resolved and an apparent vibration-rotation band which has not been interpreted. Ethylene gives a pure rotation band which indicates a moment of inertia of about $30.0 \cdot 10^{-40}$ g cm², while acetylene shows a moment of inertia of $23.52 \cdot 10^{-40}$ g cm² with alternating intensities as in hydrogen.

THE first experimental results on the Raman effect were understood theoretically with the help of the "double jump" picture of the scattering process which results from the Kramers-Heisenberg dispersion formula. This is characterized by the presence of an "intermediate state" in the transitions involved, and by a summation over all possible intermediate states. Since these are in general excited electronic states, the properties of the Raman spectra are connected by the "double jump" picture, not so much with those of the infrared, as with those of the electronic band spectra. For diatomic molecules, for which the band spectra are in many cases thoroughly understood, this was relatively satisfactory. But for polyatomic molecules the dependence upon the electronic states sharply limited the usefulness of the theory.

The problem of removing the necessity of knowing the electronic states of the molecule is primarily that of recognizing the difference in the rôles which the electronic and the nuclear motions play in the scattering process. This difference may be considered to result analytically from those properties which fundamentally distinguish the molecular problem from the atomic one. These are the approximate separability of the functions into electronic, vibrational, and rotational factors, and the difference in the order of magnitude of the energies associated with the three corresponding types of motion.

Were the functions completely separable, rotational and vibrational transitions in the Raman effect would probably be unknown, since their intensities would be several orders of magnitude smaller than they are.¹ Were they not approximately separable, no such classification of the observed lines would be possible.

Manneback² has shown, for the case of diatomic molecules, that an application of just these characteristics of the molecular problem to the dispersion formula makes it possible, in sufficient approximation, to carry out the summation over the intermediate states. The summation over the excited electronic states is the same for all vibrational or rotational Raman transitions, and accordingly need not be explicitly evaluated, while the sum over the nuclear states can be carried out. This sum over the electronic states is proportional to the electronic polarizability of the molecule when the nuclei are held fixed. The dispersion formula, with all its paraphernalia of intermediate excited states is reduced in this way to simple matrix elements

¹This has been clearly pointed out by Placzek. Cf. especially *Leipziger Vorträge*, p. 71, 1931.

Muskat has considered the case of complete separability in treating the rotational transitions of a rigid molecule equipped with an electric moment. *Phys. Rev.* **35**, 1262 (1930). This gives the nuclear scattering, which is very small indeed.

²C. Manneback, *Zeits. f. Physik* **62**, 224 (1930); **65**, 574 (1930). Cf. also p. 238 of Placzek and Teller.⁴

of the polarizability of the "rigid" molecule, which do not involve the electronic functions explicitly and can be calculated with only the nuclear functions of the initial and final states of the molecule.

It was implied by Manneback, and it has been remarked by other writers, that a similar reduction of the dispersion formula could not be carried out for polyatomic molecules, due to the lack of sufficient information with regard to their electronic functions. This, however, is not the case, since no knowledge whatever is required of these functions beyond the fact that they can be separated from the nuclear functions and that their energies are of a different order of magnitude from those of the nuclear motions. These two properties have been shown by Born and Oppenheimer³ to follow directly, to the degree of approximation employed by Manneback, from a solution of the molecular problem in which all quantities, Hamiltonian function, wave functions, and term values, are expanded in powers of the small quantity $(m/M)^{1/2}$, where m is the electronic mass and M is the nuclear mass.

Placzek has recently developed, rather completely, a method of attacking the problem which leads to the same expressions for the intensities that one obtains by Manneback's method from the dispersion formula.⁴ The process is not fundamentally different from that by which Kramers and Heisenberg reached the dispersion formula, but a simplification equivalent to that described above is introduced at the very start. The electric moment responsible for the scattered light is written as the electric field strength of the incident light multiplied by the electronic polarizability. The intensity of the light scattered in conjunction with a given transition of the molecule is then proportional to the square of the corresponding matrix element of the electric moment. Since the polarizability is taken to be independent of the positions of the individual electrons, the electronic functions do not appear in the expressions

for the computation of these matrix elements. It is the inclusion of the high frequency dependence of the electric moment upon the electronic coordinates that gives rise to the complications of the rigorous theory. The polarizability does, however, vary with the vibrations of the nuclei, since the electronic binding depends upon the internuclear distances. It also varies with the rotational motion, since the components of the polarizability relative to fixed axes depend upon the orientation of the molecule in space. The nuclear functions are therefore involved in the calculation of the polarizability matrix, and certain transitions between nuclear states will be accompanied by scattering of radiation.

The selection rules follow analytically from the expressions for the matrix elements, or they may be obtained by applying the correspondence principle to the "polarizability picture" of the scattering process. Thus, in a diatomic molecule in a Σ state, the total angular momentum, which is measured by the quantum number J , is perpendicular to the molecular axis. Since the tensor of polarizability is always a symmetrical tensor, the variation of each component of the electric moment will complete two cycles for each rotation of the molecule. By the correspondence principle this limits the changes of J to ± 2 or 0. In a diatomic molecule which is not in a Σ state, or in a molecule of the symmetrical top type in which $K \neq 0$, so that the angular momentum about the figure axis does not vanish, the total angular momentum is not perpendicular to this axis, but becomes more and more nearly parallel to it as K approaches J . In this case a rotation of the molecule through 180° about the axis of J puts it in such a position that its polarizability along the fixed Z axis is in general different from its initial value. This implies that the quantum number J can change by ± 1 also. The exception to this case arises when the total angular momentum is perpendicular to the Z axis, in which case only changes of ± 2 occur with the scattering of light polarized parallel to Z . The component of J along the Z axis is measured by the quantum number M , and so it is to be expected that M as well as K should occur as a factor in the expression for the intensity of the lines polarized in the Z direction with $\Delta J = \pm 1$. In a similar way, the other features of the

³ M. Born and J. R. Oppenheimer, *Ann. d. Physik* **84**, 457 (1927).

⁴ G. Placzek, *Zeits. f. Physik* **70**, 84 (1931); *Leipziger Vorträge*, p. 71, 1931.

G. Placzek and E. Teller, *Zeits. f. Physik* **81**, 209 (1933).

selection rules and the intensity expressions can be visualized in terms of the motion of the molecule, with the usual difficulties which arise because the initial and the final states have different motions.

In many cases the tensor of polarizability will have the same principal axes and much the same symmetry as the tensor of inertia. This is especially true in molecules of the symmetrical top type. In case the two principal values of the polarizability along the two axes perpendicular to the axis of symmetry are the same, changes in K will not occur in the Raman spectrum. If, however, these two values are different, changes in K may occur.

From considerations of this kind, much information can be obtained from the Raman spectrum concerning the shape of the molecule. We have studied the spectrum of a number of gases, with particular attention to the rotation spectra, to check these rules and to use them in the interpretation. In the study of ammonia we have measured the intensity of the lines; in the

other cases only the positions have been measured carefully.

MATRIX ELEMENTS FOR A SYMMETRICAL TOP

We have evaluated the matrix elements mentioned above for the symmetrical top type of molecule, and have obtained expressions for the intensities of the lines in a rotation band. These are identical with those recently published by Placzek and Teller,⁴ to whose extensive treatment we shall refer for all details. The assumption is made that the molecule has not only two of its principal moments of inertia equal, but that the two corresponding principal values of the polarizability are equal and that the principal axes of the tensors of inertia and of polarizability coincide. The results which we shall use are repeated here for convenience in a simplified form.

In Eqs. (1) are given the squares of the matrix elements of the polarizability averaged over all the values of M for a given J , K , and ΔJ . In all cases $\Delta K = 0$.

$$J \rightarrow J+2; \quad \bar{P}_X^2 = \bar{P}_Y^2 = -\bar{P}_Z^2 = -\frac{3}{4} \frac{1}{10} \gamma^2 \frac{\{(J+1)^2 - K^2\} \{(J+2)^2 - K^2\}}{(J+1)(J+2)(2J+1)(2J+3)}, \quad (1a)$$

$$J \rightarrow J+1; \quad \bar{P}_X^2 = \bar{P}_Y^2 = -\bar{P}_Z^2 = -\frac{3}{4} \frac{1}{5} \gamma^2 \frac{K^2 \{(J+1)^2 - K^2\}}{J(J+1)(J+2)(2J+1)}, \quad (1b)$$

$$J \rightarrow J; \quad \bar{P}_X^2 = \bar{P}_Y^2 = \frac{1}{15} \gamma^2 \frac{\{J(J+1) - 3K^2\}^2}{J(J+1)(2J-1)(2J+3)}, \quad (1c)$$

$$\bar{P}_Z^2 = \mu^2 + \frac{4}{3} \bar{P}_X^2.$$

The incident light is plane polarized with the electric vector in the Z direction, while the subscripts denote the direction of the electric vector of the scattered light.

The quantities μ and γ involve the principal values of the tensor of polarizability in the form

$$\gamma = \alpha_{zz} - \alpha_{xx}, \quad \mu = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \quad \alpha_{xx} = \alpha_{yy}.$$

When dealing with vibration rotation spectra, the polarizabilities α are replaced by the derivatives of the same quantities with respect to the normal coordinate involved in the vibration in

question. This difference between the pure rotation and the vibration rotation spectra leads to some interesting results which are described in detail by Placzek and Teller.

The matrix expressions for transitions between two given states have the same value whether J increases or decreases. However, since these quantities are customarily expressed in terms of the quantum numbers of the initial state, it is necessary in the case of decreasing J to replace J in (1) by $(J-1)$ or $(J-2)$.

To determine the intensity of a line due to a

transition between the level (J, K) and the level $(J+\Delta J, K)$, the suitable expression from (1) must be multiplied by the fourth power of the frequency of the scattered line and by the number of molecules in the initial state. This is given by

$$N_{J, K} = g_{J, K} e^{-\sigma J(J+1) - \sigma' K^2}, \quad (2)$$

where $\sigma = \hbar^2 / 8\pi^2 A k T$ and $\sigma' = \beta\sigma = (A/C - 1)\sigma$. Since the quantum number K does not change, the lines due to jumps from one value of J but from different values of K will coincide in position, as long as the energy is correctly given by the expression for the energy of a rigid molecule. To get the total intensity it is then necessary to sum the intensity expression over all of the values of K from $-J$ to J . If σ' is very small, this is simple, but if σ' is large enough to be considered, the summation is rather tedious. The quantities C and A are the moments of inertia about the axis of symmetry and an axis perpendicular to it. The quantum weight of the initial state, $g_{J, K}$, contains the factor $(2J+1)$ due to the degeneracy in M , and also depends upon the symmetry properties of the rotational functions if there are identical nuclei in the molecule. This fact is of importance in treating the spectrum of ammonia.

THE RAMAN SPECTRUM OF AMMONIA

The general features of the rotational Raman spectrum of gaseous ammonia have already been discussed by Amaldi and Placzek,⁵ and have been found to agree with the theoretical expectations. We have made a careful experimental determination of the relative intensities of the rotation lines, and have compared them with calculations based upon three different assumptions as to the shape of the molecule. These assumptions are: that the molecule is plane, that all three moments of inertia are the same, and that the case is intermediate between these two, as has been derived by Dennison and Uhlenbeck,⁶ and by Rosen and Morse,⁷ from an analysis of

the splitting of the vibrational levels. As might be expected, the agreement is the best for this intermediate case, and the spherical model can be definitely excluded.

The apparatus was essentially that used in the investigation of CO₂ and has been described previously.⁸ The source of light was a water-cooled quartz mercury arc, and only the scattering due to $\lambda 2537$ was used. The arc was cleaned after every two or three exposures to keep the intensity a maximum. The unshifted line was largely absorbed by mercury vapor from a dish of mercury inside the Hilger E1 spectrograph. The ammonia was taken from a commercial cylinder, and was used without purification, other than drying, at pressures between 75 and 100 pounds per square inch. The exposures varied from 40 to 90 hours with a slit width of about 0.08 mm. Some improvement has been made in that the quartz tube which contains the gas is no longer held by means of sealing wax, but by means of gasket material squeezed against the tube by the same scheme that is used in valve stem stuffing boxes. This facilitates the removal of the tube and can be used at temperatures at which the wax would melt.

To measure the intensities each plate was calibrated by means of density marks. These were obtained by placing a step-weakener over the slit of the spectrograph and photographing the spectrum of the mercury arc. To get uniform illumination of the slit and an exposure time not too different from that of the Raman exposures, the light from the arc was diffusely scattered, by means of a piece of white paper, into the slit. The exposures were then about 2 to 4 hours. The weakener was made by evaporating gold onto a quartz disk. It was calibrated by photographic comparison with a similar weakener, kindly loaned by Dr. D. S. Hughes. This he had calibrated with a sensitive thermocouple for the line 2537. From the density marks a density-intensity curve was plotted in the usual way.

The microphotometer used was designed by Dr. Theodore Dunham, Jr., at the Mt. Wilson Observatory, and we are deeply indebted to him for the privilege of using it. The scale of this

⁵ E. Amaldi and G. Placzek, *Zeits. f. Physik* **81**, 259 (1933).

⁶ D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.* **41**, 313 (1932).

⁷ N. Rosen and P. M. Morse, *Phys. Rev.* **42**, 210 (1932).

⁸ W. V. Houston and C. M. Lewis, *Proc. Nat. Acad.* **17**, 229 (1931).

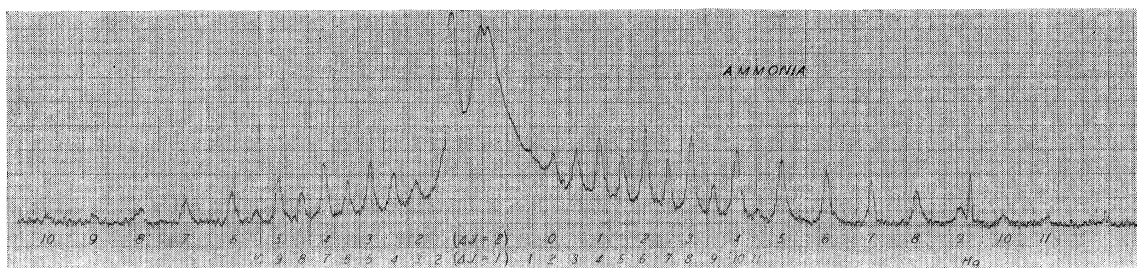
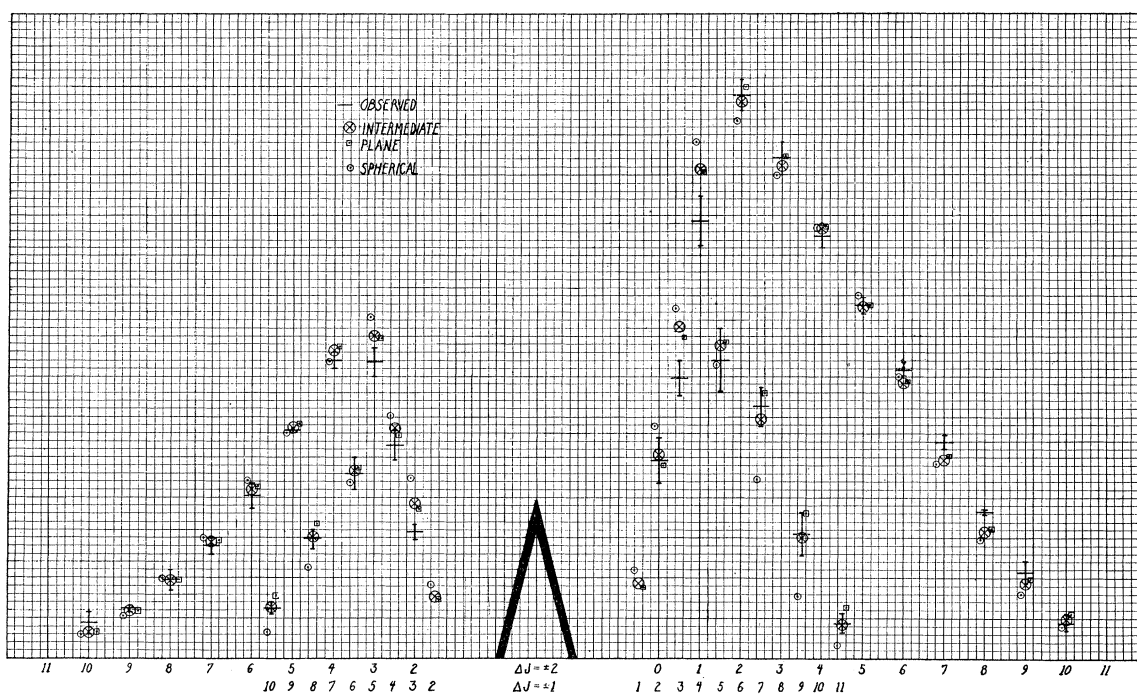


FIG. 1. Microphotometer curve of the pure rotation spectrum of ammonia.

FIG. 2. Observed and computed intensities in the pure rotation spectrum of gaseous ammonia. The different computed values refer to different relative values for the moments of inertia. They have been adjusted to agree for $J=4$, $\Delta J=2$.

instrument is so nearly linear that it is possible to use different amounts of deflection for the Raman spectrum and the intensity marks, so as to magnify as much as possible the detail in the Raman spectrum.

Fig. 1 shows a microphotometer curve of the rotation band. In this particular plate the background is so clear, except near the exciting line, that the corresponding density falls upon the extreme tail of the characteristic curve; the variation in the background can therefore not be determined accurately. Results from two plates in which this condition was just avoided,

and from three in which the background reached to the straight part of the intensity-density curve, have been averaged to give the results plotted in Fig. 2. Each set of values was adjusted by means of a constant multiplier to bring them all into the best general agreement. The straight lines extending above and below the observed intensities represent the mean deviation of the individual measurements from the average and hence give some idea of the consistency of the results. The principal uncertainty probably arises from the difficulty in properly locating the background on the microphotometer curves.

TABLE I. Constants for the ammonia molecule.

Model	Plane	Intermediate	Spherical
$A \times 10^{40}$ g cm ²	2.79	2.79	2.79
$C \times 10^{40}$ g cm ²	5.58	4.41	2.79
$d \times 10^8$ cm	0.0	0.380	0.584
N-H $\times 10^8$ cm	1.06	1.01	0.95
H-H $\times 10^8$ cm	1.84	1.63	1.30

Table I gives the constants used in calculating the values plotted in Fig. 2. The variation of the moments of inertia does not change the transition probabilities, but alters the spectrum by affecting the relative populations of the initial states. This effect is given by the exponential factor in (2). When all three moments of inertia are the same, $\sigma' = 0$ so that all values of K have the same weight. As the model becomes more nearly plane, C approaches $2A$ and σ' is negative. In this case the terms with large values of K have a large weight. This favoring of the large values of K , and hence of the large values of J since $K < J$, is largely counteracted in the cases of the O and S branches ($\Delta J = \pm 2$) by the fact that the transition probability decreases rapidly with increasing K . For the P and R branches ($\Delta J = \pm 1$) the transition probability increases with increasing K and so these branches are sensitive to the model assumed. This behavior is well illustrated by the three cases plotted in Fig. 1.

In computing the J exponentials account was taken of the dependence of the moment of inertia upon J . The constants were taken from the frequency measurements described below. The dependence of C upon J and of both A and C upon K has been neglected, since it is not known, and would probably have only a small effect. The temperature was measured by the thermometer close to the tube containing the gas. It varied slightly from one exposure to another, but was taken as 46°C in the calculations. The factor ν^4 has been included and makes a difference of about 10 percent from one end to the other. When the symmetry properties of the rotational wave functions are considered, the presence of the three identical hydrogen nuclei with spins of 1/2, doubles the quantum weight of those states for which K is a multiple of 3 (including zero).⁹ Because of the sums over

⁹ D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931).

K this is of importance only for low values of J , in contrast to the situation in O₂ and N₂ where the symmetry affects the weight as a function of J directly. It is quite necessary, however, to take account of this fact to get the agreement indicated in the figure.

The observed rotational frequency shifts for ammonia are given in Table II. They are

TABLE II. Frequency shifts of the ammonia rotation lines.

J	Observed shift	Calculated shift	Difference
$\Delta J = \pm 2$			
0	59.82 cm ⁻¹	59.48 cm ⁻¹	-0.34 cm ⁻¹
1	99.17	99.13	-.04
2	138.62	138.69	+.07
3	178.25	178.21	-.04
4	217.50	217.53	+.03
5	256.92	256.76	-.16
6	295.9	295.82	-.1
7	334.5	334.66	+.2
8	372.5*	373.37	+.9*
9	411.9	411.84	-.1
10	449.9	449.96	+.1
11	486.2	485.84	-.4
$\Delta J = \pm 1$			
1	39.67	39.66	-0.01
3	79.48	79.29	-.19
5	119.25	118.59	-.66
7	158.38	157.66	-.72
9	197.38	196.32	-1.06
11	236.5	234.38	-2.1

* A weak mercury line renders this value rather uncertain.

averages of the Stokes and the anti-Stokes lines measured relative to iron standards on the two best plates. The calculated frequencies are obtained from the following formula for the rotational energy levels:

$$E/hc = B_0 J(J+1) + B_0 \beta K^2 + B_1 J^2 (J+1)^2, \quad (3)$$

where $B_0 = h/8\pi^2 cA$. The second term in (3) does not affect the Raman lines since K does not change. The third term takes account of the increase in the moment of inertia, A , when J increases. The values used for the constants are $B_0 = 9.92$ and $B_1 = 0.00052$. These lead to the value $A = 2.79 \times 10^{-40}$ g cm² for the moment of inertia in the ground state.

According to (3) the P and Q branches should show slightly more convergence than they do,

and for large J they should not coincide as well with the lines of the O and S branches as they appear to do. The constants selected, however, give a very good representation of the O and S branches themselves. The resulting constants are remarkably close to those obtained by Dickinson, Dillon and Rasetti¹⁰ from the measurement of only ten lines, since they did not observe the P and R branches. They obtained $B_0=9.921$ and $B_1=0.00063$. Amaldi and Placzek⁵ give consistently higher values for the rotational frequencies, but without discussing them in any detail.

TABLE III. *Ammonia vibration lines.*

Intensity	Observed shift	Amaldi and Placzek	Dickinson, Dillon and Rasetti (gas)	D. D. and R. (liquid)
3	934.2	933.8		
4	964.3	964.3		
2	3219.1			3214.5
10	3334.1	3334.2	3333.6	3298.4

Table III gives the observed shifts of the vibration lines. Three of these shifts are in good agreement with those of Amaldi and Placzek; the significance of these lines and their interesting relation to the infrared spectrum have been adequately discussed by these authors and by Dennison and Hardy.¹¹ The rotational branches reported by Langseth¹² on each side of his strong line at 3312 cm^{-1} , the counterpart for solutions of 3334 in the gas, do not appear on our plates, although it appears from his reproduction that our Q branch is nearly as strong as his. We find a fourth line at 3219.1 cm^{-1} , which is slightly weaker and somewhat broader than those at 934 and 964 cm^{-1} . It appears to be the fundamental of the fourth normal mode of vibration of the molecule, which has not previously been observed in the gas. This is the unsymmetrical vibration in which the nitrogen atom takes only a small part. It should appear faintly in the Raman effect and may be expected to yield about this frequency.

¹⁰ R. G. Dickinson, R. T. Dillon and F. Rasetti, *Phys. Rev.* **34**, 582 (1929).

¹¹ D. M. Dennison and J. D. Hardy, *Phys. Rev.* **39**, 938 (1932).

¹² A. Langseth, *Zeits. f. Physik* **77**, 60 (1932).

METHANE

The results with methane confirm the work of Dickinson, Dillon and Rasetti with regard to the vibration rotation band around 3022 cm^{-1} . On account of the spherical symmetry of methane in the ground state there should be no pure rotation band at all. To check this point we have obtained plates after 100 hours exposure on which the vibration rotation lines are very clear, and on which the background is very weak to within 50 cm^{-1} of the exciting line. We would estimate that the pure rotation lines are certainly less than $1/25$ as strong as the rotation vibration lines. Because of the large difference in intensity between the unshifted line, and the Q branch of the vibration band, this means that the pure rotation spectrum is practically absent.

ETHANE

Ethane shows a pure rotation band, which, however, it has not been possible to resolve. This is disappointing, since the lines might be expected to show a separation similar to that of CO_2 . The vibration spectrum includes three lines, 993.0 (3), 2899.2 (6), and 2955.1 (7), which evidently correspond to 990 , 2890 , and 2950 obtained by Daure¹³ from the liquid, and agree well with Bhagavantam's¹⁴ values for the gas. A very weak line at 1344 cm^{-1} may possibly be related to Daure's 1460 . Three other lines of low intensity may well be connected with some of the numerous unsymmetrical vibrations of ethane which are due principally to the stretching of the C-H bonds. These are 2743.7 (2), 2778 . (0), and 2939.5 cm^{-1} (1).

In this region we have observed also a series of weak lines which can be organized into rotational branches around three of the vibration lines. Of these, the most certain are the Stokes lines associated with 2955.1 . These give shifts of 14.4 , 23.9 , 34.4 , 44.3 , and 53.7 cm^{-1} . These lines are too widely spaced to be readily explained as due to changes in J . If one assumes that the vibration is such as to permit changes in K , the spacing of the lines gives a possible moment of inertia if $\Delta K = \pm 2$. However, this assumption does not seem to fit the position of the first line.

¹³ P. Daure, *Ann. de Physique* **12**, 375 (1929).

¹⁴ S. Bhagavantam, *Indian J. Phys.* **6**, 595 (1931).

ETHYLENE

The pure rotation band of ethylene shows a structure with an apparent tendency of the lines to draw together in pairs. This tendency is much more obvious in the microphotometer curves than in the measurements of the shifts, which are given in Table IV. All of the lines can be

TABLE IV. Frequency shifts of the ethylene rotation lines.
 $B=0.920$, $\Delta J=\pm 2$, $A=30.0\cdot 10^{-40}$

J	Observed shift	Calculated shift	Difference
1	10.5 cm ⁻¹	9.20 cm ⁻¹	-1.3 cm ⁻¹
2	12.8	12.88	0.1
3	16.0	16.56	0.6
4	19.7	20.24	0.5
5	23.2	23.92	0.7
6	27.3	27.60	0.3
7	31.5	31.28	-0.2
8	35.1	34.96	-0.1
9	38.8	38.64	-0.2
10	42.5	42.32	-0.2
11	45.9	46.00	0.1
12	49.65	49.68	0.0
13	53.3	53.36	0.1
14	56.9	57.04	0.1
15	59.9	60.72	0.8
16	64.1	64.40	0.3
17	68.9	68.08	-0.8
18	72.5	71.76	-0.7
19	76.2	75.44	-0.8
20	79.3	79.12	-0.2

fitted to a formula with $\Delta J=\pm 2$, $B=0.920$. This gives $A=30.0\cdot 10^{-40}$ which is somewhat larger than the value $28.85\cdot 10^{-40}$ given by Scheib and Lueg¹⁵ from their analysis of a near infrared band.

Since the ethylene molecule is not far from a symmetrical top its spectrum should be similar in structure to that of ammonia. Presumably the lines which are resolved correspond to the strong lines for which $\Delta J=\pm 2$, while the lines for which $\Delta J=\pm 1$ merely contribute to the general background. This apparent pairing of the lines can perhaps be attributed to the lack of exact coincidence of the lines for different values of K .

¹⁵ W. Scheib and P. Lueg, *Zeits. f. Physik* **81**, 764 (1933).

ACETYLENE

From 37 lines in the pure rotation band of acetylene we obtain $A=23.52\cdot 10^{-40}$, in excellent agreement with the value of 23.509 found by Hedfield and Mecke¹⁶ from the near infrared. The alternating intensities appear in the same way as in H₂ where the odd values of J have three times the weight of the even values. The observed values given in Table V are means of

TABLE V. Frequency shifts of the acetylene rotation lines.
 $B_0=1.176$, $\Delta J=\pm 2$, $A=23.52\cdot 10^{-40}$

J	Observed shift	Calculated shift	Difference
0	—	7.06	
1	11.6	11.76	0.2
2	15.75	16.46	0.7
3	21.3	21.17	-0.1
4	26.4	25.87	-0.5
5	31.0	30.58	-0.4
6	35.6	35.28	-0.3
7	40.15	39.98	-0.2
8	44.6	44.69	0.1
9	49.65	49.39	-0.2
10	54.05	54.10	0.1
11	58.9	58.80	-0.1
12	63.6	63.50	-0.1
13	68.2	68.21	0.0
14	73.2	72.91	-0.3
15	77.6	77.62	0.0
16	83.1	82.32	-0.8
17	86.8	87.02	0.2
18	91.7	91.73	0.0
19	96.4	96.43	0.0
20	100.4	101.14	0.7
21	105.5	105.84	0.3
22	—	110.54	
23	115.6	115.25	-0.4

the Stokes and the anti-Stokes lines. We observe a vibration line at 1967.4 cm⁻¹, which is somewhat lower than the values obtained by others in the gas, but still higher than that obtained in the liquid. The weaker line at 3372 cm⁻¹ we have not observed.

¹⁶ K. Hedfield and R. Mecke, *Zeits. f. Physik* **64**, 151 (1930).

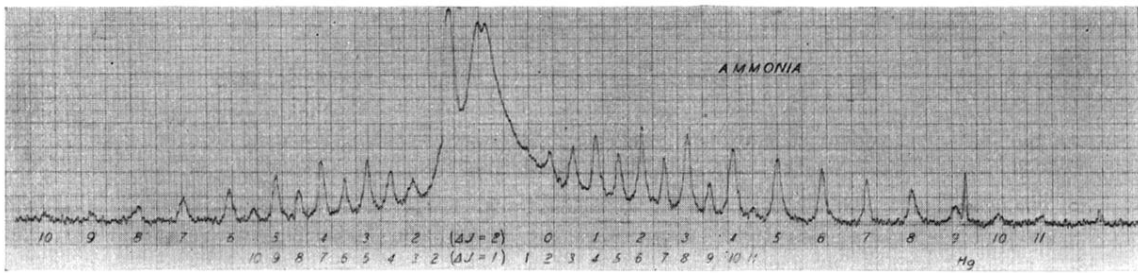


FIG. 1. Microphotometer curve of the pure rotation spectrum of ammonia.