RAMAN SPECTRA OF POLYATOMIC GASES

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Abstract

Raman spectra of gaseous CO_2, N_2O, NH_3, CH_4 and C_2H_4 have been photographed using the line $\lambda 2536$ of mercury as the exciting radiation. Vibrational transitions have been observed in all the gases investigated, and rotational transitions in the cases of NH_3 and CH_4. For the frequency shifts due to the vibrational transitions, the following numerical values (in cm^{-1}) have been found:

CO_2: 1264.5; 1285.1; 1387.7; 1408.4.
N_2O: 1281.8
NH_3: 3333.6
CH_4: 2914.8; 3022.1; 3071.5.
C_2H_4: 1342.4; 1623.3; 2880.1; 3019.3; 3240.3; 3272.3.

Raman spectra of liquid NH_3 have been photographed and found to give the two frequency shifts: 3298.4 and 3214.5. In the case of gaseous NH_3, pure rotational transitions lead to a moment of inertia having the value $I_0 = 2.79 \times 10^{-40}$. In the case of methane, the positive and negative branches of the 3022.1 band lead to the value $I_0 = 5.17 \times 10^{-40}$. The relations between these data and infra-red absorption data are discussed.

Introduction

Only one Raman line was found; this was rather weak but sharp. The frequency shift, $\Delta\nu$, was 1281.8. An infra-red absorption of this frequency would lie at 7.8μ; we are not aware of data showing any band at this wave-

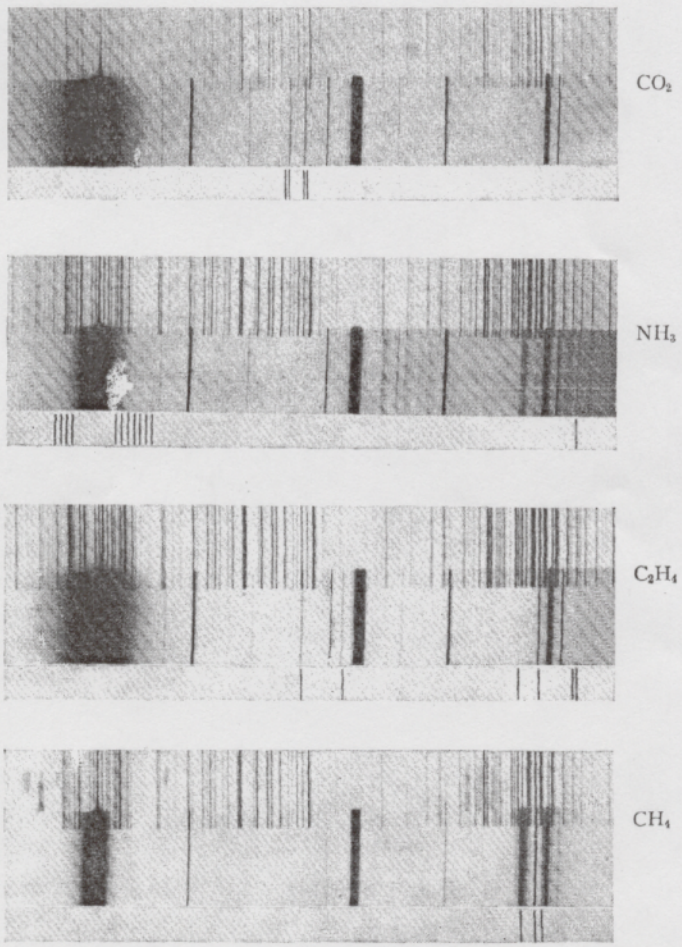


Fig. 1. Raman Spectra of Carbon Dioxide, Ammonia, Methane, and Ethylene excited by the line λ2536 of mercury; the comparison spectrum is that of the iron arc.

length. However, the at least approximate agreement of the frequency measured by us with the difference between the frequencies corresponding to the prominent absorptions given by E. v. Bahr[8] as occurring at 2.86 and 4.49μ, may be significant.

[8] E. v. Bahr, Verh. D. Phys. Ges. **15**, 710 (1913).

Ammonia. The gas was taken from a commercial cylinder, and the exposure tube was filled at a pressure slightly less than that of the saturated vapor at room temperature.

Unresolved fluorescence bands extending from λ2700 through the visible appeared on the plates; but in the region in which the Raman lines occurred, the bands were weak enough not to interfere with the measurements. The spectrum is shown in the figure. In addition to a vibrational line corresponding to $\Delta\nu = 3333.6$, rotational lines could be measured on both sides of the line λ2536. These appear to correspond to a change of ± 2 in rotational quantum number as is shown in Table II. The assumed change in rotational quantum number is given in the first column, and the observed values of the frequency shifts in the second. The calculated values of the frequency shifts given in the third column were obtained from the expression:

TABLE II. *Pure rotational Raman lines from gaseous ammonia.*

Transition	$\Delta\nu$ obs. (cm^{-1})	$\Delta\nu$ calc. (cm^{-1})	diff.
7→9	−334.8	−334.2	−0.6
6→8	−294.6	−295.5	+0.9
5→7	−256.0	−256.5	+0.5
4→6	−217.0	−217.4	+0.4
3→5	−178.7	−178.1	−0.6
2→4	−138.7	−138.7	0.0
1→3	− 99.6	− 99.1	−0.5
4→2	+138.2	+138.7	+0.5
5→3	+178.7	+178.1	−0.6
6→4	+217.4	+217.4	0.0

$$\pm\Delta\nu = (E_{m+2} - E_m)/hc$$

in which E_m, the energy of the mth rotational state was assumed to be given by:

$$E_m/hc = 9.921(m+\tfrac{1}{2})^2 - 0.00063(m+\tfrac{1}{2})^4$$

This rotational band corresponds to a moment of inertia, $I_0 = 2.792 \times 10^{-40}$. This may be compared with the value, 2.77×10^{-40}, obtained by Badger and Cartwright[9] from pure rotational absorption bands, and with the value, 2.83×10^{-40}, deduced by Stinchcomb and Barker[10] from the absorption band at 3.0μ. These authors give for the frequency of the center of this band 3337.0, which agrees fairly well with our value 3333.6.

We have thought it interesting to make an accurate comparison of the Raman shifts given by the liquid and gaseous states of ammonia. Liquid ammonia was distilled into the heavy walled glass tube in which it was to be irradiated, and was sealed up. The exciting radiation was from a mercury arc. The spectrum was photographed with a two-prism glass spectrograph of aperture f8 and a dispersion of about 100 wave-numbers per mm in the blue. The frequencies of the shifted lines were evaluated with an iron arc comparison spectrum as with the quartz instrument. The results are given in Table III.

[9] Badger and Cartwright, Phys. Rev. **33**, 692 (1929).
[10] Stinchcomb and Barker, Phys. Rev. **33**, 305 (1929).

From these results, it appears that liquid ammonia gives two Raman shifts, a strong one having $\Delta\nu = 3298.4$ and a somewhat weaker one having $\Delta\nu = 3214.5$; the disagreement between the frequency shifts in the liquid and gas lies well outside of the experimental error.

Methane. Samples of methane from two different sources were examined. The first sample was prepared by heating a mixture of sodium acetate and soda-lime. The gas was passed through a solution of KOH and then through concentrated H_2SO_4. It was then condensed to the liquid state from which it was evaporated into the apparatus under pressure.

TABLE III. *Raman spectra from liquid ammonia.*

Observed frequency.	Intensity	Exciting wave-length	Exciting frequency	Frequency shift
24176.0	weak	3650.15	27388.4	3212.4
24088.8	med. (broad)	3650.15	27388.4	3299.6
		(3663.27)	(27290.5)	(3201.7)
24053.4	weak	3654.83	27353.3	3299.9
23994.2	medium	3663.27	27290.5	3296.3
21490.9	strong	4046.56	24705.5	3214.6
21407.0	very strong	4046.56	24705.5	3298.5
19722.8	weak	4358.34	22938.1	3216.3
19638.8	weak	4358.34	22938.1	3299.3

The second sample was purified from a natural gas which originally contained 80% methane. A photograph made before purification showed a strong fluorescence which we attributed to heavier hydrocarbons. The treatment of the gas consisted in admitting it at about 800 pounds per sq. in. pressure into a cylindrical bomb filled with absorbent charcoal previously heated and evacuated. While the purified gas was slowly withdrawn from one end of the bomb and expanded into the apparatus, the pressure in the bomb was maintained at 800 pounds by admitting raw gas at the other end. Separate experiments have shown this procedure to give methane of about 99% purity. The methane so purified showed no fluorescence.

TABLE IV. *Rotation-vibrational Raman lines from methane.*

Transition	$\Delta\nu$ obs. (cm^{-1})	$\Delta\nu$ calc. (cm^{-1})	diff.
10→12	3261.2	3261.0	−0.2
9→11	3241.0	3240.7	−0.3
8→10	3220.5	3220.4	−0.1
7→ 9	3199.8	3199.9	+0.1
6→ 8	3178.4	3179.4	+1.0
5→ 7	3159.0	3158.7	−0.3
4→ 6	3137.2	3138.0	+0.8
3→ 5	3117.7	3117.1	−0.6
6→ 4	2901.5	2903.1	+1.6
7→ 5	2881.3	2881.2	−0.1
8→ 6	2859.8	2859.1	−0.7
9→ 7	2837.0	2837.0	0.0
10→ 8	2814.1	2814.7	+0.6

The spectra given by the methane from these two sources were identical; we believe, therefore, that there is little question that any of the observed lines resulted from impurities. The spectrum is shown in the figure.

Three vibrational Raman lines were found in the spectrum. One of them was very strong (relative intensity, 20); it was sharp, and corresponded to a shift $\Delta\nu = 2914.8$. One line was rather weak (intensity, 2) with $\Delta\nu = 3071.5$. The remaining line was of intermediate strength (intensity, 5); it was rather broad and shaded off on the short wave-length side. The frequency shift corresponding to its sharp edge was $\Delta\nu = 3022.1$. On both sides of this last line, a number of weak and approximately equally spaced lines were measured. These appear to constitute the positive and negative branches of the band of which the line at $\Delta\nu = 3022.1$ is the unresolved Q branch. In interpreting this band, a change of ± 2 in rotational quantum number has again been assumed. The results are given in Table IV; in the first column is given the change in rotational quantum number m, in the second, the observed shift, and in the third, the shift calculated from the following expressions for the energy in the normal state and in the excited vibrational state:

$$E_0/hc = 5.363(m+\tfrac{1}{2})^2$$
$$E_1/hc = 3022.1 + 5.313(m+\tfrac{1}{2})^2$$

For the normal state, a moment of inertia $I_0 = 5.17 \times 10^{-40}$ may be calculated from these results. The vibrational shift agrees fairly well with the value 3019, given by Cooley[11] for the band at 3.31μ. The spacing of the lines near the center of this band was found by Cooley to be 9.77 cm^{-1}, which leads to a moment of inertia, $I_0 = 5.66 \times 10^{-40}$. Although this is not very far from our value, the disagreement seems to be well outside the experimental error. The other two vibrational frequencies observed by us do not seem to correspond to any infra-red absorption.

It may be remarked that the frequency 2914.8 observed by us, practically coincides with the difference between two observed infra-red frequencies, 4217 and 1304, which Dennison[12] assumes to be fundamentals. If this is more than a coincidence, Dennison's choice of fundamental frequencies can hardly be correct, because in this case, this very strong Raman line would have its origin in molecules thermally excited with an energy corresponding to the frequency 1304; this appears highly improbable.

Ethylene. The gas used was a commercial product prepared for anaesthetic purposes, and given as 99.2% pure.

The scattering by this gas was particularly strong, so that Raman lines could be photographed in a few hours. The spectrum is shown in the figure. A strong unresolved rotational band appeared close to the exciting line. Six shifts were measured and are given in Table V.

TABLE V. *Frequency shifts for ethylene.*

$\Delta\nu$ (cm^{-1}):	1342.4	1623.3	2880.1	3019.3	3240.3	3272.3
Intensity:	20	15	3	20	2	1

[11] J. P. Cooley, Astroph. Journ. **62**, 73 (1925).
[12] D. M. Dennison, Astroph. Journ. **62**, 84 (1925).

No agreement appears to exist between these frequencies and those of the centers of the infra-red bands as given by Levin and Meyer.[13]

Discusson

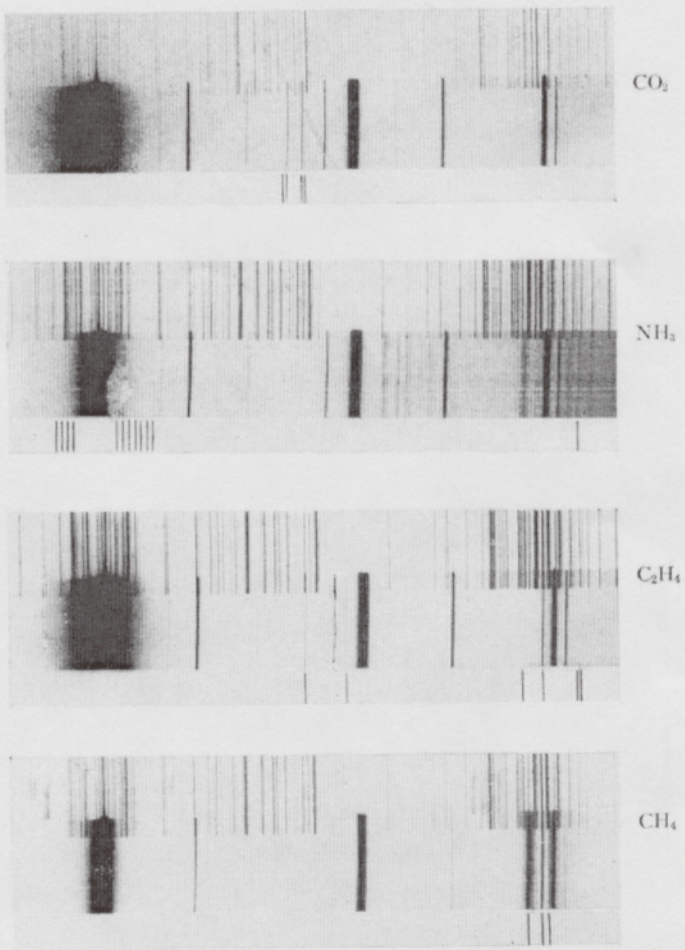
One striking fact which appears from these results is that the Raman spectra consist usually of a few sharp lines in contrast with the large number of lines observed in infra-red absorption bands. This is observed also in diatomic molecules and for these, has been discussed theoretically by Hill and Kemble.[14] The Q branch of vibrational-rotational bands (generally unresolved) is much stronger in Raman effect than the positive and negative branches and is practically always the only one observed, while in infra-red absorption spectra the Q branch is absent. The same is apparently true of the Raman spectra of polyatomic molecules. Therefore, we believe that the isolated lines generally observed in these spectra must be interpreted as unresolved Q branches, and that they usually give energy differences between vibrational levels.

Another striking fact, already well-known in the case of liquids, is that the majority of the Raman shifts do not correspond to vibrational frequencies observed in absorption. This is strikingly exemplified by the data on CO_2 where no coincidence is found between the several frequencies observed in Raman effect and the large number in absorption. In many cases, this can no doubt be attributed to the fact first pointed out by Carrelli, Pringsheim and Rosen[15] that shifts corresponding to inactive frequencies (that is, frequencies which are not associated with a variable electric moment of the molecule, and which, therefore, do not give rise to emission or absorption of radiation) can appear in the scattering process. This is due to the fact that the occurrence of a transition between two quantum states in the Raman effect does not depend on the properties of these states only; but, also, on those of all the levels which combine with both of them.[5] It also follows that it is not possible to account for the occurrence or otherwise of all the transitions between vibrational levels without taking into account electronic bands. As very little is at present known about electronic bands in polyatomic molecules, we cannot predict theoretically the intensities of vibrational and rotational lines in Raman effect.

The question arises as to which frequencies are to be considered fundamental in cases, like that of CO_2, where completely different frequencies are found in absorption and in Raman effect. It is an experimental fact and has been deduced theoretically by Manneback,[16] that in diatomic molecules shifts corresponding to the harmonics of the fundamental frequency occur with very low intensity. This appears to be true for polyatomic molecules also. It accordingly seems natural to assume that transitions from the normal state to states in which two different vibrations are simultaneously excited

[13] A. Levin and C. F. Meyer, Journ. Opt. Soc. Am. **16,** 137 (1928).
[14] E. L. Hill and E. C. Kemble, Proc. Nat. Acad. Sci. **15,** 387 (1929).
[15] A. Carrelli, P. Pringsheim and M. Rosen, Zeits. f. Physik **51,** 511 (1928).
[16] C. Manneback, Naturwissenschaften **17,** 364 (1929).

(and have energies corresponding to approximately the sum of the two frequencies), also have small probabilities. If this is true, and if we assume that in the molecules considered, we have no vibration frequencies low enough to give an appreciable proportion of molecules in excited states at room temperature, then the strong lines observed in Raman effect appear to correspond to fundamental frequencies. Combination frequencies may occur among the weaker Raman lines. It is also possible, although it does not seem very likely in the case of the molecules investigated here, that some of the Raman lines may be due to electronic transitions arising from a multiple structure of the normal electronic level as is the case for some diatomic molecules.



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