

DEFORMATION FREQUENCIES IN THE RAMAN SPECTRA OF LINEAR MOLECULES: ACETYLENE.

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1. Introduction.

THE fundamental vibrations of a linear molecule may be divided into two different types, *viz.*, the valency vibrations and the deformation vibrations. If the molecule possesses a centre of symmetry a further sub-division may be effected under the headings (i) totally symmetrical and (ii) antisymmetrical vibrations (Mecke, 1931). Of these various types, we may expect the total symmetric ones of both the valency and deformation vibrations to be 'Raman-active'. It must, however, be mentioned that the selection rules regarding the rotational structure differ very considerably in the two cases (Placzek, 1934). For valency vibrations we should expect a strong Q branch accompanied by O and S branches ($\Delta J = \pm 2$) and numerous examples of this type have already been found in the Raman spectra of gases like CO_2 , N_2O , etc. On the other hand, a deformation vibration should consist of only an extremely feeble Q branch accompanied by both O and S branches ($\Delta J = \pm 2$) and P and R branches ($\Delta J = \pm 1$) of normal intensity. No examples of this type have yet been experimentally observed in Raman spectra. Acetylene gas constitutes a very favourable case from this point of view. In this paper, is obtained and described a particularly intense Raman spectrum of this substance showing a pair of Raman bands at $\Delta \nu 600$ arising from a deformation vibration. The structure of this band agrees satisfactorily with the theoretical predictions.

2. The Normal Vibrations of the Acetylene Molecule.

The normal vibrations of the acetylene molecule have been discussed in detail by Mecke (*loc. cit.*) and by Sutherland (1935) and are represented diagrammatically in Fig. 1.

In the description of the diagram π stands for 'parallel' or valency oscillations and δ for 'perpendicular' or deformation oscillations. s and a stand for symmetric and anti-symmetric types respectively. It will be noticed

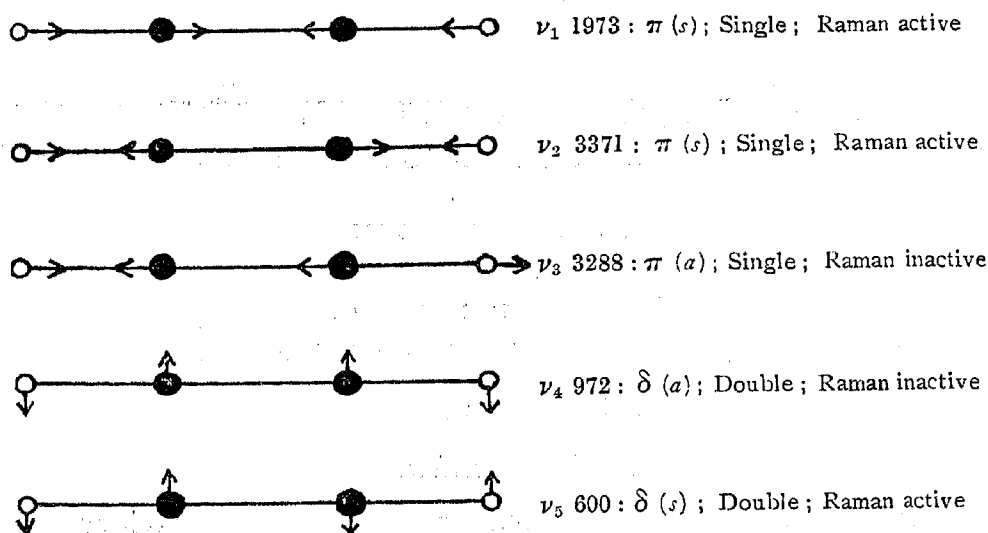


FIG. 1.

that of the three 'Raman-active' oscillations two are of the valency type and have already been observed in the Raman spectrum of acetylene gas (Bhagavantam, 1931). The third one is a deformation oscillation and has not yet been recorded in the Raman spectrum. From a detailed study of the combination bands appearing in the infra-red absorption spectrum of acetylene, Mecke and Sutherland have however deduced that its value should be about 600.

3. Raman Spectrum of Acetylene.

Using a 2-prism glass spectrograph, the Raman spectrum of acetylene gas is obtained at a pressure of 18 atmospheres by giving an exposure of about 28 days. The picture is reproduced in the plate accompanying this paper. The pair of bands at about $\Delta\nu$ 600 excited both by λ 4046 and λ 4358 and recorded here for the first time are marked with arrows. It is proposed to interpret these as the unresolved O P and R S branches of the total symmetric deformation oscillation for which the Q branch is of negligible intensity. Measurements of the individual lines are contained in Table I (see next page).

The values given below the Table for ν_1 and ν_2 are the mean figures and are in good agreement with those reported earlier (Bhagavantam, 1931). It may also be noted that the mean of the two bands excited by 4358 is 617 whereas the mean of the corresponding bands excited by λ 4046 is 613. In view of the breadth of the bands the discrepancy is not very much and an average figure of 615 is assigned for ν_5 . The very faint line with a shift of 1941 wave numbers is to be attributed to the isotopic molecule $C_{12}C_{13}H_2$. This aspect is being investigated in greater detail by extending it to similar

TABLE I.
Raman Spectrum of Acetylene.

Wave-length	Intensity	Exciting line	Frequency
4768.4	10	4358	1972
4686.3	3	4046	3372
4606.0	0	4358 (?)	1233
4484.8	1 <i>b</i>	4358	646
4473.3	1 <i>b</i>	„	589
4435.0	1	4077	1974
4397.8	10	4046	1973
4391.7	0	„	1941
4179.2	1	3663	3372
4168.0	1	3654	3368
4162.2	2	3650	3370
4154.0	0 <i>b</i>	4046	639
4145.2	0 <i>b</i>	„	587
3948.7	3	3663	1975
3938.7	3	3654	1972
3933.4	5	3650	1973

$\nu_1 = 1973$ (10); $\nu_2 = 3371$ (3); $\nu_5 = 615$ (0)
1941 (0).

molecules such as ethylene and will be dealt with by one of us in a later communication. There is, however, another very weak but a definite line at $\lambda 4605 \cdot \lambda 0$ which, if attributed to $\lambda 4358$, gives a frequency shift of 1233. The origin of this is not clear.

4. Discussion of Results.

The most outstanding feature of the present investigation is the pair of bands at about $\Delta \nu 600$. It is suggested that they represent the maximum

of the unresolved rotational wings accompanying the total symmetric deformation oscillation of acetylene. The following points constitute the evidence in favour of such a suggestion.

The mean position of the bands corresponds to a frequency shift of 615 cm.^{-1} which is in agreement with the figure derived indirectly from infrared absorption.

In a deformation vibration, we should expect the Q branch to be of negligible intensity in comparison with the O, P, R and S branches and this is confirmed.

The separation of the maxima is 57 cm.^{-1} for the pair of bands excited by $\lambda 4358$ and 52 cm.^{-1} for those excited by $\lambda 4046$. The former figure, which is more reliable, is in excellent agreement with the theory. In Fig. 2, the

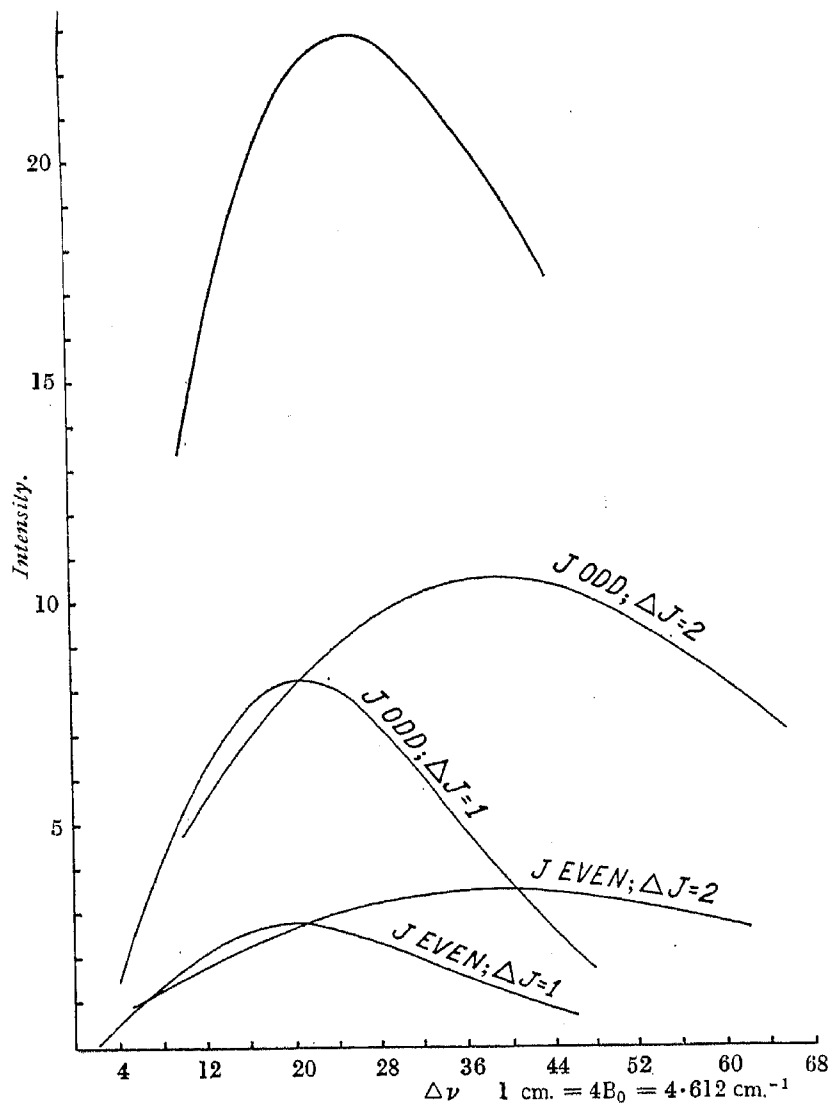
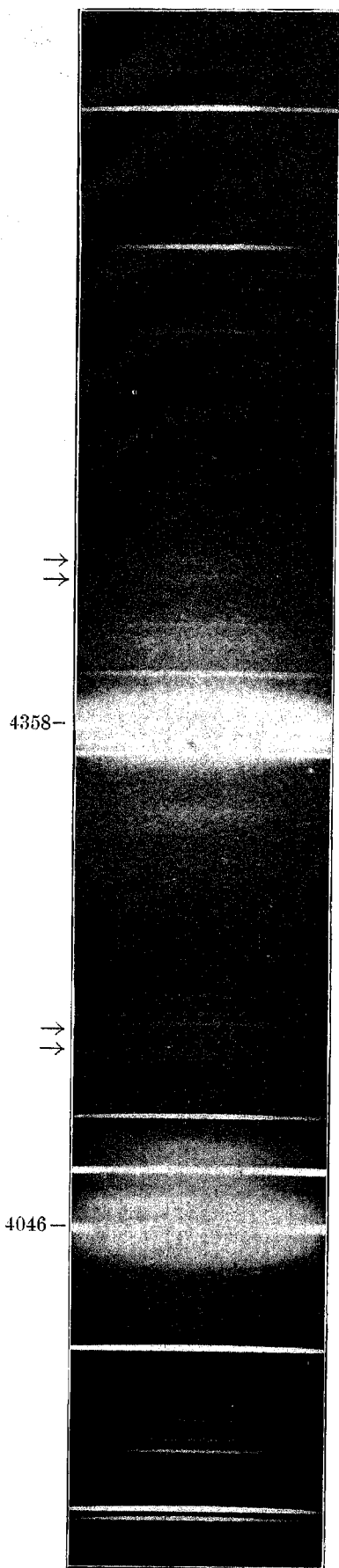


FIG. 2.



Raman Spectrum of Acetylene gas.