



Raman Effect of Acetylenes. I. Methyl, Dimethyl and VinylAcetylene

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agreement with those obtained by other methods.

Dornte^{22, 34} has reversed the procedure of Braune and Knoke, using the simplified theoretical curves for determining the x values and correlating them with experimental values taken by some undescribed procedure from microphotometer records. As mentioned above, Dornte's interatomic-distance value for carbon tetrachloride is 4 percent too high. We have repeated Dornte's work on carbonyl compounds, with the help of Mr. J. Y. Beach, and shall soon publish the results of the investigation.

³⁴ R. W. Dornte, *J. Chem. Phys.* **1**, 630 (1933); *J. Am. Chem. Soc.* **55**, 4126 (1933).

Cosslett and de Laszlo²⁵ in their short note on carbon tetrachloride do not describe their method in detail. They find, as we do, that the first two rings on a short-distance photograph have apparent diameters corresponding to too small values of the interatomic distances.

A preliminary note on carbon suboxide has been published by Boersch.³⁵

³⁵ H. Boersch, *Naturwiss.* **22**, 172 (1934). Boersch reports a structure for carbon suboxide different from that found by us (*Proc. Nat. Acad. Sci.* **19**, 860 (1933)). We have calculated the theoretical curve based on his model and find pronounced disagreement with our photographs. A more complete comparison of results will be made after his detailed publication has appeared.

Raman Effect of Acetylenes. I. Methyl-, Dimethyl- and Vinyl-Acetylene

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(Received September 27, 1934)

An improved helical discharge tube containing neon and mercury with a saturated solution of sodium nitrite as filter served as a monochromatic source of radiation (4358 Hg). A mechanical filter avoided overexposure of the exciting radiation. The vibration frequencies were studied on the basis of the symmetry properties of the molecules and the usual assignments have been made.

Faint rotation lines were found accompanying the C:C vibration in liquid dimethyl-acetylene. They are interpreted as rotation of the six hydrogen atoms around the figure axis of the molecule. The moment of inertia is $I = 10^{-39}$ g \times cm². The three compounds were studied in the liquid state.

INTRODUCTION

SEVERAL new features of experimental technique have been developed and thoroughly tried and since the resulting spectrograms are of excellent quality, it seems worth while to describe them.

NE-Hg DISCHARGE TUBE

The ordinary mercury arc is quite an expensive piece of apparatus and it is usually inconvenient to run it for long periods; if there are voltage variations it is liable to be extinguished. Further-

more, the arc runs hot and it is not possible to place it very near a Raman tube containing a liquefied gas. For these reasons a helical discharge tube on the principle of the usual "neon-sign" was developed and has been used in this laboratory for several years.² The design can best be seen from Fig. 1 (A, C and D). The helix is made of quartz, corex-D or Pyrex glass. The electrodes are made of copper or iron and are large in area so that at 6600 volts 300 milliamperes pass the tube. It contains a drop of liquid mercury and several mm of neon gas. The tube runs quite cool. One can just hold one's hand on the surface. As

¹ This article is based upon a thesis presented to the faculty of the Graduate School of the University of Minnesota by H. M. Davis in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. For a preliminary note on methyl-acetylene see *Phys. Rev.* **41**, 370 (1932).

² R. W. Wood (*J. Frank. Inst.* **208**, 617 (1929)) has used a helical discharge tube containing helium. The Hanovia Chem. & Mfg. Co., manufactures lamps similar to the one discussed here. However, the tubes used in this laboratory carry a much greater current than any others described so far.

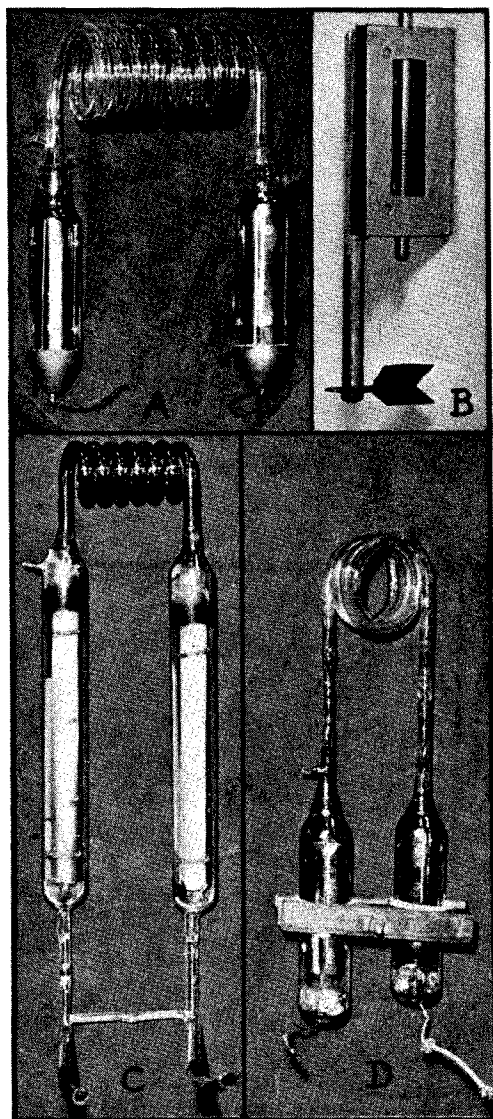


FIG. 1.

in the construction of "neon-signs" it is of great importance to out-gas the electrodes and glass-walls during the process of manufacture. One such tube has served now for 1400 hours and it is still giving good service. The area of the electrodes is determined by the rule of Claude: 1.5 dm^2 per ampere.

ELIMINATION OF OVEREXPOSURE

The exciting line for example 4358 Hg becomes greatly overexposed during the long period

needed to bring out the weaker Raman lines. The unmodified line is usually completely hidden by a complete blackening of the photographic plate which may also hide some of the scattered frequencies of small wave number. In order to avoid this difficulty a mechanical filter was placed inside of the plateholder of the spectrograph in front of the photographic plate. It prevented the scattered light (4358A) from reaching the photographic plate. However, an initial exposure of about 15 minutes served to record the unmodified line. This procedure made it possible to use 4339A Hg as a reference line for the measurement of the plate. This line appeared on the spectrogram as a very sharp line and served the purpose admirably. The mechanical filter is shown in Fig. 1B and the results which can be obtained by its use are shown in Fig. 2.

PHOTOGRAPHIC PLATES

Eastman Hyper Press Plates proved most satisfactory on account of their high speed, their insensitivity in the extreme red and their high sensitivity in the blue-green. This region in the spectrum was of most interest for 4358A Hg was used as exciting radiation rather than ultra-violet light for fear that photochemical action might become troublesome with the compounds studied. The plates mentioned above proved most satisfactory for all the work except that of photographing the C-H frequency (3300 cm^{-1}) which falls in the region 5100A when excited by 4358A. Eastman spectroscopic plates, type 1-J specially sensitized for the region were found most satisfactory.

METHYL-ACETYLENE

The maximum number of vibration frequencies (f) to be expected from a molecule depends on the number of degrees of freedom which, in turn, depends on the number of atoms (N) of the molecule reduced by six (translation and rotation) $f = 3N - 6$.

However, this number is reduced^{3,4} if the molecule has symmetry. Methyl-acetylene should

³ C. J. Brester, *Kristall-Symmetrie und Rest-strahlen*, Diss., Utrecht (1923) and *Zeits. f. Physik* **24**, 324 (1924).

⁴ G. Placzek, *Leipziger Vorträge*, Verlag S. Hirzel, Leipzig (1931).

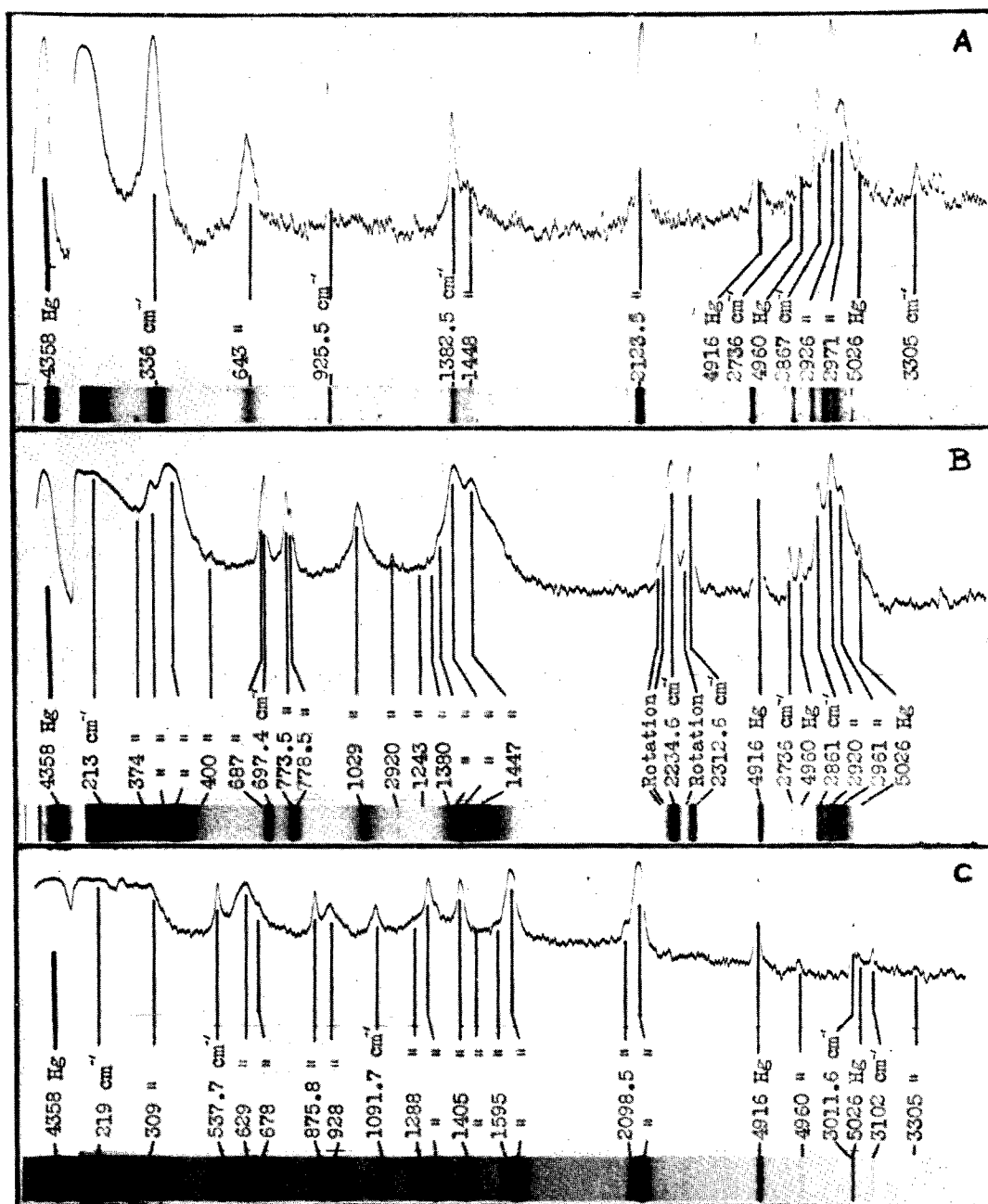


FIG. 2. Raman spectra of liquid methyl acetylene (A), dimethyl-acetylene (B) and vinyl-acetylene (C) excited by 4358 Hg.

TABLE I. Number of vibration frequencies of methyl-acetylene. Seven atoms; $f = 7 \times 3 - 6 = 15$; symmetry group = C_{3v} .³ (Molecular axis = z-axis.)

Type	Number of frequencies			Kind	Electric moment
	Total	Zero	Net		
A_1	2+4	1	5	active	$M(x) = M(y) = 0$; $M(z) \neq 0$
A_2	1	1	0	inactive	
B_1	0	0	0	inactive	
B_2	0	0	0	inactive	
C	3+4	2	5	active, double	$M(xy) \neq 0$; $M(z) = 0$
D	0	0	0		
	21	6	10		

show a maximum of 15 frequencies since it contains seven atoms. Since it, however, possesses symmetry of the type C_{3v} this number of frequencies is reduced to ten (Table I) of two groups of five each. The threefold symmetry axis of the molecule contains the three carbon atoms and the hydrogen attached to the carbon of the acetylene bond. The three hydrogen atoms of the methyl group give the molecule its threefold symmetry.

Not all of these frequencies need show up in the Raman effect or in infrared absorption. Infrared absorption is possible if the electric moment of the molecule changes during the transition and Raman lines have intensity other than zero if the polarizability of the molecule changes with changes in nuclear distances during the process of interaction with the incoming quantum.^{5, 6, 7} In general this situation depends greatly upon the constitution of the molecules and upon the type of vibration involved. In other words, the ten vibrations considered may be "infrared active" and/or "Raman-active."

The results of the experimental work show that there are eleven Raman frequencies (Fig. 2 and Table II). One of them can be interpreted as an overtone and the other ten fall into two groups: five of them are very sharp lines and the five others are broad. Within the two groups the frequencies arrange themselves in inverse proportion to the reduced mass (proportional to $m_1 \times m_2$) of the vibrating systems.

⁵ G. Placzek, Zeits. f. Physik **70**, 84 (1931).

⁶ G. Placzek and E. Teller, Zeits. f. Physik **81**, 209 (1933).

⁷ L. Tisza, Zeits. f. Physik **82**, 48 (1933).

TABLE II. Raman-lines of methyl-acetylene. Two types: $A_1(M(z) \neq 0)$ and $C(M(xy) \neq 0)$. (b = broad, s = sharp) (\downarrow) = perpendicular to valency bond; (\rightarrow) = parallel to valency bond.

Mode	cm ⁻¹	Inten- sity	μ	
			Type	C A
(H ₃ C) \downarrow , C \uparrow : C \uparrow , H \downarrow	336	9(b)	C	384
(H ₃ C) \downarrow , C \uparrow : (CH) \downarrow	643	5(b)	C	336
(H ₃ C) \rightarrow \leftarrow (C : CH)	929.5	8(s)	A	375
H \uparrow , H ₂ \downarrow , (C.C : C) \uparrow , H \downarrow	1382.5	6(b)	C	111
H \uparrow , H \downarrow , (HC.C : CH)	1448	2(b)	C	76
(H ₃ C).C \rightarrow : \leftarrow C.(H)	2123.5	11(s)	A	351
2 \times 1382.5	2736	1(b)	—	—
(H ₃) \rightarrow \leftarrow (C.C : C).H \rightarrow	2867	6(s)	A	144
(H ₃) \rightarrow \leftarrow (C.C : CH)	2926.2	10(s)	A	111
H \rightarrow \leftarrow (H ₂ C.C : CH)	2971	4(b)	C	39
(H ₃ C.C : C) \rightarrow \leftarrow H	3305	2(s)	A	39

Modes of vibration

336 and 643 cm⁻¹. The two lowest frequencies in methyl-acetylene are thought to be deformations⁸ and to the lower frequency the larger reduced mass has been ascribed.

929.5 cm⁻¹. This frequency is in the range ascribed by Dadiou and Kohlrausch⁹ to the vibration of an end methyl-group against the rest of the molecule. They trace this vibration from 990 cm⁻¹ in ethane to 870 cm⁻¹ in propane and 843 cm⁻¹ in pentane. In the odd paraffin molecules longer than ethane the frequency appears to split into three, as in propane, 870, 940, 1050 cm⁻¹.

1382.5 cm⁻¹. It seems to depend upon the presence of a methyl-group attached to an unsaturated carbon atom. It is not present in the paraffins and frequencies in this range appear in olefines only when a CH₂ or CH₃ group is adjacent to an ethylenic carbon. In substituted acetylenes a CH₂-group next to the acetylenic carbon gives a frequency of 1320–40 cm⁻¹; but a CH₃ group so located gives always the frequency found here, i.e., 1380 cm⁻¹:

Methyl acetylene	1382.5 cm ⁻¹
Dimethyl acetylene	1379.5 " ¹⁰
Methyl, <i>n</i> -amyl acetylene	1384 " ¹¹
Methyl, phenyl "	1383 " ¹¹

⁸ R. Mecke, Zeits. f. Elektrochemie **36**, 589 (1930).

⁹ Dadiou and Kohlrausch, Ber. **63**, 273 (1930).

¹⁰ See below.

¹¹ Bourguet and Daure, Bull. Soc. Chim. **47/48**, 1349 (1930).

This frequency is ascribed to a deformation involving the hydrogen atoms of the methyl group as indicated in Table II.

1448 cm^{-1} . It seems well established that this frequency occurs only when a carbon atom bearing at least two hydrogen atoms is present in the molecule. Its essential constancy found in the most different compounds indicates that it is an "inner frequency" of the CH_2 or CH_3 group. Any frequency involving the C-H binding and yet so low must be of the deformation type. It is ascribed to the transverse swing of two hydrogen atoms.^{12, 13}

2123.5 cm^{-1} . All compounds containing triply bound carbons (acetylene bond) show a vibration in this immediate neighborhood. (See, however, vinyl-acetylene below.)

2736 cm^{-1} . Because of its extreme weakness and for the fact that it lies below the usual range of C-H frequencies this line is regarded not as a fundamental but as the first harmonic of 1382 cm^{-1} . Since it is slightly less than double it would indicate that the motion is anharmonic to some extent. It might be a combination tone of 2123.5 and 643 cm^{-1} . But this assignment appears improbable when it is pointed out that isobutylene shows that frequency strongly.¹ In this case the first interpretation is the only one possible.

2867, 2926.2, 2971 cm^{-1} . These frequencies are due to the motions of the hydrogen atoms. The highest one is ascribed to the motion of one hydrogen atom only along its valency direction. Of course, the remainder of the molecule moves appropriately relative to the center of gravity, although the extent of this displacement would be very small. The reduced mass involved would be smallest if one hydrogen atom only vibrates, giving rise to the largest C-H frequency. From an appropriate model it can be seen that the electric moment is most likely changed in direction perpendicular to the symmetry axis. The symmetry axis is the Z-axis and for this motion $M(z)=0$ (see Table I). Having disposed of this vibration it is possible to ascribe 2926.2 and 2867 cm^{-1} to the symmetrical and asymmetrical frequencies as they appear also in methane. It appears that the frequencies

2926.2, 2867, 1448 and 1382.5 have to one another the same relation as have the frequencies 3022, 2915, 1520, 1304 in methane.¹⁴

3305 cm^{-1} . The hydrogen atom attached to an acetylenic carbon atom causes this motion.

It is to be pointed out that the ten frequencies considered to be fundamentals fall into two groups as concerns their appearance and that the assignments made also follow this same division. All the sharp lines are of a character such that the change of electric moment involved is along the symmetry axis (Z-axis) and the broad, diffuse lines are of a type of motion involving changes in the moment perpendicular to the symmetry axis ($M(xy) \neq 0$; $M(z)=0$). It appears that all of the fundamental frequencies of methyl-acetylene are "Raman-active." While they have been discussed on the usual basis of vibration of certain bonds or groups, it must be stated that the molecule as a whole executes the vibration. The modes of vibration, their type, intensity and character of the lines pertaining to them agree and give a satisfactory picture of the fundamental motions of this molecule.

DIMETHYL-ACETYLENE

The molecule contains ten atoms and should have twenty-four frequencies. Fifteen frequencies

TABLE III. Number of vibration frequencies of dimethyl acetylene. Ten atoms; $f=10 \times 3 - 6 = 24$; symmetry group: D_{3h} .³

Type	Number of Frequencies			Kind	Electric moment
	Total	Zero	Net		
A_1'	2+2		4	inactive; sym.	$\Delta M=0$
A_1''	2+2	1	3	active; asym.	$M(z) \neq 0$
A_2'	1	1	0	inactive; sym.	$\Delta M=0$
A_2''	1		1	inactive; asym.	$\Delta M=0$
C'	3+2	1	4	active; sym; double	$M(xy) \neq 0$
C''	3+2	1	4	inactive; asym; double	$\Delta M=0$
	30	6	16		
Symmetry group: S_6					
A	3+2	1	4	inactive; sym	$\Delta M=0$
B	3+2	1	4	active;	$M(z) \neq 0$
C	3+2	1	4	active; double	$M(xy) \neq 0$
D	3+2	1	4	inactive; double	$\Delta M=0$
	30	6	16		

¹² Dadiou and Kohlrausch, Ber. 63, 262 (1930).

¹³ Cross and Daniels, J. Chem. Phys. 1, 52 (1933).

¹⁴ R. Mecke, *Leipziger Vorträge*; Verlag von S. Hirzel, Leipzig (1931), p. 23.

TABLE IV. Raman lines of dimethyl-acetylene. Four types $A(\Delta M=0)$; $B(M(x) \neq 0)$; $C(M(xy) \neq 0)$; $D(\Delta M=0)$.

Mode	cm ⁻¹	Inten- sity	Type	$m_1 \cdot m_2$	Mode	cm ⁻¹	Inten- sity	Type	$m_1 \cdot m_2$
H ₃ ↑.C ₂ ↓ : C ₂ ↑.H ₃ ↓	213	1(b)	A	729	H↓.H↑.HC.C : C.CH ₃	1447	4(b)	D	104
H ₃ C↓.C↑ : C↓.CH ₃ ↑	374	5(b)	D	729	Rotation	2179.45	1(s)	—	—
H ₃ C↓.C : C↑.CH ₃ ↓	400	0(b)	C	720	"	2201.40	1(s)	—	—
H ₃ C↓.C.C : CH ₂ ↑.H↓	687	3(b)	C	608	H ₃ C→.C→ : ←C.CH ₃ →	2234.60	6(s)	B	504
H ₃ C↓.H↑.C↓ : C↑.H↓.CH ₂ ↑	697.4	4(s)	D	729	Rotation	2280.2	1(s)	—	—
H ₃ C→.←C : C→.←CH ₃	773.5	4(s)	A	729	H ₃ C→.C→ : ←C.←CH ₃	2312.65	6(s)	A	729
H ₃ C→.←C : C.CH ₃ →	788.5	3(s)	B	720	2×1379.5	2736.8	2.5(s)	—	—
H ₃ C→.←C : C.CH ₃	1029	3(s; b)	B	585	H ₃ →.←C.C : C.C.H ₃ →	2861.8	4(s)	B	288
H ₃ ↓.C.C : C.C.H ₃ ↓	(1243)	0(b)	D	8	H ₃ →.C.C : C.C.←H ₃	2920	7(s)	A	9
H ₂ ↓.H↑.(C.C : C.C)↓.H↑.H ₂ ↓	1379	5(b)	C	104	H→.C.C : C.CH ₃	2961	3.5(b)	C	53

were found which could be ascribed to vibrations. Another one appears to be an overtone. Three weak lines indicate rotation of the molecule. They accompany the acetylenic carbon atom vibrations. The number of vibration frequencies found is less than the maximum number expected, indicating that the molecule has symmetry. It, of course, has threefold symmetry on the ordinary views of organic chemistry. If the two sets of three hydrogen atoms of the methyl-groups are located exactly below one another, then the molecule has a threefold axis of symmetry, three planes of symmetry containing the threefold symmetry axis and another plane of symmetry perpendicular to the threefold axis. There are furthermore three twofold axes of symmetry perpendicular to the threefold axis. The four carbon atoms are located on the threefold axis. The symmetry group would be D_{3h} and sixteen fundamental frequencies are to be expected (Table III). The same agreement between number of fundamentals expected and Raman lines found is obtained, when it is proposed that the hydrogen atoms of the two methyl groups are not located directly below one another, but that they are displaced by 60°. The point-group is then S_6 . Again sixteen fundamentals are to be expected. This number also agrees with the number of vibration lines found. In the last case the molecule contains a sixfold rotation reflection axis. The details of the expected frequencies are found in Table III. Since sixteen frequencies are expected, the attempt was made to locate another line on the Raman plates and a very weak line was found at 1243 cm⁻¹. The second arrangement of symmetry would be pre-

ferred, for, if the hydrogen atoms of the two methyl groups interact at all they would assume the puckered arrangement involved in a point system symmetrical to a rotation reflection axis. The attempt was therefore made to arrange the sixteen frequencies into four groups each. The results are shown in Table IV. Within the group A the first two frequencies are deformations and the lower frequency has the larger reduced mass. The same is true of the two vibration frequencies of this group. The frequencies of group B and C are also arranged in the inverse order of the reduced mass. In the fourth group D it is found that the reduced mass is the same for the first three frequencies. It must then be assumed that the force constant varies appropriately to account for the magnitude of the frequencies themselves. It should be noted that the Raman lines could be divided into two equal groups in regard to their appearance as sharp or broad lines. The double frequencies (C and D of S_6) could be identified with the broader lines. This division fitted quite well into the usual assignments of modes of vibration. For example, the "acetylene-bond" frequencies are relatively sharp and they fit into group A and B . It is of importance to note that the division of the Raman lines as sharp and broad was made before they were assigned into the groups shown in the tables.

Modes of vibration

213, 374 and 400 cm⁻¹. These low frequencies of dimethyl-acetylene are taken to be deformations. It should be noted that the modes of vibration assigned to various frequencies indicate in some cases only the general type of mo-

tion involved. It is possible to vary them to some extent. It seems natural to involve larger moving masses for the lower frequencies.

687 and 697.4 cm^{-1} . Because of the larger value of these frequencies, hydrogen atoms were supposed to be involved in these deformations similar to 643 cm^{-1} in methyl acetylene.

773.5, 788.5 and 1029 cm^{-1} . Since these frequencies are in the neighborhood of 990 cm^{-1} they are ascribed to the C—C bond.

1379 cm^{-1} . This frequency is ascribed to a motion similar to the one which refers to 1382.5 cm^{-1} in methyl-acetylene.

1447 cm^{-1} . It is found as 1448 cm^{-1} in methyl-acetylene.

2234.6 and 2312.6 cm^{-1} . They refer to the acetylene bond and are asymmetrical and symmetrical frequencies, respectively.

2736.8 cm^{-1} . This vibration is thought to be the overtone of 1379 cm^{-1} .

2861.8, 2920 and 2961 cm^{-1} . They refer to hydrogen atoms of the methyl groups. It is to be noted that a high frequency corresponding to hydrogen attached to an acetylenic carbon atom is not found.

Rotation in dimethyl-acetylene

Three lines (2179.5, 2201.4 and 2280 cm^{-1}) are found to accompany the acetylene bond vibrations. They are interpreted as rotation changes occurring with the C : C vibration. These lines are weak requiring 97 hours exposure, but repeated measurements indicate two rotation frequencies of 33 cm^{-1} and 55 cm^{-1} . Similar rotation phenomena have been found by Bonino and Cella¹⁵ in pinene. In this latter case the rotating portion of the molecule is a simple rotator of one degree of freedom. In the present case it is similarly assumed that the rotational energy states are given by $E_{\text{rot}} = \hbar^2 k^2 / 8\pi^2 I = Bk^2$; $\Delta k = -2$; $\Delta\nu = B(4k-4)$ where "k" refers to the initial state. The change in k has been taken to be two units as is usual in the Raman effect. The moment of inertia calculated from the above formula appears to be connected with the rotation of the six hydrogen atoms around the figure axis of the

molecule. Since the interval of 22 cm^{-1} is equal to 8B:

$$I = \hbar / 8\pi^2 c B = (27.7 \times 10^{-40}) / 2.75 \\ = 10 \times 10^{-40} \text{ g} \times \text{cm}^2.$$

If it is assumed that the four carbon atoms are located on the figure axis and therefore do not contribute to the moment of inertia then the six hydrogen atoms only are responsible for this moment. Their distance from the figure axis may then be calculated:

$$6 \times 1.663 \times 10^{-24} \times r^2 \times 10^{-16} = 10 \times 10^{-40}; \\ r = 1 \text{ Angstrom.}$$

Since the C—H distance in many hydrocarbons is about 1.08A, the same value may be assumed for the methyl groups of this compound. The central angle calculated is 112° instead of the usual 109° for a regular tetrahedron.

In Table V it is seen that the even rotation

TABLE V. Rotation in dimethyl-acetylene.

Frequency				
No.	cm^{-1}	Δk	$\Delta\nu = 2.75(4k-4)$	Intensity
1	(...)	2→0	11	—
2	—	3→1	22	0
3	33	4→2	33	1
4	—	5→3	44	0
5	55	6→4	55	1
6	—	7→5	66	0

states only occur and that the odd ones are entirely missing. The rotation states found in Pinene by Bonino and Cella¹⁵ are similar in character. Further, only the P branches are found in both cases. It appears that a molecule rotating in a higher quantum state due to temperature distribution of energy can interact with the scattered quantum and give up its rotation energy, while the incoming quantum cannot excite the oscillation of the acetylene bond and at the same time cause the rotation energy of the molecule to increase. This difference does not arise from the Boltzmann factor nor from the ν^4 factor in the intensity expression pertaining to Raman scattering,¹⁶ but must arise from the

¹⁵ G. B. Bonino and P. Cella, Mem. Acad. Italia II (No. 4) 1 (1931).

¹⁶ G. Placzek, *Rayleigh Scattering and Raman Effect*, Handb. d. Radiologie by E. Marx, Akad. Verlags-Gesellschaft m.b.H. Leipzig, 1934, p. 203.

TABLE VI. Raman lines of vinyl-acetylene. Two types: $A(M(x) \neq 0)$; $B(M(yz) \neq 0)$.

Mode	cm ⁻¹	Inten- sity	Type	$m_1 \times m_2$	Mode	cm ⁻¹	Inten- sity	Type	$m_1 \times m_2$
(H ₃ C) ↓ : (CH) ↑ .C ↓ : CH ↑	219	4(b)	A	676	(H ₂ C ₂)(H) ↓ (C ₂ H)	1288	4(s)	A	51
(H ₂ C) ↓ : (C ₃ H) ↑ .H ↓	309	4(b)	"	555	H ↑ H ↓ (C ₄ H ₂)	1405	4(s)	B	100
(H ₂ C) ↑ : (C ₂ H) ↓ : (CH) ↑	538	4(s)	B	675	(H ₂ C) → : ← (CH)(C ₂ H) →	1595	5(s)	"	507
(H ₂ C) ↓ : (CH) ↑ .(C ₂) ↓ .H ↑	629	4(b)	A	532	(H ₃ C ₂) → C → : ← C. ← H	2098.5	6(s)	"	507
(H ₂ C) ↓ : (CH) ↑ .(C ₂ H) ↓	678	2(b)	"	507	(H ₂) → ← (C ₄ H ₂)	3011.6	4(s)	"	100
(H ₃ C ₂) →. ← (C ₂). (H) →	875	3(s)	B	672	H → ← (C ₄ H ₃)	3102	2(s)	"	51
(H ₃ C ₂) →. ← (C ₂ H)	928	2(s)	"	675	(C ₄ H ₃) → ← H	3305	1(s)	"	51
(H ₃ C ₂) → C ← (CH)	1091	2(s)	"	351					

difference in the expression for the scattering-tensor in the two cases.

After this research was in progress, B. Gredy¹⁷ reported a list of Raman frequencies in dimethyl-acetylene. Of the three lines 351, 971 and 2996 cm⁻¹ reported by him no trace has been found, even on exposure long enough to photograph the rotation-vibration bands mentioned above. On the other hand, he fails to report the lines at 778.5, 1029 and 2737 cm⁻¹. Since he does not mention his source of light, it is impossible to search his list for coincidence with lines of the exciting spectrum. It should be mentioned that our sample of dimethyl-acetylene was purified with extreme care; that both long and short exposures were made; that the measurements made on different plates agreed very closely and that microphotographs were made to assist in the study of the spectrum.

VINYL-ACETYLENE

The molecule contains eight atoms and eighteen fundamental frequencies may be expected. Its structure is represented by the point arrangement C_{1h} and all of the eighteen frequencies should be found, if they are "Raman-active."⁴ Only fifteen frequencies could be located with certainty. The others may be coincident with mercury lines or they may be very faint. It is possible that longer exposure may reveal them, although the spectrogram shown in Fig. 1 was obtained on 25 hour exposure. The frequencies expected fall into two classes ($A=5$ and $B=13$) and the Raman lines found on the plates were divided into sharp and broad lines as is shown in Table VI.

¹⁷ B. Gredy, Comptes rendus **197**, 327 (1933).

Modes of vibration

In some respects vinyl-acetylene is the most interesting compound studied. One can scarcely conceive of a molecule of eight atoms of only two types (carbon and hydrogen) having a greater variety of atomic bindings. One can expect to find in vinyl-acetylene almost all of the frequencies of hydrocarbon molecules. It will be noted that the organic chemists' picture of the molecule indicates (1) the presence of single, double and triple bonds between carbon atoms; (2) that the double and triple bonds are each in conjugate positions to the other; (3) that of the four hydrogen atoms three are attached to carbon atoms of distinctly different character and (4) that there are carbon atoms holding none, one and two hydrogen atoms. All of these accepted points make themselves felt in its Raman spectrum.

219 to 678 cm⁻¹. These low vibrations are considered to be due to deformations of the molecule. The assignments made are meant to indicate this situation in a general way.

As far as possible the frequencies were assigned in such a way that the masses vibrating toward one another were larger for the smaller frequencies. This point may have some significance at least within a group of vibrations involving the same bond vibration and hence the same force constant.

875, 928, 1091 cm⁻¹. These frequencies are ascribed to vibrations involving the C—C bond. The modes of vibration indicated in the table are meant to indicate the motions involved in a general way only. The types of vibration shown are to be thought of as being interchangeable among the three frequencies as no evidence exists to assign them definitely.

1288.1 cm^{-1} . This line has no counterpart in either mono-methyl or dimethyl-acetylene. Its occurrence in a Raman spectrum seems to depend upon the presence in the molecule of a lone hydrogen atom on an ethylenic carbon. This can be seen as follows: Butadiene (1277); 1-methyl-butadiene (1288); 2-methyl-butadiene (1291). However in 2-3-dimethyl-butadiene where the structure "CH" is missing, no frequency is found in the range 1024 to 1339 cm^{-1} . Again it is found in allyl alcohol (1288) and allyl sulfide (1291). The frequency reported here in vinyl-acetylene (1288.1 cm^{-1}) has also been found in divinyl-acetylene by C. E. Morrell¹⁸ as 1288.3 cm^{-1} . Since this frequency is too low for a C-H vibration along the valency direction, it is thought to be of the deformation type.

1595 cm^{-1} . As the presence of the conjugate double bond lowers the acetylene bond frequency, so it appears that the ethylene bond frequency is also lowered by the conjugate triple bond. The frequency of the carbon-carbon double bond is ordinarily in the range of 1630–40 cm^{-1} and is thus 40 cm^{-1} lower in vinyl-acetylene.

1405 cm^{-1} . A transverse motion of the two hydrogen atoms of the CH_2 group is held responsible for this vibration.

2098.5 cm^{-1} . This vibration represents the acetylene bond vibration between the two triply-bound carbon atoms. It is lower than 2119–20

cm^{-1} found in many acetylene compounds¹⁹ and the neighboring double bond may be responsible for this change.

3305 cm^{-1} . This frequency is due to the hydrogen atom attached to the acetylenic carbon atom.

3102 cm^{-1} is ascribed to the single hydrogen atom attached to the ethylenic carbon.

3011.6 cm^{-1} represents the vibration of the hydrogen atoms attached to the end carbon atom of the ethylene radical. The principle C-H line in ethylene itself is at 3019 cm^{-1} and is also found in many compounds having the CH_2 group.²⁰ It is interesting to note that the hydrogen atoms in vinyl-acetylene have a higher frequency of vibration than the hydrogen of the methyl group (Fig. 1) of methyl and dimethyl-acetylene.

It is believed that the assignments made for the motions of the molecules connecting them to certain observed frequencies is all that can be done at the present from such observations as are carried out in a scattering experiment. The symmetry of the molecules has been noted, the classes of frequencies expected have been kept in mind and the possible modes of vibration have been related to the chemical structure of the molecules.

¹⁹ Bourgel and Daure, *Comptes rendus* **190**, 1298 (1930).

²⁰ Dadiou and Kohlrausch, references 9 and 12, pp. 322–3.

¹⁸ Unpublished results obtained in this laboratory.