

[CONTRIBUTION FROM THE PHYSICAL AND CHEMICAL LABORATORIES, ILLINOIS INSTITUTE OF TECHNOLOGY]

## Raman Spectra of Acetylenes. III. Five Monosubstituted and Four Disubstituted Acetylenes

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The investigations reported in papers I and II<sup>1</sup> of this series have been extended to nine other acetylenic compounds, both monosubstituted and disubstituted, in an attempt to secure additional information in regard to the appearance of more lines in the 2200  $\text{cm}^{-1}$  region for disubstituted than for monosubstituted acetylenes. Several explanations have been offered to account for this effect. The one most generally accepted is that of Badger<sup>2</sup> in which it is suggested that the effect is due to a Fermi resonance interaction of the fundamental near 2200 with an overtone of a fundamental near 750 or 1100  $\text{cm}^{-1}$ . One difficulty with this explanation is the fact that quite often more than two lines are observed in this region.<sup>3</sup> A study of methylphenylacetylene<sup>4</sup> indicates that for the two strong lines of approximately equal intensities the frequency conditions for resonance are not very satisfactorily fulfilled. The second overtone of the 756 Raman frequency (2268) is *greater* than the mean of the doublet (2234) while the first overtone of the 1095 infrared frequency (2190) is *less* than the mean.<sup>5</sup> From theory,<sup>6</sup> one would expect that the coincidence of the overtone and the fundamental near 2234 would need to be more exact for the second overtone than for the first overtone. Since the coincidence is not very exact, this would mean that the 1095 frequency is probably the one concerned. If this is the case, then for exact coincidence it would be necessary that the anharmonicity correction *increase* the overtone frequency obtained by doubling the 1095 value, rather than *decrease* it as is the case with diatomic molecules. This may be possible since it is known

that the potential energy curves have a different shape for polyatomic molecules.

In dimethylacetylene,<sup>7</sup> the infrared fundamental was observed at 1126  $\text{cm}^{-1}$ . The first overtone (2252) is again, as for methylphenylacetylene, *less* than the mean of the doublet (2270), but the coincidence in this case is more exact. For exact coincidence, the anharmonicity correction would again have to be positive.

It may be suggested that some or all of the additional lines are due to the presence of impurities. Any such impurities would necessarily be compounds having strong lines in the 2200 region. Few compounds, however, have strong lines in this region. The single bond lines are at lower frequencies, except those involving hydrogen vibrations near 3000 and deuterium vibrations whose natural occurrence with any appreciable intensity is out of the question. The strong double line is normally near 1650 and in general no such line occurs in the disubstituted acetylenes. This leaves the triple bond carbon-nitrogen and carbon-carbon compounds, the former being ruled out by methods of preparation and by chemical analysis. As for the latter, it may be noted that the additional lines do not in general correspond to the chief lines of any of the many compounds of this type whose spectra have been reported. Furthermore, if it is a question of impurities, it is hard to understand why they do not occur generally in the monosubstituted as well as in the disubstituted acetylenes.

### Experimental

The spectrograph and the experimental technique were the same as described in the second paper of the series.<sup>1</sup> The linear dispersion was 33  $\text{\AA}/\text{mm}$ . at 4500  $\text{\AA}$ . Excitation was by the 4358  $\text{\AA}$ . mercury line. All the compounds which were liquid at room temperature were purified by distillation in a heated column. Those which were solid at room temperature were distilled at reduced pressure directly into the Raman tube without further purification and their spectra secured at elevated temperatures.

### Results<sup>8</sup>

In the list of results, the displacement  $\Delta\nu$  in  $\text{cm}^{-1}$  is written first, the estimated intensity  $I$

(7) Bryce L. Crawford, Jr., *J. Chem. Phys.*, **7**, 555 (1939).

(8) A brief report of the results for compounds I, V, VIII and IX was given at the New York meeting of the American Physical Society, February, 1940; abstract, *Phys. Rev.*, **57**, 565 (1940).

(1) M. J. Murray and Forrest F. Cleveland, *THIS JOURNAL*, **60**, 2664 (1938); *ibid.*, **61**, 3546 (1939).

(2) R. M. Badger, *J. Chem. Phys.*, **5**, 178 (1937).

(3) It has been suggested to the authors that one way out of this difficulty is to suppose that there is a resonance interaction with a fundamental (near 1100) of the  $\text{CH}_2$  or  $\text{CH}_3$  group adjacent to the triple-bond carbon. It is expected that the interaction in this case would probably be rather small and the resulting additional lines in the 2200 region correspondingly weak.

(4) M. J. Murray and Forrest F. Cleveland, *J. Chem. Phys.*, **8**, 133 (1940).

(5) The authors believe that the photographic record is sufficiently good in this region to permit the determination of the frequency of the 1095 band to  $\pm 3 \text{ cm}^{-1}$ .

(6) Cf. G. Placzek, "Handbuch der Radiologie," Volume VI, Part II, Akademische Verlagsgesellschaft, Leipzig, 1934, page 323.

in parentheses next, and the depolarization factor  $\rho$  (for the more intense lines) last. Unusually broad lines are designated by the letter *b*. Data in regard to which there is some uncertainty are enclosed in brackets. Frequencies which were observed both as Stokes and anti-Stokes lines are indicated by the symbol  $\pm$ . In certain cases, lines close together were not resolved on the polarization spectrogram and the single depolarization factor given represents the value measured for the unresolved line.

**I. 3-Methyl-1-butyne-3-ol**,  $\text{CH}_3\text{C}(\text{CH}_3)(\text{OH})\text{C}\equiv\text{CH}$ .—B. p. 103–104°; continuum weak; previous data, Bourguel and Daure.<sup>9</sup>

$\Delta\nu(\text{I})\rho$ : =184(10)0.9, =201(4), 363(2), 408(4) and 426(4)0.7, 557(5)0.7, 627(1), 645(2), 662(2), 680(1), 709(9)0.1, 892(6)0.6, 930(4)0.9, 963(6)0.9, 1133(5), 1151(5) and 1174(6)0.9, 1217(2), 1451(8b)0.9, 2089(3), 2112(10)0.4, 2719(2), 2876(4)<0.6, 2922(4)<0.6, 2939(8)0.1, 2992(8)0.9, 3296(3).

**II. 3-Methyl-1-octyne-3-ol**,  $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{CH}_3)(\text{OH})\text{C}\equiv\text{CH}$ .—B. p. 80–82° (20 mm.); continuum weak.

$\Delta\nu(\text{I})\rho$ : 176(3), =190(8)0.9, 257(1), 290(3), 344(1), 418(3b)0.6, 564(2), 600(3)<0.6, 631(2), 651(2), 715(4)<0.4, 825(1), 852(1), 913(2), 954(1), 969(1), 1036(1), 1060(2) and 1076(3)0.9, 1133(3b)0.9, 1163(2b)0.6, 1308(5)0.9, 1447(8b)0.8, 2107(10)0.4, 2729(2b), 2849(4), 2870(8)0.2, 2906(6)0.8, 2933(10)0.1, [2952(2)], 2992(5)0.9, 3302(2)0.7.

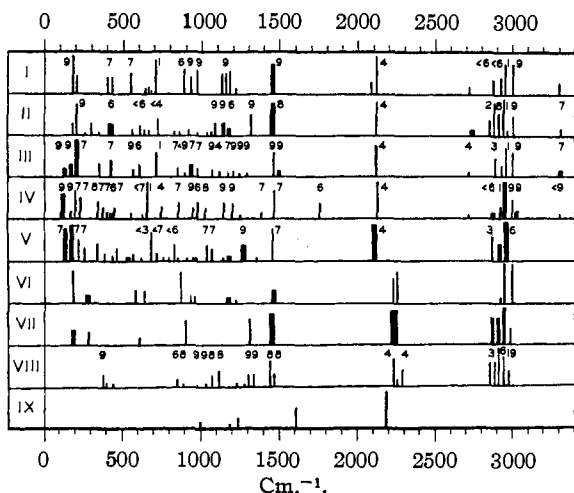


Fig. 1.—Graphical summary of Raman data for: I,  $\text{CH}_3\text{C}(\text{CH}_3)(\text{OH})\text{C}\equiv\text{CH}$ ; II,  $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{CH}_3)(\text{OH})\text{C}\equiv\text{CH}$ ; III,  $\text{CH}_3\text{C}(\text{OC}_2\text{H}_5)(\text{CH}_3)\text{C}\equiv\text{CH}$ ; IV,  $\text{CH}_3\text{C}(\text{OOCCH}_3)(\text{CH}_3)\text{C}\equiv\text{CH}$ ; V,  $\text{C}_8\text{H}_{10}(\text{OH})\text{C}\equiv\text{CH}$ ; VI,  $\text{CH}_3\text{C}(\text{CH}_3)(\text{OH})\text{C}\equiv\text{CC}(\text{CH}_3)(\text{OH})\text{CH}_3$ ; VII,  $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{CH}_3)(\text{OH})\text{C}\equiv\text{CC}(\text{CH}_3)(\text{OH})(\text{CH}_2)_4\text{CH}_3$ ; VIII,  $\text{CH}_3(\text{CH}_2)_4\text{C}\equiv\text{C}(\text{CH}_2)_4\text{CH}_3$ ; IX,  $\text{C}_6\text{H}_5\text{C}\equiv\text{CI}$ .

**III. 3-Methyl-3-ethoxy-1-butyne**,  $\text{CH}_3\text{C}(\text{OC}_2\text{H}_5)(\text{CH}_3)\text{C}\equiv\text{CH}$ .—B. p. 93°; continuum weak.

(9) M. Bourguel and P. Daure, *Bull. soc. chim.*, **47**, 1349 (1930). The frequencies found were: 185, 408, 558, 709, 891, 931, 962, 1134, 1174, 1359, 1455, 2119, 2868, 2936, 2986 and 3303.

$\Delta\nu(\text{I})\rho$ : =121(2b)0.9, 166(3b)0.9, =185(10b)0.7, 343(3)0.7, 420(4)0.7, 552(2)0.9, 593(3)0.6, 705(6)0.1, 842(2)0.7, 891(1)<0.9, 928(3b)0.7, 962(2)0.7, 1064(2)0.9, 1107(2)0.4, 1163(2)0.7, 1191(2)0.9, 1233(1)0.9, 1281(1)0.9, 1456(6)0.9, 1484(1b)0.9, 2109(9)0.4, 2710(1)0.4, 2882(5)0.3, 2921(3), 2940(8)0.1, 2992(7)0.9, 3302(1)0.7.

**IV. 3-Methyl-3-acetoxy-1-butyne**,  $\text{CH}_3\text{C}(\text{OOCCH}_3)(\text{CH}_3)\text{C}\equiv\text{CH}$ .—B. p. 131.5–132.0°; continuum weak.

$\Delta\nu(\text{I})\rho$ : =115(6b)0.9, 165(2)0.9, =186(7)0.7, =214(5)0.7, =334(4)0.6, =365(3)0.7, =391(2)0.7, 418(2)0.6, 532(3)0.7, 541(2), 614(2)<0.7, =647(9)0.1, 738(3)0.4, 845(4)0.7, 935(3)0.9, 965(4)0.6, 1016(3)0.8, 1133(4)0.7, 1193(4)0.7, 1244(1), 1380(2)0.7, 1452(7)0.7, 1745(4)0.6, 2113(10)0.4, 2720(1), 2870(2b)<0.6, 2917(3), 2938(10b)0.1, 2990(5)0.9, 3015(2b)0.9, 3306(1b)<0.9.

**V. 1-Ethynylcyclohexanol**,  $\text{H}_2\text{C} \begin{array}{l} \diagup \text{CH}_2-\text{CH}_2 \diagdown \\ \diagdown \text{CH}_2-\text{CH}_2 \diagup \end{array} \text{C} \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{C}\equiv\text{CH} \end{array}$

—B. p. 101–103° (60 mm.); continuum weak.

$\Delta\nu(\text{I})\rho$ : =133(8b)0.7, =158(9b)0.7, =215(5)0.7, =256(3), 331(4), 380(2), 430(2), 458(3), 528(1b), 558(2), 611(1), 678(7)<0.3, 713(2)<0.7, 754(1), 791(1), 827(4)<0.6, 849(1), 907(1), 945(1), 967(1), 1034(4)0.7, 1064(3)0.7, 1138(1), 1166(2b), 1264(4b)0.9, 1347(1), 1446(8)0.7, 2107(9b)0.4, 2857(6)0.3, 2918(4b), 2942(10b)0.6.

**VI. 2,5-Dimethyl-3-hexyne-2,5-diol**,  $\text{CH}_3\text{C}(\text{CH}_3)(\text{OH})\text{C}\equiv\text{CC}(\text{CH}_3)(\text{OH})\text{CH}_3$ .—M. p. 93.5–94.0°; continuum strong; spectrum incomplete.

$\Delta\nu(\text{I})$ : =183(8), 266(2b), 573(3), 634(3), 864(8), 925(2), 952(2), 1168(2b), 1219(1), 1456(3b), 2224(6), 2248(8), 2868(1), 2918(2), 2935(10), 2988(10).

**VII. 6,9-Dimethyl-7-tetradecyne-6,9-diol**,  $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{CH}_3)(\text{OH})\text{C}\equiv\text{CC}(\text{CH}_3)(\text{OH})(\text{CH}_2)_4\text{CH}_3$ .—M. p. 84–85°; continuum strong; spectrum incomplete.

$\Delta\nu(\text{I})$ : 179(3b), 279(3), 600(2), 898(6), 1305(7), 1447(8b), 2230(8b), 2868(7b), 2897(6b), 2927(10b), 2980(4).

**VIII. 6-Dodecyne**,  $\text{CH}_3(\text{CH}_2)_4\text{C}\equiv\text{C}(\text{CH}_2)_4\text{CH}_3$ .—B. p. 101–102° (18 mm.); continuum weak.<sup>10</sup>

$\Delta\nu(\text{I})\rho$ : 373(3)0.9, 383(1), 435(1), 842(2)0.6, 887(1)0.8, 970(1)0.9, 1024(1)0.9, 1067(3)0.8, 1110(4)0.8, 1221(1), 1271(1), 1300(3)0.9, 1330(3)0.9, 1436(6)0.8, 1452(3)0.8, 2231(7)0.4, 2248(2), 2294(4)0.4, 2852(6) and 2874(6)0.3, 2906(10)[0.6], 2934(8)0.1, 2967(4)0.9.

**IX. 1-Phenyl-2-iodoethyne**,  $\text{C}_6\text{H}_5\text{C}\equiv\text{CI}$ .—Prepared by directions given by Nef<sup>11</sup>; b. p. 105.5° (7 mm.); turned yellow rapidly when exposed to Hg 4358 Å.; spectrum incomplete.

$\Delta\nu(\text{I})$ : 999(2), 1177(1), 1223(3), 1599(5), 2172(10).

The results are summarized graphically in Fig. 1, in which the height of the line is proportional to its estimated intensity. The numbers written near the lines represent depolarization factors, multiplied by 10 to simplify the figure. Lines which were unusually broad on the spectrograms are drawn with greater width in the figure.

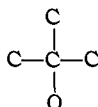
(10) For *n*-amylacetylene,  $\text{CH}_3(\text{CH}_2)_4\text{C}\equiv\text{CH}$ , Bourguel and Daure<sup>9</sup> found: 345, 633, 835, 1033, 1069, 1112, 1304, 1332, 1439, 1462, 2121, 2868, 2916, 2966, 3308.

(11) J. U. Nef, *Ann.*, **308**, 293 (1899).

### Discussion of Results

**Frequencies below 2000  $\text{cm}^{-1}$ .**—All the mono-substituted acetylenes (I–V) have a very strong depolarized frequency (or frequencies) near 200  $\text{cm}^{-1}$ . This is perhaps a deformation frequency (or frequencies) involving the group  $\text{R}-\text{C}\equiv\text{C}-\text{H}$ . The disubstituted acetylene VI also has a strong frequency near this value.

The intense, highly polarized line near 700  $\text{cm}^{-1}$  probably corresponds to the frequency (analogous to the totally symmetrical frequency  $\nu_1$  in carbon tetrachloride) of vibration of the outer atoms of the group



along the valence bonds. If one assumes that this group approximates the tetrahedral group  $\text{XY}_4$ , takes the value 15.0 as the effective mass of the Y atom and  $4.50 \cdot 10^8$  dynes/cm. for the X–Y force constant, the frequency may be calculated, using the formula given by Lechner.<sup>12</sup> The result is 714  $\text{cm}^{-1}$ . The mean of the observed values for the five monosubstituted acetylenes is 690  $\text{cm}^{-1}$ . This is, of course, only a rough calculation, but it indicates that the assignment of the frequency is probably correct.

**Frequencies near 2200  $\text{cm}^{-1}$ .**—In general only one frequency is observed in this region for monosubstituted acetylenes. This rule holds for four of the monosubstituted acetylenes (II–V) listed above. For I, however, two lines were observed, although Bourguel and Daure<sup>9</sup> reported only one. It may be that they failed to observe the weaker line because of continuous background or because of its proximity to the exceedingly strong line at 2112. On the other hand, it may be that the line 2089 observed in the present study is due to an impurity. The only acetylenic compounds listed in "Tables Annuelles"<sup>13</sup> having Raman frequencies below 2100 are those having a double bond conjugated with a triple bond, as in vinylacetylene. This type of compound is a reasonable impurity because of the ease with which tertiary alcohols lose water. If such a compound had been present in the sample, however, there should have been a line (corresponding to the

double bond) in the neighborhood of 1600  $\text{cm}^{-1}$ . No such line was observed, even on considerably over-exposed spectrograms.

Furthermore, distillation in a heated column, using a high reflux ratio, failed to produce a separation, for the ratio of the estimated intensities ( $I_{2112}/I_{2089}$ ) was the same on spectrograms made with the first and last fractions. Of course, such distillation would not have eliminated an impurity if an azeotropic mixture were present or if the boiling points were almost identical.

Finally, the alcohol was acetylated. The spectrum of the resulting ester showed only a single line. However, when this ester was then hydrolyzed to give the alcohol, the line was again double and showed the same ratio of the estimated intensities as before. If an impurity had been present, it seems that it should either have shown its presence in the spectrum of the ester or have been absent from the spectrum of the alcohol formed by the hydrolysis.

For the disubstituted acetylenes, two lines were observed in the 2200 region for VI, three for VIII, and only one for VII and IX. The line for VII was broad, however, and may have been double, while for IX the spectrum was incomplete due to the short exposures required by the rapid yellowing of the liquid upon exposure to the exciting light. It is possible, therefore, that a weak companion could have been present, but unobservable, in the latter case. In neither of the cases where more than one line was observed is there a Raman frequency near 750 whose overtone would satisfy the frequency condition for resonance interaction. In VIII, where three lines were observed, the assignments given in Table I could be assumed:

Obsd. frequency	Tentative assignment
2231(7)0.4	Fundamental, involving chiefly the triple bond
2248(2)—	970 + 1271 or 1024 + 1221
2294(4)0.4	1024 + 1271

However, while the frequencies are well accounted for by this assignment, it is to be noted that the intensities of the lines thus ascribed to combinations are much greater than would normally be expected. The validity of the assignment is therefore questionable. It is possible that the intensities might be increased by proximity to the strong fundamental, but in this case it seems that 2248 should be stronger than 2294, which is contrary to the observations.

(12) F. Lechner, *Anz. Akad. Wiss. Wien., Math. Naturw., Klasse*, **70**, 126 (1933).

(13) M. Magat, "Tables annuelles de constants et données numériques," Volumes XI and XII, Gauthier-Villars and Hermann et Cie., Paris, 1936 and 1937.

TABLE II  
 TENTATIVE ASSIGNMENT OF C-H FREQUENCIES

Compd.	—CH <sub>3</sub> Groups	—CH <sub>2</sub> — Groups	$\nu_{  }$	—CH <sub>3</sub>	$\nu_{\perp}$	$\nu_{  }$	—CH <sub>3</sub> —	$\nu_{\perp}$
V	0	5	.....		.....	2857(6)0.3		2942(10b)0.6
VIII	2	8	2934(8)0.1		<sup>b</sup> 2967(4)0.9	<sup>a</sup> 2863(6)0.3		<sup>b</sup> 2967(4)0.9
VII	4	8	2927(10b)		2980(4)	2868(7b)		.....
II	2	4	2933(10)0.3		2992(5)0.9	2870(8)0.2		[2952(2)]
III	3	1	2940(8)0.1		2992(7)0.9	2882(5)0.3		.....
I	2	0	2939(8)0.1		2992(8)0.9	2876(4)<0.6		.....
IV	3	0	2938(10b)0.1		2990(5)0.9	2870(2b)<0.6		.....
VI	4	0	2935(10)		2988(10)	2868(1)		.....

<sup>a</sup> Mean of the doublet, 2852, 2874. <sup>b</sup> Probably an unresolved doublet.

**Frequencies near 3000 cm.<sup>-1</sup>.**—Vibration frequencies involving the C—H bond lie in this region. The frequency near 3300 cm.<sup>-1</sup> is due to the vibration involving chiefly the ≡C—H group. The line corresponding to this frequency was rather weak and, in the two cases where it was possible to measure the depolarization factor, rather highly depolarized.

In a previous paper,<sup>14</sup> the frequencies near 2931 (polarized) and 2968 (depolarized) were tentatively assigned to parallel ( $\nu_{||}$ ) and perpendicular ( $\nu_{\perp}$ ) vibrations of the —CH<sub>3</sub> group, respectively, while the one near 2867 (polarized) was less definitely suggested as a parallel ( $\nu_{||}$ ) vibration of the —CH<sub>2</sub>— group. It may be interesting to see how well the C—H frequencies observed in the present investigation agree with these assignments. The pertinent data are summarized in Table II. The compounds are listed in such a way that the ratio of the number of CH<sub>2</sub> groups to the number of CH<sub>3</sub> groups steadily decreases as one reads down the table. In the main, the results are consistent with the assignments made for the ethers, but there are some differences. The mean of the first column, 2935, is very close to the mean value of this frequency in the ethers, 2931. The mean of the second column, 2986, is, however, considerably greater than the value, 2968, previously observed. There is some indication that  $\nu_{\perp}$  (CH<sub>3</sub>) and  $\nu_{\perp}$  (CH<sub>2</sub>) may overlap and that the value 2968, previously assigned to  $\nu_{\perp}$  (CH<sub>3</sub>), may in reality have been a doublet made up of  $\nu_{\perp}$  (CH<sub>2</sub>) near 2945 and  $\nu_{\perp}$  (CH<sub>3</sub>) near 2990, both depolarized. The mean

of the third column, 2869, is also very close to the mean value, 2867, previously obtained. The situation in this instance is complicated, however, by the fact that the frequency occurs also in compounds I, IV and VI which contain no CH<sub>2</sub> groups, although it may be noted that the intensities in these cases are less than in the ones that do contain this group. It seems probable that two frequencies may be involved, one ( $\nu_{||}$  CH<sub>2</sub>) near 2857, which occurs in V where there are no CH<sub>3</sub> groups, and another near 2871 whose origin is not clear.

The remaining frequencies observed in this region may be overtones (the overtone of the C—H deformation frequency falls in this region) or combination frequencies whose intensities are augmented by resonance interactions.

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### Summary

Raman displacements, estimated intensities, and depolarization factors are reported for: 3-methyl-1-butyn-3-ol, 3-methyl-1-octyn-3-ol, 3-methyl-3-ethoxy-1-butyne, 3-methyl-3-acetoxy-1-butyne, 1-ethynylcyclohexanol, 2,5-dimethyl-3-hexyne-2,5-diol, 6,9-dimethyl-7-tetradecyne-6,9-diol, 6-dodecyne, and 1-phenyl-2-iodoethyne. Tentative assignments are made for certain of the observed frequencies.

(14) Cleveland, Murray, Haney and Shackelford, *J. Chem. Phys.*, **88**, 156 (1940).