The Assignment of the Vibrational Spectra of the C4 Hydrocarbons Butyne−1, Butene−1, and Vinyl Acetylene, to the Normal Modes of Vibration of These Molecules

N. Sheppard

Articles you may be interested in

The Assignment of the Vibrational Spectra of the C₄ Hydrocarbons Butyne-1, Butene-1, and Vinyl Acetylene, to the Normal Modes of Vibration of These Molecules*

N. Sheppard**

Department of Physics, The Pennsylvania State College, State College, Pennsylvania

(Received June 25, 1948)

An attempt has been made to assign all the normal modes of vibration of the C₄ hydrocarbons butyne-1, butene-1, and vinyl acetylene, in terms of frequencies observed in the infra-red and Raman spectra. It has been found to be possible to do this in a satisfactory manner which takes into account the structural similarities of these and other hydrocarbon molecules. With the help of these assignments previous data on the frequency ranges characteristic of the various hydrogen deformation modes of the groups ethyl, vinyl, and $-C\equiv CH$ can be extended to include all such modes.

INTRODUCTION

THE detailed assignment of the vibrational spectra of the smaller hydrocarbons, together with the identification of the characteristic frequencies of particular structural groups in larger molecules, are two parallel methods which can be used to increase our understanding of the spectra of polyatomic hydrocarbons. The isolation and identification of characteristic frequencies in the infra-red and Raman spectra is in itself a method which can be applied with advantage as an aid to the complete analysis of the spectra of the smaller molecules. This has recently been shown in the case of n-butane,[1] and will be demonstrated again in the present communication. In recent years fairly complete assignments have been made for all the non-cyclic hydrocarbons of the C_2[2-5] and C_3[6-9] classes, and for the molecules n-butane,[1] isobutane,[10,11] isobutene,[7] *cis*- and *trans*-butene-2,[7] butadiene 1–2,[12] butadiene 1–3,[13] and dimethyl acetylene,[14] of the C₄ class. Assignments of a lesser degree of completeness have previously been made for the remaining well established C₄ hydrocarbons, and it is the purpose of this paper to bring up to date the work on these remaining molecules, with the exception of diacetylene (see reference 4, p. 323) for which further experimental work appears to be necessary. These three molecules, *viz.*, butyne-1, butene-1, and vinyl acetylene, also form a convenient series for examination as each of the structural groups, ethyl, vinyl, and $-C\equiv CH$, occurs in two of these molecules. An attempt will be made to assign specifically all the fundamental modes of vibration of these molecules in a manner which is consistent with the results on already reliably assigned molecules, and with the results of previous investigations on characteristic frequencies.

A. THE EXPERIMENTAL DATA

Experimental data on the infra-red and Raman spectra of all these molecules are now available.

In the case of butyne-1 (ethyl acetylene) Cleveland, Murray, and Taufen[15] have published

* This research was carried out on Contract N6onr-269 Task V of the Office of Naval Research.

** Now at Department of Colloid Science, Cambridge University, Cambridge, England.

[1] G. J. Szasz, N. Sheppard, and D. H. Rank, J. Chem. Phys. 16, 704 (1948).

[2] F. Stitt, J. Chem. Phys. 7, 297 (1939).

[3] W. S. Gallaway and E. F. Barker, J. Chem. Phys. 10, 88 (1942).

[4] G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 325.

[5] T. Y. Wu, *Vibration Spectra and Structure of Polyatomic Molecules* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1946), p. 176.

[6] K. S. Pitzer, J. Chem. Phys. 12, 310 (1944).

[7] J. E. Kilpatrick and K. S. Pitzer, J. Research Nat. Bur. Stand. 38, 191 (1947).

[8] B. L. Crawford, J. Chem. Phys. 8, 526 (1940).

[9] J. W. Linnett and W. H. Avery, J. Chem. Phys. 6, 686 (1938).

[10] K. S. Pitzer and J. E. Kilpatrick, Chem. Rev. 6, 686 (1938).

[11] N. Sheppard, J. Chem. Phys. 16, 690 (1948).

[12] G. J. Szasz, J. S. McCartney, and D. H. Rank, J. Am. Chem. Soc. 69, 3150 (1947).

[13] Aston, Szasz, Woolley, and Brickwedde, J. Chem. Phys. 14, 67 (1946).

[14] B. L. Crawford, J. Chem. Phys. 7, 555 (1939).

[15] F. F. Cleveland, M. J. Murray, and H. J. Taufen, J. Chem. Phys. 10, 172 (1942).

the Raman spectrum together with the depolarization data for the lines. The infra-red spectrum has also been obtained recently.[16] Wagman, Kilpatrick, Pitzer, and Rossini[17] have previously made a semi-schematic assignment for this molecule.

The Raman spectrum of butene-1 (ethyl ethylene) has been independently determined by Kohlrausch and Stockmair,[18] and Bourguel and Piaux,[19] and the infra-red spectrum has been published by Rasmussen and Brattain.[20] A fairly detailed assignment has been made by Aston, Szasz, Woolley, and Brickwedde,[13] for the purpose of determining the contribution of the vibrational degrees of freedom to the thermodynamic properties of this molecule. This requires slight correction to bring it in line with data on the other molecules.

The Raman spectrum of vinyl acetylene has been studied by Glockler and Davis,[21] and Timm and Mecke,[22] and the infra-red spectrum has been obtained by Bartholomé and Karweil.[23] The most satisfactory previous assignment seems to be that of Kohlrausch,[24] made on the basis of the Raman frequencies.

There are possibilities of rotational isomerism in the case of the molecule butene-1. However, the number of lines in the infra-red and Raman spectra suggest that one form only is present in considerable quantity. It is probable that the energy difference between the two types of rotational isomer is greater than in the case of butane,[1] where several Raman frequencies caused by the higher energy form have been observed.

TABLE I. Collected experimental data on the vibrational spectra of butyne-1, butene-1, and vinyl acetylene.

Butyne-1		Butene-1		Vinyl acetylene	
Raman[a]	Infra-red[b]	Raman[c]	Infra-red[d]	Raman[e]	Infra-red[f]
3305 (2) 0.6	3300 (8)	3074 (4)	3075	3305 (1)	
2986 (5) 0.8		2998 (7)		3102 (2)	
2941 (8) 0.2		2968 (4)	2970	3012 (4)	
2919 (7) 0.2	2900 (10)	2936 (7)		2099 (6)	
2885 (5b) 0.4		2898 (7)		1595 (5)	1600 (8)
2851 (3) 0.4		2872 (4)		1405 (4)	1410 (2)
2118 (10) 0.5	2120	2850 (4)		1288 (4)	
1459 (3b) 0.8	1450 (9)	1636 (7)	1645 (9)		1245 (20)
1438 (4b) 0.8			1550 (1) D	1091 (2)	1090 (4)
1375 (1)		1450 (2)	1457 (9)		1058 (4)
1314 (4) 0.6	1325 (8) D	1416 (3)	1412 (½)		950 (30)
1252 (1b) 0.6	1250 (10) PQR		1391 (1)	928 (2)	935 (30)
1068 (6) 0.3	1070 (7) D	1376 (0)		875 (3)	
1023 (1)	1030 (½) Q		1307 (3) PQR	678 (2b)	
1005 (3) 0.6	1005 (1) D	1293 (5)		629 (4b)	
	910 (3) PQR	1257 (2)			615 (100)
840 (7) 0.2			1182 (1) D	538 (4)	535 (2)
784 (½)	783 (3) PQR	1166 (0)			515 (2)
642 (3b) 0.7	650 (6)		1135 (1)	309 (4b)	
563 (3) 0.5			1116 (1)	219 (4b)	
509 (4) 0.5		1068 (1)	1080 (4)		
348 (5b) 0.7		1019 (2)			
290 (1) p		(980) (2)	993 (9) PQR		
206 (8b) 0.7		908 (2)	912 (10) PQR		
		850 (4)	853 (1) PQR		
			802 (1)		
			788 (1) D		
		623 (½)			
		533 (0)			
		437 (2)			
		320 (0)			
		282 (½)			
		237 (0)			

a See reference 15.
b See reference 16.
c See reference 18.
d See reference 19.
e See reference 21.
f See reference 23.

In Table I are given the collected experimental data on vibrational spectra that have been used to make the assignments. In cases where several independent determinations of the spectra have been made, the values given are taken from the work of the authors of the most complete data, controversial frequencies being enclosed in brackets. The relative intensities of all the observed lines are given after the frequencies, and the degrees of depolarization or band contours of Raman or infra-red frequencies are given, when available, after the intensity values. PQR denotes an infra-red band with a marked Q branch, and D, a doublet contour. The designation b after the intensity value for a Raman line indicates a broad appearance to the line. Wherever possible, Table I is set out so that corresponding infra-red and Raman frequencies are opposite each other. The infra-red frequencies are estimated values taken from the center of each band contour. No frequencies greater than 3350 cm⁻¹ are included, nor are any in the region 2800–1700 cm⁻¹, except for the obvious C≡C stretching frequencies, as it is well known that these regions are otherwise free of fundamentals.

[16] American Petroleum Institute Research Project 44, at the National Bureau of Standards. Catalog of Infra-Red Spectrograms. Serial No. 13, contributed by the Phillips Petroleum Company, Bartlesville, Oklahoma, and the University of Oklahoma Research Institute, Norman, Oklahoma.

[17] D. D. Wagman, J. E. Kilpatrick, K. S. Pitzer, and F. D. Rossini, J. Research Nat. Bur. Stand. 35, 467 (1945).

[18] K. W. F. Kohlrausch and W. Stockmair, Zeits. f. physik. Chemie B29, 292 (1935).

[19] M. Bourguel and L. Piaux, Bull. Soc. Chem. Fr. 2, 1958 (1935).

[20] R. S. Rasmussen and R. R. Brattain, J. Chem. Phys. 15, 120 (1947).

[21] G. Glockler and H. M. Davis, J. Chem. Phys. 2, 881 (1934).

[22] B. Timm and R. Mecke, Zeits. f. physik. Chemie B35, 442 (1937).

[23] E. Bartholomé and J. Karweil, Zeits. f. physik. Chemie B35, 442 (1937).

[24] K. W. F. Kohlrausch, "Ramanspektren," Hand und Jahrbuch der Chemischen Physik (Akad. Verlag Becker and Erler, Leipzig, 1943), Vol. 9, pp. 306, 309.

TABLE II. An assignment of the fundamental vibration frequencies of butyne-1, butene-1, and vinyl acetylene.

Group	Description of vibration	Frequency range previously assigned	References	n-butane[1]	Butyne-1	Butene-1	Vinyl acetylene	Frequency ranges from present assignments
	CH₃ symm. stretching	ca. 2870 cm⁻¹	29	2880, (2880)	2885	2872		2890–2870
	CH₃ asymm. stretching	ca. 2960	29	(2950), (2960), 2964, (2950)	2941, 2986	2936, 2968		2990–2935
Ethyl	CH₂ symm. stretching	ca. 2850	29	2860, (2860)	2851	2850		2860–2850
	CH₂ asymm. stretching	ca. 2930	29	2934, (2934)	(2925)	(2936)		2940–2920
	CH₃ asymm. deformation	1470–1440	26	1455(2), 1466(2)	1459, 1438	1457, 1450		1470–1435
	CH₃ symm. deformation	1390–1360	26	1370, 1390	1375	1391		1395–1365
CH₃–CH₂–	CH₃ wagging (in-plane)	1200–900	1	1148, 1134	1005	1019		1150–1000
	CH₃ wagging (out-of-plane)	1200–900	1	959, 956	910	(910)		960–900
	CH₂ bending	1470–1440	11	1455, 1466	1450	1450		1470–1440
	CH₂ wagging	1340–1290	11	1304, 1297	1325	1307		1330–1290
	CH₂ twisting	(1350–1100)	11	1244, (1250)	1252	1257		1260–1240
	CH₂ rocking	760–720	11	751, (740)	785	788		790–740
	CH₂ symm. stretching	ca. 2980	29			2998	3012	3020–2990
Vinyl	CH₂ asymm. stretching	ca. 3080	29			3074	3102	3110–3070
	CH stretching	ca. 3020	29			(2998)	(3012)	(3020–2990)
	CH₂ bending (in-plane)	1430–1390	28			1416	1410	1440–1380
	–CH=CH– bending (in-plane)	1320–1280	28			1293	1288	1300–1270
CH₂=CH–	CH₂ rocking (in-plane)	?	—			1166	1090	1170–1090
	CH₂ wagging (out-of-plane)	920–900	28			912	935	940–900
	–CH=CH– wagging (out-of-plane)	1010–980	28			993	950	1025–950
	CH₂ torsion (out-of-plane)	?	—			623	678	680–600
CH≡C–	CH stretching	ca. 3300	5, 8		3305		3305	ca. 3305
	CH deformation	700–600	5, 8		642, (605)		615, 629	650–600
	C–C stretching	1200–800	27	1058, 970, 835	1068, 840	1068, 850	875	1100–830
Skeletal and torsional modes	C=C stretching	1700–1600	26			1645	1600	1650–1590
	C≡C stretching	ca. 2050	26		2118		2099	2120–2090
	Skeletal deformation (in-plane)			432, (365)	509, 348	437, 320	538, 309	540–300
	Skeletal deformation (out-of-plane)	<600 cm⁻¹	26	?	206	282	219	(350)–200
	CH₃ torsion			200(?)	?	237 (?)		(240–200)

B. THE ASSIGNMENT OF FUNDAMENTALS

Our final assignments for these three molecules are summarized in Table II together, for comparison purposes, with that recently worked out for the n-butane molecule.[1] When the same frequency has slightly different values in the infra-red and Raman spectra, the infra-red frequency of the molecule in the gaseous state is usually chosen. Exceptions occur in the region above 2000 cm⁻¹ where the resolution of the Raman spectra is usually superior, and in cases where it is difficult to estimate the precise center of an infra-red band contour. Detailed points with respect to the various assignments are discussed below region by region. Table II is subdivided into the frequencies of different molecular groups so that closely related frequencies in different molecules can be easily compared. The third and fourth columns of this table give, respectively, the characteristic frequency ranges which have previously been assigned to the various modes of vibration, and the appropriate references.[1, 5, 8, 11, 25–28] Although all of these molecules are asymmetric rotators and hence infra-red band contours are difficult to predict, the type C fundamentals of the planar molecules (see reference 4, p. 469), i.e., change in electric moment perpendicular to the skeletal plane of the molecule, would be expected to have fairly marked Q branches.

(a) The Region 3350–2800 cm⁻¹

It is generally recognized that the CH stretching modes of vibration occur in this region. Fox and Martin[28] have systematized the assignment of frequencies in this region to the specific CH stretching modes, and their conclusions are summarized in Table II, column 3. In addition to the frequencies listed there, others occur close to 2900 cm⁻¹, caused by overtones of the bending modes near 1450 cm⁻¹. The various assignments in this region shown in Table II have been made with these points in mind, and taking into

---

[25] See reference 4, p. 195, and discussions of individual hydrocarbon spectra.

[26] K. W. F. Kohlrausch and F. Köppl, Zeits. f. physik. Chemie B26, 209 (1934).

[27] N. Sheppard and G. B. B. M. Sutherland, Proc. Roy. Soc. (London) (to be published shortly).

[28] J. J. Fox and A. E. Martin, Proc. Roy. Soc. (London) A175, 208 (1940).

account the polarization data on the Raman lines they are fairly self-explanatory. When an insufficient number of lines have been observed schematic assignments have been made, and these values are enclosed in brackets. They are probably close to the correct values.

(b) The Region 2900–1700 cm⁻¹

The only fundamentals that can occur in this region are the $C \equiv C$ stretching modes. This frequency occurs at 2118 cm⁻¹ in butyne-1 and at 2099 cm⁻¹ in vinyl acetylene. The slight lowering of this frequency in the latter molecule is probably due to a weakening of the linkage caused by conjugation with the neighboring $C = C$ linkage.

(c) The Region 1700–1550 cm⁻¹

The $C = C$ stretching modes occur in this region and are to be identified with the frequencies at 1650 cm⁻¹ in butene-1, and 1600 cm⁻¹ in vinyl acetylene. As in the case of the $C \equiv C$ frequency discussed above, the $C = C$ stretching mode of the conjugated molecule has a lower frequency than in the case of butene-1.

(d) The Region 1550–600 cm⁻¹

This is the most difficult region to analyze because of the occurrence of all the various CH deformation modes as well as the skeletal stretching vibrations of $C - C$ linkages. The assignment of each molecule is discussed separately.

Butyne-1

This molecule is effectively made up of an ethyl group and a $-C \equiv CH$ group. The latter will have only a few frequencies in this region, viz., two CH bending modes between 700 and 600 cm⁻¹ and a strong overtone or combination frequency involving these modes between 1300 and 1200 cm⁻¹ in the infra-red.[5,8] The in-plane CH bending mode can be identified with the polarized Raman line at 642 cm⁻¹, and the infra-red frequency at ca. 650 cm⁻¹. The expected strong infra-red line occurs at 1250 cm⁻¹, and from this we deduce 608 cm⁻¹ as an approximate value of the other CH bending mode. The remainder of the Raman lines and medium or strong infra-red lines in this region can probably

be attributed to fundamental modes of the ethyl group. If we make the assumption that the two strong and highly polarized lines at 1068 and 840 cm⁻¹ in the Raman spectrum correspond to the two skeletal stretching modes, the rest of the observed frequencies can be assigned with fair confidence using the correlation rules of Table II. The only Raman frequency in this region which has not been assigned to a fundamental is the weak line at 1023 cm⁻¹. This probably corresponds to the overtone of the 509-cm⁻¹ frequency. The final assignment appears to be very satisfactory and is in most cases in agreement with the correlation rules, and with the previous assignment for n-butane.

Butene-1

The assignment for this molecule is fairly easily arrived at, taking into account the frequencies of the ethyl group found for butyne-1, and the correlation rules for the vinyl group modes. Apart from being satisfactory on these grounds, it also accounts for all the Raman lines in this region, and all the infra-red bands except a few weak absorptions of intensity (1) or less. One of the CH₃ wagging modes has been assigned in a schematic fashion by analogy with the butyne-1 spectrum. Although derived from a more extensive knowledge of the spectra of related molecules as summarized in the characteristic frequencies of Table II, this assignment is in good agreement with the earlier results of Aston, Szasz, Woolley, and Brickwedde.[13]

Vinyl Acetylene

The frequencies of the $C \equiv CH$ group in this region can once again be picked out with little difficulty (CH bending modes at 615 and 629 cm⁻¹). The remaining frequencies of the vinyl group can be assigned as shown in a straightforward manner despite the fact that several of them are somewhat shifted from their usual positions. Although the infra-red data of Bartholomé and Karweil[28] did not give the contours of the lines, those of the closely similar spectrum of vinyl cyanide[29] help in the assignment of the out-of-plane modes of the vinyl group.

[29] H. W. Thompson and P. Torkington, J. Chem. Soc. (London) 597 (1944).

(e) The Region below 600 cm^{-1}

Butyne-1

In this region butyne-1 should have four fundamentals—three of them corresponding to bending modes of the carbon skeleton, and one to the methyl torsional mode. We have assigned the three strongest Raman lines (509, 348, and 206 cm^{-1}) to the skeletal modes, and the frequencies at 563 and 290 cm^{-1} may perhaps be the combination transitions 910–348 cm^{-1} and 509–209 cm^{-1}. A possible alternative would be to assign the 563-, 509-, and 348-cm^{-1} lines to the skeletal vibrations, and the 206-cm^{-1} line to the methyl torsion mode. Points against this latter assignment are that the methyl torsion mode is usually weak or non-observable in the Raman spectrum, and that it seems unlikely that both the in-plane (Raman, polarized) skeletal modes would be as high as 500 cm^{-1}.

Butene-1

This molecule should also have four low frequency modes of a similar type to those of butyne-1. We assign the lines at 437, 320, and 282 cm^{-1} to the skeletal modes, and that at 237 cm^{-1} to the methyl torsional oscillation. The weak line at 533 cm^{-1} can be explained as a difference band 853–320 cm^{-1}, although it may possibly be an in-plane skeletal bending mode of another rotational isomer.

Vinyl Acetylene

In this case there are just three observed Raman lines corresponding to the three skeletal modes, and the assignment is thus straightforward.

C. DISCUSSION OF RESULTS

The assignments given above for these C_4 hydrocarbons seem to be fairly satisfactory in that they explain all the strong infra-red and Raman frequencies of each molecule in a manner which is consistent with the assignments of corresponding frequencies in other structurally related hydrocarbons. Perhaps the most important advance is the systematization of the frequencies in the region 1500–600 cm^{-1}. It is clear that despite the effect of different neighbor-ing groups on the hydrogen deformation frequencies of the ethyl, vinyl, and C≡CH structural units, these maintain a closely parallel series of fundamental frequencies in the infra-red and Raman spectra. The most notable exceptions are the higher frequency in-plane methyl wagging mode of the ethyl group, and the CH_2 in-plane rocking mode of the vinyl group. The variability of these frequencies is almost certainly due to the fact that these are the two hydrogen deformation modes which are closest to the frequencies associated with the C−C stretching modes for these molecules (1100–840 cm^{-1}). They will interact strongly with these skeletal modes as all of these are in-plane frequencies. Other deformation modes are either further away from the C−C stretching frequency range, or are out-of-plane modes which cannot interact with them.

The characteristic frequencies which were used as an aid in the assignments had been obtained from the spectra of closely related molecules. However, for such a characteristic frequency to be found consistently in the spectra of a series of molecules it must have some distinctive feature such as considerable strength in the infra-red or Raman spectrum. As a result, several frequencies cannot be found in this manner because of weakness in both types of spectra. Such cases are the CH_2 twisting mode of the ethyl group, the in-plane CH_2 rocking mode, and the torsional mode of the vinyl group. The detailed analysis of the spectra of these smaller molecules, however, has enabled these frequencies to be identified in the regions 1260–1240 cm^{-1}, 1170–1090 cm^{-1}, and 680–600 cm^{-1}, respectively. These values, together with the regions of the spectrum corresponding to the various other modes of vibration, are summarized in the last column of Table II, and have been taken directly from the data of the preceding columns. These data are supplementary to the data already given earlier in the third column of the same table on the characteristic frequencies of various modes, in that they are usually less precise in range. On the other hand, they are of wider application, and are probably fairly accurately obeyed in most hydrocarbon spectra.

The assignments that we have made in the frequency region below 600 cm^{-1} are probably the least reliable because of the lack of infra-red data.