

The Vibrational Spectrum of 4-chlorobutene-3-yne

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IR spectra were recorded of 4-chlorobutene-3-yne in the vapor phase, in CCl_4 ($4000\text{--}400\text{ cm}^{-1}$) and cyclohexane ($500\text{--}100\text{ cm}^{-1}$) solutions, and in the solid state. Raman spectra including polarization measurements were recorded of the liquid and of the solid at liquid air temperature.

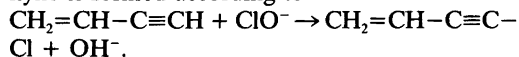
The vapor IR spectrum contains a number of A/B hybrid bands and C contour bands. The spectrum is interpreted in terms of the C_s symmetry group, hence assuming a planar structure. A 27 parameter valence force field, transferred from similar molecules, was refined to make the fit between observed and calculated frequencies satisfactory.

4-chlorobutene-3-yne, henceforth to be called CVA, has been subject to microwave and electron diffraction studies by our group^{1,2}. The vibrational and rotational spectra of the unsubstituted compound have also been reported³. The present investigation of the vibrational spectrum therefore fills a gap in the structural information on the molecule, by contributing to our understanding of its bonding properties.

A provisional force field for CVA was derived both in the microwave and in the electron diffraction study^{1,2}. A refined force field, obtained in the present investigation does not differ substantially from the force field of the unsubstituted butenyne, except for the part containing chlorine.

Experimental

The sample was prepared according to Jacobson and Carothers⁴: Butene-3-yne is added to a hypochlorite solution at 0°C , whereby chlorobutenyne is formed according to



The product was purified by distillation and gas-liquid chromatography at 100°C , using a 1.5 m diethylhexylsebacate column (15% on chromosorb).

The substance tends to polymerize at room temperature and has to be stored at -70°C . Recording of spectra, on the other hand, can be performed without any extra precautions and the sample shows no sign of decomposition after exposure to the *ca* 100 mW power of the 515.4 nm laser line during the Raman experiments.

The IR spectra were recorded on three different instruments: The vapor spectrum in the $4000\text{--}600\text{ cm}^{-1}$ region was recorded on a Digilab FTS-14 FTIR spectrometer, equipped with a KBr beamsplitter and a 10 cm vapor cell with KBr windows. Sample pressures were *ca* 90 and 30 mbar.

Far-IR vapor, solution (*ca* 15% in cyclohexane) and solid phase spectra were recorded on a Bruker 114C FTIR spectrometer, using mylar beamsplitters of 3.5, 6, and 12 μm thicknesses for the different wavelength regions. The vapor cell has 18 cm path length and the sample pressure was *ca* 90 mbar. A 0.5 mm polyethylene cell was used for the solution spectrum, whereas that of the solid was recorded at *ca* -180°C in a cryostat with polyethylene windows.

The mid-IR solution spectrum was recorded on a Perkin-Elmer model 225 spectrometer, using a 0.1 mm KBr liquid sample cell.

The same spectrometer was employed for recording the solid state spectrum. Here the sample vapor was allowed to deposit on a cooled KBr

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window of a cryostat. Spectra were obtained of the sample in both amorphous and annealed solids.

The Raman spectra were run on a modified Cary 81 Raman spectrometer with an argon ion laser source; the 515.4 nm line was used for excitation. The liquid sample was contained in a 4 mm evacuated tube during recording of the spectrum and the polarization measurements.

Spectra of solid phase deposits on a cooled copper block at the temperature of liquid air were recorded before and after annealing.

The program used for normal coordinate analyses of the spectra^{11,12} uses Cartesian displacement coordinates. In addition to force constants and normal coordinates, it calculates centrifugal distortion constants, which in this molecule can be compared to those observed for CVA¹ listed at the lowest lines in Table 3.

Interpretation of the spectra

General. CVA belongs to the C_2 point group with only two symmetry species, a' and a'' . All normal vibrations are active in both Raman and IR. Of the 18 modes, five belong to the a'' species. In the spectrum they often are easily identified as giving rise to C-type contour bands in the vapor, with prominent Q peaks and depolarized Raman counterparts (Figs. 1a and b, Fig. 2).

The anticipated A/B type band contours of the a' species bands are frequently encountered in the vapor phase spectrum (Fig. 1).

With the help of the observed rotational constants' the separation between the P and R branches was calculated to be 9.5, 12, and 18 cm^{-1} for the A, B and C type bands resp³.

The above-mentioned information regarding the vapor spectra, together with well resolved

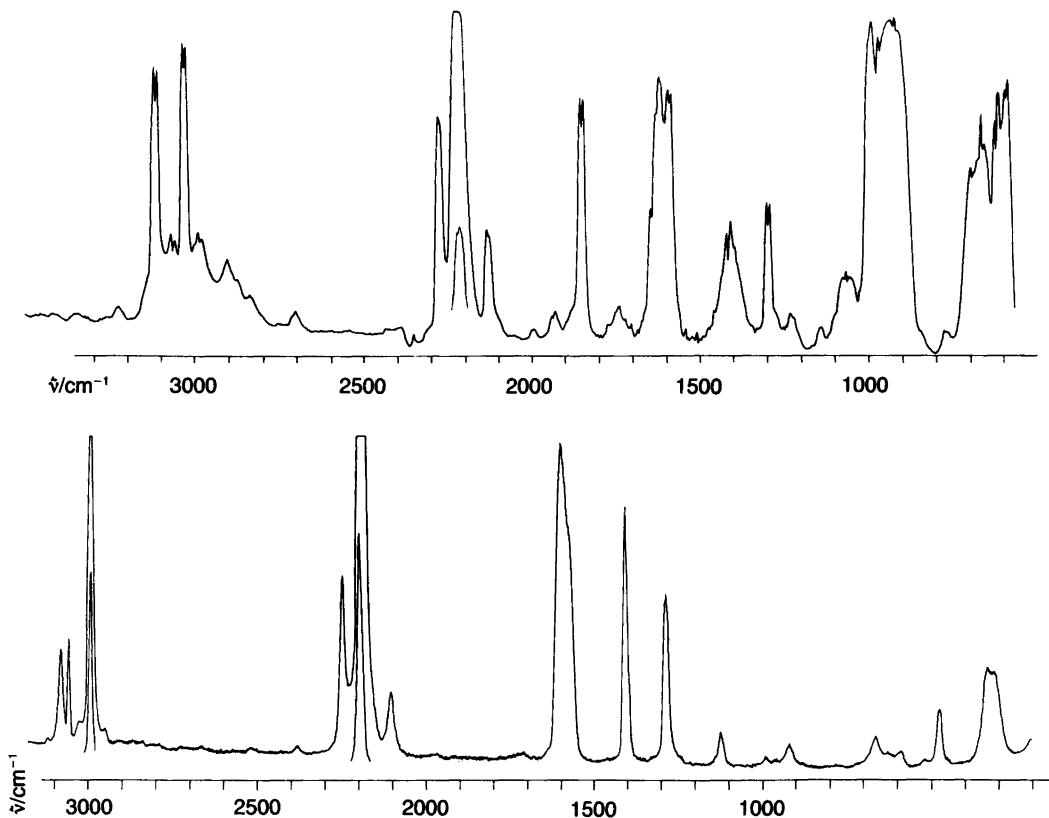


Fig. 1. The CVA vibrational spectrum.
a. The IR spectrum. (10 cm cell, 90 and 30 mbar pressure.)
b. The Raman spectrum.

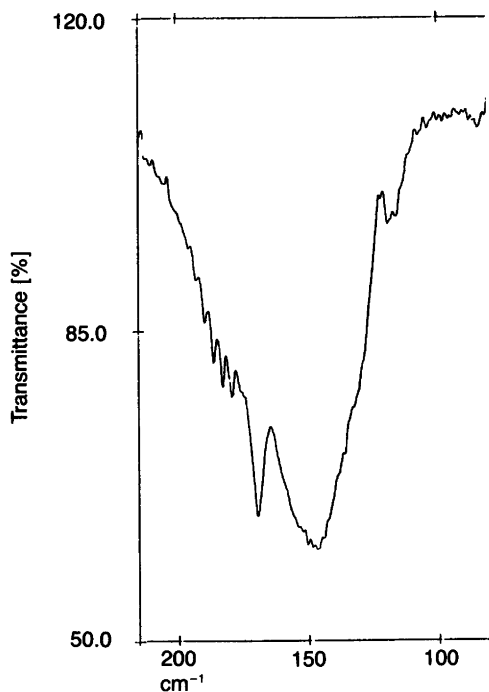


Fig. 2. The IR absorption around 150 cm^{-1} (18 cm cell, 80 mbar).

spectra of CVA(l) and CVA(s) in IR and far-IR, Raman recordings of CVA(l) and (s) and with polarization data make the spectral interpretation fairly straightforward.

Stretching vibrations. The three C–H stretching coordinates of Table 1 are immediately identified in the IR spectra as ν_1 at 3114 cm^{-1} (asymmetric $=\text{CH}_1$ stretch), ν_2 , the weak absorption at 3064 cm^{-1} ($-\text{CH}$ stretch) and ν_3 at 3030 cm^{-1} (symmetric $=\text{CH}_2$ stretch). Both ν_1 and ν_3 give rise to very strong bands. The wave numbers are almost equal to those found for 4-deuterobutene-3-yne by Tørneng et al.³, however slightly shifted to lower frequencies as compared to the unsubstituted butenyne. The very strong peak at 2228 cm^{-1} is interpreted as being due to the $\text{C}\equiv\text{C}$ stretch, ν_4 . This band is shifted 113 wave numbers to higher frequencies compared to the unsubstituted butenyne. In deuterobutenyne it is predominantly mixed with the ν_5 fundamental at 1994 cm^{-1} . According to our PED (Potential En-

ergy Distribution) calculations the ν_4 of CVA is a fairly localized $\text{C}\equiv\text{C}$ stretch.

$\text{C}\equiv\text{C}$ stretching coordinate is predominantly contributing to the ν_5 band at 1589 cm^{-1} , almost equal to the absorption frequencies for the corresponding mode in butenyne and deuterobutenyne, 1599 cm^{-1} and 1596 cm^{-1} , respectively. The band in CVA, however, is slightly perturbed by Fermi resonance with two neighbouring combination bands, see later.

The $\text{C}\equiv\text{C}$ stretching coordinate contributes to both ν_8 and ν_9 by almost equal amounts. The former band is found at 1140 cm^{-1} , being weak and broad in IR with a more distinct Raman counterpart. The ν_9 band at 996 cm^{-1} is one of the strongest bands of the spectrum with prominent A/B features. In butenyne and deuterobutenyne the mode is also distributed between two bands, at 1096 cm^{-1} and 874 cm^{-1} in the former, at 1096 cm^{-1} and 865 cm^{-1} in the latter. The ν_9 band also contains contributions from CCl stretch. So does the ν_{10} fundamental at 622 cm^{-1} . The corresponding band occurs at 756 cm^{-1} in vapor IR of monochloroacetylene and at 575 cm^{-1} in monochlorodiacetylene and 747 cm^{-1} in dichlorodiacetylene⁷.

The band at 622 cm^{-1} is tentatively assigned to ν_{10} due to the support given by our calculations and by the better explanation of the 594 cm^{-1} band as a combination; see below.

In-plane bendings. All in-plane bending modes of CVA are more or less mixed. The C–H bond angle deformations mainly contribute to ν_6 at 1414 cm^{-1} , to ν_7 at 1296 cm^{-1} , as well as to ν_9 at 996 cm^{-1} . The A/B contour of the 1414 cm^{-1} band is somewhat obscured by rotational fine structure belonging to a nearby A'' combination band, but the corresponding Raman band is very strong and definitely polarized. The A/B character of ν_7 and ν_9 is quite obvious (Fig. 1a).

Also in butenyne and deuterobutenyne, the bending modes are mixed and the absorption bands are found between 874 cm^{-1} and 1415 cm^{-1} (butenyne), and between 543 cm^{-1} and 1415 cm^{-1} (deuterobutenyne).

Bending of the C–Cl bond angle is predominantly contributing to ν_{12} at 305 cm^{-1} . Frequencies reported for this coordinate of related compounds are: Monochloroacetylene 326 cm^{-1} , methylchloroacetylene 184 cm^{-1} ⁶, monochlorodiacetylene 129 cm^{-1} ⁷. The remaining a' funda-

Table 1. Infrared and Raman spectral data of 4-chlorobutene-3-yne.

Infrared				Raman				Interpretation
Vapour	Solution	Solid (-180°C)		Liquid	Solid (-180°C)			
		Amorphous	Annealed		Amorphous	Annealed		
			3167 w	3146 vw				
3139 vs 3114 vs 3130 vs	A/B } 3105 w	3101	3097 m	3108 m P	3100 s	3100 s	ν_1 A'	
3070 w 3066 vw 3062 vw 3058 w	A/B } 3052 vw	3048 vw	3048 vw	3053 vw P	3052 w	3052 m	ν_2 A'	
3035 vs 3030 vs 3025 vs	A/B } 3017 m	3014 s	3015 m 3010 m	3019 vs P	3011 vs	3017 s,sh 3011 s	ν_3 A'	
2990 w 2988 w	A/B(?)	2970 m	2968 m	2979 vw	2970 w	2970 w	$\nu_5 + \nu_6 = 3003$ A'	
2975 w		2956 vw						
		2925 vw	2930 vw					
2902 w		2885 w	2880 vw				$\nu_7 + \nu_8 = 2885$ A'	
2867 w,br		2868 vw,br					$\nu_5 + \nu_{10} = 2846$ A'	
2832 vw,br		2830 w			2831 vw		$2\nu_6 = 2828$ A'	
2700 vw,br		2689 vw	2660 vw				$\nu_6 + \nu_7 = 2712$ A'	
	2658 vw			2540 vw P				
				2403 vw P	2400 vw		$\nu_6 + \nu_9 = 2413$ A'	
		2331 vw					$\nu_6 + \nu_{15} = 2338$ A''	
2277 s 2270 s,sh	A/B? } 2268 m	2263 s	2266 s	2268 s P	2267 s	2267 s	$2\nu_8 = 2280$ A' or $\nu_9 + \nu_7 = 2293$ A' FR	
2228 vs,sh	A/B } 2215 vs	2212 vs	2217 vs	2217 vvs P	2218 vs,sh	2219 vs	ν_4 A'	
2220 vs	2207 vs,sh		2213 vs	2209 vs,sh P	2215 vvs	2215 vs	$\nu_5 + \nu_{10} = 2211$ A' FR	
		2174 m	2175 vw,br		2177 w	2177 w	$\nu_1 - \nu_{15} = 2190$ A''	
2132 m 2124 m	A/B } 2120 w	2115 m	2122 w 2116 vw	2122 m,P	2120 m	2120 m	$\nu_8 + \nu_9 = 2137$ A'	
			1944 w				$\nu_9 + \nu_{14} = 1969$ A'' or $2\nu_{14} = 1944$ A''	
1929 vw	1930 vw,br		1936 w				$\nu_9 + \nu_{15} = 1921$ A'' or $\nu_5 + \nu_{17} = 1928$ A''	
1854 vs 1845 vs	A/B } 1850 m		1878 w,sh 1875 m,sh 1870 m 1865 m,sh				$2\nu_{15} = 1850$ A' or $\nu_6 + \nu_{11} = 1894$ A'	

VIBRATIONAL SPECTRUM OF 4-CHLOROBUTEN-3-YNE

Infrared			Raman				Interpretation
Vapour	Solution	Solid (-180°C)		Liquid	Solid (-180°C)		
		Amorphous	Annealed		Amorphous	Annealed	
1737 w,br							$\nu_8 + \nu_{17} = 1753A''$
1645 m			1650 w 1640 w				$\nu_9 + \nu_{16} = 1666$ A''
1629 s	1631 w,sh	1620 1615	1630 w 1620 w	1617 vs P	1619 s	1621 s	$\nu_8 + \nu_{11} = 1616 A''$ FR
1620 vs	1613 m,sh	1604 s					$\nu_7 + \nu_{12} = 1601 A'$
1612 vs,sh	1602 m,sh	1596 s	1597 s	1609 vs,sh P	1597 s	1598 s	$\nu_7 + \nu_{12} = 1701 A'$ or $\nu_{15} + \nu_{16} =$ 1594 A' FR
1593 vs 1584 vs } A/B	1586 m,sh	1584 vs	1584 s	1591 s P	1584 s	1586 s	$\nu_5 a'$
		1568 w	1567 w				$\nu_8 + \nu_6 = 1583 A''$ $\nu_{11} + \nu_{14} = 1448 A''$
	1450 m						
1420 m 1411 m } A/B	1407 s	1408 vs	1413 w 1411 w 1408 w 1405 vs	1411 vs P	1412 vs	1413 s	$\nu_6 a'$
1408 w 1405 w 1402 w 1400 w 1394 m } C			1397 vw				$\nu_{15} + \nu_{11} = 1403 A''$?
		1366 w					?
	1358 vw						?
		1355 w 1336					$\nu_9 + \nu_{17} = 1336$
1300 s 1291 s } A/B	1292 w	1291 s	1294 m	1294 s P	1294 s	1295 s	$\nu_7 a'$
		1277 w	1277 s				$\nu_{12} + \nu_{14} = 1279 A''$
1229 w		1236 s					$2\nu_{10} = 1244 A'$
1228 vw	1218 m	1215 m	1215 m				$\nu_{12} + \nu_{15} = 1229 A''$
1149 w,br A/B?		1132 m	1133 m	1134 w P	1134 m	1134 w	$\nu_8 a'$
		1092 w	1098 w,br				$\nu_{13} + \nu_{14} = 1102 A''$
1076 w							$\nu_{10} + \nu_{11} = 1098 A'$
1066 w C							$\nu_{15} + \nu_{18} = 1093 A'$
1058 w 1049 w		1045 w,br					$\nu_{13} + \nu_{15} = 1054 A''$
1001 vs 993 vs } A/B	994 s	993 vs	998 vs 996 w 994 vs	996 w P	998 vw		$\nu_9 a'$

Infrared				Raman			Interpretation
Vapour	Solution	Solid (-180°C)		Liquid	Solid (-180°C)		
		Amorphous	Annealed		Amorphous	Annealed	
Rotational fine structure							
972 vs C	970 s	973 vs	977 vs 972 vs	969 vw, D	974 ν_{14} a''		
Rotational fine structure							
024 vs C	924 vs	931 vs	932 vs 929 vs	928 w D	932 m	932 m	ν_{15} a''
Rotational fine structure							
		755 m					$\nu_{11} + \nu_{12} = 781$ A'
		738 vw					$\nu_{10} + \nu_{13} = 752$ A''
668 vs	670 w	670 s	680 s 670 m 559 m,sh 668 w,sh	670 w,br D	673 m	682 m,sh 673 m	ν_{16} a''
627 vs 618 vs	}A/B	625 s	623 s	635 vw,br P	626 w	627 w	ν_{10} a'
598 vs 590 vs		595 vs	598 s	596 s	596 w P	596 w	596 w
524 w	525 w,br	540 m					?
479 m	477 m	477 m	478 m	481 m P	481 s	481 m	ν_{11} a'
			415 w,br				$\nu_{12} + \nu_{13} = 435$ A' ?
	351 w		348 w 346 w	339 m D	348 s	349 s	ν_{17} a''
305 w,br	304 2		305 w,br	318 m P	307 s	307 s	ν_{12} a'
	280 vw						$\nu_{13} + \nu_{16} = 229$ A''
	246 vw						$2\nu_{13} = 260$ A'
	225 w,sh	225 m					impurity?
192 w 189 w 186 w 182 w 176 w 169 s	}C	178 vs	198 m				ν_{18} a''
149 s					185 vw,br		
130 m,sh	139 s	150 s		130 m P			ν_{13} a'

mentals are mixed skeletal bending modes, with small contributions from bending of the C-H bonds and from bond stretching. The ν_8 band at

1140 cm^{-1} could only be assigned with the help of Raman data. The ν_{11} band is found at 476 cm^{-1} , ν_{13} at 130 cm^{-1} , thus in accordance to what is ob-

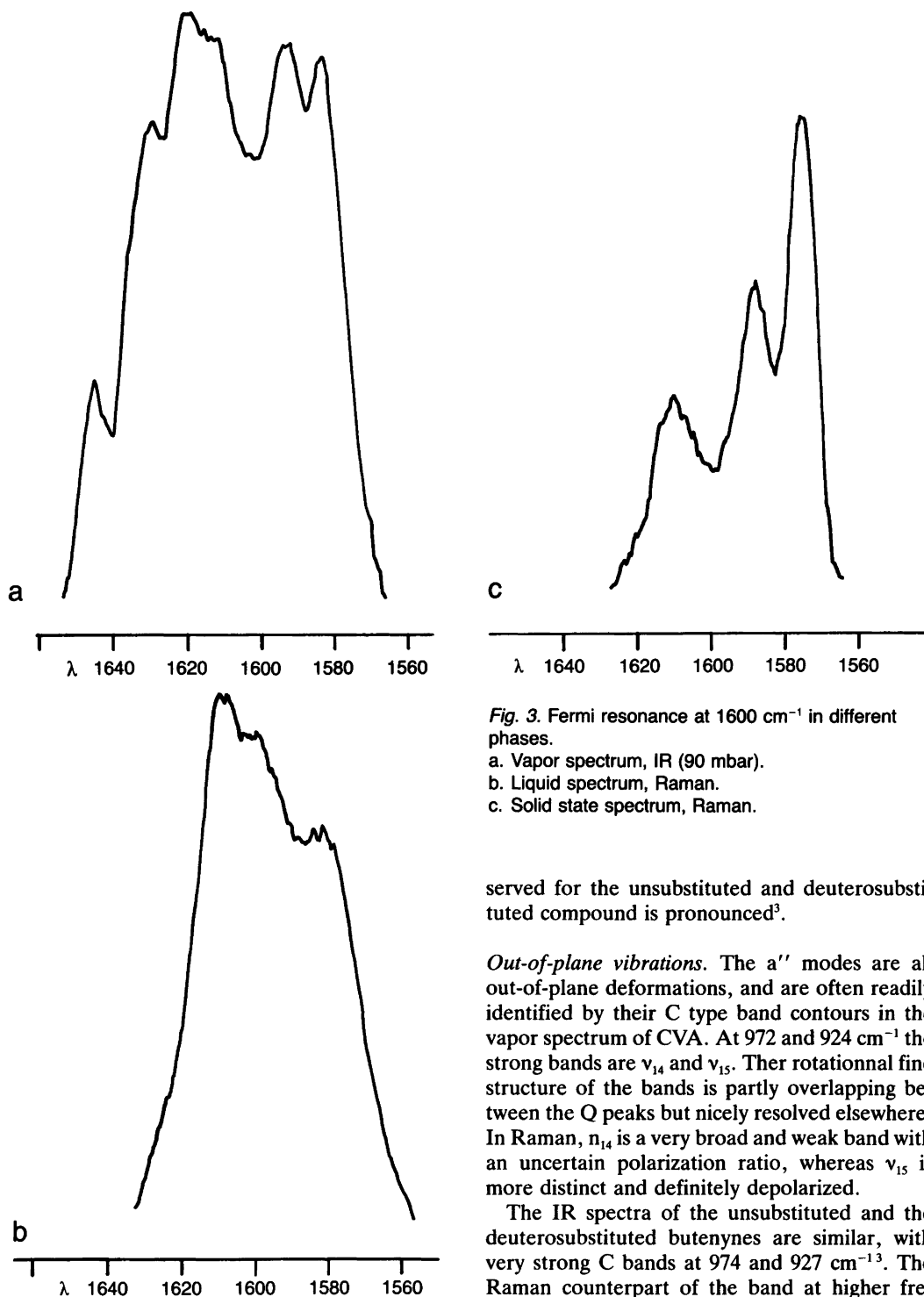


Fig. 3. Fermi resonance at 1600 cm^{-1} in different phases.

- a. Vapor spectrum, IR (90 mbar).
- b. Liquid spectrum, Raman.
- c. Solid state spectrum, Raman.

served for the unsubstituted and deuterio-substituted compound is pronounced³.

Out-of-plane vibrations. The a'' modes are all out-of-plane deformations, and are often readily identified by their C type band contours in the vapor spectrum of CVA. At 972 and 924 cm^{-1} the strong bands are ν_{14} and ν_{15} . Their rotational fine structure of the bands is partly overlapping between the Q peaks but nicely resolved elsewhere. In Raman, ν_{14} is a very broad and weak band with an uncertain polarization ratio, whereas ν_{15} is more distinct and definitely depolarized.

The IR spectra of the unsubstituted and the deuterio-substituted butenyne are similar, with very strong C bands at 974 and 927 cm^{-1} ³. The Raman counterpart of the band at higher fre-

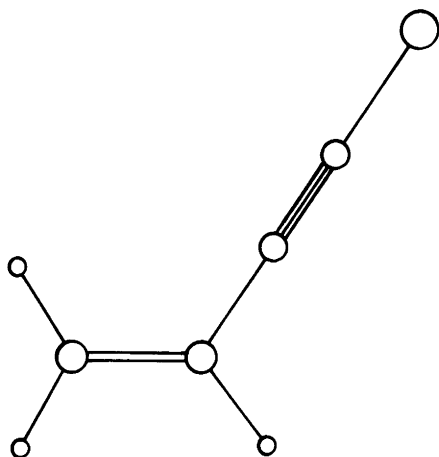


Fig. 4. Molecular model of 4-chlorobutene-3-yne and the numbering of atoms.

quency is weak and broad, that for the lower one is more distinct, just as for CVA. The interpretation differs, however. Our PED calculations show that these absorptions are related mainly to the bending of carbons 6 and 4 out of the plane spanned by atoms 4,2,6 and 7,8,3, respectively. (Fig. 4.) Mode ν_{14} of the unsubstituted and deuterated compounds is supposedly mixed with torsion³.

The ν_{16} band at 668 cm^{-1} mainly involves out-of-plane bending of the linear chain. It is a strong band with definite C contour in the vapor spectrum, its Raman counterpart weak and depolarized.

C-type, depolarised bands at 677 and 676 cm^{-1} are reported for butenyne and deuterobutyne resp.³, in both cases interpreted as torsions (twistings around the vinyl bond).

In the far-IR vapor spectrum ν_{17} of CVA does not appear. The Raman band at 339 cm^{-1} , on the other hand, is depolarized and of substantial intensity, which supports the assignment of this band. Our calculations indicate torsion as the main contributor to this band, thus corresponding to what is reported for this mode in similar molecules^{6,9,10}.

Due to its sharp Q branch and five resolved peaks of the R branch, the band centered at 169 cm^{-1} is easily identified as due to an a'' coordi-

Table 2. Simplified Valence Force Field of 4-chlorobutene-3-yne.

Definition* k (10^2Nm^{-1})	I butenyne†	II CVA
1 C1≡C2	15.334	14.755
2 C2-C3	5.252	5.252
3 C3=C4	9.148	9.148
4 C1-Cl (C1-H)	5.976	5.531
5 C3-H6	5.111	5.111
6 C4-H†	5.144	5.144
$k_{\theta,ip}$ ($\text{nN}\cdot\text{nm rad}^{-2}$)		
7 C=C-H†	0.582	0.582
8 HCH	0.3654	0.365
9 C-C-H	0.572	0.572
10 C=C-C	0.842	0.842
11 C-C≡C	0.2721	0.267
12 C≡C-Cl (C≡C-H)	0.2206	0.366
$k_{\theta,op}$ ($\text{nN}\cdot\text{nm rad}^{-2}$)		
13 C-C≡C	0.3041	0.326
14 C≡C-Cl (C≡C-H)	0.2057	0.765
k_{τ} ($\text{nN}\cdot\text{nm rad}^{-2}$)		
16 C4	0.3823	0.382
17 C4=C3	0.2383	0.238
k_{τ} (10^2Nm^{-1})		
18 C-C/C=C	0.09744	0.106
19 C-C/C≡C	0.5	0.500
20 C-H7/C-H8	0.2	0.200
$k_{r\theta,ip}$ ($\text{nN}\cdot\text{nm rad}^{-2}$)		
21 C=C/C=C-H† C-C/C=C-H	0.039	0.051
22 C=C/C=C=C	0.336	0.336
$k_{\theta,ip,\theta,op}$ ($\text{nN}\cdot\text{nm rad}^{-2}$)		
23 C=C-H8/C=CH6 C=C-H7/C=C-X	0.276	0.276
24 C=C-H7/C=CH6 C=C-H8/C=C-	0.067	0.067
25 C-C≡C/C≡C-Cl (.../C≡C-H)	-0.034	-0.034
$k_{\gamma\gamma}$ ($\text{nN}\cdot\text{nm rad}^{-2}$)		
26 C3/C4	0.010	-0.119
$k_{\theta,\gamma,\gamma,op}$ ($\text{nN}\cdot\text{nm rad}^{-2}$)		
27 C-C≡C/C≡C-Cl (.../C≡C-H)	0.044	0.059
	0.040	0.058

* The molecular model is given in Figure 4.

The k subscripts mean: r , stretching; θ,ip , in-plane bending; θ,op , out-of-plane bending; γ , out-of-plane bending of a central atom in a planar group of 4 atoms; τ , torsion.

† All possible combinations with hydrogen according to the k definition.

‡ Force constants as in Ref. 3.

nate, ν_{18} (Fig. 2). In the Raman spectrum of the liquid it is found at 185 cm^{-1} .

Combinations and overtones. Bands attributed to combined modes are noted in Table 1 along with their symmetry. In a few cases Intensities are enhanced by Fermi interaction, which is also noted in the Table.

In the group of bands at 1589 (ν_5), 1620 (ν_{15} , ν_{16}), and 1629 ($\nu_7\nu_{12}$) cm^{-1} , the intensities of individual bands relative to the others change according to phase. See Figs. 3a-c.

The combination band of ν_{15} and ν_{11} at 1394 cm^{-1} has a very distinct C type contour with four rotational transitions clearly outlined in the vapor spectrum.

The strong band with a typical A/B contour at 1850 cm^{-1} is no fundamental but either the first overtone of ν_{15} or the combination of ν_{11} with ν_6 .

Discussion

In Fig. 4, a model of the CVA molecule is depicted in accordance to Fukuyama et al¹³, and its

atoms numbered. The force constants for stretching, bending and some interaction constants are defined in Table 2. Comparison with values of the force field for butenyne is also done in the Table³. Force constants for vibrations involving chlorine were transferred from similar fragments of other molecules^{7,9} and allowed to refine during the iteration process of the normal coordinate analysis¹².

In Table 3 observed and calculated fundamental frequencies are tabulated, along with the potential energy distribution according to our calculations. The mixing of the vibrational modes is in some cases substantial.

The substitution of hydrogen for chlorine in the ethynyl group of butenyne changes the stretching force constants with only *ca* 5%. This is in agreement with the results of the electron diffraction study, where minor deviations of the ethynyl bond distances due to substitution are reported². No increase in the force constant of the central single bond similar to that recently reported for dimethyldiacetylene¹⁴ was detected.

The substitutional effects on the bending modes are quite large. In particular, the resis-

Table 3. Observed and Calculated Fundamental Frequencies of 4-chlorobutene-3-yne.

Species	No	Observed	Calculated	PED [†]
a'	ν_1	3114	3114	6(99)
	ν_2	3064	3064	5(93)
	ν_3	3030	3030	6(94)
	ν_4	2224	2224	1(83), 2(10)
	ν_5	1589	1592	3(85), 7(11), 21(-18)
	ν_6	1414	1411	7(49), 8(34), 9(13)
	ν_7	1297	1307	3(12), 7(44), 8(16), 9(12)
	ν_8	1140	1140	2(27), 4(13), 7(30), 9(17)
	ν_9	996	995	2(24), 4(27), 7(43)
	ν_{10}	622	617	2(13), 4(32), 7(22), 10(25)
	ν_{11}	476	474	2(16), 4(18), 10(21), 11(28), 12(13), 25(-15)
	ν_{12}	305	304	10(13), 11(29), 12(90), 25(-40)
	ν_{13}	130	129	11(54), 12(13), 25(21)
a''	ν_{14}	972	972	15(88)
	ν_{15}	924	924	16(103), 26(-10)
	ν_{16}	668	668	13(22), 14(62)
	ν_{17}	339 [§]	339	17(87)
	ν_{18}	169	169	13(72), 14(31), 27(-11)
Δ_J (kHz)		0.12	0.12	
Δ_K (kHz)		-28.55	-23.39	

[§] Raman liquid value.

[†] Contributions (%) in parenthesis and numbering as given in Table 2. Values below 10% are omitted.

tance to out-of-plane bending of the chloro-ethynyl chain increases *ca* 270 %. We made attempts to constrain this force constant to values similar to the force constant for the corresponding in- and out-of-plane bending modes in butenyne. This procedure, however, in some cases created unacceptably large differences between observed and calculated frequencies. In particular ν_{16} was affected. It is possible that a valence force field with a more detailed set of interaction constants or a different type of force field would better explain this substitutional effect.

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