

Infrared Spectra and Tentative Vibrational Assignments of Some Halogeno Cyanoacetylenes

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The infrared spectra of the halogeno cyanoacetylenes $X-C\equiv C-C\equiv N$ ($X = Cl, Br, \text{ and } I$) have been recorded in the gaseous phase and in carbon disulphide or cyclohexane solutions in the region $4000-280\text{ cm}^{-1}$. These spectra can be interpreted in terms of a linear structure and 6 of the fundamental frequencies have been observed. A tentative assignment of the vibrational spectra has been made and a force constant calculation has been carried out.

Chloro,¹ bromo,² and iodo³ cyanoacetylenes have recently been synthesized by one of us, and they are found to be quite stable at room temperature. These compounds are expected to be linear and preliminary micro-wave investigations⁴ support this prediction. The molecules are also being studied by electron diffraction methods with special reference to the shrinkage effect,⁵ and iodo cyanoacetylene has been studied by X-ray crystallographic methods⁶ in the solid state.

In the present paper we shall report the infrared spectra of these compounds as observed in the gas phase and in solution. A tentative assignment of the infrared spectra will be proposed, partly based on reported work on related linear molecules. The assignments were partly confirmed by force constant calculations.

No attempts were made to obtain the Raman spectra since only small samples were available. Moreover, bromo cyanoacetylene (Br) and iodo cyanoacetylene (I) slowly became coloured in carbon tetrachloride solutions when exposed to daylight. Thus, it seems likely that only chloro cyanoacetylene (Cl) might successfully be exposed to the Raman irradiation.

EXPERIMENTAL

(Cl), (Br), and (I) were prepared by halogenation of cyanoacetylene, according to the procedures described previously.¹⁻³

(Cl), m.p. $42.0-42.5^\circ\text{C}$, was purified by gas liquid chromatography on a Beckman GC-2 gas chromatograph, using a column of 3 m length and 1/4 inch inner diameter with

25 % Apiezon L on Chromosorb W and helium as a carrier gas. The flow rate was 60 ml/min and the operating temp. 64°C.

(Br), m.p. 96.0–96.5°C was purified by sublimation 3 times over phosphorus pentoxide at 32°C at 10 mm Hg.

(I), m.p. 152.0–152.5°C was purified by sublimation 2 times at 1 mm Hg pressure from 20°C to dry ice temperature.

The (uncorrected) melting points of (Br) and (I) were measured in sealed capillaries on a Hoover Capillary Melting Point Apparatus and (Cl) in an evacuated tube in an alcohol bath.

Carbon tetrachloride, cyclohexane, and carbon disulphide, all *Uvasole* from Merck, were used as solvents for the infrared measurements. They were used without further purification after their infrared spectra had been checked for impurity bands.

The infrared spectra were obtained with the aid of a Unicam SP-100 spectrophotometer equipped with a rock salt prism and gratings, ruled at 1500 and 3000 lines/inch for the 650–2150 cm^{-1} and the 2150–3650 cm^{-1} regions, respectively. A potassium bromide prism without grating was employed in the region 650–400 cm^{-1} . Finally, the spectral region 400–280 cm^{-1} was covered with a Perkin-Elmer model 21 spectrophotometer, having CsBr optics.

(Cl) has a high vapour pressure at room temperature and was studied in a 10 cm gas cell having KRS-5 windows. (Br) was studied in a 1 m folded gas cell with KRS-5 windows. (I) has a very low vapour pressure and no absorption spectrum was obtained in the 1 m gas cell at room temperature. However, the strongest bands were recorded at 60°C in a 10 cm cell in the sodium chloride region. The solution spectra were obtained in carbon disulphide, carbon tetrachloride or cyclohexane, using matched pairs of sealed cells of thickness 0.02 cm with sodium chloride and KRS-5 windows.

RESULTS

The infrared spectrum of (Cl) in the gaseous phase is shown in Fig. 1. The wave numbers of the observed absorption maxima (or in some cases unresolved "shoulders") of (Cl), (Br), and (I) are listed in Tables 1–3. (I) is only slightly soluble in the solvents and a complete infrared spectrum of this compound was not obtained either in gas or in solution. We believe that 6 of the fundamentals were recorded, but most of the weaker overtone and combination bands are not included in Table 3.

INTERPRETATION

Fundamentals. The halogeno cyanoacetylenes undoubtedly have a linear configuration of point group $C_{\infty, v}$ and hence have 4 normal vibrations of species $A_1 = \Sigma^+$ and three doubly degenerate of species $E_1 = \Pi$. The former should be bond stretching vibrations of higher frequencies, the latter bending vibrations and one of these are expected to lie outside the range of the CsBr prism. All the seven fundamentals should be both infrared and Raman active, and an assignment of the vibrational spectra can be based upon the infrared data alone.

We assumed the following interatomic distances: $\text{C}\equiv\text{C}$, 1.205; $\text{C}\equiv\text{N}$, 1.158; $\text{C}-\text{C}$, 1.375; $\text{C}-\text{Cl}$, 1.635; $\text{C}-\text{Br}$, 1.793, and $\text{C}-\text{I}$, 1.991 Å. These values have been reported on similar molecules by microwave and electron diffraction and should be approximately valid for the present molecules. The principal moments of inertia are accordingly: $I = 613.2$, 886.8, and

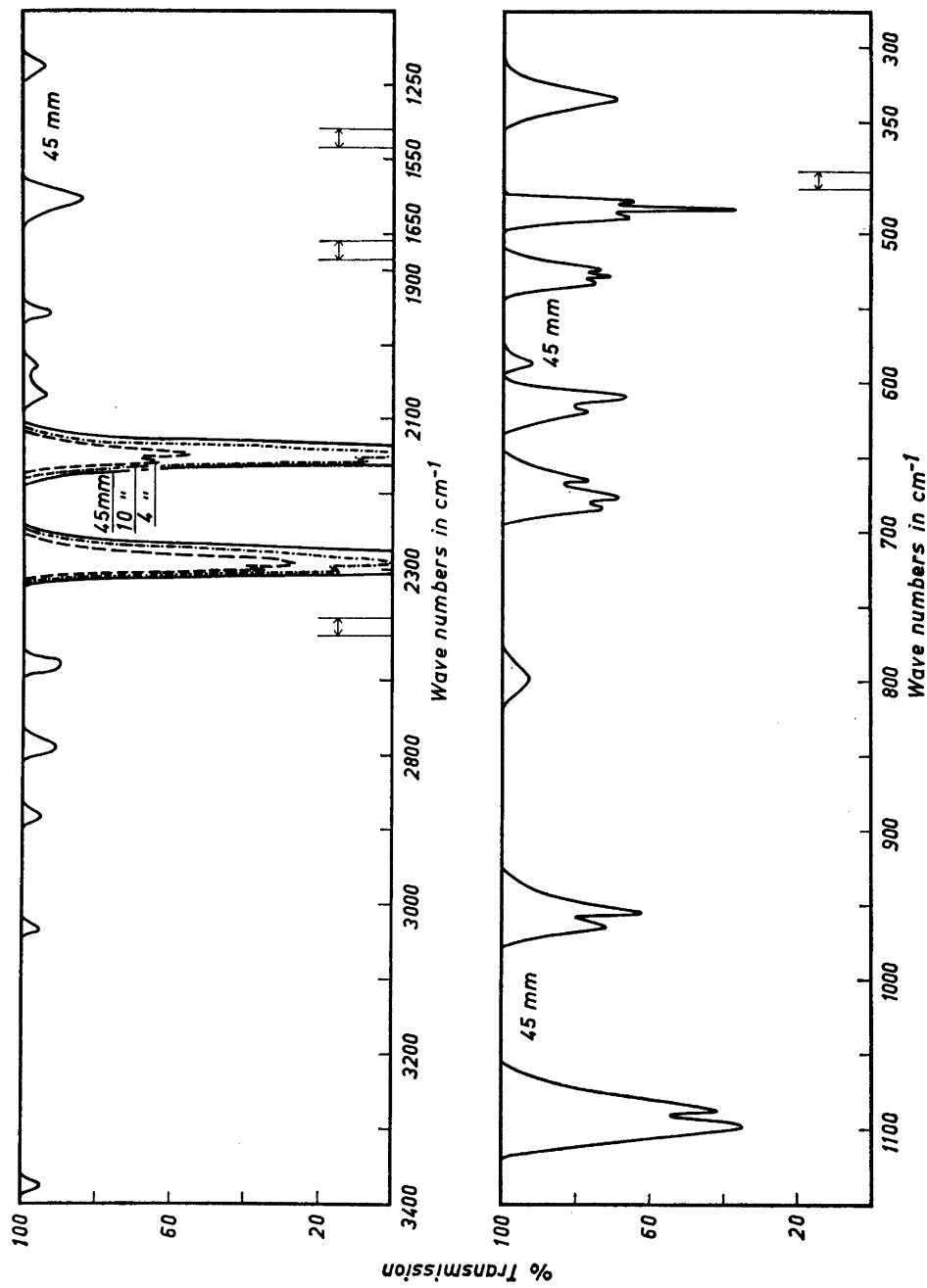


Fig. 1. The infrared spectrum of gaseous chloro cyanoacetylene at 25°C and 10 cm path length.

Table 1. Infrared spectral data for Cl—C≡C—C≡N (in cm⁻¹).

Gas		Contour	Solution		Interpretation	
Wave number	Description ^a		Wave number	Description ^a		
3378	vw		3370 ^b	vw	$\nu_1 + \nu_3 = 3390$	
3032	vw		3030 ^b	vw	$\nu_2 + \nu_3 = 3342$	
			2910 ^b	m	$\nu_1 + \nu_4 = 2910$	
2827	w		2818 ^b	m	$\nu_1 + \nu_5 = 2824$	
2778	w				$\nu_1 + \nu_6 = 2780$	
2673	vw		2676 ^b	vw	$\nu_2 + \nu_5 = 2676$	
2301	vs		2629 ^b	vw	$\nu_2 + \nu_5 = 2632$	
2293			vs	2283 ^b	vs	ν_1
2153						
2145	s		2146 ^b	s	ν_2	
2066	vw					
2027	vw					
1956	w					
1600	w				$\nu_3 + \nu_5 = 1620$	
1270	vw				$\nu_3 + \nu_7 = 1260$	
1098	s		1098 ^c	s	ν_3	
1089						
964	m		963 ^c	m	$2\nu_6 = 966$	
955						
797	vw		785 ^c	vw		
683	m		762 ^c	vw	$\nu_4 + \nu_7 = 780$	
676			m	677 ^c	m	$\nu_5 + \nu_7 = 694$
667	m				$\nu_6 + \nu_7 = 650$	
618	m		623 ^d	m	ν_4	
609						
588	w					
531	m	⊥	528 ^d	m	ν_5	
527						
524						
488	s	⊥	482 ^d	s	ν_6	
483						
479						
334	m		333 ^d	m	$2\nu_7$	
[167] ^e					ν_7	

^a The following abbreviations have been used: w, weak; m, medium; s, strong and v, very.

^b Solvent: carbon tetrachloride.

^c Solvent: carbon disulphide.

^d Solvent: cyclohexane.

^e Unobserved.

$1098.1 \times 10^{-40} \text{ g cm}^2$ for (Cl), (Br), and (I), respectively. Accordingly, the PR separation can be calculated from the formula:⁷

$$\Delta\nu = 8kTB/hC \quad \text{where } B = h/8\pi^2CI$$

giving the values 8.7, 7.2 and 6.5 cm⁻¹ for (Cl), (Br), and (I), respectively. The stretching frequencies of species Σ^+ should correspond to parallel bands

Table 2. Infrared spectral data for Br-C≡C-C≡N (in cm⁻¹).

Gas			Solution		
Wave number	Description ^a	Contour	Wave number	Description ^a	Interpretation
			3225 ^b	vw	$\nu_2 + \nu_3 = 3212$
			2892 ^b	w	$\nu_1 + \nu_5 = 2898$
			2750 ^b	w	$\nu_2 + \nu_5 = 2764$
2635	w		2622 ^b	m	$\nu_1 + \nu_4 = 2763$
					$\nu_3 + \nu_6 = 2643$
					$\nu_2 + \nu_4 = 2621$
2295)	vs		2558 ^b	vw	
2289)			2272 ^b	vs	ν_1
2161)	s		2137 ^b	s	ν_2
2155)					
2108	w				$2\nu_3 = 2108$
			1650 ^b	m	$\nu_3 + \nu_5 = 1660$
1180	m				$2\nu_5 = 1212$
					$\nu_3 + \nu_7 = 1210$
1105	w				$\nu_5 + \nu_6 = 1091$
			1054 ^b	w	ν_3
959	w		956 ^c	m	$\nu_4 + \nu_6 = 956$
950	w		946 ^c	m	$2\nu_4 = 942$
			751 ^c	m	$\nu_5 + \nu_7 = 762$
635	m		633 ^d	m	$\nu_6 + \nu_7 = 641$
609)	m	⊥	601 ^d	m	ν_5
606)					
602)					
489					
485)	s	⊥	483 ^d	s	ν_6
483)					
471)	w		472 ^d	w	ν_4
312					
[156] ^e					ν_7

^a For abbreviations, see footnotes to Table 1.

^b Solvent: carbon tetrachloride. ^d Solvent: cyclohexane.

^c Solvent: carbon disulphide. ^e Unobserved.

with missing *Q* branches. On the other hand, the doubly degenerate bending frequencies of species *II* should give rise to perpendicular bands. It was found that the *P* and *R* branches were not well resolved for the perpendicular bands because of the intense *Q* branches and because the spectrometers had lower dispersion in the KBr and CsBr regions. The *PR* separations which can be measured agree quite well with the predicted values, but for (I) the absorption bands were too weak to permit any conclusions regarding the band contours.

The spectra of the (Cl), (Br), and (I) resemble those of cyanoacetylene,^{8,9} deuterio cyanoacetylene⁹ and dicyanoacetylene.¹⁰ Moreover, the spectra were closely related to other linear molecules as chloroacetylene,¹¹ cyanogen,¹² different diacetylenes,¹³ and halogenated methyl acetylenes.¹⁴ The assignments of fundamentals reported for these compounds were therefore of some help in assigning the fundamentals in the present compounds. Table 4 summarizes the notations,¹⁵ selection rules and the tentative assignments of fundamentals.

Table 3. Infrared spectral data for I—C≡C—C≡N (in cm⁻¹).

Gas ^a		Solution		
Wave number	Description ^b	Wave number	Description ^b	Interpretation
		3280 ^c	vw	$\nu_1 + \nu_3 = 3301$
		2610 ^c	w	$\nu_2 + \nu_6 = 2623$
		2502 ^c	w	$\nu_2 + \nu_4 = 2526$
		2405 ^c	vw	$\nu_1 + \nu_7 = 2419$
2270	s	2260 ^c	m	ν_1
2131	m	2128 ^c	m	ν_2
		2120 ^c	vw	$\nu_1 - \nu_7 = 2121$
2041	w			$2\nu_3 = 2062$
		1990 ^c	vw	$\nu_2 - \nu_7 = 1982$
1098	w	1080 ^d	m	$\nu_5 + \nu_6 = 1105$
1031	s	1029 ^d	s	ν_3
1010	w			$\nu_4 + \nu_5 = 1008$
		786 ^d	m	$2\nu_4 = 790$
		756 ^d	m	$\nu_3 + \nu_7 = 762$
		613 ^e	m	ν_5
not		492 ^e	s	ν_6
		395 ^e	m	ν_4
recorded		306 ^e	vw	
		297 ^e	m	$2\nu_7$
		[149] ^f		ν_7

^a Recorded at 60°C in a 10 cm cell.

^b For abbreviations see footnotes to Table 1.

^c Solvent: carbon tetrachloride.

^d Solvent: carbon disulphide.

^e Solvent: cyclohexane.

^f Unobserved.

Each of the compounds had a very strong infrared band in the region 2250—2300 cm⁻¹ with parallel contours. This band was situated at a considerably lower frequency in the solution, and it is undoubtedly the ν_1 fundamental, mainly connected with the C≡N stretching mode. Likewise, the strong, parallel infrared band which appeared around 2150 cm⁻¹ for each molecule is undoubtedly the ν_2 fundamental, involving mainly the C≡C stretching mode.

Table 4. Tentative vibrational fundamentals for X—C≡C—C≡N.^a

Species	Notation	Cl	Br	I	Approx. motion
Σ^+	ν_1	2297 vs	2292 vs	2270 vs	C≡N stretch
	ν_2	2149 s	2158 s	2131 s	C≡C stretch
	ν_3	1093 s	1054 vw	1031 s	C—C stretch
	ν_4	613 s	471 s	395 m	C—X stretch
Π	ν_5	527 s	606 m	613 m	C—C≡N bend
	ν_6	483 s	485 s	492 s	C—C≡C bend
	ν_7	[167] ^b	[156] ^b	[149] ^b	C≡C—X bend

^a For abbreviations, see footnotes to Table 1.

^b Unobserved, inferred from combination bands.

The ν_3 fundamental is much less straightforward. It should be noted that for cyanoacetylene and deuterio cyanoacetylene the C—C stretching mode was not observed in the gas spectrum but appeared in the liquid spectra in infrared⁸ as well as in Raman.⁹ Moreover, for the halogeno methylacetylenes this fundamental was not observed in Raman,¹⁵ but from normal coordinate calculations¹⁴ they were expected to lie in the region 1000—1080 cm^{-1} . The force constant calculations in Table 5 indicate that the ν_3 fundamental should be situated in the approximate region 1100—1000 cm^{-1} for the present molecules. In (Cl) the strong, parallel band at 1094 cm^{-1} is assigned as the ν_3 fundamental. In (Br) the peaks at 950 and 959 cm^{-1} might be interpreted as *PR* branches of a parallel type band assigned as ν_3 . However, the two peaks at 956 and 946 in carbon disulphide solution seem to correspond to the former, and they can be explained as combination bands. Thus, the weak band at 1054 cm^{-1} in solution having no counterpart in the gas spectrum is assigned as the ν_3 fundamental in (Br). In (I) we observed a strong, sharp band at 1031 cm^{-1} in the gas corresponding to a strong band at 1029 cm^{-1} in solution and they have been assigned as the ν_3 fundamental in this molecule.

There is not much information available in the literature concerning the position and intensity of the C—X stretching vibration (X = Cl, Br, I) with the carbon atom in a state of *sp* hybridization. Wojtkowiak¹⁷ listed the observed C—X stretching frequencies for halogeno propyne, heptyne and octyne. He observed that the stretching frequencies are generally much lower for the propyne than for the higher homologs and are found in the regions 573—605, 464—572, and 405—563 cm^{-1} for the chloro, bromo and iodo compounds, respectively. The frequency calculations in Table 5 suggest that this fundamental should be situated at a somewhat lower frequency in the present molecules. In (Cl) the medium intense bands at 676, 613, or 527 cm^{-1} might all be possible choice for ν_4 . However, the 676 cm^{-1} band has undoubtedly a perpendicular contour, 613 cm^{-1} is a parallel band and for 527 cm^{-1} the contour is probably perpendicular. In spite of the fact that the 527 cm^{-1} band fits very well with the frequency calculations in Table 5 it is assigned as ν_5 and the 613 cm^{-1} band has been assigned as ν_4 . The shoulder at 471 cm^{-1} partly overlapping the strong 485 cm^{-1} band in (Br) is assigned as ν_4 and in (I) the weak band observed at 410 cm^{-1} in solution is tentatively assigned as ν_4 .

Among the doubly degenerate *II* fundamentals, the lowest ν_7 mainly connected with $\text{C}\equiv\text{C}-\text{X}$ bending must definitely lie outside the range of our CsBr prism and remains unobserved. However, infrared bands with uncertain contours were observed at 334, 312, and 297 cm^{-1} in (Cl), (Br), and (I), respectively. They might possibly be assigned as the ν_6 fundamentals, however, it seems more likely that they are overtones of ν_7 . Since the contours are not known it cannot be definitely decided whether they are fundamentals or overtones. The ν_7 fundamentals might tentatively be assigned to unobserved bands at 167, 156, and 149 cm^{-1} in (Cl), (Br), and (I), respectively. These frequencies are somewhat higher than those predicted in Table 5. They agree fairly well with those calculated by Bjorvatten¹⁸ from the *l*-type splitting of the microwave spectra. His calculations gave the values 147 and 144 cm^{-1} in (Br) for the 81 and the 79 isotopes of bromine, respectively. In (I) his calculated value was 132 cm^{-1} .

Table 5. Estimated fundamental frequencies for $X-C\equiv C-C\equiv N$

	Force constants	Cl	Br	I
$C\equiv N$ stretch	15.7 ^a	2430	2419	2413
$C\equiv C$ stretch	15.799 ^b	2114	2104	2097
$C-C$ stretch	7.83 ^a	1096	1033	1004
$C-X$ stretch	5.52 ^c	529		
	4.3525 ^b		413	
	3.5707 ^b			358
$C-C\equiv N$ bend	0.210 ^a	579	582	585
$C-C\equiv C$ bend	0.209 ^a	352	352	354
$C\equiv C-X$ bend	0.15 ^d	123	115	111

^a Force constants adopted from Ref. 8.

^b Force constants adopted from Ref. 14.

^c Force constants adopted from Ref. 11.

^d This bending force constant was used for all the molecules.

Table 6. F-matrix elements (m dyne/Å) for the Σ^+ vibrations in chloroacetylene.*

	C-Cl	$C\equiv C$	C-C	$C\equiv N$
C-Cl	6.48(5.52)			
$C\equiv C$	1.08	16.0(15.799)		
C-C	0.771	1.27	8.31(7.83)	
$C\equiv N$	0.629	- 0.286	0.589	15.9(15.7)

* The original valence force field given in parentheses.

Table 7. Potential energy distribution for the Σ^+ normal vibrations (Q) in chloroacetylene. (Frequencies in cm^{-1}).

	Q_1 (2297)	Q_2 (2149)	Q_3 (1093)	Q_4 (613)
C-Cl	0.05	0.05	0.47	0.46
$C\equiv C$	0.60	0.29	0.01	0.13
C-C	0.29	0.03	0.50	0.20
$C\equiv N$	0.22	0.62	0.14	0.03

A very strong band was observed around 485 cm^{-1} in each of the infrared spectra. In (Cl) and (Br) the bands had definite perpendicular contours. They must be fundamentals and have been assigned as ν_6 in the three compounds. These frequencies are close to those reported for dicyanoacetylene¹⁰ in which two fundamentals are situated at 504 and 472 cm^{-1} . Miller *et al.*¹⁰ list these fundamentals as mainly connected with the symmetrical and asymmetrical $C-C\equiv N$ bending modes. The frequency calculations in Table 5 suggest that the ν_6 should be mainly connected with the $C-C\equiv C$ bending mode, however, these bending modes are highly mixed for the present molecules.

The ν_5 fundamental is mainly connected with the C—C \equiv C skeletal bending mode and the expected range for this fundamental is quite uncertain. In (Cl) the medium intense band at 527 cm⁻¹ which seems to have perpendicular contours with a *PR* separation of 7 cm⁻¹, is assigned as ν_5 , and in (Br) it is assigned to the medium intense band at 606 cm⁻¹ with perpendicular contour.

The medium intense band at 613 cm⁻¹ is assigned to ν_5 in (I). Since the infrared spectrum of (I) was only recorded in solution in this region, no information was available about the contour.

Explanation of the remaining frequencies. Most of the remaining infrared bands in Tables 1—3 have been satisfactorily explained as overtones or combination bands, some have been explained as difference bands and a few very weak bands have remained unexplained. The latter may be tertiary combination bands or caused by impurities.

FORCE CONSTANTS

Attempts were made to confirm the assignments by force-constant calculations. Following the procedure of Turrell *et al.*⁸ a valence force field was estimated as a first approximation. A C—Cl stretching force constant was tentatively transferred from chloroacetylene,¹¹ the C—Br and C—I force constants from the halogeno methylacetylenes.¹⁴ After some trials the best calculated frequencies were obtained with $f(\text{C}\equiv\text{N})$ and $f(\text{C—C})$ from cyanoacetylene⁸ and $f(\text{C}\equiv\text{C})$ from halogeno methylacetylene.¹⁴ The calculated frequencies are listed in Table 5. For (Cl) the force field was modified to fit accurately the observed frequencies with the result given in Table 6. The procedure is the same as has been used for cyanoacetylene¹⁹ and should be considered mainly as a mathematical adjustment. Hence, too much physical significance should not be given to the introduced interactional force constants.

The derived force constants were used to evaluate the potential energy distribution, following the method of Morino and Kuchitsu²⁰ for classification of fundamental frequencies. The results are listed in Table 7 and show that the normal mode with the frequency 1093 cm⁻¹ (ν_3) contains almost equal contributions from both the C—C and the C—Cl stretchings. More surprising was the observation of the mixed character of 2297 cm⁻¹ (ν_1) with main contribution from C \equiv C, while 2149 cm⁻¹ (ν_2) was found to have a main contribution from the C \equiv N stretching. The latter observation is in disfavour of the evaluated force field, but it is interesting to notice that the highly mixed character of some of the normal modes also was found in cyanoacetylene.¹⁹

Very few bending force constants are available in the literature which can be transferred to the present molecules. As a first approximation, the C \equiv C—C bending and the C—C \equiv N bending force constants were transferred from cyanoacetylene⁸ and the C \equiv C—X bending force constants were set equal to 0.15 $r_1 r_2$ md/Å. It appears that the calculated *II* fundamentals in Table 5 differ greatly from the assigned fundamentals in Table 4, indicating that the proposed force field should be drastically changed. However, since the assigned *II* fundamentals in Table 4 should be considered as tentative and particularly because the ν_7 frequency is unobserved, no attempts were made to alter the force constants

in order to obtain a fit with the experimental values. A lower $C\equiv N$ stretching force constant would undoubtedly bring the ν_1 fundamental closer to the observed values. We expect that higher values for the $C-X$ stretching force constants^{11,14} would give a better agreement with the observed frequencies.

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