

Cyanoacetylene: Mean Amplitudes of Vibration and Bastiansen-Morino Shrinkage Effects

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A harmonic force field has been derived for cyanoacetylene. The mixed character of some of the normal modes is discussed. In particular, the mode assigned to C≡N stretching and with the characteristic frequency of 2271 cm⁻¹ has been found to possess considerable contributions from C≡C and CC stretchings. Calculated mean amplitudes of vibration for all the ten different types of distances are reported, along with the six independent shrinkage effects. These results are in good agreement with previous calculations for hydrogen cyanide, acetylene and cyanogen.

The presently reported computations on cyanoacetylene from spectroscopic data are believed to be of special interest for studies in electron-diffraction. They are also of particular interest in connection with recently undertaken studies on the infrared spectra of halogen substituted cyanoacetylenes.

FORCE FIELD

The computations are based on a harmonic valence force field as given by Turrell *et al.*¹ First the normal-coordinate matrix (L) was calculated, along with the vibrational frequencies, which are given in Table 1 (as "Calc."). In the final calculations the *observed* frequencies^{1,2} were used without changing the L matrix. By this procedure the force constants were slightly changed, and small interaction constants introduced. In Table 2 this modified force field is given, along with the original valence force constants¹ included in parentheses.

CLASSIFICATION OF NORMAL MODES

In Table 3 we give the terms $X_{ik} = F_{ii} L_{ik}^2 / \lambda_k$ rather than the L-matrix elements themselves. These terms may be interpreted as the contributions from the various internal coordinates (i) to the potential energy for a normal

Table 1. Vibrational frequencies of HCCCN (cm⁻¹).

	Calc.	Obs.	Description	
ν_1	3312	3328 ^{1,2}	CH	} Σ^+
ν_3	2008	2078 ^{1,2}	C≡C	
ν_4	877	877 ²	CC	
ν_2	2342	2271 ^{1,2}	C≡N	
ν_5	668	663 ^{1,2}	HCC	} Π
ν_7	238	230 ^{1,2}	CCC	
ν_6	491	500 ²	CCN	

Table 2. F-matrix elements (mdyne/Å).

	$\Delta r_{12}(\text{CH})$	$\Delta r_{23}(\text{C}\equiv\text{C})$	$\Delta r_{34}(\text{CC})$	$\Delta r_{45}(\text{C}\equiv\text{N})$
Δr_{12}	5.92 (5.86)*			
Δr_{23}	0.013	15.2 (14.9)		
Δr_{34}	0.029	0.166	7.70 (7.83)	
Δr_{45}	-0.114	-0.825	0.253	15.8 (15.7)
	$\varrho_1 \Delta \varphi_{123}(\text{CCH})$	$\varrho_2 \Delta \varphi_{234}(\text{CCC})$	$\varrho_3 \Delta \varphi_{345}(\text{CCN})^{**}$	
$a_1 \Delta \varphi_{123}$	0.149 (0.150)			
$a_2 \Delta \varphi_{234}$	0.0010	0.203 (0.209)		
$a_3 \Delta \varphi_{345}$	-0.0041	-0.0092		0.208 (0.210)

* In parentheses the valence force field from Turrell *et al.*¹

** $\varrho_1 = (r_{12}r_{23})^{1/2}$, $\varrho_2 = (r_{23}r_{34})^{1/2}$, $\varrho_3 = (r_{34}r_{45})^{1/2}$.

Table 3. Potential energy distribution for the normal vibrations (Q).

Σ^+	Q_1	Q_2	Q_3	Q_4
CH	0.96	0.02	0.02	0.00
C≡C	0.04	0.30	0.51	0.15
CC	0.00	0.32	0.00	0.68
C≡N	0.00	0.43	0.42	0.15
Π	Q_5	Q_6	Q_7	
CCH	0.77	0.20	0.03	
CCC	0.18	0.26	0.56	
CCN	0.06	0.49	0.45	

Table 4. Mean amplitudes of vibration, u , and Bastiansen-Morino shrinkage effects, δ (Å units).

Atom pair	u (298°K)*	δ	
		$T = 0$	298°K
12 (CH)	0.074		
23 (C≡C)	0.036		
34 (CC)	0.042		
45 (C≡N)	0.035		
13 (C...H short)	0.079	0.018	0.020
24 (C...C)	0.046	0.007	0.010
35 (C...N short)	0.046	0.007	0.010
14 (C...H long)	0.084	0.031	0.039
25 (C...N long)	0.050	0.016	0.025
15 (H...N)	0.086	0.042	0.059

* Values at absolute zero are almost the same.

Table 5. Mean amplitudes of vibration, u , and shrinkage effects, δ , in cyanoacetylene and related molecules at 298°K (Å units).

	HC≡N ⁶	HC≡CH ⁷	N≡CC≡N ⁸	HC≡CC≡N
$u(\text{CH})$	0.0731	0.0783		0.074
$u(\text{C}\equiv\text{C})$		0.0358		0.036
$u(\text{CC})$			0.0419	0.042
$u(\text{C}\equiv\text{N})$	0.0342		0.0349	0.035
$u(\text{C}\dots\text{H})$		0.0730		0.079 (short)
$u(\text{C}\dots\text{N})$			0.0458	0.046 (short)
$\delta(\text{C}\dots\text{H})$		0.019		0.020 (short)
$\delta(\text{C}\dots\text{N})$			0.011	0.010 (short)

vibration (Q_k). Morino and Kuchitsu ³ have shown the X_{ik} terms to be suitable for classification of the normal vibrations. Following their procedure we have confirmed the assignment of frequencies by Turrell *et al.*¹ (*cf.* Table 1), as far as the highest contribution from each internal coordinate is considered. But it is also interesting to notice that some of the normal vibrations have considerably mixed character. In particular, the normal mode assigned to C≡N stretching ($\nu_2 = 2271 \text{ cm}^{-1}$) has considerable character of C≡C and CC stretchings. Also the Q_3 mode (2078 cm^{-1}) is a mixture of C≡C and C≡N rather than a pure C≡C stretching vibration. Finally, the bending mode of Q_7 should be assigned to a mixture of CCC and CCN bendings. It should be noted, however, that these conclusions have been drawn from Table 3, where the terms depend on the particular force field here adopted.

MEAN AMPLITUDES OF VIBRATION AND SHRINKAGE EFFECTS

The mean amplitudes of vibration ⁴ (u) and Bastiansen-Morino shrinkage effects ⁵ (δ) are of great interest in electron-diffraction investigations of molecular structures. If some of these quantities could be determined from electron-diffraction with sufficiently high precision, they might be used for improved determination of the force field. Here we give the calculated values of u and δ (Table 4) based on the presently adopted force constants (see Table 2). The shrinkage effects of Table 4 are all based on the bonded distances, viz.

(C...H short)	$-\delta_{13} = r_{13}^g - (r_{12}^g + r_{23}^g)$
(C...C)	$-\delta_{24} = r_{24}^g - (r_{23}^g + r_{34}^g)$
(C...N short)	$-\delta_{35} = r_{35}^g - (r_{34}^g + r_{45}^g)$
(C...H long)	$-\delta_{14} = r_{14}^g - (r_{12}^g + r_{23}^g + r_{34}^g)$
(C...N long)	$-\delta_{25} = r_{25}^g - (r_{23}^g + r_{34}^g + r_{45}^g)$
(H...N)	$-\delta_{15} = r_{15}^g - (r_{12}^g + r_{23}^g + r_{34}^g + r_{45}^g)$

Here r_{ij}^g denotes the average internuclear distance between the atoms i and j . In the last table (Table 5) the values of u and δ are compared with corresponding ones in related molecules. There is observed good correspondence which supports the applied force field.

REFERENCES

1. Turrell, G. C., Jones, W. D. and Maki, A. *J. Chem. Phys.* **26** (1957) 1544.
2. Job, V. A. and King, G. W. *Can. J. Chem.* **41** (1963) 3132.
3. Morino, Y. and Kuchitsu, K. *J. Chem. Phys.* **20** (1952) 1809.
4. Cyvin, S. J. *Kgl. Norske Videnskab. Selskabs, Skrifter* **1959** No. 2.
5. Cyvin, S. J. *Tidsskr. Kjem. Bergvesen Met.* **21** (1961) 236; **22** (1962) 44, 73.
6. Meisingseth, E. and Cyvin, S. J. *Acta Chem. Scand.* **16** (1962) 1321.
7. Meisingseth, E. and Cyvin, S. J. *Acta Chem. Scand.* **15** (1961) 2021.
8. Cyvin, S. J. and Meisingseth, E. *Acta Chem. Scand.* **15** (1961) 1289.

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