

MOLECULAR FORCE FIELDS FOR CH_3CN , CH_3NC AND SiH_3CN

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Molecular constants of methyl cyanide, methyl isocyanide and silyl cyanide containing $\text{C} \equiv \text{N}$ were determined by the use of kinematic methods. It has been shown that L' matrix approximation method suggested by Torkington gives a reasonably accurate force field for these molecules.

1. Introduction

A number of studies [1-7] have been devoted to the analysis of the Raman and infrared spectra of small molecules containing the $\text{C} \equiv \text{N}$ group and some of these [5, 6] have included the normal coordinate analysis of the vibrational frequencies. In earlier papers [8, 9] the kinematic methods of Herranz [10] and Torkington [11] were applied to molecules containing the linear chain $-\text{N} = \text{C} = \text{X} (\text{X} = \text{S}, \text{O})$ and the relative merits and limitations of the two methods were discussed. In the present paper the molecular constants of methyl cyanide, methyl isocyanide and silyl cyanide (containing the $\text{C} \equiv \text{N}$ bond) are determined by these kinematic methods in order to see how far are these methods suitable for the series of molecules under study.

2. Potential energy constants

Both methyl and silyl cyanides belong to the C_{3v} point group with twelve fundamental vibrations, four falling under the a_1 species and four under the doubly degenerate e species. In the present calculations the vibrational assignments given by Nakagawa and Shimanouchi [6], Williams [2] and Linton and Nixon [7] are made use of. The structural parameters were taken from Thomas *et al.*, [12], Kessler *et al.*, [13] and Sheridan and Turner [14]. Since the force field does not change appreciably due to small variations in angles,

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tetrahedral angles were taken. The vibrational assignments and structural parameters are given in Table I. The symmetry coordinates are essentially the same as those given by Duncan [15].

TABLE I

Vibrational frequencies (cm^{-1}), internuclear distances (\AA) and interbond angles for CH_3CN , CH_3NC and SiH_3CN

Species	CH_3CN	CH_3NC	SiH_3CN
a_1	2954	2966	2212
	2267	2166	2205
	1385	1429	920
	920	945	608
e	3009	3014	2227
	1454	1467	941
	1041	1129	682
	362	263	235
d	1.092	1.094	1.480
D_1	1.459	1.427	1.847
D_2	1.158	1.167	1.156

tetrahedral angles — $109^\circ 28'$

$d = \text{C—H}$ or Si—H ; $D_1 = \text{C—C}$ or C—N or Si—C
 $D_2 = \text{C}\equiv\text{N}$; $\alpha = \text{H}\hat{\text{C}}\text{H}$ and $\beta = \text{H}\hat{\text{C}}\text{N}$

TABLE II

Symmetrized F elements¹ for CH_3CN

Present study		Duncan	Nakagawa and Shimanouchi	Present study		Duncan	Nakagawa and Shimanouchi
F_{11}	5.0525	4.938	5.020	F_{55}	4.8541	4.937	4.854
F_{22}	0.5916	0.605	0.597	F_{66}	0.5654	0.535	0.533
F_{33}	4.7501	5.1509	5.065	F_{77}	0.6714	0.677	0.746
F_{44}	20.9502	18.11	18.65	F_{88}	0.3046	0.351	0.308
F_{12}	0.0400	0.066	-0.049	F_{56}	-0.0817	-0.093	-0.111
F_{13}	0.1839	0	0.747	F_{57}	0.0788	0.093	0.291
F_{14}	0.0990	0	0	F_{58}	-0.0099	0	0
F_{23}	-0.4016	-0.387	-0.449	F_{67}	-0.0856	0.041	0.044
F_{24}	-0.2162	0	0	F_{68}	-0.0175	0	0
F_{34}	2.5574	0.299	0.500	F_{78}	0.0568	-0.088	0

¹ The stretching force constants are in $\text{mdyn}/\text{\AA}$, bending force constants in $\text{mdyn}/\text{\AA}$ and stretch-bend interaction constants in mdyn

Following the procedure outlined in earlier papers [8, 9] the L matrix of maximum trace was constructed by the method of „characteristic set of valence coordinates”. In Torkington’s method the elements of the lower triangular matrix were obtained directly from the inverse kinetic energy matrix. The potential energy matrix was evaluated using the relation

$$F = \tilde{L}^{-1} \wedge L^{-1} \quad (1)$$

Symmetrized F elements for CH_3NC

TABLE III

Present study		Duncan	Present study		Duncan
F_{11}	5.0943	4.972	F_{55}	4.8723	4.950
F_{22}	0.6317	0.653	F_{66}	0.5786	0.514
F_{33}	5.0118	5.404	F_{77}	0.7867	0.859
F_{44}	18.9360	16.65	F_{88}	0.1708	0.176
F_{12}	0.0429	0.094	F_{56}	-0.0852	-0.133
F_{13}	0.1940	0	F_{57}	0.0954	0.133
F_{14}	0.0896	0	F_{58}	-0.0059	0
F_{23}	-0.4245	-0.528	F_{67}	-0.0983	0.029
F_{24}	-0.1959	0	F_{68}	-0.0097	0
F_{34}	2.3135	0.250	F_{78}	0.0302	-0.042

Symmetrized F elements for SiH_3CN

TABLE IV

Present study		Duncan	Present study		Duncan
F_{11}	2.8541	2.901	F_{55}	2.8120	2.832
F_{22}	0.5123	0.550	F_{66}	0.4597	0.449
F_{33}	3.0851	3.229	F_{77}	0.5674	0.640
F_{44}	19.5294	18.00	F_{88}	0.1564	0.140
F_{12}	0.0129	0.030	F_{56}	-0.0233	-0.036
F_{13}	0.0577	0	F_{57}	0.0245	0.040
F_{14}	0.0311	0	F_{58}	-0.0018	0
F_{23}	-0.1708	-0.228	F_{67}	-0.0930	-0.123
F_{24}	-0.0920	0	F_{68}	-0.0078	0
F_{34}	1.6610	0.385	F_{78}	0.0315	-0.080

The elements of the F matrix obtained by the method of Torkington for CH_3CN , CH_3NC and SiH_3CN are given in Tables II, III and IV along with the values reported by earlier workers [6, 15]. The valence force constants are summarized in Table V.

TABLE V

Valence force constants (in mdyn/Å) for CH₃CN, CH₃NC and SiH₃CN

	CH ₃ CN		CH ₃ NC		SiH ₃ CN	
	Method I	Method II	Method I	Method II	Method I	Method II
f_d	4.9967	4.9202	5.0244	4.9463	2.8359	2.8261
F_{D_1}	6.7352	4.7501	6.3553	5.0118	6.6269	3.0851
f_{D_1}	26.0026	20.9502	22.1959	18.9360	26.9361	19.5294
$f_{D_1 d}$	0.3784	0.1062	0.3741	0.1120	0.1503	0.0333
f_{dd}	0.0510	0.0661	0.0579	0.0740	0.0129	0.0140
$f_{D_1 D_2}$	8.9949	2.5574	7.0928	2.3135	10.9878	1.6610
f_α	0.4138	0.3988	0.4246	0.4103	0.1839	0.1789
f_β	0.3722	0.3428	0.4362	0.4034	0.1800	0.1696
f_φ	0.2247	0.1912	0.1508	0.1095	0.0645	0.0572
$f_{D_1 \alpha}$	-0.1642	-0.1029	-0.1620	-0.1110	-0.0593	-0.0255
$f_{D_1 \beta}$	0.1642	0.1029	0.1620	0.1110	0.0593	0.0255

Method I — Herranz method

Method II — Torkington's method

3. Mean amplitudes of vibration

The mean amplitudes of vibration were obtained after solving the secular determinant given by Cyvin [16]. The bonded mean amplitudes of vibration obtained for the three molecules are presented in Table VI.

TABLE VI

Mean amplitudes of vibration (Å) for CH₃CN, CH₃NC and SiH₃CN

	CH ₃ CN		CH ₃ NC		SiH ₃ CN	
	Method I	Method II	Method I	Method II	Method I	Method II
σ_{C-H}	0.0785 (0.0781)	0.0779	0.0787	0.0778	—	—
σ_{Si-H}	—	—	—	—	0.0885 (0.0888)	0.0883
σ_{C-C}	0.0539	0.0499	—	—	—	—
σ_{C-N}	—	—	0.0514	0.0485	—	—
σ_{Si-C}	—	—	—	—	0.0575	0.0508
σ_{C-N}	0.0359	0.0339	0.0361	0.0347	0.0389	0.0343

The values in the parantheses refer to experimental values for similar bonds

4. Rotational distortion constants

The values of the rotational distortion constants for the symmetric tops CH_3CN , CH_3NC and SiH_3CN were constructed using the τ elements defined by Kivelson and Wilson [17]. These τ elements in turn were constructed from a knowledge of the matrix of transformation (1) between mass weighted Cartesian and normal coordinates, making use of the relations given by Oka and Morino [18] and De Alti *et al.*, [19].

The explicit relations between the rotational distortion constants and the τ elements are

$$D_J = -\frac{\hbar}{4}(\tau_{xxxx})$$

$$D_K = D_J - \frac{\hbar}{4}(\tau_{zzzz} - 2\tau_{xxzz} - 4\tau_{xzxz})$$

$$D_{JK} = -D_J - D_K - \frac{\hbar}{4}(\tau_{zzzz}). \quad (2)$$

The values of the rotational distortion constants along with the values of other workers are given in Table VII.

TABLE VII

Rotational distortion constants for CH_3CN , CH_3NC and SiH_3CN in kc/s

	CH_3CN				CH_3NC			SiH_3CN	
	Present study ¹	Exp. 24	Ref. [6]	Ref. [15]	Present study	Ref. [5]	Ref. [15]	Present study	Ref. [25]
D_J	3.41	3.8	3.74	3.72	4.10	5.0	4.53	1.31	1.21
D_{JK}	147	176.9	136	176	208	188	234	48.6	45.2
D_K	4019	—	3141	—	4115	2175	—	358	726

¹ Values obtained using the method of "progressive rigidity"

5. Coriolis coupling constants

The Coriolis coupling constants were evaluated using the relations given by Meal and Polo [20]. The molecular axis was taken to be the z-axis. The values of the zeta elements along with the available experimental values are presented in Table VIII.

Coriolis coupling constants for CH_3CN , CH_3NC and SiH_3CN

	CH_3CN		CH_3NC		SiH_3CN	
	Present study	Ref. [6]	Present study	Ref. [2]	Present study	Ref. [7]
ζ_5	0.1006	0.062	0.1006	0.08	0.0457	0.04
ζ_6	-0.2671	-0.384	-0.2671	-0.35	-0.2298	-0.16
ζ_7	0.2575	0.422	0.2546	0.36	0.2689	0.20
ζ_8	0.9381	(0.945) ¹	0.9438	0.94	0.9441	(0.95)
$\sum \zeta_i$	1.0291		1.0319		1.0289	
$\frac{I_B}{2I_A}$	1.0292		1.0319		1.0289	

¹ Observed indirectly

6. Results and discussion

The F elements obtained by Duncan [15] and Nakagawa and Shimanouchi [6] are quoted in Tables II–IV for comparison with the present values obtained using the method of “Progressive rigidity”. Except for the difference in F_{44} and F_{34} , the elements of the F matrix are in substantial agreement with the reported values of earlier workers.

The values of the C–H and Si–H stretching force constants obtained in the present study by both the methods of “characteristic set” and “progressive rigidity” conform well with the values of Duncan [15] and Krishna Pillai and Cleveland [5] ($f_{\text{C-H}} = 4.9430$ md/A in CH_3CN and 4.9160 md/A in CH_3NC). Aldous and Mills [21] have explained the nature and sign of F_{23} on the basis of the changes in the hybridisation character of the orbitals for XY_3Z type molecules. The sign of F_{23} obtained in the present study is in agreement with the expectations of Aldous and Mills [21]. Taking the bond order corresponding to the average value of the $\text{C} \equiv \text{N}$ stretching force constants given by Duncan [15] as unity, the bond order calculated from the average value of the force constants was found to be 1.12. This indicates that though the value of the $\text{C} \equiv \text{N}$ force constant is slightly higher, the bond order does not differ much.

The mean amplitudes of vibration for the C–H and Si–H bonds obtained in the present study using the “L matrix approximation method” conform well with the electron diffraction results of Bartell *et al.*, [22] and with those reported by Cyvin [23], in molecules containing similar bonds.

As may be seen from Table VII, the present values of D_J , D_{JK} and D_K agree well with the values reported by other workers. [24, 25]. The Coriolis coupling constants are quite sensitive to off diagonal F elements and therefore one cannot expect very good agreement between the observed and calculated values, particularly when the kinematic methods are used which are approximate only. Nevertheless there is reasonable agreement between calculated and observed values in all cases. The zeta sum rule is verified.

Thus it may be concluded that the "L matrix approximation" method gives a reasonable set of potential energy constants which are quite consistent with the values of other workers indicating that the method is suitable for the normal coordinate analysis of the series of molecules under consideration. This set of potential energy constants can be used as an initial set for further refinements and suitable modifications, if necessary, to give the best fit for all other molecular constants.

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