Substituted Propanes

Part IV. Harmonic Force Fields and Mean Amplitudes for 2-Chloro-, 2-Bromo-, 2-Iodo-, and 2-Cyanopropane

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Harmonic force fields have been developed for 2-chloropropane, 2-bromopropane, and 2-iodopropane. They are presented as F matrices on the basis of specified symmetry coordinates. The force fields were used to calculate mean amplitudes of vibration and perpendicular amplitude correction coefficients. These quantities are of great interest in modern gas electron diffraction studies.

Computations of the same type were also performed for 2-cyanopropane. The F matrix for this molecule is not given for the sake of brevity.

Systematic studies of spectra and structures of substituted propanes are in progress. The reports on vibrational spectra of 2-chloro-, 2-bromo-, 2-iodo, and 2-cyanopropane,[1] and of 2,2-dichloro- and 2,2-dibromopropane [2] are considered as Parts I and II, respectively, of this series. Part III [3] contains a normal coordinate analysis with calculated mean amplitudes for 2,2-dichloro- and 2,2-dibromopropane. In the present work a normal coordinate analysis was performed for the monosubstituted propanes with chlorine, bromine, iodine, and the cyano group.

2-HALOPROPANES

Molecular model. The molecular symmetry of propane (C_{2v}) is lowered to C_s by the substitutions in question. Fig. 1 shows the identification of atoms in $(CH_3)_2CHX$. The interatomic distance values of 1.75 Å, 1.97 Å, and 2.106 Å were used for C−Cl, C−Br, and C−I, respectively. Otherwise the structural parameters from propane [4] were adopted. (The applied structural data are given implicitly in terms of interatomic separations in subsequent tables.)

Internal coordinates. The notation for valence coordinates in the molecular vibration analysis is adopted from Vizi and Cyvin.[5] Because of the lowered symmetry these coordinates are grouped into some more sets of symmetrically
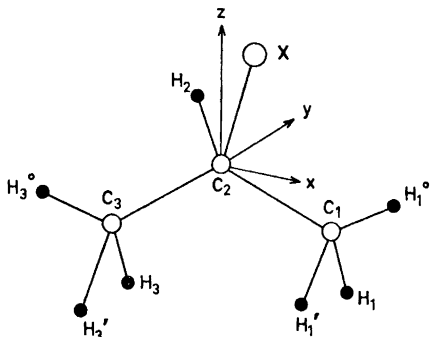
Fig. 1. Identification of atoms in the 2-halopropane molecule model. X is the halogen atom.

equivalent members than is the case in propane.[5] The appropriate sets are specified in the following.

d_1: $C_2 - H$ stretching
d_2: $C - X$ stretching
r_1, r_2: $C - C$ stretchings
s_1, s_2: $C - H^\circ$ stretchings
t_1, t_3: $C_1 - H_1'$ and $C_3 - H_3'$ stretchings
t_2, t_4: $C_1 - H_1$ and $C_3 - H_3$ stretchings
α: CCC bending
β_1, β_3: CCH_2 bendings
β_2, β_4: CCX bendings
γ_1, γ_3: $H_1^\circ C_1 H_1'$ and $H_3^\circ C_3 H_3'$ bendings
γ_2, γ_4: $H_1^\circ C_1 H_1$ and $H_3^\circ C_3 H_3$ bendings
δ_1, δ_3: $C_2 C_1 H_1'$ and $C_2 C_3 H_3'$ bendings
δ_2, δ_4: $C_2 C_1 H_1$ and $C_2 C_3 H_3$ bendings
ε_1, ε_2: CCH° bendings
τ_1, τ_2: $CCCH^\circ$ torsions

The above valence coordinates were used to construct a complete set of independent symmetry coordinates, which are given in the following.

$$S_1(A') = d_1, \quad S_2(A') = d_2, \quad S_3(A') = 2^{-\frac{1}{2}}(r_1 + r_2)$$
$$S_4(A') = 2^{-\frac{1}{2}}(s_1 + s_2), \; S_5(A') = 2^{-\frac{1}{2}}(t_1 + t_3), \; S_6(A') = 2^{-\frac{1}{2}}(t_2 + t_4)$$
$$S_7(A') = R\alpha, \; S_8(A') = (RD_1/2)^{\frac{1}{2}}(\beta_1 + \beta_3), \; S_9(A') = (RD_2/2)^{\frac{1}{2}}(\beta_2 + \beta_4)$$
$$S_{10}(A') = (ST_1/2)^{\frac{1}{2}}(\gamma_1 + \gamma_3), \qquad S_{11}(A') = (ST_2/2)^{\frac{1}{2}}(\gamma_2 + \gamma_4)$$
$$S_{12}(A') = (RT_1/2)^{\frac{1}{2}}(\delta_1 + \delta_3), \qquad S_{13}(A') = (RT_2/2)^{\frac{1}{2}}(\delta_2 + \delta_4)$$
$$S_{14}(A') = (RS/2)^{\frac{1}{2}}(\varepsilon_1 + \varepsilon_2), \qquad S_{15}(A') = (RS/2)^{\frac{1}{2}}(\tau_1 - \tau_2)$$
$$S_1(A'') = 2^{-\frac{1}{2}}(r_1 - r_2), \qquad S_2(A'') = 2^{-\frac{1}{2}}(s_1 - s_2)$$
$$S_3(A'') = 2^{-\frac{1}{2}}(t_1 - t_3), \qquad S_4(A'') = 2^{-\frac{1}{2}}(t_2 - t_4)$$
$$S_5(A'') = (RD_1/2)^{\frac{1}{2}}(\beta_1 - \beta_3), \qquad S_6(A'') = (RD_2/2)^{\frac{1}{2}}(\beta_2 - \beta_4)$$
$$S_7(A'') = (ST_1/2)^{\frac{1}{2}}(\gamma_1 - \gamma_3), \qquad S_8(A'') = (ST_2/2)^{\frac{1}{2}}(\gamma_2 - \gamma_4)$$
$$S_9(A'') = (RT_1/2)^{\frac{1}{2}}(\delta_1 - \delta_3), \qquad S_{10}(A'') = (RT_2/2)^{\frac{1}{2}}(\delta_2 - \delta_4)$$
$$S_{11}(A'') = (RS/2)^{\frac{1}{4}}(\varepsilon_1 - \varepsilon_2), \qquad S_{12}(A'') = (RS/2)^{\frac{1}{4}}(\tau_1 + \tau_2)$$

The capital letters R, D_1, D_2, etc. in the scaling factors, are used to designate the appropriate equilibrium distances.

Harmonic force field. In the first run it was attempted to transfer diagonal force constants from propane [3] with special values for C−X stretchings (X = Cl, Br, I), and neglecting most of the interaction terms. The calculated frequencies from this run gave rather poor agreement with the experimental values.[1]

Therefore a different approach was followed in order to set up an initial approximate force field, by which also the interaction force constants were taken into account. This was accomplished in the easiest way by using a preliminary set of symmetry coordinates constructed exactly as in the case of propane [5] except for the d_1 and d_2 stretchings, which were left as such. In this set a mixing between not exactly equivalent valence coordinates was tolerated, such as combinations between t_1 and t_3 on one hand and t_2 and t_4 on the other. By this approach it was possible to transfer most of the diagonal and off-diagonal force constants from propane.[3] The force constant values for C−Cl and C−Br stretchings were taken from the respective 2,2-dihalopropanes.[3] Force constants for β bendings were taken as average values between the appropriate values in propane and 2,2-dihalopropanes.[3] For the C−I stretching the value of 2.0 mdyn/Å was tentatively assumed. With this force field (F_0) the secular equation [6]

$$G\ F_0\ L_0 = L_0\ \Lambda_0 \qquad (1)$$

gave a set of calculated frequencies represented by Λ_0, and the normal-coordinate transformation matrix L_0. The frequencies calculated from F_0 are included in Tables 1 − 3 for the three molecules of our study.

The force field was adjusted to fit exactly the observed frequencies [1] (represented by Λ) according to the relation

$$F = \widetilde{L}_0^{-1}\ \Lambda\ L_0^{-1} \qquad (2)$$

Table 1. Vibrational frequencies (cm^{-1}) and potential energy distribution terms (PED) for 2-chloropropane.

Frequency Species	No.	Initial approx.	Final	PED [a]
A'	1	2982	3005	$54t$
	2	2975	2955	$52s + 37t'$
	3	2956	2927	$77d_1$
	4	2886	2878	$34t + 33t' + 32s$
	5	1474	1472	22γ
	6	1442	1454	$110\gamma' + 47\gamma + 24\delta'$
	7	1411	1390	$77\gamma + 37\delta + 34\varepsilon + 33\delta' + 21\gamma'$
	8	1691	1270	$58\beta_H + 35\delta$
	9	1149	1163	$62\varepsilon + 40\delta'$
	10	1064	1065	$55\delta + 22\beta_H$
	11	891	888	$58r$
	12	705	633	$53\beta_X + 26d_2$
	13	411	418	$57d_2 + 26\beta_X$
	14	314	336	$129\alpha + 62\beta_H + 25r$
	15	194	253	86τ

Table 1. Continued.

A''	16	2970	2997	$53t' + 47t$
	17	2968	2985	$67s$
	18	2886	2947	$33t + 32s + 32t'$
	19	1471	1472	$76\gamma + 74\gamma'$
	20	1433	1454	$51\gamma' + 51\gamma + 27\varepsilon + 26\delta' + 26\delta$
	21	1343	1377	21δ
	22	1653	1334	$103\beta_H$
	23	1131	1123	$51\varepsilon + 27r$
	24	983	972	$51\varepsilon + 38\delta' + 32r$
	25	939	936	$73\delta + 48\delta'$
	26	406	317	$90\beta_X + 25r$
	27	207	276	91τ

^{a} Terms below 20 are neglected.

Table 2. Vibrational frequencies (cm^{-1}) and potential energy distribution terms (PED) for 2-bromopropane.

Frequency Species	No.	Initial approx.	Final	PED ^{a}
A'	1	2983	2985	$54t$
	2	2975	2960	$52s + 37t'$
	3	2956	2931	$77d_1$
	4	2886	2875	$33t + 33t' + 32s$
	5	1475	1471	21γ
	6	1443	1463	$107\gamma' + 48\gamma + 24\delta'$
	7	1411	1390	$76\gamma + 36\delta + 34\varepsilon + 33\delta' + 22\gamma'$
	8	1702	1234	$57\beta_H + 36\delta + 22\beta_X$
	9	1148	1162	$62\varepsilon + 40\delta'$
	10	1066	1043	$56\delta + 22\beta_H$
	11	888	882	$59r$
	12	700	552	$70\beta_X + 29d_2$
	13	350	403	$53d_2$
	14	311	290	$141\alpha + 72\beta_H + 26r$
	15	192	249	85τ
A''	16	2971	3003	$50t + 49t'$
	17	2968	2985	$67s$
	18	2886	2935	$33t + 32s + 32t'$
	19	1471	1471	$75\gamma + 73\gamma'$
	20	1433	1436	$52\gamma' + 52\gamma + 28\varepsilon + 26\delta' + 26\delta$
	21	1343	1376	21δ
	22	1653	1321	$103\beta_H$
	23	1130	1123	$52\varepsilon + 25r$
	24	981	944	$50\varepsilon + 43\delta' + 32r$
	25	938	919	$73\delta + 46\delta' + 20r$
	26	385	282	$94\beta_X + 26r$
	27	206	267	91τ

^{a} Terms below 20 are neglected.

Table 3. Vibrational frequencies (cm⁻¹) and potential energy distribution terms (PED) for 2-iodopropane.

Frequency Species	No.	Initial approx.	Final	PED [a]
A'	1	2984	2978	$54t$
	2	2975	2961	$52s + 37t'$
	3	2955	2925	$77d_1$
	4	2886	2882	$33t + 33t' + 32s$
	5	1475	1468	22γ
	6	1443	1459	$106\gamma' + 47\gamma + 23\delta'$
	7	1411	1389	$75\gamma + 35\delta + 34\varepsilon + 33\delta' + 22\gamma'$
	8	1699	1210	$57\beta_H + 38\delta$
	9	1148	1153	$63\varepsilon + 40\delta'$
	10	1067	1020	$57\delta + 23\beta_H + 20\gamma'$
	11	882	879	$64r$
	12	692	499	$72\beta_X + 22\delta + 20d_2$
	13	319	398	$70\alpha + 31\beta_H + 21r$
	14	294	269	$68d_2 + 47\alpha$
	15	191	192	89τ
A''	16	2971	2997	$51t + 47t'$
	17	2968	2937	$67s$
	18	2886	2890	$33t + 32t' + 32s$
	19	1471	1468	$74\gamma + 73\gamma'$
	20	1433	1428	$52\gamma' + 52\gamma + 27\varepsilon + 27\delta + 26\delta'$
	21	1343	1375	21δ
	22	1652	1325	$103\beta_H$
	23	1129	1113	$52\varepsilon + 25r$
	24	981	937	$49\varepsilon + 45\delta' + 32r$
	25	938	925	$71\delta + 44\delta' + 21r$
	26	382	250	$100\beta_X + 30r$
	27	206	217	92τ

[a] Terms below 20 are neglected.

The observed frequencies taken from Klæboe[1] are shown in Tables 1 – 3, and are as usually numbered in the sequence of falling wave numbers within each symmetry species. By re-arranging the elements of A in eqn. (2) different force fields may be produced, which all fit the observed frequencies. This kind of re-arrangements has a great influence on the potential energy distribution[7,8] for the normal modes. In the present calculations a sequence with two frequencies violating the sequence of falling wave numbers was chosen as the basis of the final force field. These frequencies are $\nu_8(A')$ and $\nu_{22}(A'')$. Accordingly the initial approximate frequencies as listed in Tables 1 – 3 do not follow strictly the sequence of falling wave numbers.

The most important ones of the potential energy distribution terms, which are defined by

$$X_{ik} = 100\, F_{ii}\, L_{ik}^2/\lambda_k$$

are given in Tables 1 — 3. The descriptions of normal modes on the basis of the present analysis of the potential energy distribution are fairly well consistent with the approximate descriptions reported in the experimental work.[1]

The final force fields in terms of the above specified symmetry coordinates are shown in Tables 4 — 6 for the three molecules of this work.

Table 4. Symmetry force constants (mdyn/Å) for 2-chloropropane.

Species A'

1	4.68							
2	−0.04	2.41						
3	−0.00	−0.04	3.47					
4	0.01	−0.02	−0.05	4.66				
5	0.02	−0.02	−0.01	0.06	4.67			
6	−0.03	0.03	−0.01	0.01	0.01	4.71		
7	−0.04	−0.08	−0.04	−0.08	−0.01	0.06	0.70	
8	−0.05	−0.11	0.34	−0.04	−0.04	0.06	0.47	0.99
9	0.04	0.22	0.07	0.02	0.01	−0.03	0.08	0.11
10	−0.00	0.01	0.09	−0.01	−0.01	0.03	0.05	−0.01
11	−0.00	−0.00	0.08	−0.01	0.02	−0.00	0.04	−0.01
12	−0.00	0.01	0.18	0.00	−0.01	0.03	−0.03	−0.04
13	0.01	0.02	0.14	0.02	0.03	−0.03	0.07	0.12
14	−0.01	0.00	0.34	−0.01	0.02	0.03	0.03	−0.02
15	0.00	0.01	−0.00	0.00	−0.00	−0.00	−0.01	0.00

Species A' (continued)

9	1.22						
10	0.01	0.88					
11	−0.01	0.45	0.88				
12	0.00	0.40	0.41	0.82			
13	−0.03	0.41	0.41	0.33	0.79		
14	0.01	0.38	0.39	0.30	0.32	0.75	
15	−0.04	−0.02	0.02	−0.01	0.01	−0.00	0.071

Species A''

16	3.08					
17	−0.01	4.80				
18	−0.04	0.08	4.82			
19	−0.05	0.08	0.07	4.82		
20	0.28	0.02	−0.03	−0.00	0.45	
21	0.19	−0.00	−0.01	0.02	0.02	0.46
22	−0.05	−0.02	−0.00	0.03	−0.01	0.02
23	−0.02	−0.02	0.03	−0.00	0.01	−0.01
24	0.12	0.01	−0.02	0.03	0.00	0.02
25	0.16	0.01	0.04	−0.02	0.01	−0.01
26	0.12	−0.01	0.03	0.03	0.03	0.03
27	0.01	0.00	0.00	0.00	−0.00	−0.01

Species A'' (continued)

22	0.83					
23	0.40	0.83				
24	0.30	0.35	0.72			
25	0.35	0.31	0.32	0.73		
26	0.35	0.35	0.26	0.26	0.70	
27	−0.03	0.03	−0.02	0.02	0.00	0.084

Table 5. Symmetry force constants (mdyn/Å) for 2-bromopropane.

Species A'

1	4.68						
2	−0.06	2.78					
3	−0.01	0.15	3.44				
4	−0.01	−0.02	−0.06	4.66			
5	0.01	−0.02	−0.01	0.04	4.66		
6	−0.01	0.05	−0.01	0.03	0.02	4.67	
7	−0.04	0.00	−0.08	−0.09	−0.01	0.06	0.61	
8	−0.05	−0.09	0.36	−0.04	−0.04	0.07	0.44	0.93
9	0.06	0.51	0.22	0.03	0.02	−0.02	0.08	0.07
10	−0.00	0.02	0.11	−0.01	−0.01	0.03	0.06	−0.01
11	−0.00	−0.01	0.08	−0.01	0.02	−0.00	0.05	−0.01
12	−0.00	0.05	0.20	0.00	−0.01	0.04	−0.04	−0.05
13	0.01	0.01	0.12	0.02	0.04	−0.03	0.08	0.12
14	−0.01	0.01	0.35	−0.01	0.02	0.03	0.05	−0.02
15	0.00	0.02	0.00	0.00	−0.00	−0.00	−0.01	−0.00

Species A' (continued)

9	1.14					
10	−0.00	0.88				
11	−0.01	0.44	0.88			
12	−0.01	0.39	0.41	0.81		
13	−0.01	0.42	0.41	0.34	0.78	
14	0.01	0.38	0.39	0.30	0.32	0.74	
15	−0.04	−0.02	0.02	−0.01	0.01	−0.00	0.069

Species A''

16	2.99					
17	−0.01	4.79				
18	−0.04	0.07	4.81			
19	−0.05	0.06	0.04	4.81		
20	0.27	0.02	−0.04	−0.00	0.44	
21	0.21	−0.00	−0.01	0.03	0.02	0.41
22	−0.04	−0.02	−0.00	0.03	−0.01	0.03
23	−0.00	−0.02	0.03	−0.00	0.01	−0.00
24	0.11	0.02	−0.02	0.03	0.00	0.03
25	0.16	0.01	0.04	−0.02	0.00	−0.01
26	0.14	−0.01	0.04	0.03	0.03	0.04
27	0.01	0.00	0.00	0.00	−0.00	−0.01

Species A'' (continued)

22	0.82				
23	0.39	0.83			
24	0.30	0.35	0.71		
25	0.35	0.30	0.32	0.72	
26	0.34	0.34	0.26	0.26	0.68	
27	−0.02	0.02	−0.01	0.02	0.00	0.079

Table 6. Symmetry force constants (mdyn/Å) for 2-iodopropane.

Species A'

1	4.66					
2	−0.05	1.79				
3	−0.02	0.10	3.61			
4	−0.01	−0.01	−0.04	4.66		
5	0.01	−0.02	−0.02	0.04	4.66	
6	−0.01	0.03	−0.01	0.04	0.04	4.66
7	−0.04	0.14	0.08	−0.08	−0.01	0.07	0.70

Table 6. Continued.

8	− 0.05	− 0.06	0.35	− 0.04	− 0.05	0.07	0.41	0.89
9	0.07	0.28	0.21	0.04	0.02	− 0.04	0.11	0.05
10	0.00	− 0.01	0.09	− 0.02	− 0.01	0.03	0.04	− 0.01
11	− 0.00	− 0.03	0.07	− 0.02	0.02	− 0.00	0.04	− 0.01
12	0.00	0.03	0.21	0.00	− 0.01	0.04	− 0.03	− 0.05
13	0.01	0.01	0.13	0.02	0.04	− 0.03	0.09	0.13
14	− 0.00	− 0.03	0.33	− 0.01	0.02	0.03	0.02	− 0.02
15	0.00	0.02	0.02	0.00	0.00	− 0.00	0.01	− 0.00

Species *A'* (continued)

9	0.90						
10	− 0.04	0.87					
11	− 0.00	0.45	0.87				
12	− 0.04	0.38	0.41	0.80			
13	0.01	0.43	0.40	0.35	0.77		
14	− 0.02	0.37	0.39	0.29	0.33	0.74	
15	− 0.01	− 0.01	0.01	− 0.00	0.00	− 0.00	0.043

Species *A''*

16	2.93					
17	− 0.01	4.64				
18	− 0.04	0.07	4.72			
19	− 0.05	0.06	− 0.02	4.73		
20	0.27	0.02	− 0.03	− 0.00	0.44	
21	0.26	− 0.00	− 0.01	0.03	0.01	0.35
22	− 0.05	− 0.02	− 0.00	0.03	− 0.08	0.04
23	− 0.01	− 0.02	0.03	− 0.00	0.01	− 0.00
24	0.10	0.01	− 0.02	0.03	0.00	0.03
25	0.16	0.01	0.04	− 0.02	0.00	− 0.01
26	0.13	− 0.01	0.03	0.02	0.03	0.05
27	0.00	− 0.00	− 0.00	0.00	− 0.00	− 0.01

Species *A''* (continued)

22	0.81					
23	0.40	0.81				
24	0.30	0.36	0.71			
25	0.36	0.30	0.32	0.72		
26	0.34	0.34	0.26	0.26	0.67	
27	− 0.01	0.01	− 0.01	0.01	0.00	0.053

Mean amplitudes of vibration. The developed force fields were used to calculate mean amplitudes of vibration [9] for the molecules of the present study. For the interatomic distances involving halogen the mean amplitudes (u) at the temperatures of absolute zero and 298 K are shown in Tables 7 − 9.

Table 7. Mean amplitudes (u) and perpendicular amplitude corrections (K) for some distances in 2-chloropropane; Å units.

Distance	(R, Å)	$u(0)$	$u(298)$	$K(0)$	$K(298)$
$C_2 - Cl$	(1.750)	0.0506	0.0543	0.0013	0.0016
$C_1 \cdots Cl$	(2.666)	0.0638	0.0749	0.0005	0.0007
$H_2 \cdots Cl$	(2.354)	0.1181	0.1213	0.0054	0.0057
$H_1^{\circ} \cdots Cl$	(2.870)	0.1458	0.1671	0.0058	0.0080
$H_1 \cdots Cl$	(2.878)	0.1489	0.1728	0.0061	0.0086
$H_1' \cdots Cl$	(3.649)	0.1003	0.1057	0.0058	0.0082

Table 8. Mean amplitudes (u) and perpendicular amplitude corrections (K) for some distances in 2-bromopropane; Å units.

Distance	(R, Å)	$u(0)$	$u(298)$	$K(0)$	$K(298)$
C_2-Br	(1.970)	0.0476	0.0517	0.0009	0.0012
$C_1\cdots Br$	(2.853)	0.0600	0.0725	0.0004	0.0006
$H_2\cdots Br$	(2.554)	0.1225	0.1275	0.0049	0.0051
$H_1^\circ\cdots Br$	(3.019)	0.1483	0.1732	0.0054	0.0076
$H_1\cdots Br$	(3.027)	0.1519	0.1794	0.0058	0.0084
$H_1'\cdots Br$	(3.851)	0.0978	0.1035	0.0058	0.0085

Table 9. Mean amplitudes (u) and perpendicular amplitude corrections (K) for some distances in 2-iodopropane; Å units.

Distance	(R, Å)	$u(0)$	$u(298)$	$K(0)$	$K(298)$
C_2-I	(2.106)	0.0506	0.0593	0.0008	0.0011
$C_1\cdots I$	(2.971)	0.0628	0.0807	0.0004	0.0005
$H_2\cdots I$	(2.679)	0.1271	0.1349	0.0046	0.0048
$H_1^\circ\cdots I$	(3.115)	0.1575	0.1976	0.0057	0.0092
$H_1\cdots I$	(3.124)	0.1624	0.2075	0.0060	0.0099
$H_1'\cdots I$	(3.977)	0.0990	0.1082	0.0065	0.0111

Also included are the perpendicular amplitude correction coefficients or K values.[9] The quantities of u and K are of great interest in modern gas electron diffraction studies.

For all the distances not involving halogen atoms the mean amplitudes are found to be similar in the three molecules in question. They are also similar to the previously published data for 2,2-dihalopropanes.[3] For the sake of brevity we give here only the calculated mean amplitudes at 298 K, compressed in one table for the three molecules; see Table 10.

2-CYANOPROPANE

The normal coordinate analysis was performed in principally the same way as in the case of 2-halopropanes.

The internal coordinates had to be extended with three coordinates: The C_2-C_2' stretching comes instead of $C-X$. In addition we need the $C\equiv N$ stretching, the linear CCN bending in the symmetry plane (σ), say $(D_2D_3)^{\frac{1}{2}}\ \xi$, and the linear CCN bending perpendicular to σ, say $(D_2D_3)^{\frac{1}{2}}\ \eta$. Here D_2 and D_3 in the scaling factors denote the equilibrium C_2-C_2' and $C\equiv N$ distances, respectively, *viz.* $D_2=1.375$ Å, $D_3=1.158$ Å.

Initial force constants were transferred from propane[3] and supplemented with 16.5 for the $C\equiv N$ stretching, 6.5 for C_2-C_2', 0.14 for the linear bendings, and 0.25 for the $C\equiv N/C_2-C_2'$ interaction; all values in mdyn/Å.[10] The calculated vibrational frequencies with this initial force field are shown in Table 11.

Table 10. Mean amplitudes at 298 K for distances not involving halogen atoms; Å units.

Distance	$(R, \text{Å})$	$2\text{-}C_3H_7Cl$	$2\text{-}C_3H_7Br$	$2\text{-}C_3H_7I$
$C_1 - H_1^{\circ}$	(1.091)	0.0785	0.0785	0.0788
$C_1 - H_1$	(1.091)	0.0784	0.0785	0.0786
$C_1 - H_1'$	(1.091)	0.0783	0.0784	0.0786
$C_2 - H_2$	(1.096)	0.0787	0.0787	0.0787
$C_1 - C_2$	(1.526)	0.0554	0.0562	0.0560
$C_1 \cdots C_3$	(2.536)	0.0855	0.0931	0.0816
$C_2 \cdots H_1^{\circ}$	(2.173)	0.1078	0.1081	0.1086
$C_2 \cdots H_1$	(2.173)	0.1080	0.1088	0.1089
$C_2 \cdots H_1'$	(2.173)	0.1095	0.1109	0.1110
$C_1 \cdots H_3^{\circ}$	(3.486)	0.1104	0.1138	0.1091
$C_1 \cdots H_3$	(2.801)	0.1689	0.1780	0.1734
$C_1 \cdots H_3'$	(2.801)	0.1665	0.1741	0.1810
$C_1 \cdots H_2$	(2.146)	0.1063	0.1069	0.1071
$H_1 \cdots H_1^{\circ}$	(1.762)	0.1290	0.1293	0.1297
$H_1^{\circ} \cdots H_1'$	(1.762)	0.1291	0.1293	0.1297
$H_1 \cdots H_1'$	(1.761)	0.1301	0.1303	0.1305
$H_1^{\circ} \cdots H_2^{\circ}$	(4.324)	0.1404	0.1409	0.1404
$H_1 \cdots H_3^{\circ}$	(3.802)	0.1798	0.1867	0.1833
$H_1^{\circ} \cdots H_3'$	(3.802)	0.1774	0.1829	0.1912
$H_1 \cdots H_3$	(2.625)	0.2479	0.2611	0.2565
$H_1' \cdots H_3'$	(2.625)	0.2436	0.2538	0.2737
$H_1 \cdots H_3'$	(3.161)	0.2539	0.2650	0.2849
$H_1^{\circ} \cdots H_2$	(2.491)	0.1695	0.1712	0.1772
$H_1 \cdots H_2$	(3.064)	0.1290	0.1295	0.1300
$H_1' \cdots H_2$	(2.497)	0.1749	0.1765	0.1858

The force constants were adjusted to fit the observed frequencies[1] (see also Table 11) by the same method as described above. Approximate descriptions of normal modes according to the potential energy distribution are included in Table 11.

Table 11. Calculated frequencies (cm^{-1}) and approximate descriptions of normal modes.

Species	Initial	Final[a]	Approx. description
A'	2982	2989	$C_1 - H$ stretch
	2975	2950	$C_1 - H$ stretch
	2957	2933	$C_2 - H$ stretch
	2886	2888	$C_1 - H$ stretch
	2233	2255	$C \equiv N$ stretch
	1475	1482	C_2C_1H bend
	1442	1466	C_2C_1H bend
	1412	1396	C_2C_1H bend
	1732	1296	C_1C_2H bend
	1158	1175	C_2C_1H bend
	1064	1068	C_2C_1H bend
	977	769	$C_2 - C_2'$ stretch
	812	738	$C_1 - C_2$ stretch
	571	537	$C_1C_2C_2'$ bend

Table 11. Continued.

	320	459	$C_1C_2C_3$ bend
	258	220	linear bend
	181	197	torsion
A''	2970	2999	C_1-H stretch
	2968	2941	C_1-H stretch
	2886	2922	C_1-H stretch
	1471	1482	C_2C_1H bend
	1433	1450	C_2C_1H bend
	1344	1376	C_2C_1H bend
	1656	1326	$C_1C_2C_2'$ bend
	1149	1104	C_1-C_2 str./C_2C_1H bend
	994	932	C_1-C_2 str./C_2C_1H bend
	940	916	C_2C_1H bend
	558	355	C_1C_2H bend/lin. bend
	213	316	torsion
	196	264	torsion/lin. bend

[a] Adjusted to the observed frequencies from Ref. 1.

The final force field was used to calculate the mean amplitudes of vibration for all the thirty-eight types of interatomic distances in the molecule. The results are given in Table 12.

Table 12. Mean amplitudes of vibration (Å).

Distance	$(R, \text{Å})$	$T=0$	298 K
$C_1-H_1^{\circ}$	(1.091)	0.0787	0.0787
C_1-H_1	(1.091)	0.0785	0.0785
C_1-H_1'	(1.091)	0.0785	0.0785
C_2-H_2	(1.096)	0.0786	0.0786
C_2-C_2'	(1.375)	0.0457	0.0465
$C_2'\equiv N$	(1.158)	0.0356	0.0356
C_1-C_2	(1.526)	0.0555	0.0578
$C_1\cdots C_3$	(2.536)	0.0678	0.0753
$C_3\cdots C_2'$	(2.359)	0.0696	0.0795
$C_2\cdots H_1^{\circ}$	(2.173)	0.1100	0.1116
$C_2\cdots H_1$	(2.173)	0.1077	0.1094
$C_2\cdots H_1'$	(2.173)	0.1086	0.1098
$C_1\cdots H_3^{\circ}$	(3.486)	0.1055	0.1089
$C_1\cdots H_3$	(2.801)	0.1452	0.1667
$C_1\cdots H_3'$	(2.801)	0.1426	0.1618
$C_1\cdots H_2$	(2.146)	0.1067	0.1076
$C_2'\cdots H_2$	(2.024)	0.1138	0.1162
$C_2'\cdots H_1^{\circ}$	(2.640)	0.1488	0.1708
$C_2'\cdots H_1$	(2.647)	0.1481	0.1715
$C_2'\cdots H_1'$	(3.310)	0.1037	0.1079
$C_1\cdots N$	(3.351)	0.0734	0.0908
$C_2\cdots N$	(2.533)	0.0515	0.0526
$H_1\cdots H_1^{\circ}$	(1.762)	0.1287	0.1290
$H_1^{\circ}\cdots H_1'$	(1.762)	0.1289	0.1291
$H_1\cdots H_1'$	(1.761)	0.1302	0.1304

Table 12. Continued.

$H_1^\circ \cdots H_3^\circ$	(4.324)	0.1435	0.1454
$H_1 \cdots H_3^\circ$	(3.802)	0.1646	0.1846
$H_1^\circ \cdots H_3'$	(3.802)	0.1617	0.1795
$H_1' \cdots H_3$	(2.625)	0.2145	0.2588
$H_1' \cdots H_3'$	(2.625)	0.2107	0.2507
$H_1 \cdots H_3'$	(3.161)	0.2052	0.2372
$H_1^\circ \cdots H_2$	(2.491)	0.1661	0.1757
$H_1 \cdots H_2$	(3.064)	0.1293	0.1300
$H_1' \cdots H_2$	(2.497)	0.1685	0.1796
$H_2 \cdots N$	(3.077)	0.1290	0.1409
$H_1^\circ \cdots N$	(3.434)	0.1648	0.2013
$H_1 \cdots N$	(3.444)	0.1695	0.2133
$H_1' \cdots N$	(4.375)	0.1034	0.1123

A similar analysis of 2,2-dicyanopropane (dimethylmalonitrile) is in progress.

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