

Harmonic Force Fields and Mean Amplitudes for 2,2-Dichloro- and 2,2-Dibromopropane

INGER-LILL ANDRESEN, S. J. CYVIN, B. LARSEN and O. TØRSET

Institutt for teoretisk kjemi, Norges tekniske høgskole, N-7034 Trondheim, Norway

Harmonic force fields have been developed for 2,2-dichloro- and 2,2-dibromopropane, and are presented in terms of symmetry force constants. The force field was used to calculate the mean amplitudes of vibration and perpendicular amplitude correction coefficients for all types of interatomic distances. These quantities are of great importance in modern gas electron diffraction studies.

The propane molecule has been subjected to extensive spectroscopic analyses by several authors, and recently the mean amplitudes of vibration and related quantities for propane and propane- d_8 have been reported.¹ Also the different kinds of substituted propanes have attained considerable interest. Extensive electron diffraction studies of chloro- and bromo-substituted propanes are in progress.² For some molecules of this type Klæboe^{3,4} has produced complete vibrational assignments from new observations and careful interpretations of infrared and Raman spectra. These excellent studies make it feasible to calculate the mean amplitudes of vibration for the molecules in question with good confidence. In the present work, such calculations have been performed for 2,2-dichloro- and 2,2-dibromopropane, which are treated in one of the papers by Klæboe.³ The results are believed to be of prime interest for the electron diffraction studies. More general spectroscopical applications of the here reported harmonic force fields are also possible.

HARMONIC FORCE FIELD

Harmonic force fields were developed for 2,2-dichloro- and 2,2-dibromopropane, hereafter denoted (Cl) and (Br), respectively. The values of 1.75 Å and 1.90 Å were assumed as the C-Cl and C-Br equilibrium distances. Otherwise the structural parameters from propane⁵ were adopted, as also used in the previous calculations of mean amplitudes for that molecule.¹ Especially the Cl-C-Cl and Br-C-Br angles were assumed as tetrahedral like the corresponding H-C-H angle in propane.

Preliminary force fields were constructed with most of the force constants transferred from propane.¹ Through some few iterative steps of refinements, which need not be reported here in details, the final force fields of (Cl) and (Br) were constructed in exact agreement with the observed vibrational frequencies.³

Since a detailed specification of a set of symmetry coordinates for the molecular model in question has been published⁶ it is possible to present the developed force fields in a fairly condensed form. It may be of interest to compare the force fields of (Cl) and (Br) with the original force field for propane. Therefore, the symmetry force constant matrix of C_3H_8 is shown in Table 1. This is the force field which was used in the previous computations,¹ but has not been published before. Tables 2 and 3 show the final force constants for (Cl) and (Br), respectively, in terms of the same symmetry coordinates specified elsewhere.⁶

Table 1. Symmetry force constants (mdyne/Å) for propane.

Species A_1										
1	4.62									
2	-0.00	3.47								
3	-0.01	-0.05	4.70							
4	0.01	-0.02	0.04	4.73						
5	0.08	-0.11	-0.06	0.02	0.82					
6	1.04	0.30	0.00	-0.01	0.72	2.24				
7	-0.01	0.13	-0.02	0.02	0.08	0.05	1.33			
8	-0.02	0.23	0.01	0.02	-0.01	0.01	0.81	1.16		
9	0.01	0.35	-0.01	0.04	0.05	0.01	0.54	0.44	0.75	
Species A_2										
1	4.67									
2	0.01	0.43								
3	-0.03	-0.01	0.42							
4	-0.05	-0.03	-0.05	0.41						
5	0.00	0.00	0.01	0.01	0.048					
Species B_1										
1	4.89									
2	-0.06	4.68								
3	0.91	0.01	0.56							
4	-0.00	-0.03	-0.01	0.42						
5	0.02	-0.03	-0.03	-0.01	0.50					
6	0.00	0.00	0.00	0.01	0.00	0.043				
Species B_2										
1	3.32									
2	-0.01	4.70								
3	-0.04	0.04	4.73							
4	0.29	0.01	-0.01	0.45						
5	-0.02	-0.03	0.03	0.01	1.19					
6	0.23	0.02	0.02	-0.00	0.62	1.00				
7	0.15	-0.01	0.04	-0.00	0.49	0.36	0.71			

Table 2. Symmetry force constants (mdyne/Å) for 2,2-dichloropropane.

Species A_1										
1	2.95									
2	-0.11	3.89								
3	0.01	0.01	4.82							
4	-0.01	-0.01	0.06	4.94						
5	0.13	0.04	-0.01	0.01	1.02					
6	-0.32	-0.07	0.01	-0.01	0.70	2.28				
7	-0.05	-0.07	-0.00	-0.02	0.02	-0.04	0.86			
8	0.00	-0.01	0.02	-0.01	0.03	-0.02	0.34	0.79		
9	-0.12	0.06	0.00	0.00	-0.01	-0.05	0.30	0.05	0.66	
Species A_2										
1	4.51									
2	-0.05	1.28								
3	-0.01	0.00	0.31							
4	0.09	-0.13	0.08	0.71						
5	-0.01	0.01	0.02	-0.04	0.107					
Species B_1										
1	2.11									
2	-0.02	4.45								
3	0.17	0.00	0.41							
4	-0.01	-0.00	0.01	0.42						
5	0.05	-0.02	0.00	-0.04	0.33					
6	-0.02	0.00	0.00	0.00	0.01	0.047				
Species B_2										
1	3.80									
2	-0.02	4.80								
3	-0.00	0.08	4.92							
4	0.01	0.00	0.00	0.51						
5	-0.04	-0.01	-0.01	0.00	0.84					
6	0.08	0.01	0.00	-0.01	0.29	0.73				
7	-0.03	-0.00	-0.00	0.01	0.27	0.02	0.65			

Table 3. Symmetry force constants (mdyne/Å) for 2,2-dibromopropane.

Species A_1										
1	2.36									
2	-0.38	3.71								
3	-0.00	-0.01	4.82							
4	-0.02	-0.01	0.06	4.92						
5	-0.03	-0.14	-0.01	0.00	0.97					
6	-0.36	-0.08	0.01	-0.01	0.63	2.14				
7	-0.03	-0.01	-0.00	-0.01	0.02	-0.05	0.85			
8	-0.03	-0.02	0.02	-0.01	0.01	-0.03	0.34	0.76		
9	-0.09	0.09	0.00	0.00	-0.01	-0.06	0.28	0.05	0.67	

Table 3. Continued.

Species A_1							
1	4.49						
2	0.01	0.91					
3	0.01	-0.03	0.39				
4	0.03	-0.10	0.00	0.48			
5	-0.00	0.01	-0.01	-0.02	0.087		
Species B_1							
1	2.65						
2	-0.02	4.46					
3	0.36	-0.01	0.46				
4	-0.00	-0.00	0.00	0.42			
5	0.15	-0.02	-0.02	-0.04	0.31		
6	-0.06	0.00	-0.01	0.00	0.01	0.048	
Species B_2							
1	3.62						
2	-0.02	4.79					
3	-0.02	0.10	4.87				
4	-0.19	0.00	-0.01	0.36			
5	-0.06	-0.00	-0.01	-0.01	0.84		
6	0.04	0.01	0.00	-0.03	0.29	0.72	
7	-0.07	0.00	-0.00	-0.03	0.26	0.02	0.64

Table 4. Mean amplitudes of vibration (\AA units) for 2,2-dichloro- and 2,2-dibromopropane: u at 0 and 298.16°K.

Distance type (X = Cl, Br)	2,2- $C_3H_6Cl_2$			2,2- $C_3H_6Br_2$		
	(R)	u (0)	u (298)	(R)	u (0)	u (298)
$C_1-H_1^\circ$	(1.091)	0.0782	0.0782	(1.091)	0.0782	0.0782
C_1-H_1'	(1.091)	0.0787	0.0787	(1.091)	0.0787	0.0787
C_2-X	(1.750)	0.0505	0.0543	(1.900)	0.0482	0.0536
C-C	(1.526)	0.0503	0.0513	(1.526)	0.0504	0.0520
C...C	(2.536)	0.0638	0.0691	(2.536)	0.0657	0.0722
$C_3\cdots H_1^\circ$	(2.173)	0.1050	0.1059	(2.173)	0.1050	0.1064
$C_3\cdots H_1'$	(2.173)	0.1060	0.1070	(2.173)	0.1080	0.1097
$C_1\cdots H_3^\circ$	(3.486)	0.1008	0.1031	(3.486)	0.1017	0.1048
$C_1\cdots H_3'$	(2.801)	0.1401	0.1584	(2.801)	0.1436	0.1639
$C_1\cdots X$	(2.666)	0.0614	0.0713	(2.793)	0.0606	0.0742
$H_1\cdots H_1^\circ$	(1.762)	0.1311	0.1316	(1.762)	0.1289	0.1295
$H_1\cdots H_1'$	(1.761)	0.1406	0.1416	(1.761)	0.1411	0.1422
$H_1^\circ\cdots H_3^\circ$	(4.324)	0.1371	0.1385	(4.324)	0.1371	0.1389
$H_1^\circ\cdots H_3'$	(3.802)	0.1610	0.1779	(3.802)	0.1629	0.1804
$H_1\cdots H_3^\circ$	(2.625)	0.2110	0.2498	(2.625)	0.2145	0.2535
$H_1\cdots H_3'$	(3.161)	0.2040	0.2360	(3.161)	0.2115	0.2538
$X\cdots X'$	(2.858)	0.0579	0.0764	(3.103)	0.0490	0.0785
$H_1^\circ\cdots X$	(2.870)	0.1427	0.1643	(2.970)	0.1458	0.1734
$H_1\cdots X$	(2.878)	0.1568	0.1899	(2.979)	0.1639	0.2041
$H_1\cdots X'$	(3.649)	0.0989	0.1041	(3.786)	0.0987	0.1061

MEAN AMPLITUDES OF VIBRATION

The calculated mean amplitudes of vibration (u -values) for (Cl) and (Br) are shown in Table 4. The designation of distance types follows the system of Ref. 1, where H_1° and H_3° are used to designate the hydrogen atoms in the CCC plane. For further identification of the distances, the calculated equilibrium separations (R -values) in Å are included in the table.

PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS

The calculated perpendicular amplitude correction coefficients (K -values) are given in Table 5. Therein, the atom pairs are identified by numbers according to the conventions of Ref. 6, also adopted in Ref. 1.

Table 5. Perpendicular amplitude correction coefficients (Å units) for 2,2-dichloro- and 2,2-dibromopropane: K at 0 and 298.16°K.

Distance type (X=Cl, Br)	Atom pair	2,2-C ₃ H ₆ Cl ₂		2,2-C ₃ H ₆ Br ₂	
		K (0)	K (298)	K (0)	K (298)
C ₁ -H ₁ [°]	3-6	0.0210	0.0306	0.0214	0.0325
C ₁ -H ₁	3-8	0.0243	0.0369	0.0257	0.0405
C ₂ -X	1-5	0.0014	0.0019	0.0012	0.0019
C-C	3-5	0.0021	0.0025	0.0023	0.0029
C...C	3-4	0.0012	0.0015	0.0017	0.0024
C ₂ ...H ₁ [°]	5-6	0.0107	0.0157	0.0113	0.0170
C ₂ ...H ₁	5-8	0.0126	0.0197	0.0136	0.0221
C ₁ ...H ₃ [°]	3-7	0.0069	0.0102	0.0077	0.0121
C ₁ ...H ₃	3-10	0.0084	0.0128	0.0093	0.0151
C ₁ ...X	1-3	0.0009	0.0012	0.0008	0.0013
H ₁ ...H ₁ [°]	6-8	0.0303	0.0508	0.0320	0.0556
H ₁ ...H ₁ '	8-9	0.0329	0.0557	0.0353	0.0618
H ₁ [°] ...H ₃ [°]	6-7	0.0089	0.0116	0.0101	0.0147
H ₁ ...H ₃ [°]	6-10	0.0120	0.0196	0.0131	0.0222
H ₁ ...H ₃	8-10	0.0141	0.0192	0.0160	0.0237
H ₁ ...H ₃ '	8-11	0.0128	0.0202	0.0139	0.0226
X...X'	1-2	0.0003	0.0004	0.0001	0.0001
H ₁ [°] ...X	1-6	0.0065	0.0097	0.0063	0.0097
H ₁ ...X	1-8	0.0071	0.0110	0.0069	0.0113
H ₁ ...X'	1-9	0.0071	0.0111	0.0074	0.0132

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