

Normal Coordinate Analysis of Methanethiol

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A normal coordinate analysis was performed for methanethiol. Harmonic force fields, potential energy distribution, and calculated mean amplitudes of vibration are reported.

Recently a normal coordinate analysis has been performed for methanol.¹ As structural and spectroscopic data are available for the homologue molecule methanethiol,^{2,3} the analogous calculations for this molecule were performed.

SYMMETRY COORDINATES

Methanethiol has the same symmetry (C_s) as methanol. This allows us to use the symmetry coordinates given in Ref. 1 for the calculations reported in the following.

STRUCTURAL AND SPECTRAL DATA

Kojima² has reported structural parameters for methanethiol based on microwave spectra. His data were used only with the slight modification that all interbond angles of the methyl group were assumed to be tetrahedral.

May and Pace³ have reported infrared vibrational frequencies for the isotopic molecules CH_3SH and CH_3SD , observed in the gas phase and assigned by means of normal coordinate calculations. These frequencies are given in Table 1.

FORCE FIELD

An approximate force field, defined on the basis of the symmetry coordinates,¹ was constructed from the reported force field for methanol.¹ Some of the force constants pertaining to the S atom were exchanged (Ref. 4), *viz.* $F_{33} = 3.16$, $F_{44} = 3.72$, $F_{55} = 0.72$, $F_{56} = 0.15$, and $F_{88} = 0.33$; all in mdyn/Å.

After a few iterations it was arrived at the force field of Table 2, which is consistent with the experimental frequencies of CH_3SH given in Table 1. The

Table 1. Experimental frequencies (in cm^{-1}) for methanethiol and methanethiol- d_1 , reported by May and Pace.³

		CH_3SH	CH_3SD
A'	C-H stretching	3015	3015
	C-H stretching	2948	2949
	S-H ^a stretching	2605	1893
	Methyl deformation	1453	1453
	Methyl deformation	1332	1332
	Methyl wagging	1072	1007
	CSH ^a bending	802	623
	C-S stretching	710	717
A''	C-H stretching	3012	3011
	Methyl deformation	1444	1444
	Methyl wagging	956	963
	C-S torsion	236 ^b	196 ^b

^a For CH_3SD put deuterium instead of hydrogen.

^b Calculated by the author.

Table 2. Symmetry force constants (in $\text{mdyn}/\text{\AA}$) for methanethiol. The force constants are defined according to the coordinates given in Ref. 1.

A'	4.897							
	-0.009	4.682						
	-0.050	-0.060	3.093					
	0	-0.010	0.010	3.904				
	0.056	0.203	0.240	0.021	0.651			
	-0.143	-0.208	-0.027	0.001	0.217	0.881		
	0.109	0.076	0.190	-0.010	0.115	0.334	0.735	
	0.008	-0.009	0.062	0	0.044	0.031	-0.007	0.271
A''	4.809							
	-0.037	0.375						
	-0.029	-0.057	0.375					
	-0.001	-0.003	-0.002	0.0258				

Table 3. Calculated and observed frequencies (in cm^{-1}) for methanethiol- d_1 , CH_3SD .

	Calc.	Obs.
A'	3015	3015
	2948	2949
	1872	1893
	1453	1453
	1330	1332
	1064	1007
	714	717
	587	623
A''	3012	3011
	1444	1444
	956	963
	196	—

only noteworthy discrepancy with the results of May and Pace³ is that their reported interaction force constant between methyl wag and CSH bend in the A' species is not reproduced in the present results.

Calculated frequencies for CH_3SD by means of the final force field are given in Table 3. The agreement with observed values³ is altogether satisfactory. The discrepancy for 1007 cm^{-1} (obs.) and 1064 cm^{-1} (calc.) may possibly be traced back to the above-mentioned interaction force constant.

POTENTIAL ENERGY DISTRIBUTION

The approximate description of the normal modes of CH_3SH on the basis of the potential energy distribution is given in Table 4. Again the only considerable disagreement with Ref. 3 is the absence of mixing of the coordinates for methyl wag and CSH bend.

Table 4. Approximate description of normal modes and potential energy distribution^a for CH_3SH .

A'	1	C-H stretching	$(42r + 55d)$
	2	C-H stretching	$(55r + 38d)$
	3	S-H stretching	$(100t)$
	4	HCH bending/SCH bending	$(10d + 50\phi + 92\beta + 41\epsilon)$
	5	SCH bending	$(43\phi + 79\epsilon)$
	6	HCH bending/SCH bending	$(20\phi + 37\beta + 5\epsilon)$
	7	CSH bending	(97γ)
	8	C-S stretching	$(102s)$
A''	1	C-H stretching	$(99r)$
	2	HCH bending	$(20\phi + 67\beta)$
	3	SCH bending	$(82\phi + 32\beta)$
	4	C-S torsion	(96τ)

^a P.E.D. terms smaller than 5 are omitted.

Table 5. Calculated mean amplitudes of vibration (\AA units) for methanethiol and methanethiol- d_1 (CH_3SD). For numbering of atoms, see figure in Ref. 1.

Distance type (i-j)	Equil. dist. in \AA	CH_3SH		CH_3SD^a	
		0 K	298 K	0 K	298 K
S-H(1-2)	(1.336)	0.0814	0.0814	0.0690	0.0690
C-H(3-6)	(1.091)	0.0791	0.0791	0.0791	0.0791
C-H(4-6)	(1.091)	0.0781	0.0781	0.0781	0.0781
C-S(2-6)	(1.819)	0.0501	0.0517	0.0501	0.0517
C...H(1-6)	(2.376)	0.1289	0.1313	0.1110	0.1166
S...H(2-3)	(2.413)	0.1015	0.1021	0.1014	0.1021
S...H(2-4)	(2.413)	0.1070	0.1080	0.1070	0.1080
H...H(3-4)	(1.782)	0.1332	0.1335	0.1331	0.1335
H...H(4-5)	(1.782)	0.1376	0.1381	0.1376	0.1381
H...H(1-3)	(3.316)	0.1420	0.1436	0.1289	0.1323
H...H(1-4)	(2.627)	0.2011	0.2311	0.1832	0.2209

^a Atom number 1 is deuterium.

MEAN AMPLITUDES OF VIBRATION

The developed force constants (Table 2) were used to calculate the mean amplitudes for CH₃SH and CH₃SD. The results at absolute zero and 298 K are summarized in Table 5.

REFERENCES

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