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NORMAL COORDINATE ANALYSIS OF CH_3COSH AND CH_3 COSD

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Normal vibration analysis of CH_3 COSH and CH_3 COSD has been carried out employing the Urey-Bradley Shimanouchi force field. Vibrational frequencies are assigned on the basis of normal coordinate calculations and are compared with the earlier assignments.

Key Words : CH_3 COSH; CH_3 COSD; Normal Coordinate Analysis

INTRODUCTION

In an earlier research,[1] the author has proposed a vibrational assignment for CH_3COSH which is supported by the extensive infrared and Raman spectral data obtained for CH_3 COSD, CD_3 COSH and CD_3 COSD in the vapour and liquid states. Normal coordinate analysis of CH_3COSH has not attracted considerable attention. The only report employing modified valence force field (MVFF) is by Crowder *et al.*[2] The author has now made the normal coordinate analysis for the in-plane vibrations of CH_3 COSH and CH_3 COSD employing Urey-Bradley-Shimanouchi force field (UBSFF)[3] in order to (*i*) substantiate the assignment of these motions based on infrared and Raman spectral data[1,4,5] and normal coordinate analysis by MVFF[2] and (*ii*) quantize the contribution of the fundamental modes.

The normal coordinate analysis for the in-plane vibrations of CH_3 COSH and CH_3COSD was carried out as an eight-body problem and C_s point group. The structural parameters used in the calculations are given in Table I. The structure and internal coordinates of CH_3 COSH are shown in Fig. 1 and the symmetry coordinates are reported in Table II. By employing a set of force constants taken from thioformaldehyde,[6] thiol acids,[7] methylthionformate,[8] formic acid, acetic acid and related molecules,[9] the author carried out initial calculations and progressively impoved the results by an iterative procedure. The final set of force constants which give good agreement between observed and calculated frequencies is recorded in Table I. A comparison of calculated and observed frequencies as well as the potential energy distribution (PED) in the symmetry coordinate for CH_3 COSH and CH_3 COSD (calculated from normalized L-matrix) is given in Tables III and IV, respectively.

The data reveal that the percentage deviation (Δ) between the observed and calculated values is generally small and within the jurisdiction of force field applied ($< 20\%$) except for the two frequencies associated with C-C stretch

TABLE I

The structural parameters and force constants of CH_3COSH

Bond distances (Å)	Bond angles (deg)
$r(C-H) = 1.09$	$H-\hat{C}-H = 109.47122$
$r(C-C) = 1.50$	$H-\hat{C}-C = 109.47122$
$r(C-S) = 1.78$	
$r(C-O) = 1.24$	$C-\hat{C}=O = C-\hat{C}-S = 120$
$r(S-H) = 1.34$	$C-\hat{S}-H = 107.8$
Force constants (millidynes/Å)	
$K(C-H) = 4.50$	$H(H-C-H) = 0.30$
$K(S-H) = 3.67$	$F(O \ldots S) = 2.20$
$K(C-C) = 2.80$	$F(O \ldots C) = 0.40$
$K(C-S) = 2.26$	$F(S \ldots C) = 0.40$
$K(C=O) = 9.948$	$F(C \ldots H) = 0.10$
$H(O-C-S) = 1.25$	$F(H \ldots C) = 0.04$
$H(O=C-C) = 0.60$	$F(H \ldots H) = 0.03$
$H(S-C-C) = 0.60$	$F' = -F/10$
$H(C-S-H) = 0.49$	$T = 0.04$
$H(H-C-C) = 0.50$	

($1000cm^{-1}$) and CCS bend ($330cm^{-1}$) where it is about 26 and 32 in CH_3COSH while 20 and 32% in CH_3COSD correspondingly. Such deviation may arise due to the improper selection of the internal coordinates and some fixed force constants. But for these minor discrepancies, our calculations provide satisfactory assignments of all the vibrational frequencies and predict the observed isotopic effects. However, a few comments on the assignment of some of the fundamental modes and their nature would be in order. From our calculations, we are able to confirm the assignment of the controversial band at $438cm^{-1}$ which is not affected on deuteration to OCS bending motion. This is inconfirmity with our earlier results.[1] Secondly the CH_3 rock have been found to be almost pure (80%)

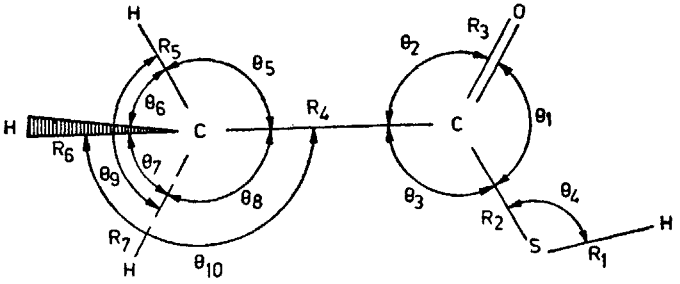

FIG 1 Internal coordinates of CH_3COSH

TABLE II

Symmetry coordinates of CH_3COSH[a]

Species	Symmetry coordinate	Assignment
A[a]	$S_1 = \frac{1}{\sqrt{6}}$ $(2 R_5 - R_6 - R_7$	CH_3 asym str
	$S_2 = \frac{1}{\sqrt{3}} (R_5 + R_6 + R_7)$	CH_3 sym str
	$S_3 = R_1$	SH str
	$S_4 = R_3$	C=O str
	$S_5 = \frac{1}{\sqrt{6}} (2\theta_7 - \theta_6 - \theta_9)$	CH_3 asym bend
	$S_6 = \frac{1}{\sqrt{6}} (\theta_5 + \theta_{10} + \theta_8 + \theta_6 + \theta_9 + \theta_7$	CH_3 sym str
	$S_7 = \frac{1}{\sqrt{6}} (2\theta_5 - \theta_{10} - \theta_8)$	CH_3 rock
	$S_8 = R_4$	C—C str
	$S_9 = \theta_4$	CSH bend
	$S_{10} = R_2$	C—str
	$S_{11} = \frac{1}{\sqrt{6}} (2\theta_1 - \theta_2 - \theta_3)$	SCO bend
	$S_{12} = \frac{1}{\sqrt{2}} (\theta_3 - \theta_2)$	CCS bend
Redundant coordinates	$S_{13} = \frac{1}{\sqrt{3}} (\theta_1 + \theta_2 + \theta_3)$	
	$S_{14} = \frac{1}{\sqrt{6}} (\theta_5 + \theta_6 + \theta_7 + \theta_8 + \theta_9 + \theta_{10})$	

[a]Abbreviations used are : str—stretch; asym—asymmetric; sym—symmetric.

TABLE III

Observed and calculated frequencies and PED of CH_3COSH

Obs[a] (cm^{-1})	Calc (cm^{-1})	Δ (%)[b]	Approx. PED in the symmetry coordinates (%)
3020	3010	0.33	$99\, S_1$
2940	2930	0.34	$100\, S_2$
2585	2580	0.19	$100\, S_3$
1735	1710	1.44	$88\, S_4$
1425	1428	0.21	$88\, S_5 + 10\, S_7$
1365	1360	0.36	$95\, S_6$
1128	1132	0.35	$80\, S_7 + 10\, S_5$
1000	732	26.80	$27\, S_8 + 34\, S_{10} + 18\, S_9 + 16\, S_{11}$
830	835	0.60	$79\, S_9 + 16\, S_{11}$
628	628	0.00	$30\, S_{10} + 47\, S_8 + 11\, S_{12}$
438	450	2.73	$64\, S_{11} + 28\, S_{10}$
330	438	32.72	$77\, S_{12} + 10\, S_{11}$

[a]Ref. 1

[b]$\Delta = /(\nu_{obs} - \nu_{calc})/ \times 100/\nu_{obs}$;

*$(F_{ii} L_{in}^2/\lambda N) \times 100$; PED below 10% is not considered; average error = 5.5%

TABLE IV

Observed and calculated frequencies and PED of CH_3COSD

obs[a] (cm^{-1})	calc (cm^{-1})	(%)[b]	Approx. PED in the symmetry coordinates (%)[*]
3020	3010	0.33	$99\ S_1$
2940	2930	0.34	$100\ S_2$
1890	1854	1.90	$100\ S_3$
1735	1710	1.44	$89\ S_4$
1425	1428	0.21	$88\ S_5 + 10\ S_7$
1365	1360	0.36	$95\ S_6$
1128	1132	0.35	$80\ S_7 + 10\ S_5$
960	763	20.52	$42\ S_8 + 28\ S_{10} + 21\ S_{11}$
658	574	12.76	$65\ S_9 + 32\ S_8$
628	647	3.02	$42\ S_{10} + 23\ S_9 + 13\ S_8 + 10\ S_{12}$
438	446	1.82	$41\ S_{11} + 26\ S_{10} + 30\ S_{12}$
325	429	32.00	$55\ S_{12} + 30\ S_{11}$

[a] Ref. 1

[b] $\Delta = / (\nu_{obs} - \nu_{calc}) / \times 100/\nu_{obs}$;

[*] $(F_{ii}\ L_{in}^2/\lambda N) \times 100$; PED below 10% is not considered; average error = 6.25%.

and not mixed with C-C stretch, but C-C stretch has significant contribution due to CSH bend, C-S stretch and SCO bend and not from CH_3 rock as the calculations of Crowder *et al.*[2] reveal.

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