

## NORMAL COORDINATE ANALYSIS OF METHANETHIOL AND ISOTOPIC ANALOGS

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### ABSTRACT

Gas-phase infrared frequencies for 55 fundamentals of methanethiol ( $\text{CH}_3\text{SH}$ ) and its  $d_1$ ,  $d_3$ ,  $d_4$ , and  $^{13}\text{C}$ -substituted analogs have been used to calculate a nineteen-parameter symmetry valence force field. The final refinement resulted in an average error of less than  $5\text{ cm}^{-1}$  (ca. 0.4%) between the calculated and observed frequencies for the five isotopomers. In general, the calculations support presently accepted vibrational assignments for these species. One revision indicated, however, is the transposition of  $\delta\text{CSH}$  and  $\nu\text{CS}$  for  $\text{CD}_3\text{SH}$ . The calculations show that the band observed at  $643\text{ cm}^{-1}$  is associated with  $\delta\text{CSH}$ , while  $\nu\text{CS}$  is assigned to the absorption at  $688\text{ cm}^{-1}$ . Comparisons are made between the present force field and one previously reported for  $\text{CH}_3\text{SH}$ , as well as one for the selenium analog,  $\text{CH}_3\text{SeH}$ . The calculated symmetry valence force field was then transformed into a set of valence force constants in terms of internal coordinates for comparison with available data for  $\text{CH}_3\text{OH}$ , a series of alkanethiols and alkyl sulfides, and an ab initio force field for  $\text{CH}_3\text{SH}$ .

### INTRODUCTION

Volatile sulfur-containing compounds are important in a variety of agricultural contexts. For example, trace quantities of hydrogen sulfide, as well as dimethyl sulfide, methanethiol, and dimethyl disulfide contribute to the flavor and aroma of fresh citrus juices [1]. These same simple, organosulfur species also have significant roles in the chemistry of sludge-amended soils. Here they arise from decomposition of sulfur-containing amino acids [2], in some cases under both aerobic and anaerobic conditions [3]. Evidence that these compounds are powerful inhibitors of the nitrogen-fixation process further underscores their importance [4].

Thiols, in particular, are biochemically important from yet another standpoint. They are precursors in the formation of thionitrites (*S*-nitrosothiols) [5]. These reactive species have, in turn, been implicated as possible key intermediates in such processes as vasodilation by organonitrites and nitroglycerin [6], and in the inhibition of bacterial growth observed in nitrite-treated food products [7].

Because methanethiol is the smallest alkyl mercaptan, spectroscopists

have studied it extensively by both infrared and Raman techniques [8]. Siebert, in 1952, calculated an eight-parameter simple valence force field based solely on data for the normal molecule [9]. Some years later (1968), May and Pace reinvestigated the infrared and Raman spectra of  $\text{CH}_3\text{SH}$ , and obtained vibrational data for its S-deuterated analog. In addition, they calculated a symmetry valence force field (SYMFF) which included just one off-diagonal force constant [8]. Scott and El-Sabban included normal methanethiol as part of an "overlay" calculation of a valence force field for a series of alkanethiols and alkyl sulfides [10].

More recently, two general valence force fields (GVFF) have been published. One by Gebhardt [11] is "empirical" and is based on May and Pace's infrared data for the normal molecule only [8]. Because of the severely limited data set, questions arise with respect to the validity of a force field resulting from such a calculation. For example, the calculated frequency fit for  $\text{CH}_3\text{SD}$  is very poor [11]. The other GVFF is an ab initio calculation by Schlegel et al. [12], using Cartesian-Gaussian basis sets. These researchers concluded that a re-examination of the experimental force field is warranted.

Vibrational frequencies are now available for the two C-deuterated species [13]. In addition, we have synthesized  $^{13}\text{C}$ -substituted  $\text{CH}_3\text{SH}$  and measured its gas-phase infrared spectrum (Fig. 1). With these new data in hand, we have calculated a new, more complete symmetry valence force field for methanethiol which includes eleven diagonal and eight interaction force

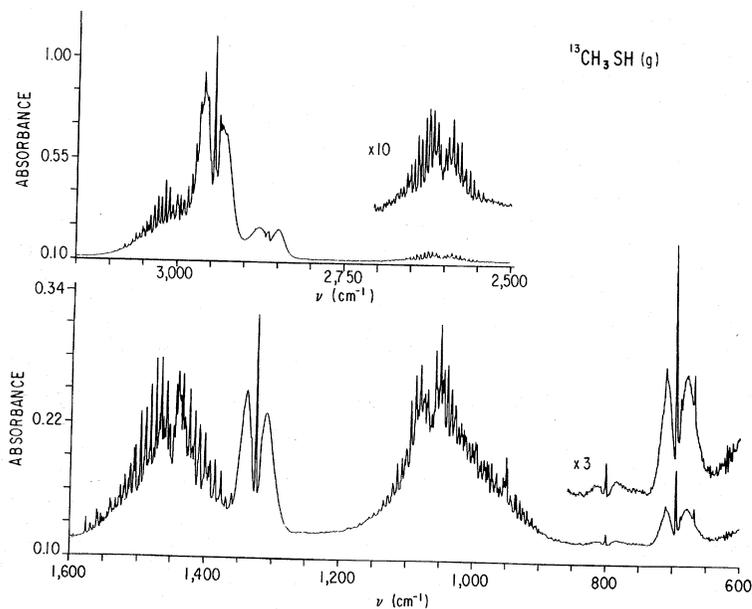


Fig. 1. FTIR spectrum of  $^{13}\text{CH}_3\text{SH}$  from 3150–2500 and 1600–600  $\text{cm}^{-1}$ .  $P = 78.8$  torr; resolution = 1.0  $\text{cm}^{-1}$ .

constants. (The unobserved torsional mode was omitted.) We have also obtained a set of valence force constants for comparison with force fields of related molecules and with ab initio calculations for methanethiol.

#### EXPERIMENTAL

Table 1 summarizes the measured frequencies of the observed fundamentals for the five methanethiol isotopomers. The gas-phase infrared frequencies for the normal molecule, CH<sub>3</sub>SH, and for CH<sub>3</sub>SD are those of May and Pace [8]. Saur et al. reported the spectra for the C-deuterated analogues, CD<sub>3</sub>SH, and CD<sub>3</sub>SD [13].

Gas-phase infrared spectra for the <sup>13</sup>C-substituted species (Fig. 1) were obtained between 4000 and 400 cm<sup>-1</sup> at 1 cm<sup>-1</sup> resolution using a Nicolet 7199 Fourier-transform infrared spectrometer. This instrument has a KBr beamsplitter, a TGS detector, and a Globar source. The spectral data are an average of 200 scans; the interferogram was apodized with the Happ-Genzel function prior to Fourier transformation. The spectra were run at ambient temperature in a 10-cm gas cell; *P* = 78.8 torr.

The <sup>13</sup>C-enriched compound was prepared by one of the authors in conjunction with an earlier study of methyl thionitrite [14].

*Caution:* Methanethiol is a flammable, moderately toxic gas characterized by an obnoxious, evil stench. It should always be handled in an efficient exhaust hood.

TABLE 1

Observed and calculated frequencies (cm<sup>-1</sup>) for five isotopomers of methanethiol (SYMFF1)

Band No.	Approximate assignment <sup>a</sup>	CH <sub>3</sub> SH		CH <sub>3</sub> SD		CD <sub>3</sub> SH		CD <sub>3</sub> SD		<sup>13</sup> CH <sub>3</sub> SH			
		Obs. <sup>b</sup>	Calc.	Obs. <sup>b</sup>	Calc.	Obs. <sup>c</sup>	Calc.	Obs. <sup>c</sup>	Calc.	Obs. <sup>d</sup>	Calc.		
A <sub>1</sub>	ν <sub>1</sub>	ν <sub>a</sub>	CH <sub>3</sub>	3015	3015.9	3015	3015.8	2261	2260.4	2260	2260.1	3004.8	3002.1
	ν <sub>2</sub>	ν <sub>s</sub>	CH <sub>3</sub>	2948	2951.2	2949	2951.2	2150	2146.4	2148	2146.4	2946.8	2945.2
	ν <sub>3</sub>	ν	SH	2605	2612.3	1893	1876.4	2605	2612.3	1892	1876.3	2604.1	2612.3
	ν <sub>4</sub>	δ <sub>a</sub>	CH <sub>3</sub>	1453	1449.7	1453	1449.7	1060	1055.2	1058	1051.8	1449.7	1446.7
	ν <sub>5</sub>	δ <sub>s</sub>	CH <sub>3</sub>	1332	1334.8	1332	1334.8	1022	1016.3	1021	1016.3	1325.5	1327.7
	ν <sub>6</sub>	ρ <sub>  </sub>	CH <sub>3</sub>	1072	1077.5 <sup>e</sup>	1007	1008.8	643	649.0	822	815.6 <sup>e</sup>	1066.9	1072.3
	ν <sub>7</sub>	δ	CSH	802	805.0	623	616.1	977	972.6	568	565.9	799.4	804.1
	ν <sub>8</sub>	ν	CS	710	713.2	717	726.7	688	673.3	679	671.7	695.1	697.8
A <sub>2</sub>	ν <sub>9</sub>	ν <sub>a</sub>	CH <sub>3</sub>	3012	3014.7	3011	3014.7	2260	2256.9	2260	2256.9	3001.3	3001.0
	ν <sub>10</sub>	δ <sub>a</sub>	CH <sub>3</sub>	1444	1450.3	1444	1450.3	1051	1050.4	1052	1050.4	1441.1	1447.4
	ν <sub>11</sub>	ρ <sub>⊥</sub>	CH <sub>3</sub>	956	959.1	963	959.1	726	714.9	717	714.9	950.7	954.8

<sup>a</sup>ν, stretch; δ, bend; ρ, rock; subscripts: a (or s), antisym. (or sym.) with respect to methyl C<sub>3v</sub> axis; || or ⊥, parallel or perpendicular to molecular symmetry plane. <sup>b</sup>Ref. 8. <sup>c</sup>Ref. 13. <sup>d</sup>This work. <sup>e</sup>For CH<sub>3</sub>SH and CD<sub>3</sub>SD, ρ<sub>||</sub> CH<sub>3</sub> (ν<sub>6</sub>), and δCSH (ν<sub>7</sub>) mix heavily (see Table 4).

### Numerical methods and structural considerations

The computational procedures for solving the vibrational secular equation were based on Wilson's  $GF$ -matrix formulation [15]. Evaluation of the SYMFF potential constants by application of the least squares criterion was performed using programs and procedures previously described by Susi and Scherer [16].

Microwave data for methanethiol [17] served as the source of bond lengths ( $r$ ) and bond angles ( $\angle$ ):

$$\begin{array}{ll} r(\text{CS}) = 1.819 \text{ \AA} & \angle \text{CSH} = 96.50^\circ \\ r(\text{CH}) = 1.092 \text{ \AA} & \angle \text{HCH} = 109.75^\circ \\ r(\text{SH}) = 1.335 \text{ \AA} & \angle \text{HCS} = 109.20^\circ \end{array}$$

The angle between the CS bond and the  $C_3$  symmetry axis of the methyl group is  $2.17^\circ$ . To determine the  $G$ -matrix elements [15], certain structural simplifications were made:

(1) The CS bond was assumed to coincide with the symmetry axis of the methyl group.

(2) All angles around the carbon atom were idealized to tetrahedral values. (Calculations based on a  $G$ -matrix in which experimental values for the HCH and HCS bond angles were used showed no significant differences between the force constant values based on observed geometry and those obtained assuming a tetrahedral configuration.)

(3) The molecular configuration chosen was that for which one CH bond and the SH bond lie in the same  $C_s$  symmetry plane, *anti*- (or *trans*-) to each other. Thus, the dihedral angle HCSH equals  $180^\circ$ . (Numerical experiments show that if one chooses angle HCSH equal to  $0^\circ$  the only resulting change is that the values of a few interaction terms take on the opposite sign from that calculated for the *anti*-configuration.)

### Symmetry coordinates and force field

Even in its most symmetrical conformations (*anti*- and *syn*-), methanethiol has only  $C_s$  symmetry. It has 12 fundamentals:  $8 A' + 4 A''$ . Despite its low formal symmetry classification, methanethiol is very nearly a symmetric top [8]. Under high resolution, the two symmetric  $\text{CH}_3$  vibrations (corresponding to  $A_1$  modes for true  $C_{3v}$  symmetry) exhibit infrared bands with obvious PQR structures (Fig. 1). The three antisymmetric  $\text{CH}_3$  modes (stretching, bending, and rocking) are nearly degenerate; the  $A'$  and  $A''$  components overlap extensively [8, 13]. One may thus choose to calculate a force field based on any one of three sets of internal displacement coordinates:

(1) Local  $C_{3v}$  symmetry coordinates may be defined for the methyl group modes [8, 14, 18].

(2) Methyl group symmetry coordinates may be written such that the mirror plane is the only symmetry element [11, 19].

(3) Simple bond stretching and bond angle deformation coordinates may be used as a basis for all force constants [12, 20].

Advantages and disadvantages are inherent in each choice. No matter which alternative one selects, even spectroscopic data from five isotopomers is insufficient to calculate a convincing, empirical general valence force field (GVFF). Simplifying assumptions must be made. Unfortunately, exactly the same simplifications cannot be used in each of these three cases. Hence, a direct comparison of the calculated force fields which result from each of the above choices of internal coordinates is not always feasible.

Employing local symmetry coordinates has certain advantages. For molecules having methyl groups or other approximately symmetric moieties, calculated displacements of the local symmetry coordinates rather closely approximate many of the normal vibrations [14, 16]. Thus, the potential energy contributed by each local symmetry force constant to a particular normal vibration is interpretable as arising from characteristic vibrational motions involving specific, symmetrical parts of the molecule. One can also readily compare force constants of one molecule with others having analogous symmetry and structure. Because we wished to compare our calculated force field with that reported by May and Pace [8], and with the published SYMFF for methaneselenol [18], we chose to define our coordinates in terms of approximate  $C_{3v}$  symmetry, using a  $U$ -matrix as defined in these reports [8, 18]. To facilitate comparison with force fields based on other types of coordinates, we transformed our final symmetry force field (SYMFF1) into one based on simple bond stretching and bending coordinates.

#### *Refinement of force constants*

Because the methyl group closely approximates  $C_{3v}$  symmetry, the two diagonal force constants for each of the three pairs of nearly degenerate modes were constrained throughout every calculation to be equal: i.e.,  $F(1) = F(9)$ ,  $F(4) = F(10)$ , and  $F(6) = F(11)$ . In a similar manner, the interaction constants for these modes were required to refine to equal values:  $F(15) = F(19)$  and  $F(17) = F(20)$ .

For an initial trial calculation, 11 diagonal constants (the torsional constant was neglected) and one off-diagonal,  $F(13)$ , were assigned non-zero values transferred from May and Pace [8]. One by one new interactions were added. Generally, the only interactions considered for refinement were those for which the two coordinates involved shared at least one atom in common [15]. If the refinement diverged, or if the estimated error in the new interaction force constant was greater than 50% of the calculated value of the constant, that interaction was constrained to zero. Six  $A'$  and two  $A''$  off-diagonal terms could ultimately be determined with reasonable precision. Table 2 gives the values for all force constants calculated in the

## Symmetry valence force constants for methanethiol and methaneselenol

Force constant <sup>a</sup>	Symmetry coordinate <sup>b</sup>	CH <sub>3</sub> SH			CH <sub>3</sub> SeH <sup>e</sup>
		SYMFF1 <sup>c</sup>	SYMFF2 <sup>c</sup>	M & P <sup>d</sup>	
Diagonal					
A'	A''				
$F(1) \equiv F(9)^f$	$\nu_a$ CH <sub>3</sub>	4.77(3) <sup>f</sup>	4.75(5) <sup>g</sup>	4.81	4.89
$F(2)$	$\nu_s$ CH <sub>3</sub>	4.86(5)	4.86(8)	5.00	4.86
$F(3)$	$\nu$ SH	3.925(10)	3.926(15)	3.934	3.20
$F(4) \equiv F(10)^f$	$\delta_a$ CH <sub>3</sub>	0.573(10)	0.583(16)	0.528	0.530
$F(5)$	$\delta_s$ CH <sub>3</sub>	0.588(15)	0.589(23)	0.487	0.613
$F(6) \equiv F(11)^f$	$\rho$ CH <sub>3</sub>	0.610(4)	0.620(8)	0.623	0.585
$F(7)$	$\delta$ CSH	0.829(9)	0.901(17)	0.846	0.773
$F(8)$	$\nu$ CS	3.12(3)	3.16(5)	3.26	2.62
	$F(12)$	$\tau$		0.006	—
Interaction					
A'	A''				
$F(13)$	$\rho_{  }$ CH <sub>3</sub> , $\delta$ CSH	0.144(4)	-0.281(10)	-0.150	-0.145
$F(14)$	$\delta_s$ CH <sub>3</sub> , $\nu$ CS	-0.29(3)	-0.31(5)	—	-0.261
$F(15) \equiv F(19)^f$	$\nu_a$ CH <sub>3</sub> , $\delta_a$ CH <sub>3</sub>	0.14(6)	0.18(8)	—	-0.041
$F(16)$	$\nu_s$ CH <sub>3</sub> , $\delta_s$ CH <sub>3</sub>	-0.36(7)	-0.35(11)	—	-0.453
$F(17) \equiv F(20)^f$	$\delta_a$ CH <sub>3</sub> , $\rho_{\perp}$ CH <sub>3</sub>	-0.07(2)	-0.11(4)	—	—
$F(18)$	$\delta$ CSH, $\nu$ CS	0.05(2)	-0.01(3)	—	—
	Average error <sup>h</sup> in frequencies	4.6 cm <sup>-1</sup> (0.41%)	5.9 cm <sup>-1</sup> (0.57%)		

<sup>a</sup>Units: Str., mdyn Å<sup>-1</sup>; bend, mdyn Å rad<sup>-2</sup>; str.—bend interaction, mdyn rad<sup>-1</sup>. <sup>b</sup>Same as Table 1, note <sup>a</sup>. <sup>c</sup>The major distinction between SYMFF1 and SYMFF2 are for  $F(7)$  and  $F(13)$ . In the latter, note the change in sign. See Results and discussion section for details. <sup>d</sup>Ref. 8. <sup>e</sup>Ref. 18. <sup>f</sup>Each pair of constants associated with the approximately degenerate modes of the methyl group were constrained so that the A' and A'' components would refine to the same value. <sup>g</sup>Numbers in parentheses represent the error in the last decimal place(s) of the force constant values as estimated from the standard error in the frequency parameters. <sup>h</sup>I.e., the average of the absolute value of the observed frequency minus the calculated frequency for all vibrations.

final refinements. As discussed below, SYMFF1 and SYMFF2 result from two calculations which differed only in the initial values assigned to  $F(13)$ , 0.00 and -0.10 mdyn Å rad<sup>-2</sup>, respectively.

Later the set of force constants for SYMFF1 ( $F_{\text{sym}}$  in matrix notation) was desymmetrized by means of the matrix transformation

$$\mathbf{F} = \mathbf{U}'\mathbf{F}_{\text{sym}}\mathbf{U} \quad (1)$$

to give the equivalent force field (VFF1) in terms of simple bond stretching and bending coordinates ( $\mathbf{F}$  in matrix notation).  $\mathbf{U}$  is the orthogonal matrix,

as defined by May and Pace [8], which transforms the internal coordinates into the desired local symmetry coordinates;  $U'$  is its transpose. Constraining a minimal number of interactions to zero, VFF1 was then refined to give the best set of empirical force constants based on internal coordinates (VFF2). Table 3 presents these two sets of constants.

TABLE 3

Valence force constants for methanethiol, alkanethiols, and methanol

Force constant <sup>a</sup>	Internal coordinate <sup>b,c</sup>	CH <sub>3</sub> SH		RSH and RSR <sup>f</sup>	CH <sub>3</sub> OH <sup>g</sup>
		VFF1 <sup>d</sup>	VFF2 <sup>e</sup>		
Diagonal					
$f(1)$	$\nu$ CH	4.80	4.79(3) <sup>h</sup>	4.663(6) <sup>h</sup>	4.661(7) <sup>h</sup>
$f(2)$	$\delta$ HCH	0.480	0.582(9)	0.563(2)	0.576(3)
$f(3)$	$\delta$ HCS	0.504	0.541(14)	0.615(8)	0.766(8)
$f(4)$	$\nu$ CS	3.12	3.21(3)	3.21(6)	5.28(4)
$f(5)$	$\delta$ CSH	0.829	0.846(10)	0.814(19)	0.737(6)
$f(6)$	$\nu$ SH	3.925	3.925(10)	3.800(16)	7.568(12)
$f(7)$	$\tau$	—	—	0.0115(9)	0.0263(10)
Interaction					
$f(8)$	$\nu$ CH, $\nu$ CH	0.029	0.058(5)	0.026(5)	0.177(14)
$f(9)$	$\nu$ CH, $\delta$ HCH <sup>i</sup>	0.010	—	—	—
$f(10)$	$\nu$ CH, $\delta'$ HCH <sup>j</sup>	-0.133	-0.21(4)	—	—
$f(11)$	$\nu$ CH, $\delta$ HCS	0.086	—	—	—
$f(12)$	$\delta$ HCH, $\delta$ HCH	-0.093	—	—	—
$f(13)$	$\delta$ HCH, $\delta$ HCS <sup>i</sup>	-0.150	-0.080(18)	—	-0.060(5)
$f(14)$	$\delta$ HCH, $\delta'$ HCS <sup>j</sup>	-0.072	—	—	—
$f(15)$	$\delta$ HCH, $\nu$ CS	-0.117	-0.127(13) <sup>k</sup>	—	—
$f(16)$	$\delta$ HCS, $\nu$ CS	0.117	0.127(13) <sup>k</sup>	0.35(5)	0.454(13)
$f(17)$	$\delta$ HCS, $\delta$ HCS	-0.0105	-0.068(14)	-0.015(6)	-0.044(2) <sup>l</sup>
$f(18)$	$\delta_i$ HCS, $\delta$ CSH <sup>m</sup>	0.118	0.182(5)	0.184(5)	0.096(5)
$f(19)$	$\delta_o$ HCS, $\delta$ CSH <sup>n</sup>	-0.059	—	—	-0.010(5)
$f(20)$	$\nu$ CS, $\delta$ CSH	0.05	0.30(2)	0.32(4)	0.41(2)

<sup>a</sup>Units: (same as Table 2, note a.) <sup>b</sup>Same as Table 1, note a. <sup>c</sup>For CH<sub>3</sub>OH, substitute O for S in the internal coordinate descriptions. <sup>d</sup>VFF1 is the unrefined force field obtained when SYMFF1 is transformed by eqn. (1). <sup>e</sup>VFF2 results from a refinement of VFF1 with  $f(9)$ ,  $f(11)$ ,  $f(12)$ ,  $f(14)$ , and  $f(19)$  constrained to zero. <sup>f</sup>R = alkyl; ref. 10. <sup>g</sup>Ref. 20. <sup>h</sup>Same as Table 2, note f. <sup>i</sup>For  $f(9)$  and  $f(13)$ , two coordinates involved in the interaction have only the C atom in common, and do not share a CH bond. <sup>j</sup>For  $f(10)$  and  $f(14)$ , two coordinates involved in the interaction always share a CH bond in common. <sup>k</sup>For VFF2,  $f(15)$  and  $f(16)$  were refined so that  $f(15) \equiv -f(16)$ . <sup>l</sup>This value is estimated from a linear combination of two interaction constants reported in ref. 20:  $(\Delta H_\phi + 2h'_{\phi\phi})/3$ . <sup>m</sup>In-plane HCS bend. <sup>n</sup>Out-of-plane HCS bend.

In general, assignments based on the calculated potential energy distribution (PED) for the five methanethiol molecules (Table 1) agree with those previously published [8, 13]. One notable exception is the transposition in the assignment of  $\nu$ CS and  $\delta$ CSH for  $\text{CD}_3\text{SH}$ . As is clear from the PED for the best symmetry force field, SYMFF1 (Table 4),  $\rho_{\parallel}\text{CH}_3$  and  $\delta$ CSH mix heavily for all five isotopomers. In the specific cases of  $\text{CH}_3\text{SH}$  and  $\text{CD}_3\text{SH}$ , the interaction is so great that one can no longer speak of group vibrations even as a first approximation. On the other hand,  $\nu$ CS mixes appreciably with  $\delta$ CSH only for  $\text{CD}_3\text{SH}$ . The CS stretch also couples to a moderate degree with  $\delta_s\text{CH}_3$  for the two C-deuterated species. The selenium analog  $\text{CH}_3\text{SeH}$  exhibits similar behavior [18], although the degree of mixing with the methyl group vibrations is smaller because both  $\delta\text{CSeH}$  and  $\nu\text{CSe}$  occur at lower frequencies than do the corresponding thiol vibrations.

The present study provides an excellent example of a pitfall encountered in any attempt to determine a convincing empirical force field for all but the smallest of molecules: by what criteria can one choose the most realistic set of force constants from two or more similar sets resulting from calculations whose initial parameters differ only slightly? In the present instance, a small change in the initial value of just one interaction,  $F(13)$ , yielded two different force fields: SYMFF1 (initial  $F(13) = 0.0$  or  $-0.05$  m dyn  $\text{\AA}$  rad $^{-2}$ ) and SYMFF2 (initial  $F(13) = -0.10$  m dyn  $\text{\AA}$  rad $^{-2}$ ). The calculated frequencies and force constants do not clearly indicate which of these two sets is the better. SYMFF1 gave a better frequency fit ( $4.6$  cm $^{-1}$  vs.  $5.9$  cm $^{-1}$  for SYMFF2) and had smaller estimated errors in the calculated force constants. But are these criteria sufficient? Most of the final calculated force constant values for these two VFF's are quite similar. Just two force constants show significant differences:  $\delta$ CSH [ $F(7)$ ] and the interaction constant  $F(13)$ , [ $\rho_{\parallel}\text{CH}_3$ ,  $\delta$ CSH]. For SYMFF1,  $F(13) = 0.144$  m dyn  $\text{\AA}$  rad $^{-2}$ ; for SYMFF2,  $F(13) = -0.281$  m dyn  $\text{\AA}$  rad $^{-2}$ . This change in the value and sign of the interaction constant results in a very small increase in value of the diagonal force constants for  $\rho_{\parallel}\text{CH}_3$  and a somewhat larger value for  $\delta$ CSH (Table 2). A more detailed examination of the calculations for each set reveals additional distinctions:

(1) Mixing of  $\rho_{\parallel}\text{CH}_3$  and  $\delta$ CSH is greater for SYMFF2. This observation is reflected by a marked increase in the contribution of  $F(13)$  to the potential energy term for these modes in SYMFF2. For several isotopomers,  $F(13)$  has an absolute value of greater than 40%.

(2) As suggested by May and Pace [8], a negative value for  $F(13)$  does, in general, better reproduce the observed splitting of the approximately degenerate methyl deformation (SYMFF2). On the other hand, the calculated splitting for the methyl rocking vibrations of the two S-deuterated species is much better generally for SYMFF1, where  $F(13)$  has a positive value.

(3) Most telling in favor of SYMFF1 is the relatively small number of large

TABLE 4

Potential energy distribution<sup>a</sup> (PED) for four isotopomers of methanethiol (SYMFF1)

Band No.	Approximate assignment <sup>b</sup>	F(1) <sup>c</sup>	F(2)	F(3)	F(4)	F(5)	F(6)	F(7)	F(8)	F(13)	F(14)	F(15)	F(16)	F(17)	F(18)
$\nu_4$	$\delta_a\text{CH}_3$	3 <sup>d</sup>			102		2					-3		-4	
		3			102		2					-3		-4	
		5			93			6				-4			
		5			99			1				-3			-1
$\nu_5$	$\delta_s\text{CH}_3$		11			109			3		-8		-14		
			11			109			3		-8		-15		
			15			104			15		-17		-17		
			15			104			15		-17		-18		
$\nu_6$	$\rho_{  }\text{CH}_3$						48	35		16					
							81	8		10					
					2	1	66	24	22	-16	2				1
$\nu_7$	$\delta\text{CSH}$						55	66	5	-24					1
							20	87	8	-17					2
					8		12	70	1	12				-3	
							48	68	5	-23	1				1
$\nu_8$	$\nu\text{CS}$						1	3	96	-1	-1				1
							3	9	93						2
						3	27	5	66	-5	5				-1
						3	10	2	81	-2	7				1

<sup>a</sup>For each of the three  $A'$  stretching vibrations ( $\nu_1, \nu_2, \nu_3$ ) and the three  $A''$  bands ( $\nu_{10}, \nu_{11}, \nu_{12}$ ), the respective contributions of the diagonal force constants ( $F_1, F_2, F_3; F_{10}, F_{11}, F_{12}$ ) to the PED was 91–102%. The absolute value of contributions to the PED for these modes from other force constants was in all cases less than 6%. <sup>b</sup>See Table 1, note <sup>a</sup>. <sup>c</sup>See Table 2. <sup>d</sup>Listed in the order:  $\text{CH}_3\text{SH}$ ,  $\text{CH}_3\text{SD}$ ,  $\text{CD}_3\text{SH}$ , and  $\text{CD}_3\text{SD}$ . The PED for  $^{13}\text{CH}_3\text{SH}$  is very nearly the same as for  $\text{CH}_3\text{SH}$ .

deviations ( $\Delta\nu > 8 \text{ cm}^{-1}$ ) between the observed and calculated frequencies (Fig. 2). SYMFF1 has but four large deviations:  $15 \text{ cm}^{-1}$  for  $\nu\text{CS}$ ,  $11 \text{ cm}^{-1}$  for  $\rho_{\perp}\text{CD}_3$  of the  $\text{CD}_3\text{SH}$ , and  $16 \text{ cm}^{-1}$  for  $\nu\text{SH}$  and  $\nu\text{SD}$  (Table 1 and Fig. 2). SYMFF2, by contrast, exhibits one deviation of  $33 \text{ cm}^{-1}$ , two between 20 and  $25 \text{ cm}^{-1}$ , and twelve between 8 and  $20 \text{ cm}^{-1}$ . Figure 2 provides a graphical representation of the distribution of the calculated frequency errors. For SYMFF1, 90% of all calculated frequencies have an error smaller than  $2 \text{ cm}^{-1}$ ; but for SYMFF2, only 75% do.

(4) Finally, SYMFF2 shows significantly larger differences between the calculated and observed isotope shifts for many of the fundamental frequencies than does SYMFF1.

Thus, SYMFF1 (where  $F(13)$  is positive) appears to be the more realistic empirical force field for methanethiol. The published value of the analogous interaction constant for methaneselenol is negative [18]. These results suggest that the reported force field of  $\text{CH}_3\text{SeH}$  [18] be re-examined to determine whether a set of constants for which the  $\rho_{\parallel}\text{CH}_3$ ,  $\delta\text{CSeH}$  interaction is positive may exist for this molecule also.

SYMFF1 gives calculated  $^{34}\text{S}$  isotope frequency shifts of 2.4, 1.5, 1.2, and  $5.7 \text{ cm}^{-1}$  for  $\nu^{34}\text{SH}$ ,  $\rho_{\parallel}\text{CH}_3$ ,  $\delta\text{C}^{34}\text{SH}$ , and  $\nu\text{C}^{34}\text{S}$ , respectively. In the Raman spectrum of liquid methanethiol, a weak shoulder appears at  $698 \text{ cm}^{-1}$  on the side of the very strong  $\text{C}^{32}\text{S}$  stretching band at  $704 \text{ cm}^{-1}$  (Fig. 3). This feature is probably attributable to  $\nu\text{C}^{34}\text{S}$  (4.2% natural abundance). A second weaker shoulder at  $689 \text{ cm}^{-1}$  is due to  $\nu^{13}\text{C}^{32}\text{S}$  (1.1% natural abundance).

Taking SYMFF1 as the best empirical force field for  $\text{CH}_3\text{SH}$  and its four isotopomers, the symmetry force constants were transformed into valence force constants based on simple stretching and bending coordinates, as

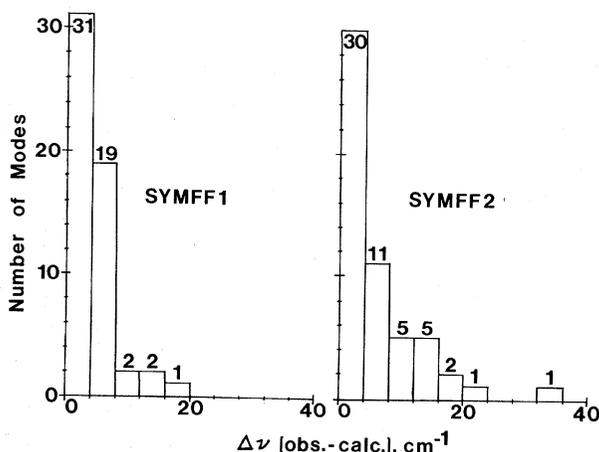


Fig. 2. Distribution of deviations ( $\Delta\nu$ ) between the observed and calculated frequencies for SYMFF1 and SYMFF2.

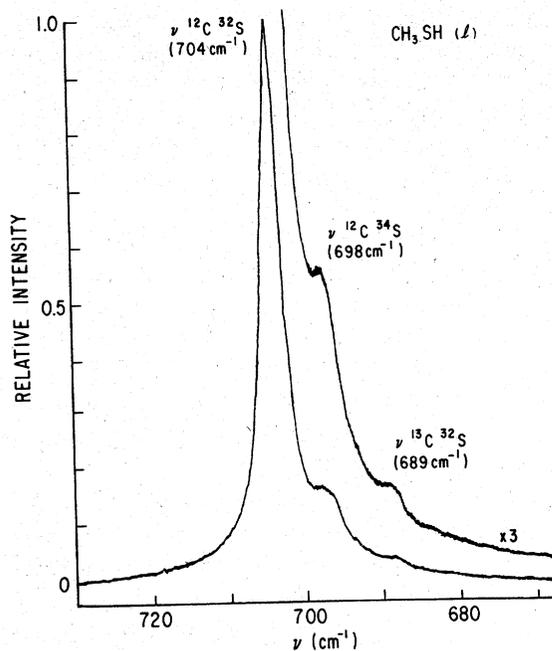


Fig. 3. Laser Raman spectrum of the  $\nu_{CS}$  bond of pure liquid methanethiol (natural isotopic abundance) sealed inside a 0.25 in. Pyrex tube. ( $T \sim 20^\circ\text{C}$ . Spectra-Physics model 165-03  $\text{Ar}^+$  laser:  $\lambda_0 = 514.5 \text{ nm}$ ,  $P = 400 \text{ mW}$  at the sample. Spex 1401 double monochromator with RCA 31034 photomultiplier: spectral slit width  $\sim 1 \text{ cm}^{-1}$ ).

previously described. The force field obtained (VFF1), consists of six diagonal constants (the torsional constant was again ignored) and 13 interactions (Table 3). Even with five isotopically substituted molecules, one cannot refine this number of constants simultaneously. So following traditional simplifying assumptions [20], five of these interactions were fixed at zero. In addition, one pair was constrained to refine to equal values but of opposite sign:  $f(15) = -f(17)$ . With the values from VFF1 as an initial parameter set, a new refinement led to VFF2. This force field appears just as satisfactory as SYMFF1 and has the same number of non-zero force constants. The average error between the observed and calculated frequencies is  $4.5 \text{ cm}^{-1}$  (0.37%). Again, no individual frequency deviations are greater than  $11 \text{ cm}^{-1}$ , except for the  $\nu_{SH}$  and  $\nu_{SD}$  stretching modes. These two vibrations exhibit a  $\Delta\nu$  value of about  $16 \text{ cm}^{-1}$ .

The largest difference in the values of the diagonal force constants in VFF1 and VFF2 is for  $f(2)$  [ $\delta\text{HCH}$ ] and  $f(3)$  [ $\delta\text{HCS}$ ]. As shown in Table 3, both increase markedly upon refinement:  $f(2)$  changes from 0.480 to 0.582  $\text{mdyn \AA rad}^{-2}$  and  $f(3)$ , from 0.504 to 0.541  $\text{mdyn \AA rad}^{-2}$ . Table 3 also compares the force constants obtained in this study with those reported by Serrallach et al. for  $\text{CH}_3\text{OH}$  [20] and with the relevant constants determined

by Scott and El-Sabban by overlay calculations for a series of simple alkane-thiols and alkyl sulfides [10]. In every case, the interactions reported are of the same sign and of similar magnitude to those calculated in this investigation. Differences observed in the values of  $f(2)$  [ $\delta\text{HCH}$ ] and  $f(3)$  [ $\delta\text{HCS}$ ] can be associated with the fact that the earlier authors used fewer interaction terms and in certain cases have made alternative assumptions with respect to which interactions should be constrained to zero.

Another notable distinction between VFF1 and VFF2 is the sixfold increase (from 0.05 to 0.30) in the value of  $f(20)$ , the interaction constant for  $\nu\text{CS}$  and  $\delta\text{CSH}$  (Table 3). Whatever the reason for this change, one may note that the valence force fields for RSH and RSR and for methanol also have values for  $f(20)$  which are similar to that for VFF2. For SYMFF1 and SYMFF2, the analogous constant  $F(18)$  is 0.05 and  $-0.01$ , respectively (Table 2). If  $F(18)$  is constrained to zero, the resulting symmetry valence force field differs little from either SYMFF1 or SYMFF2.

A detailed comparison of our empirical force constants (VFF2) with the ab initio values reported by Schlegel et al. [12], would be most interesting. Unfortunately, the latter authors do not employ the conventional type of angle bending internal coordinates (as defined by Wilson et al. [15]) for the methyl group deformation modes. A comparison of all force constants is, therefore, not feasible. Table 5 compares some values which are not directly affected by the choice of these methyl bending coordinates. Ab initio quadratic force constants apply to harmonic frequencies ( $\omega$ ) and not to the observed anharmonic frequencies ( $\nu$ ) used in the present work. So in general, the ab initio values will be larger than those based on empirical data uncorrected for anharmonicity. Indeed, for four of the six force constants compared in Table 5, the ab initio value is 11–16% larger than the empirical value. Standing as conspicuous exceptions here are the constant for the  $\nu\text{CS}$  stretching vibration and the associated interaction constant between  $\nu\text{CS}$  and  $\delta\text{CSH}$ . For these two cases, the ab initio quadratic constant is smaller than the empirical constant. In addition to a complete set of quadratic force constants, Schlegel et al. [12] calculate values for five stretching cubic force constants,  $f_{\text{rrr}}$ . With these data, they then calculated anharmonic frequencies

TABLE 5

Comparison of some ab initio and some empirical force constants for methanethiol

	$f(1)^a$		$f(6)$ $\nu\text{SH}$	$f(4)$ $\nu\text{CS}$	$f(5)$ $\delta\text{CSH}$	$f(13)$ ( $\nu\text{CS}$ , $\delta\text{CSH}$ )
	$\nu_{\text{ip}}\text{CH}^{b,c}$	$\nu_{\text{op}}\text{CH}^d$				
Ab initio <sup>e</sup>	5.426	5.358	4.368	3.036	0.988	0.224
VFF2 <sup>f</sup>	4.79	4.79	3.925	3.21	0.846	0.30

<sup>a</sup>See Table 3; units: (same as Table 2, note <sup>a</sup>.) <sup>b</sup>Same as Table 1, note <sup>a</sup>. <sup>c</sup>In-plane CH stretch. <sup>d</sup>Out-of-plane CH stretch. <sup>e</sup>Ref. 12. <sup>f</sup>From Table 3.

for CH<sub>3</sub>SH and three deuterated analogs. Except for  $\nu$ CS, their calculated anharmonic frequencies are generally larger than the observed values. They attribute this deviation from the overall trend in the calculated frequencies to the theoretically determined value of the equilibrium CS bond length being appreciably larger than the empirical value. This fact may also account for the somewhat low ab initio value determined for  $f(\nu$ CS). Nonetheless, the overall agreement between the ab initio and empirical values for the quadratic force constants which we can compare appears to be reasonable.

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