

Tentative Assignment of Fundamental Vibrations of Thio- and Selenocarboxylates

I. The Dithioacetate Ion

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In recent papers¹⁻³ the infrared spectra of several compounds containing the CSS and CSeSe groups have been discussed from an empirical point of view. The principal aim of the present series of papers is to present a more detailed assignment of the fundamental vibrations of selected compounds containing these groups. This paper summarises the results obtained by studying the infrared spectra of solid lead(II) dithioacetate and the trideuterio derivative in the range 40–4000 cm⁻¹ together with the Raman spectrum of an aqueous solution of sodium dithioacetate in the same range. Both sodium and lead(II) dithioacetate are probably ionic, since the infrared spectra of their solids in the range 700–4000 cm⁻¹ appeared to be identical. Lead(II) dithioacetate was, however, found to be the more convenient for solid state investigations since it is not susceptible to oxidation. A normal coordinate analysis based on a generalized valence force field has been employed to help assign the fundamentals.

The bond lengths and bond angles of the dithioacetate ion are listed in Table 1. It has been assumed that the methyl group is tetrahedral (*cf.* acetates⁹). The structure of the CSS group has been based on that reported for the dithiocarbamate ion.¹⁰

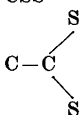
The corresponding internal coordinates are given in the third column of Table 1. In addition to the changes in the valence bond lengths (*r*, *R*, and *D*) and interbond angles (α , β , μ , and π), a coordinate de-

scribing the CSS out-of-plane bending (wagging) motion (*Δ*) has been used. From these internal coordinates, symmetry coordinates were constructed analogous to those previously reported for CX₂NO₂.¹¹ The dithioacetate ion was assumed to have effectively C_{2v} symmetry and described according to the representation 5A₁+A₂+5B₁+4B₂. The torsional vibration (species A₂) was omitted in the normal coordinate analysis, since it is not observable in C_{2v} molecules.

The force constants of the final calculation are given in the fourth column of Table 1. The initial values for the methyl group were obtained from the valence force field so successfully used for alkanes by Snyder and Schachtschneider,¹² and apart from the *F*_{Rβ} value it required only small modifications. With the exception of the wagging motion where $\bar{H}_\Delta = 0.4$ mdyne·Å/(rad)² and which was transferred from nitromethane,¹⁶ the initial values for the CSS group were estimated from those reproducing the spectrum of the trithio-carbonate ion.¹³

The normal vibrations of the dithioacetate ion were assigned on the basis of the calculations as indicated in Tables 2 and 3. The following procedure was used: (1) Two of the fundamentals of species A₁ at 1105 and 608 cm⁻¹ were identified by the Raman depolarisation ratios of 0.3(±0.2) and 0.1(±0.1), respectively. The methyl deformation vibration of this species was, owing to its position and strength, assigned to the band at 1349 cm⁻¹ in the IR spectrum of lead(II) dithioacetate. The CH stretching frequency of species A₁ had to be transferred from dithioacetic acid,¹⁴ but the exact value has almost no influence on the frequencies calculated in the region below 1500 cm⁻¹. This left only three possibilities for the remaining fundamental of species A₁: 464, 348, or 372 cm⁻¹. (2) A force field was set up to fit either of these demands. Since the calculations showed that the low frequency fundamental of species A₁ should be almost unchanged on isotopic substitution, it was identified with the band at 372 cm⁻¹, displaced to 368 cm⁻¹ in the trideuterio derivative. (3) The force field was finally applied to the two other species and adjusted to the best possible overall fit with the values found for the solid state. The validity of the local force field of the CSS group was finally confirmed by carrying out preliminary normal coordinate analyses on (CH₃)₂NCSSK. This will be the subject of a following paper.

Table 1. Molecular parameters of CH_3CSS^- and CD_3CSS^- .

Bond length or bond angle	Atoms involved	Internal coordinate	Force constants ^a
1.10 Å	CH/CD	r	$K_r = 4.77$, $F_r = 0.065$
109°28'	HCH/DCD	α	$H_\alpha = 0.53$
109°28'	HCC/DCC	β	$H_\beta = 0.68$, $F_\beta = -0.03$
1.53 Å	CC	R	$K_R = 4.45$
1.709 Å	CS	D	$K_D = 3.5$, $F_D = 0.95$
118°20'	CCS	μ	$H_\mu = 1.15$
123°20'	CSS	π	$H_\pi = 1.6$
(180°)		Δ	$H_\Delta = 0.41$

^a In units of $\text{mdyn}/\text{Å}$ (stretching constants), mdyn/rad (stretch-bend interaction constants), and $\text{mdyn}\cdot\text{Å}/(\text{rad})^2$ (bending constants). The nomenclature of Ref. 12 has been used in this work. In addition to the force constants given in the table, the following were included in the final calculation: $F_{RD} = 0.35$, $F_{R\beta} = 0.6$, $F_{R\mu} = 0.28$. All interaction force constants between the methyl and the dithiocarboxylate group were omitted with one exception: In the F matrix of species B_1 (arranged according to Ref. 11) it was necessary to assume $F_{45} = 0.05$ to obtain a reasonably good fit to the observed frequencies. This corresponds to a small interaction between CH_3 rock and CS_2 rock.

Table 2. Observed infrared spectra of $(\text{CH}_3\text{CSS})_2\text{Pb}$ and $(\text{CD}_3\text{CSS})_2\text{Pb}$ in KBr (cm^{-1}). Raman spectrum of an aqueous solution of CH_3CSSNa (cm^{-1}).

CH_3CSS^- IR ^c	CH_3CSS^- Raman ^c	CD_3CSS^- IR ^c	Assignment ^b
1449wbr		1020msh	$\nu_8(B_1), \nu_{13}(B_2)$
1420wbr			
1349m	1354w	992m	$\nu_3(A_1)$
		1311vw	576 + 734?
1141s	1150w	734vs	$\nu_9(B_1)$
1115m	1105m,P	1162s	$\nu_5(A_1)$
1065wsh		816w	$\nu_{14}(B_2)$
983vw			602 + 372?
921vw			2 × 464?
865vs	875w	1053vs	$\nu_{10}(B_1)$
		892vw	576 + 314?
602m	608vs,P	576m	$\nu_4(A_1)$
	515m ^d		1105 - 608?
464m		421m	$\nu_{15}(B_2)$
372s	370w	368s	$\nu_5(A_1)$
348w	341vw	314vw	$\nu_{11}(B_1)$
160m		160m	} lattice modes
141m		141m	
119m		119m	

^b The numbering of the fundamentals refers to the undeuterated compound.

^c The following abbreviations have been used: vs=very strong, s=strong, m=medium, w=weak, vw=very weak, br=broad, and sh=shoulder. The polarisation of a Raman line is indicated by P.

^d The estimated depolarisation ratio is 0.6, however, fluorescence is present in this region of the spectrum.

Table 3. Calculated (ν_{calc} , cm^{-1}) and observed (ν_{obs} , cm^{-1}) frequencies and potential energy distribution for the dithioacetate ion from a 15-parameter valence force field.

	CH_3CSS^-			CD_3CSS^-		
	ν_{calc}	ν_{obs}^f	Assignment ^e	ν_{calc}	ν_{obs}	Assignment ^e
A_1	2916	(2915)	$\nu\text{CH}(100)$	2098	—	$\nu\text{CD}(98)$
	1353	1349	$\delta\text{CH}_3(92)$	987	992	$\delta\text{CD}_3(82)$
	1121	1115	$\nu\text{CC}(56)$	1152	1162	$\nu\text{CC}(59)$
	604	602	$\nu_s\text{CSS}(67)$	577	576	$\nu_s\text{CSS}(66)$
	372	372	$\delta\text{CSS}(74)$	368	368	$\delta\text{CSS}(76)$
B_1	2977	(2976)	$\nu\text{CH}(100)$	2224	—	$\nu\text{CD}(98)$
	1445	1449	$\delta\text{CH}_3(90)$	1039	1020	$\delta\text{CD}_3(90)$
	1143	1141	$\rho\text{CH}_3(53), \nu_{\text{as}}\text{CSS}(23)$	703	734	$\rho\text{CD}_3(69), \nu_{\text{as}}\text{CSS}(28)$
	860	865	$\nu_{\text{as}}\text{CSS}(49), \rho\text{CH}_3(36)$	1059	1053	$\nu_{\text{as}}\text{CSS}(44), \rho\text{CSS}(29)$
	348	348	$\rho\text{CSS}(70)$	319	314	$\rho\text{CSS}(70)$
B_2	2975	(2976)	$\nu\text{CH}(100)$	2219	—	$\nu\text{CD}(98)$
	1444	1449	$\delta\text{CH}_3(90)$	1036	1020	$\delta\text{CD}_3(95)$
	1056	1065	$\rho\text{CH}_3(87)$	840	816	$\rho\text{CD}_3(84)$
	457	464	$\omega\text{CSS}(95)$	426	421	$\omega\text{CSS}(90)$

^e The following abbreviations have been used: ν =stretching, δ =deformation, ρ =rocking, ω =wagging, and, as subscripts, s=symmetric, as=antisymmetric. The rounded percentage potential energy distribution values are shown in parenthesis; small values have been neglected. In cases where several vibrations contribute significantly, the most important is printed in italics.

^f Since absorption was not observed in the CH stretching region, the values in parenthesis were transferred from dithioacetic acid.¹⁴

The mixed asymmetric CSS stretching motion occurs in the region around 1000 cm^{-1} as previously stated.³ The assignment of the corresponding symmetric stretching absorption to the region around 600 cm^{-1} is in agreement with the proposal by Anthoni¹⁸ that this band occurs in dithiocarbamic acids in the 680–691 cm^{-1} range. To our knowledge, the present paper presents the first positive assignment of the wagging, deformation, and rocking frequencies of the CSS group to bands at 464/421, 372/368, and 348/314 cm^{-1} in $\text{CH}_3\text{CSS}^-/\text{CD}_3\text{CSS}^-$.

Experimental. Dithioacetic acid was prepared from methyl magnesium iodide and carbon disulfide¹⁴ and the deuterated compound analogously from trideuteriomethyl iodide. The purity of the lead(II) salts was demonstrated by elemental analysis.

The infrared spectra in the range 400–4000 cm^{-1} were recorded in KBr discs using a Perkin-

Elmer model 337 grating infrared spectrophotometer. In the range 40–400 cm^{-1} the infrared spectra were obtained on a RIIK Fourier Spectrophotometer FS-720 in polyethylene pellets. We thank Dr. Kjeld Rasmussen for providing us with the latter spectral data.

The Raman spectrum was recorded on a freshly prepared solution of sodium dithioacetate, prepared from the dithioacid and 1 N NaOH. It was recorded on a Coderg PHI Raman spectrometer using a Spectra Physics 125 He/Ne-laser with perpendicular illumination in polarisation measurements. The help of Dr. O. Faurskov Nielsen in the recording and interpretation of the Raman spectrum is gratefully acknowledged.

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The Valence Electron Density Distribution of Strained Single Bonds in the Iterative Extended Hückel Approach

III. Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (Cubane)*

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With cubanes we mean organic or inorganic compounds, the basic valence structure of which is cubic (Fig. 1; for a review see Ref. 1). Within organic chemistry the name cubane is used as a trivial name for pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, C₈H₈, the parent hydrocarbon in its

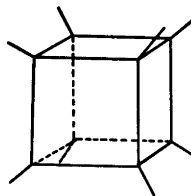


Fig. 1. The valence skeleton of cubanes.

class of compounds. The classical valence angle of the cubic structure, 90°, is the limiting angle for orthogonal hybrids built up from atomic orbitals of *s* and *p* type directed along the interatomic vectors. Complex hybrids may also be used for this description.² Since the cubanes are strained compounds, with the valence angles differing substantially from the tetrahedral angle, it is not unreasonable to expect bent bonds, *i.e.* bonds with the electron density forming maxima outside the interatomic vectors. If a hybrid interpretation of such a bond is desired, "best" hybrid orbitals may be chosen as those providing the highest localization of the MO-LCAO over-

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