Tentative Assignment of Fundamental Vibrations of Thio- and Selenocarboxylates

I. The Dithioacetate Ion

K. A. JENSEN, H. MYGIND and P. H. NIELSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark
and

G. BORCH

Chemistry Department A, The Technical University of Denmark, Lyngby, Denmark

In recent papers [1-8] 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.* acetates [9]). The structure of the CSS group has been based on that reported for the dithiocarbazate 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 describing 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 CX_3NO_2.[11] The dithioacetate ion was assumed to have effectively C_{2v} symmetry and described according to the representation $5A_1+A_2+5B_1+4B_2$. The torsional vibration (species A_2) 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 $F_{R\beta}$ value it required only small modifications. With the exception of the wagging motion where $H_\Delta = 0.4$ mdyn·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 trithiocarbonate 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 A_1 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 A_1 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 A_1: 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 A_1 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 $(CH_3)_2NCSSK$. 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°)	C–C(S)S	Δ	$H_\Delta = 0.41$

[a] In units of mdyn/Å (stretching constants), mdyn/rad (stretch-bend interaction constants), and mdyn·Å/(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 $(CH_3CSS)_2Pb$ and $(CD_3CSS)_2Pb$ 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	$\nu_2(A_1)$
		1311vw	576+734?
1141s	1150w	734vs	$\nu_9(B_1)$
1115m	1105m,P	1162s	$\nu_3(A_1)$
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)	νCH(100)	2098	—	νCD(98)
	1353	1349	δCH_3(92)	987	992	δCD_3(82)
	1121	1115	νCC(56)	1152	1162	νCC(59)
	604	602	ν_sCSS(67)	577	576	ν_sCSS(66)
	372	372	δCSS(74)	368	368	δCSS(76)
B_1	2977	(2976)	νCH(100)	2224	—	νCD(98)
	1445	1449	δCH_3(90)	1039	1020	δCD_3(90)
	1143	1141	*ϱCH_3(53)*,ν_{as}CSS(23)	703	734	*ϱCD_3(69)*,ν_{as}CSS(28)
	860	865	*ν_{as}CSS(49)*,ϱCH_3(36)	1059	1053	*ν_{as}CSS(44)*,ϱCSS(29)
	348	348	ϱCSS(70)	319	314	ϱCSS(70)
B_2	2975	(2976)	νCH(100)	2219	—	νCD(98)
	1444	1449	δCH_3(90)	1036	1020	δCD_3(95)
	1056	1065	ϱCH_3(87)	840	816	ϱCD_3(84)
	457	464	ωCSS(95)	426	421	ωCSS(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 Anthoni[15] that this band occurs in dithiocarbazic 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 CH_3CSS^-/CD_3CSS^-.

Experimental. Dithioacetic acid was prepared from methyl magnesium iodide and carbon disulfide[14] 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 PH1 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.

The calculations were made according to the Wilson FG-method. We owe special thanks to Dr. G. O. Sørensen for placing the computer program at our disposal and for very helpful discussions. Finally, we wish to thank the operational staff of D.T.H.-Gier for competent service.

1. Jensen, K. A. and Nielsen, P. H. *Acta Chem. Scand.* **17** (1963) 547, 549.
2. Jensen, K. A., Carlsen, J. B., Holm, A. and Nielsen, P. H. *Acta Chem. Scand.* **17** (1963) 550.
3. Jensen, K. A. and Henriksen, L. *Acta Chem. Scand.* **22** (1968) 1107.
4. Anthoni, U., Dahl, B. M., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **23** (1969) 1061.
5. Jensen, K. A. and Anthoni, U. *Acta Chem. Scand.* **24** (1970). *In press.*
6. Jensen, K. A. and Henriksen, L. *Acta Chem. Scand.* **24** (1970). *In press.*
7. Jensen, K. A. and Krishnan, V. *Acta Chem. Scand.* **24** (1970) 1088.
8. Jensen, K. A. and Mygind, H. *Acta Chem. Scand. To be published.*
9. Ferrari, A., Braibanti, A., Bigliardi, G. and Lanfredi, A. M. *Acta Cryst.* **19** (1965) 548.
10. Braibanti, A., Lanfredi, A. M., Tiripicchio, A. and Loqiudice, F. *Acta Cryst.* **B 25** (1969) 93.
11. Castelli, A., Palm, A. and Alexander, Jr., C. *J. Chem. Phys.* **44** (1966) 1577.
12. Snyder, R. G. and Schachtschneider, J. H. *Spectrochim. Acta* **21** (1965) 169.
13. Müller, A. and Fadini, A. *Z. physik. Chem. Neue Folge* **54** (1967) 129.
14. Mecke, R. and Spiesecke, H. *Chem. Ber.* **89** (1956) 1110.
15. Anthoni, U. *Acta Chem. Scand.* **20** (1966) 2742.
16. Wilson, T. P. *J. Chem. Phys.* **11** (1943) 361.

Received April 10, 1970.

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)*

OLLE MÅRTENSSON

Quantum Chemistry Group, Uppsala University, Box 518, S-751 20 Uppsala, Sweden

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, C_8H_8, the parent hydrocarbon in its

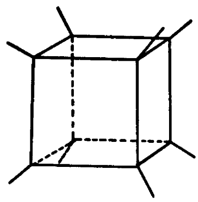

Fig. 1. The valence skeleton of cubanes.

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-

* Sponsored in part by *King Gustaf VI Adolf's 80-Year Fund for Swedish Culture, Knut and Alice Wallenberg's Foundation* and in part by the *Swedish Natural Science Research Council.*