Vibrational Spectra and Structure of Crystalline Potassium Perthiocarbonate–Methanol K_2CS_4,CH_3OH

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The i.r. and Raman spectra of polycrystalline K_2CS_4,CH_3OH and K_2CS_4,CH_3OD addition compounds have been investigated in the 4 000—50 cm^{-1} range. Most of the intramolecular fundamentals have been assigned and the spectroscopic and *X*-ray diffraction data are correlated. The hydrogen bonded CH_3OH molecules are characterized by 3 400 and 3 240 cm^{-1} OH stretching frequencies corresponding to OH · · · O and OH · · · S interactions, respectively. The valence force field determined for the two nonequivalent CS_4^{2-} anions gives four different C–S stretching force constants varying from 3.4 to 4.2 mdyn Å^{-1} and consistent with the C–S distances; however, no C=S double bond is expected from the spectroscopic data.

THE crystalline structure of potassium perthiocarbonate addition compound with methanol, K_2CS_4,CH_3OH, was determined recently by *X*-ray diffraction.[1,2] We were interested in a correlation between the crystallographic and spectroscopic data concerning the nonequivalence of CS_4^{2-} anions and the type and strength of hydrogen bonds involving CH_3OH molecules. We have thus investigated the i.r. and Raman spectra of K_2CS_4,CH_3OH and K_2CS_4,CH_3OD and determined the valence force field of CS_4^{2-} anions. No previous spectroscopic study of this compound has been published as far as we know.

EXPERIMENTAL AND CALCULATIONS

The method of preparation of this compound has already been described;[2,3] the deuteriated derivative was obtained in the same way using CH_3OD. The i.r. spectra of samples examined as emulsions in Nujol and Fluorolube or as pressed KBr pellets (with identical results for both techniques) were recorded on Perkin-Elmer 225 and Polytec FIR-30 instruments for the 4 000—200 and 400—50 cm^{-1} regions, respectively. Raman spectra of polycrystalline material sealed in glass tubes were investigated on a Coderg PH1 double monochromator apparatus using a Spectraphysics krypton laser with the 6 471 Å line of 150 mW as exciting source. Spectra at 100 K were also investigated.

A valence force field of CS_4^{2-} ion was determined using the force constant matrix method, F_{XSM}, following a program similar to that described by Shimanouchi.[4] The calculations were performed on a 360/180 I.B.M. computer.

RESULTS AND DISCUSSION

(1) *Crystal Structure and Symmetry Considerations.*—The K_2CS_4,CH_3OH crystal is triclinic ($P\bar{1}$-C_i; $Z = 4$).[1,2] There are two nonequivalent planar anions occupying general positions (Figure 1). In anion A, electrons corresponding to a formal C=S double bond appear to be delocalized, whereas the situation seems much closer to a localization in anion B. There are also two types of methanol molecules. The first forms a hydrogen bonded cyclic dimer with O · · · O distance 2.875 Å and the second corresponds to an OH · · · S interaction with the CS_4^{2-} anion, the O · · · S distance being 3.10 Å.

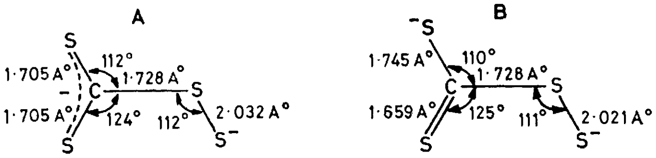

FIGURE 1 Structure of CS_4^{2-} anions [1,2] in K_2CS_4,CH_3OH addition compound

Each intramolecular vibration of each nonequivalent species is expected to split into two components, one i.r. (A_u) and one Raman (A_g) active, *i.e.* the i.r. or Raman band splitting is thus due to nonequivalence of molecules and not to a correlation field splitting.

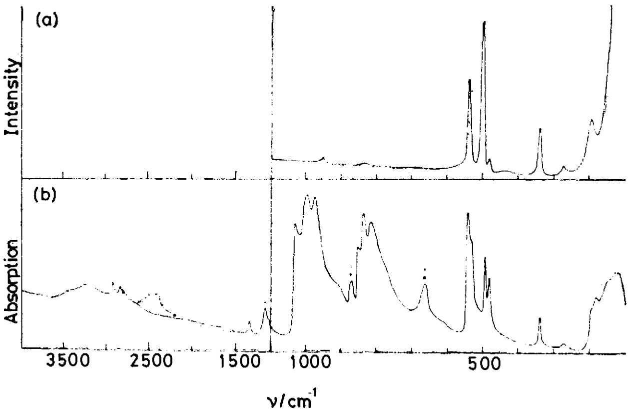

FIGURE 2 Raman (a) and i.r. (b) spectra of K_2CS_4,CH_3OH; dotted line corresponds to ν(OD) absorption band of the deuteriated derivative. The arrows denote impurity bands

(2) CH_3OH *Vibrations and Hydrogen Bonding.*—The i.r. and Raman spectra of K_2CS_4,CH_3OH are shown in Figure 2. The bands of methanol and CS_4^{2-} anion can be distinguished. Six methanol bands are observed in the i.r. spectrum (Table 1) but no Raman equivalent was found. The most interesting fundamentals are two OH stretching bands at 3 400 and 3 240 cm^{-1} which shift to 2 500 and 2 400 cm^{-1} on deuteriation yielding a 1.35

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[2] D. Zins, M. Robineau, and M. C. Brianso-Perucaud, *Compt. rend.*, 1975, **280C**, 875.

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isotopic frequency ratio. The 3 400 cm^{-1} band can be assigned to O–H $\cdots$ O hydrogen bonded molecules forming a cyclic dimer and the 3 240 cm^{-1} band to the O–H $\cdots$ S interactions. The 3 400 cm^{-1} frequency is consistent with a 2.875 Å O $\cdots$ O distance following the frequency–distance relationship.[5] At any rate, it implies an O–H $\cdots$ O hydrogen bond much weaker than in pure methanol crystal characterized by a lower ν(OH) frequency [6] at 3 245 cm^{-1} and a shorter, 2.66 Å, O $\cdots$ O distance.[7]

TABLE 1

I.r. frequencies (cm^{-1}) of methanol in $K_2CS_4,CH_3OH(OD)$

CH_3OH	CH_3OD	Attribution
3 400sh	2 500m	ν(OH) (OH $\cdots$ O)
3 240m	2 400m	ν(OH) (OH $\cdots$ S)
2 920 2 820 } w	2 930 2 820 } w	$\nu(CH_3)$
1 373vw	1 373vw	$\delta(CH_3)$
1 021sh	1 018sh	ν(C–O)

Very little is known about O–H $\cdots$ S hydrogen bonds. However, the O $\cdots$ S distance of 3.10 Å can be considered as relatively short by analogy with N–H $\cdots$ S systems studied recently.[8] In the case of pyridine-2-thione and 2,4-dithiouracil for instance, an N $\cdots$ S distance of *ca.* 3.3 Å gives rise to an NH stretching absorption band near 2 900 cm^{-1}, *i.e.* in the same region as an N–H $\cdots$ O hydrogen bonded group corresponding to an N $\cdots$ O distance of 2.8 Å. So the O $\cdots$ S distance of 3.10 Å can be compared with the O $\cdots$ O length of 2.6—2.7 Å found in crystalline methanol.[7] This justifies our assignment of the low frequency OH stretching band to the O–H $\cdots$ S hydrogen bond.

(3) CS_4^{2-} *Vibrations and Valence Force Field.*—Nine fundamentals (7 A' + 2 A'') are expected for each of the CS_4^{2-} anions. In terms of group frequencies a different classification for each anion (A or B) is needed if anion B contains a C=S double bond. However, inspection of the spectra reveals that there is no band above 1 000 cm^{-1} characteristic of such a bond and that the general pattern is reminiscent of the spectra of compounds containing CS_3^{2-} ions.[9–12,*] We shall thus distinguish for each anion, to a first approximation, six vibrations of the CS_3 group (5 A' + 1 A'') and three vibrations of the C–S–S group (2 A' + 1 A''). The former can be derived from the four fundamentals of CS_3^{2-} anion of D_{3h} point symmetry and are denoted by ν_1 (A'_1), ν_{3a}, ν_{3b} and ν_{4a}, ν_{4b} derived from the degenerate species (E') for stretching and bending modes, respectively, and ν_2 an out-of-plane mode (A''_2) (Table 2).

TABLE 2

I.r. and Raman frequencies (cm^{-1}) of CS_4^{2-} anions in K_2CS_4,CH_3OH; calculated values and potential energy distributions (p.e.d.)

Species and description	I.r.	Raman	Calc.	Anion type	P.e.d.*
A' ν_{3a} CS_3	994vs		999	B	$14\ r_1 + 70\ r_2 + 25\ r_3 + 20\ \alpha_2$
	974vs		976	A	$99\ r_{2.3} + 36\ \alpha_{2.3} + 11\ \beta$
A' ν_{3b} CS_3	838vs		843	A	$82\ r_1 + 43\ r_{2,3} + 18\ \alpha_1 + 18\ \alpha_{2.3}$
	818vs		817	B	$72\ r_1 + 49\ r_3 + 18\ \alpha_1 + 23\ \alpha_3$
A' ν_1 CS_3	539vs	537s	541	A	$10\ r_1 + 33\ r_{2.3} + 36\ s$
	535sh		540	B	$14\ r_1 + 19\ r_2 + 23\ r_3 + 22\ s$
A' ν SS	494s	495vs	505	A	$29\ r_{2.3} + 32\ s + 15\ \beta$
			512	B	$17\ r_2 + 48\ s + 16\ \beta$
A'' ν_2 CS_3	478m	481w	482	A	$98\ \gamma$
			483	B	$97\ \gamma$
A' ν_{4a} CS_3	334m	338m	340	A	$14\ r_{2.3} + 15\ s + 27\ \alpha_1 + 37\ a_{2.3} + 20\ \beta$
			335	B	$14\ r_3 + 13\ s + 29\ \alpha_1 + 35\ \alpha_3 + 22\ \beta$
A' ν_{4b} CS_3	273w	273w	272	A	$15\ s + 28\ \alpha_1 + 57\ \alpha_{2.3}$
			268	B	$16\ s + 28\ \alpha_1 + 58\ \alpha_2$
A' δ CSS		194m	179	A	$34\ \alpha_{2.3} + 55\ \beta$
			178	B	$28\ \alpha_3 + 52\ \beta$
A'' t CS_2			101	A	$98\ t$
			101	B	$97\ t$

* Contributions <10% are not given.

Observed spectra. There are two groups of very strong i.r. bands near 980 and 830 cm^{-1} which are assigned to the C–S stretching vibrations ν_{3a} and ν_{3b} derived from the ν_3 mode of the CS_3^{2-} ion near 905 cm^{-1}. Each group has two components due to nonequivalent ions (Table 2, Figure 2), the splitting being close to 20 cm^{-1}. The assignment of the other pair of bands resulting from the second CS_3^{2-} degenerate vibration near 320 cm^{-1} is straightforward: the 334 and 273 cm^{-1} frequencies correspond to ν_{4a} and ν_{4b} bending modes observed both in i.r. and Raman. There is a slight *g–u* correlation field splitting for the ν_{4a} mode but no splitting due to the nonequivalency of anions. The 500 cm^{-1} region is more complicated since ν_1, ν_2,[9–12] and ν(S–S) [13,14] vibrations are expected there: the first mode doubtless corresponds to a strong Raman band at 537 cm^{-1}, its i.r. equivalent giving rise to a 539—535 cm^{-1} nonequivalence doublet while the out-of-plane ν_2 mode must be due to the 480 cm^{-1} band, very weak in the Raman spectrum. The ν(S–S) vibration is very strong in the Raman spectrum at 495 cm^{-1} as expected; the fact that the ν(S–S) absorption band is also strong may be associated with some coupling between the ν_1 and ν(S–S) motions. Finally, the remaining intense Raman band at 194 cm^{-1}

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[*] ν(C=S) Vibrations at frequency lower than 1 000 cm^{-1} can be expected only when some vibrational coupling with vibrations at higher frequencies are important (*e.g.* thioamides).

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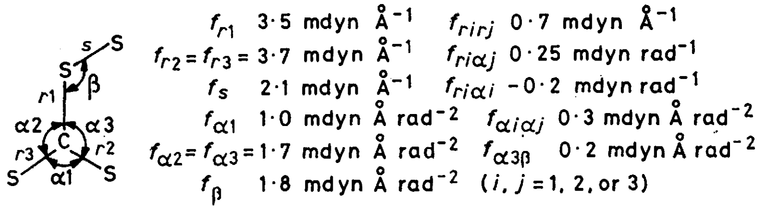
is likely to be due to the δ(CSS) bending motion. The far i.r. spectra show several ill-resolved bands in the 200—100 cm^{-1} region but their interpretation is not clear since many lattice modes besides the last two internal vibrations are expected in this region.

Force Field of CS_4^{2-} *Anions.*—In order to check the experimental assignment, to give a quantitative description of the intramolecular vibrations, and to characterize different C–S bonds in both anions, a normal co-ordinate calculation was carried out. The parameters given in Figure 1 were used and the internal co-ordinates are defined in Figure 3. Lack of data on isotopic species limited our force field to the most important force constants: besides the ten principal force constants, five interaction force constants only were different from zero. Moreover, the same force constants, except for $f_{\alpha 3}$, f_{r2}, and f_{r3}, were used for both anions A and B.



f_{r1} 3·5 mdyn Å^{-1} f_{rirj} 0·7 mdyn Å^{-1}

$f_{r2} = f_{r3} =$ 3·7 mdyn Å^{-1} $f_{ri\alpha j}$ 0·25 mdyn rad^{-1}

f_s 2·1 mdyn Å^{-1} $f_{ri\alpha i}$ −0·2 mdyn rad^{-1}

$f_{\alpha 1}$ 1·0 mdyn Å rad^{-2} $f_{\alpha i\alpha j}$ 0·3 mdyn Å rad^{-2}

$f_{\alpha 2} = f_{\alpha 3} =$ 1·7 mdyn Å rad^{-2} $f_{\alpha 3\beta}$ 0·2 mdyn Å rad^{-2}

f_β 1·8 mdyn Å rad^{-2} ($i, j = 1, 2,$ or 3)

FIGURE 3 Internal co-ordinates and values of the valence force constants in type A CS_4^{2-} anion: f(wagging) 0.625 and f(torsion) 0.19 mdyn Å rad^{-2} have been used for out-of-plane deformations; in type B anion, only three force constants have been adjusted to new values: f_{r2} 4.2 mdyn Å^{-1}, f_{r3} 3.4 mdyn Å^{-1}, and $f_{\alpha 3}$ 1.5 mdyn Å rad^{-2}

Agreement between the observed and calculated values appears to be satisfactory (Table 2). In particular, the calculation reproduces very well the effect of degeneracy splitting and nonequivalence of anions on the ν_3 vibration; specific assignment of all four components can thus be given. The p.e.d. confirms the coupling between ν_1 and ν(S–S) vibrations expected on intensity grounds and shows that there is another coupling between ν_{4a} and δ(CSS) motions. The latter interaction may also explain why the degeneracy splitting of the ν_4 vibration is larger (20%) than that of ν_3 (16%).

The C–S stretching force constants of type A CS_4^{2-} ion are similar (f_{r1} 3.5 and $f_{r2} = f_{r3} =$ 3.7 mdyn Å^{-1}) while a large difference is observed for type B (f_{r1} 3.5, f_{r2} 4.2, and f_{r3} 3.4 mdyn Å^{-1}). These values can be well correlated with the corresponding C–S distances varying from 1.66 to 1.75 Å and with the force constant of the CS_3^{2-} anion, f_{C-S} 3.71 mdyn Å^{-1}.[9,10] A real C=S double bond would imply a force constant between 6.3 and 7.9 mdyn Å^{-1}.[15-18] The value f_{r2} found for anion B shows some degree of delocalization. Finally, the internal consistency of C–S stretching force constants and distances is shown in Table 3 where the calculated force constants are compared with those determined by the Badger's relationship of the $f_{(C-S)} = a/r(C-S)^3$ type.[19]

The S–S stretching force constant, on the other hand, is 2.1 mdyn Å^{-1} and appears to be slightly lower than those calculated for $(CH_3)_2S_2$ (2.2 mdyn Å^{-1} [13]) and H_2S_2 (2.5 mdyn Å^{-1} [14]) molecules with similar S–S distances.

TABLE 3

Comparison of some f(C–S) force constants determined by Badger's rule [19] and by force field calculations

Entity	Distance r(C–S) (Å)	Ref.	Force constant f(C–S) (mdyn Å^{-1}) Badger [19]	Force field	Ref.
CS_3^{2-}	1.712	*a*		3.712	9, 10
CS_4^{2-}	1.659	1, 2	4.08	4.2	This work
	1.705		3.76	3.7	
	1.728		3.61	3.5	
	1.745		3.50	3.4	
$(CH_3)_2S$	1.802	*b*	3.18	3.15	*d*
				3.20	*e*
CH_3SH	1.819	*c*	3.09	3.09	*f*

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